Turbulent drag reduction by additives

Kulmatova, D.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
LITERATURE REVIEW

2.1 Drag Reduction Additives

Drag reduction in turbulent flow can be achieved by several types of additives. These include surfactants, fibers, aluminum disoaps, and high polymers. These drag reducing additives can dramatically affect the turbulent structures of the flowing fluid, increase the flow rate and decrease the energy consumption. This section gives an overview of drag reduction and the commonly used DRA.

2.1.1. Drag reduction characterisation

The addition of a minute amount of drag reducing additives to a turbulent fluid flow can cause a large reduction in the frictional drag relative to a pure solvent at the same flow rate. The amount of drag reduction is generally expressed as the pressure gradient differences between the solvent and the drag reducing solution. Savins [16] was the first in using the term “Drag Reduction” with the definition:

\[
\%DR = \left( 1 - \frac{\Delta P_{\text{Polymer}}}{\Delta P_{\text{Solvent}}} \right) \times 100
\]

where \( \Delta P_{\text{Polymer}} \) and \( \Delta P_{\text{Solvent}} \) signify the pressure drops in friction in the presence and absence of drag reduction.

Drag reduction efficiency can also be expressed in terms of the friction factors of the solvent and the drag reducing fluids as:

\[
\%DR = \left( 1 - \frac{f_{\text{Polymer}}}{f_{\text{Solvent}}} \right) \times 100
\]
The effect of drag reduction is also presented in the terms of wall shear stress \( \left( \tau_w = \frac{D\Delta P}{4L} \right) \), friction factor \( \left( f = \frac{D}{2pU^2} \frac{\Delta P}{L} \right) \) and Reynolds number \( \left( \text{Re} = \frac{pUD}{\eta} = \frac{UD}{v} \right) \).

Where \( \tau_w \) is the wall shear stress, \( d \) is the pipe diameter, \( U \) is the mean fluid velocity in the pipe and \( p, \eta \) and \( v \) are the dynamic viscosity and kinematic viscosity of the fluid respectively.

In order to analyze the drag reducing additive effectiveness, the best known method of representing the data in terms of these parameters is the classical \( f \) versus \( \text{Re} \) as shown in Figure 2.

As illustrated in the Figure 6, with the drag reducing agent, above a particular Reynolds number, the friction factor falls below that for the case of pure solvent flow.

\[ 
\begin{align*}
\text{Figure 2: Methods of representing drag reduction data (Virk [8]).}
\end{align*}
\]
Prandtl–Karman coordinates \((f^{1/2} \text{ vs } Re f^{1/2})\) are normally used to illustrate drag reduction. The advantage of this representation is that the Newtonian turbulent flow forms a straight line.

\[
f^{-1/2} = \frac{u}{\sqrt{2}u_r} \text{ as ordinate}
\]

\[
Re f^{1/2} = \sqrt{2} \frac{D u_r}{v} \text{ as abscissa}
\]

describe ratios of bulk to turbulent velocities and pipe to turbulent length scales respectively. According to Newtonian flow, the relationship between \(1/f^{1/2}\) and \(Re f^{1/2}\) are given by

\[
\frac{1}{f^{1/2}} = 4.0 \log_{10} \left(Re f^{1/2}\right) - 0.4 \quad \text{or} \quad f = \frac{16}{Re}
\]

In the case of the absence of drag reduction, the frictional factor can be expressed using the Prandtl–van Karman law for Newtonian turbulent pipe flow

\[
\frac{1}{f^{1/2}} = 4.0 \log_{10} \left(Re f^{1/2}\right) - 0.4
\]

### 2.1.2 Drag reduction by polymers

Polymer solutions are the most widely studied and most employed of drag reduction systems. The addition of a small amount of polymer to a turbulent fluid flow can greatly reduce the amount of drag a fluid creates on its vessel. Drag reduction can occur in water, but also in a range of organic solvents. The most important aspects of the polymers are that they possess a high molecular weight, chain flexibility, and long linear chain structure. It is also important that polymers are very soluble in the fluid (Morgan S.E. et al [17]).

Table 1 provides a list of the most common polymer drag reducers. Previous studies on polymer drag reduction indicate that the most polymers meeting parameters described above are able to reduce the drag in a turbulent flow.
Table 1: Most Widely Used Drag Reducing Polymer agents [15].

<table>
<thead>
<tr>
<th>Water-soluble polymers</th>
<th>Hydrocarbon soluble polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (PEO)</td>
<td>Polyisobutylene (PIV)</td>
</tr>
<tr>
<td>Polyacrylamide (PAM)</td>
<td>Polystyrene (PS)</td>
</tr>
<tr>
<td>Guar gum (GGM)</td>
<td>Polymethylmethacrylate (PMMA)</td>
</tr>
<tr>
<td>Xanthan gum (XG)</td>
<td>Polydimethylsiloxane (PDMS)</td>
</tr>
<tr>
<td>Carboxymethyl cellulose (CMC)</td>
<td>Polycisisoprene (PCIP)</td>
</tr>
</tbody>
</table>

Polyethylene oxide (PEO) and polyacrylamide (PAM) have been much studied in fundamental research and industry because of their low cost and high rates of availability. PEO, with its linear and flexible molecular structure, has been widely studied for commercial applications, such as fire prevention and marine propulsion. On the other hand, its usefulness in most practical applications is limited because of its extreme sensitivity to shear degradation. Conversely, polymer mixtures and DRA additives, such as grafted PEO polymers and soap mixtures, and polymer/dye mixtures are quite effective and have shown different levels of drag reduction effectiveness [18, 19]. The search for shear-stable drag reducing polymers continues to be a challenging task.

Biopolymers, being environmental friendly, show great resistance to mechanical degradation. Biopolymers, such as high molecular weight polysaccharides, are made by living organisms and exhibit effective drag reduction [20]. For instance, polysaccharides of several fresh water and marine algae, fish slime, seawater slime and other fresh water biological growths are excellent drag reducers. Yet, due to their production of fouling substances, these biological additives can substantially reduce DRA efficiency. It has been found that industrial polysaccharides such as xanthan gum (XG) show significant resistance to mechanical degradation compared to flexible polymers with similar molecular weights. Xanthane is one of the most popular commercial drag reducing biopolymers. Taofeqa [21] has proven that XG polymer has greater shear stability compared to other drag-reducing additives. The following sequence: PAM>XG>PEO>GG demonstrates the decreasing factor of shear stability, and resistance to shear degradation of flexible and rigid polymers.
2.1.3. Drag reduction by surfactants

Surface-active molecules are known as surfactants, and some of them are effective DR agents. Early publications on drag reduction by additives deal with surfactant solutions, however these kinds of additives have recently obtained less attention than polymers. Studies of drag reduction have increased during the last twenty years to use surfactants as drag reducing additives. These compounds have a self-assembled structure, and after mechanical degradation they are assembled which permits them to be used in recirculation systems such as district heating and cooling systems [22]. Surfactants have been utilized as drag reducing agents in many research studies. Surfactant molecules have unique self-repairing ability that keeps the drag-reducing effect through mechanical shear stress. Drag reducing surfactant molecules form “aggregates,” called wormlike micelles. As fluid comes into a shear region, the micelles change their structure. Furthermore, surfactants are commercially available and, during operations, are easy to handle. Therefore, surfactants are more desirable than many types of polymers in certain commercial applications, such as in district heating or cooling systems [23].

2.1.4 Drag reduction by fibres

Fibres, which are stable both chemically and mechanically in aqueous surroundings, are also used as DRA for many practical applications, which has a significant practical importance to the papermaking industry, the food industry and in the production of fiber-reinforced plastics. Since the most fibrous materials are not affected by water chemistry, piping substances, and temperature, they can withstand a wide temperature range [24, 25]. Drag-reducing fibers are considered not to cause an envorimental pollution because they do not react with any material and do not produce toxic substances. Lee et al. [26] and Doulah et al. [27] believed that fiber drag reduction might be caused by suppression of turbulent eddies in the turbulent core areas. It was observed that a 95 percent drag reduction occurred due to mixtures of fiber systems and polymers [28, 29]. Compared to the drag reduction of polymers and fibers alone, this drag reduction level is greater. In this system, the actual polymer was also more resistant to degradation. However, it is difficult to use fibers in these surroundings because they can create plugging problems in pipelines as a result of the high concentration (as high as a few percent required for drag reduction).


2.1.5 DRA applications

Using polymer and surfactant additives provides benefit to various industries, such as long-distance transportation of liquids, district heating and cooling, fire-fighting operations, irrigation systems and the oil servicing and transportation industries for designing the optimal operation of oil pipelines. The use of drag reducing additives to enhance flow in petroleum pipelines has received the greatest attention due to its great commercial success in reducing cost and energy consumption.

The best known practical application is the use of polymers to enhance the crude oil flow in Trans-Alaska Pipeline system where 1 ppm of drag reducer increased the flow rate by 33 per cent. Burger et al. [30] reports that DRAs are used in petroleum product pipeline installations, like the Oseberg Field in the North Sea. Many other great benefits can be obtained by drag reduction in oil fields by increasing the water injection rate and hence the oil production rate, energy saving and reducing the level of corrosion [31]. The use of the drag reducing agents in sewerage pipes and storm-water drains to increase the flow rate can be much cheaper than constructing new larger pipes. Polymer additives can reduce the pumping power costs of transportations of ash, coal, sediments, etc. by pipelines. This application is very important for the transport of high weight solids in many locations worldwide [32]. In military applications, the drag reduction phenomenon can be applied to operations, like increasing the speed of underwater bodies (e.g., torpedoes and submarines). Of great importance, a 20% drag reduction creates an increase in speed of 6.8% [33]. For the past forty years, drag reducing polymers have also been used in the biomedical industry. One such application of drag reducing polymers is the treatment of circulatory or cardiovascular diseases [34].

Surfactants have been widely used in district heating and cooling systems (DHC) for reducing pumping power or increasing flow rate as they are very stable and recover from degradation quickly compared to polymers. The use of drag reducing surfactant additives in large scale district heating systems has lowered pipe flow energy significantly. Saeki [35] has reported that cationic surfactants in aqueous systems have been maintained in over 130 buildings in Japan, and they have helped to decrease pumping energy by 20%-60%. In addition, surfactant DRA were also used to aid in the prevention of the agglomeration of ice slurries [36]. Due to their ice-dispersion ability and drag reduction effectiveness, the ice slurry systems showed improved performance in
advanced cold heat storage, transportation, and heat exchange systems [37]. As the drag reducing additives bear a close relationship to energy conservation, they will receive more attention and exhibit increased usage in the near future.

2.2 Drag Reduction Behavior of Polymers

The addition of a minute amount of polymer additives to a turbulent fluid flow can result in a large drag reduction. Many studies have confirmed that the effectiveness of polymer's drag reduction in a turbulent flow is strongly influenced by polymer degradation, molecular-weight, concentration, preparation of polymer solutions, solvent properties, solution temperature, turbulent intensity, flow rate, geometry and types of pumps used (Den Toonder et al. [38] and Lee et al. [39]).

2.2.1 Polymer Degradation

An important problem in the application and study of drag reduction by polymer additives is the degradation of the polymers. It is well known that the drag reducing capability of a polymer is limited by two types of degradation: chemical and mechanical (Den Toonder et al. [38]).

Chemical degradation occurs when a change in the polymer structure is caused by a chemical reaction. It can be caused by the presence of metals or free radical initiators where oxygen is present and a high level of salinity or calcium in the solvent may also cause chemical degradation (Choi et al. [40]). In comparison, mechanical degradation occurs due to mechanical energy acting on the polymers in the solution. In practical terms, this means passing the fluid through pumps or pipes or both. Den Toonder [38] suggested that this mechanical stress causes the polymer to break, thereby reducing the molecular weight of the polymer and thus its drag-reducing capability.

Mechanical degradation is linked to shear-flow, causing degradation of dilute polyethylene oxide solutions when present (Sellin et al. [41]). Bueche [42] showed evidence that the mechanical degradation of the polymer within elongated flows, which exist in some regions of turbulent pipe flow, is extremely severe. This is because a polymer molecule in a turbulent flow is subjected to stretching and rotation, due to interaction of the vortices. The practical use of polymers in a turbulent DR application is consequently mostly hindered by mechanical shear degradation.
There have been numerous investigations (Patterson et al. [43], Nakano and Minoura [44], Tabata et al. [45], Hunston and Zakin [46] and Moussa and Tiu [47]) regarding mechanical degradation of both dilute and concentrated polymer solutions. Yet these studies show conflicting results depending on a number of variables in the experiment, including laminar, turbulent flow and polymer concentration range.

Molecular chains in polymer may undergo scission due to a range of external actions. Polymer chains can be stretched due to weak extensional flows, and they can be broken in a strong extensional flow, according to Choi et al. [48]. This degradation decreases the polymer’s average molecular weight, causing the drag reducing properties of the polymer to become weaker and eventually vanish.

Several studies have been performed to determine the conditions that can affect a polymer’s ability to reduce turbulent drag. Fabula [49] found that an increase in turbulent flow and a drop in pressure occurred at a certain pipe diameter and attributed this effect to either molecular disentanglement and/or degradation. Nakano and Minoura [44] observed that a polymer degrades faster in a good solvent than in a poor solvent at a low concentration by noting that the interaction between polymer molecules weakens at low concentrations. Their results suggest that a decrease in concentration of polymer solution positively affects the scission of chains, implying that mechanical degradation is affected by the stretching of the polymeric chains (Yu et al. [50]).

Many experiments have illustrated mechanical shear degradation using turbulent flow conditions. Zakin and Hunston [51] evaluated DR efficiency in a capillary tube, which is very sensitive to changes in polymer molecular weight at extremely low concentrations. Culter et al. [52] showed that mechanical degradation in turbulent flow occurs at the entrance of capillary tubes. In an effort to reduce the entrance effect, Horn and Merrill [53] established that fitting a conical funnel at the entrance from the feed solution reservoir. Bueche [42] demonstrated that in shear flows, the polymer molecule rotates along the principal axis of strain much too quickly, causing the flow to stretch. In elongational-types of flows, vorticity is much lower relative to the stretching and aligning actions of the strain than in shear flows, in relation to the strain of stretching and aligning actions. In these elongational flows, stretching is generally expected and scission of polymer molecules may occur.
2.2.2 Effect of Molecular Weight of Polymer on Drag Reduction

It is important to determine which property is mainly responsible for a polymer's drag reduction efficiency. The most important property is often believed to be the molecular weight but other properties may contribute as well, including the polymer's chain length, radius of gyration or hydrodynamic volume. The effect of a polymer's molecular weight on drag reduction is shown in Figure 3. As the molecular weight of a polymer increases, the onset of drag reduction occurs at a lower Reynolds number, which in turn implies greater drag reduction. The high molecular weight fraction of polyethylenoxide contributes more to drag reduction for a mixture of highly fractionated polymers than any other trait, as illustrated in the work of Gampert et al. [54].

Polymers with higher molecular weight fractions are believed to be able to interact with bigger vortices and are responsible for higher levels of drag reduction, as suggested by Hunston et al. [55]. The decrease in the overall turbulent dissipation of energy leads to higher values of drag reduction, according to Liberatore et al. [56], who systematically investigated the link between degradation and molecular weight distribution. Their results supported the notion that not only single molecules of the highest polymer molecular weight tail are responsible for drag reduction but polymer aggregates could also be important for drag reduction.

Figure 3: Drag reduction data for PEO with various molecular weight (Virk [8]).
2.2.3 Effect of polymer concentration on drag reduction

Polymer concentrations of as low as 0.02 ppm can create polymer drag reduction (Oliver and Bakhtiyarov [57]). An increase in polymer concentration results in an increase in drag reduction. Kim et al. [58] studied the concentration of different chemical additives on drag reduction. Their result is illustrated in Figure 4.

Figure 4: Effectiveness of synthetic polymers (PEO, PAM) and different polysaccharides in pipe flows, Kim et al. [58].

Figure 4 shows that a small amount of a polymer is needed to reduce drag in a solution. The figure demonstrates a large drag reduction attainable with various concentrations of natural and synthetic polymers. Research shows that drag reduction is at a maximum at a certain concentration for a given Reynolds number. Increasing the polymer concentration further after the maximum does not lead to an increase in drag reduction.
Figure 5 provides another look on the effect of polymer concentrations on drag reduction (Bewersdorff et al. [59]). The figure 4 shows a decreasing Fanning friction factor with increasing polymer concentrations, indicating an increase in drag reduction. It is worth noting that the friction factor increases after a certain Reynolds number value, a phenomenon which can possibly be explained by polymer degradation.

![Figure 5: Xanthane (Rhodopol 23) concentration influence on friction factor as a function of Reynolds number in water in a 5.2 m pipe [59].](image)

Litte [60] investigated the influence of polymer concentration and molecular weight on drag reduction. He found a general relation between polymer concentration and drag reduction for a certain Reynolds number value. The relationship is defined by

\[
\frac{C}{DR} = \frac{[C]}{DR_{\text{max}}} + \frac{C}{DR_{\text{max}}}
\]

where \( DR_{\text{max}} \) is the maximum level of drag reduction, \( C \) is the polymer concentration and \([C]\) is the intrinsic concentration (in wppm) defined by

\[
[C] = \frac{DR_{\text{max}}}{\lim_{C \to 0} \left( \frac{DR}{C} \right)}
\]
2.2.4 Effect of polymer degradation on drag reduction

Over the past few decades, extensive research on drag reduction has shown that there is no common model explaining the mechanisms corresponding to macromolecules that reduce polymer friction. Drag-reducing polymers are found to lose their effectiveness when subjected to an intense turbulent flow for sufficient amounts of time. These losses are due to the polymer degradation that is suspected to occur as a result of polymer chain and/or the breakdown of molecular aggregates. Some researchers observed polymer backbone scission (Rho et al. [61], and Choi et al. [62]) others the breakup of polymer aggregates (Cox R.H. et al. [63] and Malik et al. [64]). The different conclusions of various researchers could be explained by different shear rates in the testing apparatus. An experiment carried out under sufficiently low shear rates may reveal the presence only of aggregates while at high shear rates both aggregates and molecules may manifest themselves in reducing drag. The same polymer solution may therefore have quite different characteristics in experiments performed under different shear rates. Gadd [65] established the aging effect of polyethylene oxide (PEO) solutions on friction reduction was small at high concentrations. The results were obtained when the concentration fell to 10 ppm suggesting that large molecular aggregates were initially present but were broken because of aging. Elias [66] observed the aggregation of polymer molecules in solution. They showed that the degradation process is caused by breaking of polymer aggregates based on a free energy calculation. The result that was obtained in the experiments can not be reconciled with the breaking of chemical bonds and the degradation hypothesis, but it is in accord with disaggregation hypothesis.

Kowalski and Brundrett [67] developed macromolecular entanglement hypothesis based on measurements of the turbulent energy spectrum collectively with and without polymer solutions. Major changes in the dissipative scales correspond to much larger molecules than were nominally present but could correspond to large intertwined chains which entrap large amounts of the solvent. A large amount of evidence has been obtained for molecular aggregates (Dunlop et al. [68], Warholic et al. [69], Liberatore et al. [56] and Khan et al. [70]). Dunlop observed PEO and PAM samples at different MW and concentrations in rotating-disk apparatus. Their results showed that transient existence of aggregates was more effective than drag reducers in comparisons to individual polymer molecules. Virk [8] provided the results of a drag reducing solution of polyethylene oxide. He observed that the individual polymer molecules are involved at lower
volume fraction than entanglement aggregates. It is estimated that the volume fraction occupied by polymer coils is 0.1. This suggests that individual polymer molecules are involved at lower volume fraction than the entanglement concentration C*.

Warholic et al. [69] studied turbulent flow in a channel with heterogeneous polymer systems. They found different levels of DR at varied concentrations of injected polymer at constant mixed polymer concentration and Re. They suggest that aggregates form before injection, and that these aggregates have a positive effect on drag reduction.

Liberatore and his coworkers [56] observed a link between degradation and molecular weight distribution. Their experimental results also suggest the existence of aggregates of molecules. This could be important in understanding polymer drag reduction; the action of shear might be break up these aggregates rather than breaking up the constituent molecules.

Khan et al. [70] used light scattering to study aggregation. He found that aggregation occurred in low molecular weight samples; however, in higher molecular weight samples little evidence for aggregation both in water and methanol. Kim et al. [71] suggested that above concentrations of 3000 ppm, macromolecular aggregates should be present. This showed that when macromolecular aggregates are present, the drag reduction roughly doubles. They also found that onset Re is slightly higher for unstructured polymer solutions than for solutions containing aggregates.

Although some researchers have observed the polymer backbone scission others polymer aggregates break up (Den Toonder et al. [72] and Vanapalli et al. [73]). The various conclusions of researchers could be explained by different shear rates in the testing apparatuses. Kalashnikov [74] was capable of demonstrating the complex process of degradation, which depends on variables such as hydrodynamic variables, which describes the polymeric fluid in support of a single homogeneous continuum without consideration of the micro-domain structure. The hydrodynamic variables are in consideration of dimensionless parameters, the Reynolds number

\[ \text{Re} = \frac{\omega r^2}{v} \]

the Weissenberg number \( (We = \theta \omega) \) and the relative amplitude of the shear-thinning viscosity \( \left( \frac{\eta_0 - \eta_\infty}{\eta_\infty} \right) \).

Where \( \omega \) is the angular velocity of the rotor, \( v \) is the solvent kinematic viscosity of the fluid respectively, \( r \) is the radius of the cylindrical surface of the rotor, \( \theta \) is the natural time of the
polymer solution and $\eta_0$ and $\eta_\infty$ are the limiting viscosities at zero and infinite shear rates respectively.

In demonstration, Kalashnikov discovered in his earlier work [75] that the decisive role of these parameters for describing initial drag reduction was unchanged due to degradation in the flows when considering polymeric liquid. The study showed that degradation is determined by the characteristics of network structures of the solution although these characteristics have no direct impact on the initial drag reduction there was not observed a direct dependence on the individual properties of macromolecules.

Polymer degradation can usually be expressed using an exponential expression. Brostow [76] introduced an empirical model. He assumed a midpoint polymer chain scission in turbulent flow. Brostow model was adopted by many research groups [77, 78]. Brostow's model is given as:

$$\frac{DR(t)}{DR(0)} = \frac{1}{1 + W(1 - e^{-ht})}$$

(11)

Where DR(t) stands for level of drag reduction in time $t$ and DR(0) for initial drag reduction. Parameter $h$ is the decay constant and a large value of $h$ is in relation to the rapid degradation, and a larger value of $W$ indicates lower shear stability. The Brostow model was an empirical model over the past few decades for the polymer degradation or chain scission phenomenon. However, there has been no development in formulating a clear understanding of this. Recent evidence suggests that aggregates of molecules existed, but polymer degradation is suspected to occur through polymer chain scission and/or the breakdown of molecular aggregates, although this is also unclear.

### 2.3 Drag Reduction Behavior of Surfactants.

Drag-reducing surfactants have been successfully applied in industrial applications. Surfactants have an advantage over polymers due to their quick self-repairing ability after mechanical degradation and they can consequently keep the drag-reducing effect for a long time. This self-repairing ability of surfactants has great potential in district heating and cooling systems (DHC) for reducing pumping power.
2.3.1 Surfactant drag reducing additives

Drag reduction with surfactant additives was first studied by Mysels [79]. These kinds of additives have received less attention than other drag reducing additives, especially polymers. During the past years this has changed due to their self-repairing advantages and their ability to keep the drag-reducing effect over long periods of time. Many authors have reported that the surfactant molecules come together, forming rod-like micelles that are necessary for drag reduction. The drag reducing surfactant solutions are described with the presence of cylindrical micelles, which form above a critical micellar concentration. They are mainly effective within a certain range of temperatures and concentrations. The drag reduction correlates to the alignment of cylindrical micelles in the flow direction (Bewersdorff and Gyr [80]). To improve drag reducing power, it is possible to mix counterions with surfactants. Lin et al. [81] described that, by adding sodium salicylate (NaSal) to cetyltrimethyl ammonium bromide surfactant (CTAB) provided significant the drag reduction qualities. However, this solution lost solubility in an effective temperature range. When fluid temperature returns to the effective range, the drag reducing ability can easily be recovered.

\[
\text{Figure 6: The chemical structure of CTAB and NaSal.}
\]

2.3.2 Aggregation of surfactants

Surface-active agents or “surfactants” are molecule, having one hydrophobic group (nonpolar end) and one hydrophilic group (polar end). The nonpolar tail is generally made up of a long carbon chain. This unique structure makes it easy to modify physical properties. Having this particular chemical nature (hydrophilic and hydrophobic) in the same molecule causes the self-aggregation of the surfactant molecules when dissolved in water at concentrations above the CMC. These
aggregates are known as micelles [82]. The micelles are formed by the balance of two opposing forces: the attractive, tail–tail, hydrophobic interaction creates the aggregation of the surfactant molecules. Conversely, the electrostatic repulsion among the polar head groups decreases the size of the micelle. The environment of aggregates is found to be tuned by controlling solution conditions, such as temperature, concentration, and ionic strength. Many types of aggregates are formed, having a variety of shapes and sizes, such as spherical or ellipsoidal, cylindrical or thread-like micelle, disk-like micelle, membrane, and vesicles [83, 85]. It is worth studying the formation of these different structures because surfactant solutions are often used in various industrial and research applications [86]. The behavior of surfactants in aqueous solutions depends on concentration and temperature. Ekwall et al. [87] found that ionic surfactants generally form spherical micelles in dilute solutions. In solution with low concentrations, the molecules are present in the liquid in the shape of monomers. Once the concentration goes just above the first critical concentration "CMC₁," surfactant monomers associate forming spherical micelles. When the concentration is further increased, the number of surfactant molecules per micelle will increase and surfactants form rodlike micelles. The concentration at which surfactants form rodlike micelles is called CMC II [88]. As is shown in the figure 7, the critical micelle concentration (CMC₁) is almost independent of temperature, while temperature goes up, the value of the CMC II increases.

Figure 7: Critical micelle concentrations CMC₁ and CMC II [88].
2.3.3 Main classes of surfactants in drag reduction

The classification of surfactants depends on the chemical nature of the hydrophilic polar group. There are four distinguishable groups of surfactants:

- **Anionic**: ![Chemical structure of anionic surfactant]
- **Cationic**: ![Chemical structure of cationic surfactant]
- **Zwitterionic**: ![Chemical structure of zwitterionic surfactant]
- **Nonionic**: ![Chemical structure of nonionic surfactant]

These surfactants have been used as drag as drag reducing agents in many industrial and research studies. Savins [89] investigated drag reduction of anionic surfactants in aqueous media and obtained a reduction of more than 80%. However, anionic surfactants have limited applications because of their precipitation after the salt formation with the calcium and magnesium ions (Zakin and Jacques [90]) that are present in water. In addition, due to their tendency to form foams, anionic surfactants also cause some problems when exposed to air. This can cause complications in some systems that cannot handle the formation of foam. Thus they are not thought to be as good candidates as drag reducing agents. The drag reduction effect by anionic surfactants can be achieved at very high concentrations (about a few thousands ppm) [91, 92]. This situation creates high costs and severe environmental problems.

Cationic surfactants, unlike anionic surfactants, possess a positive charge in aqueous solutions. As opposed to anionic surfactants, these surfactants are not affected by metal ions found in tap water. Also, cationic surfactants have superior drag reduction results over a wide temperature range and therefore have larger potential for industrial applications. Other positive characteristics of cationic surfactants include relatively stability and self-reparability. Their major disadvantage is that they are not readily biodegradable, and this creates problems when leaks or spills occur [93].

Because cationic surfactants are not easily biodegradable, many researches focused on testing other types of surfactants that are more biodegradable with the intention of finding more environmental friendly surfactants with equal drag reducing ability. Zwitterionic surfactant and combinations of zwitterionic with anionic surfactants have been studied as drag reducers by many
researchers [94, 96]. Zwitterionic surfactants have both negative and positive charges on the molecule’s head group. As these surfactants have both charges, the surfactant molecule is sensitive to the presence of ions in water or solutions. This situation can reduce the stability of these surfactants. Beneficial characteristic of zwitterionic surfactants are biodegradability and low toxicity. Due to their environmentally friendly nature, if leaks or spills happen in the system, these additives can not represent an environmental risk.

Unlike the three, aforementioned surfactants, nonionic surfactants do not have charged head groups. These stable surfactants can self-repair quickly after degradation due to high shear. Zakin [90] noticed that nonionic surfactants, having straight chain alkyl groups were very effective. Moreover, mixtures of nonionic surfactants at 1% concentration effectively reduced drag at temperatures around the cloud point, which is the temperature where the phase separation of mixture starts to occur, thus becoming cloudy. Lu et al. [97] demonstrated that these kinds of surfactants are not toxic, and easily degradable. Like zwitterionic surfactants, nonionic surfactants have low toxicity and rapid biodegradability. A large number of studies have shown that the effectiveness of drag reduction depends strongly on surfactant type and temperature range. The investigations demonstrate that the surfactants’ unique structure makes them widely used in district heating and cooling systems and research applications.

2.3.4 Heat transfer reduction of surfactant drag reducing flow

Along with drag reduction, the heat transfer ability of surfactant solutions is also significantly reduced from 10 to 65% of heat transfer. The nature of the heat transfer reduction of drag reducing surfactant solutions is still not clearly understood. Many research studies that compared to Newtonian fluids, the viscous sublayer of drag reducing solutions is extended. Sellin et al. [94] suggested that the extended viscous sublayer increases the thermal resistance between the wall and bulk fluid. Therefore, the heat transfer effectiveness of the solution decreases. Moreover, the velocity fluctuations of drag reducing surfactant solutions in turbulent flow along radial and tangential directions are suppressed compared with Newtonian fluids [98, 100]. Authors have explained that the velocity fluctuations in the radial direction are strongly associated with a fluid’s heat transfer ability. Therefore, in the radial direction, the heat transfer is significantly decreased due to a reduction in the radial velocity fluctuations.
2.3.5 Rheologic behavior of surfactant drag reducing solutions

The knowledge of rheological properties of non-Newtonian materials is a key factor in understanding the nature of surfactants in solution. The drag reducing surfactant solutions have an unusual rheological behavior because of the presence of the micelles. Surfactant solutions with micellar structure present complex rheological properties such as shear thinning, shear thickening, viscoelastic and elongational characteristics [101].

Figure 8: (a) Viscosity of the surfactant solution measured in a Couette cell: two concentric cylinders spaced by 1 mm or 3 mm. Inset: visualization in the gap between crossed polarizers; the fluid becomes birefringent at the viscosity increase. b) The elongational viscosity [101].
The structure of surfactant solutions changes, when they self repair upon removal from high shear. When studying a solution’s behavior, it is necessary to look at its rheological properties. It is generally believed that the surfactant solution flows have viscoelastic characteristics and the drag reduction by surfactant additives is due to interaction between viscoelasticity and turbulence in the flow. Lu et al. [97] found that the certain surfactant solutions do not exhibit any viscoelastic character. Gyr and Bewersdorff [102] declare that elongational viscosity has a minor effect on the drag reduction. Furthermore, local shear-thickening is not a characteristic of pressure loss in drag reducing surfactants. Despite many studies on surfactant drag reducing flow, the precise nature of complex rheological features of surfactant systems is not fully understood and it still continues to be a challenging subject of controversy.

2.3.6 Shear induced structure (SIS)

Many research studies have been devoted to a solutions’ rheology of surfactants [103, 107]. The behavior of surfactant solutions changes as a result shear effects. The change in the rheological properties is explained by the formation of the micelles structure in the surfactant solution. It was observed that at high concentration, with quite long surfactants chains, the micelles can form complicated structures with three-dimensional forms. These superstructures are formed under the action of shear stress, and therefore the condition at which this happens, we call this shear-induced structure (SIS) phase a “gel” [105]. The precise nature of shear-induced structure is not clearly understood. It was examined that the rheological characteristics of this kind of solutions have an enormous industrial importance. Yunying Qi [108] explained this with a change in the structure of the micelles at a critical shear rate causing formation of a “shear induced structure”. A particular complex rheological behavior may occur for some surfactant solutions at a critical shear rate at which the shear viscosity and elasticity have a sudden increase. This phenomenon is known as shear induced structure (SIS). It has been observed that the sizes of these structures may be roughly twice the size of a surfactant molecule and a length that can be thousands of times the molecular size resulting in a large increase in viscosity [109]. The results show that with increasing shear rate, shear induced structure becomes unstable and viscosity begins to decreases with shear rate. Hu et al. [110] observed that the micelles are completely aligned in the direction of flow at the viscosity peak by the birefringence [111] and scattering methods, such a light
scattering (LS) or small-angle-neutron scattering (SANS) [112, 113]. From rheological behavior studies, it was noted that the critical shear rate for SIS is dependent on surfactant concentration, chemical structure, counterion, temperature, and geometry of the rheological measuring devices [108]. Several studies have been performed to determine the nature of shear induced structure. According to several authors, SIS of surfactants may relate to the drag reduction phenomenon in turbulent flow [114, 117]. They concluded that SIS is not a phase transition caused by the micellar alignment or elongation, but rather a shear induced inhomogeneity and phase separation. Despite numerous studies, the complex nature of SIS is not clearly understood. The relationship between SIS and drag reduction still continues to be controversial and needs to be further investigated.

2.4 Flow Properties of Drag Reduction Additives

2.4.1 Maximum drag reduction asymptote

One of the most significant characteristics of the data for polymer drag reduction is that there is a maximum drag reduction asymptote (MDA). The effectiveness of drag reduction by polymers is limited by the “maximum drag reduction asymptote”. Virk et al. [118] described the empirical laws in which all diluted polymer systems demonstrate asymptotic behavior. They found that the maximum drag reduction obtainable using DRA in turbulent pipe flow is limited due to the “maximum drag reduction” asymptote, which is a function of Reynolds number. The magnitude of DR increases with the DRA concentration in the system, until the MDR asymptote is reached. Subsequent addition of DRA to the system has not further effect on the frictional drag. Virk et al formulated the following correlation to data for the MDR friction factor. He described that the equation is the formula, which gives the maximum possible drag reduction asymptote, where the drag reduction is unaffected by polymer properties.

\[
\frac{1}{f} = 19 \log_{10} \left( \text{Re} \sqrt{f} \right) - 32.4 \quad \text{or} \quad f = 0.58 \text{Re}^{-0.58}
\]  

(12)
However, the surfactant drag reducer differs from the polymeric reducer, in several aspects particularly having a greater level of drag reduction that crosses the Virk’s maximum drag reduction asymptote. Zakin et al. [119] offered an alternative drag reduction asymptote for surfactant systems, demonstrating that this assumption probably does not always hold in its full generality.

$$C_f = 0.32 \text{Re}^{-0.55}$$

Thus, it shows that the effect is more complicated because different additives behave differently. It is still open to conjecture whether or not certain additives have their own MDA asymptotes.

### 2.4.2 Mean velocity profiles and turbulence structures

Drag reduction is accompanied by changes in the strength of the turbulent fluctuations and in the velocity profiles. Mean velocity profiles exhibit changes between a drag reducing polymer solution and a pure solvent. The velocity profiles are generally expressed in non-dimensional semilogarithmic coordinates of the fluid velocity $U+$ versus distance from the wall $y+$ defined as follows.
$U^+ = \frac{U}{u_\tau}$ \hfill (14) \hfill \quad y^+ = \frac{y u_\tau}{V} \hfill (15)$

where $U$ is the average local velocity at a distance $y$ from the wall and $u_\tau$ stands for the friction velocity. Figure 10 illustrates a typical representation of mean velocity profiles in flows with a drag reducing agent.

![Figure 10: Non-dimensional velocity profiles for a system with drag reduction (Virk [118]).](image)

The average local velocity alters with distance from the wall. As a result, the mean velocity profile for a Newtonian fluid can be divided into 3 regions:

**Viscous sublayer:** $u^+ = y^+$ \quad $y^+ \leq 5$

**Buffer layer:** $u^+ = y^+$ \quad $y^+ \leq 30$

**Logarithmic region:** $U^+ = 2.5 \ln y^+ + 5.5$ \quad $y^+ > 30$ \hfill (16)

The area between the viscous sublayer and the Newtonian plug is called the elastic sublayer. When maximum drag reduction occurs, the elastic area extends into the pipe’s center and the Newtonian region disappears. Virk’s maximum drag reduction asymptote is given by

$U^+ = 11.7 \ln y^+ - 17.0$ \hfill (17)
It is possible to compare the velocity profile of a drag reducing fluid to the model and to a Newtonian fluid at any Reynolds number. The ultimate profile for maximum drag reduction by polymers is also represented in a similar way. Based on the asymptote found for polymers, Virk proposed a model to describe the mean velocity profiles of drag reducing fluids in the turbulent region, analogous to those of Newtonian fluids.

Viscous sublayer: \( u^+ = y^+ \quad y^+ < 11.6 \)

Transition zone: \( U^+ = 11.7 \ln y^+ - 17.0 \quad 11.6 > y^+ < y_e^+ \) (18)

Turbulent core: \( u^+ = 2.5 \ln(y^+) - 5.5 + \Delta B \quad y^+ > y_e^+ \) (19)

\( \Delta B \) is the difference between the core and the profile for a Newtonian fluid and \( y_e^+ \) is the joint point of the elastic sublayer and the transition zone.

For the case of surfactants, Chara [120] proposed a model to describe the average profile of velocities in the limiting case of maximum drag reduction. The model consists of three different layers (Fig.11).

Viscous sublayer: \( u^+ = y^+ \quad y^+ < 15 \)

Transition zone: \( u^+ = 5 \ln(y^+) - 3.05 \quad 15 > y^+ < y_e^+ \) (20)

Turbulent core: \( u^+ = 23.41 \ln(y^+) - 65 \quad y^+ > y_e^+ \) (21)

Figure 11: Velocity profiles in wall coordinates for a flow with a Newtonian fluid and Non-Newtonian flow: polymers (Virk) and surfactants (Chara [120]).
Many authors have measured a turbulent velocity field when using additives. They investigated the turbulence in the flow using by Laser Doppler Velocimetry (LDV) (Hibberd et al. [121], Harder and Tiederman [122], Ptasinski et al. [123], and Kim and Sirbiente [124]). Measurements using Particle Image Velocimetry (PIV) are reported by Warholic et al. [125] and by White et al. [126]. The overall conclusion of PIV and LDV measurements is that, the addition of DRA gives rise to a decrease in the spanwise velocity fluctuations and a rise in streamwise fluctuations. This is illustrated by two examples in Figure 12. The figure clearly demonstrates that the addition of DRAs to a solvent increases the intensity of the streamwise fluctuation $\text{rms}(u_z^+)$ but on the other hand suppresses the spanwise turbulence fluctuation $\text{rms}(u_r^+)$. 

Figure 12 Results for streamwise and spanwise velocity fluctuations showing influence of polymer addition (Ptasinski et al. [123]).
2.4.3 Drag reduction in other geometries

Most of the drag reduction studies reported are concerned with straight channel flows. However, other systems have also been studied to understand the nature of the drag reduction mechanism.

Rotating disc cells. As shown in Figure 10, turbulent flows can be created by two counter-rotating discs (either with baffles or without baffles). Tests for this kind of apparatus are reported by Bonn et al. [127], Cadot et al. [128] and Sohn et al. [129]. They found that polymers hinder the formation of coherent-vorticity filaments while slowing the rate of formation of large eddies, for which high-vorticity filaments provide nuclei. Cadot et al. [128] discovered drag reduction for the smooth discs; however, they found no drag reduction for the baffled discs (see Figure 13). They concluded that the drag reduction effect happens in the viscous boundary layers. If there is no boundary layer (b), there is no DR. In this case, the dissipation of energy does not change even when the turbulent flow structure in the bulk is altered using polymers.

Figure 13: Schematic of counter-rotating cell apparatus with smooth discs (a) and with discs with baffles (b) (Cadot et al. [128]).
Grid turbulence. Using PIV with DRA solutions, Van Doom et al. [130] examined the turbulence decay behind a towed grid. Unlike pure water, the turbulent energy components demonstrate marked anisotropy and decay very slowly.

Coiled tubing (CT) has been used in the oil and gas industry because of various advantages. Zhou and Shah [131] have provided measurements of drag reduction in terms of coiled tubing. When compared with straight tubing, coiled tubing caused a delay in the onset of turbulence and drag reduction. Also, the effect of polymer concentration on drag reduction was small.

2.5 Mechanism of Polymer and Surfactant Drag Reduction

2.5.1 Theoretical studies of drag reduction

In the last 50 years, many papers have illustrated the experimental, numerical and theoretical aspects of drag reduction of turbulent flows by polymer additives. The explanation for drag reduction can generally be divided into two classes based on the proposed effects of polymer stretching on the flow. The first class focuses on viscous effects (Lumley [132], L’vov et al. [133] and Ryskin [134]), whereas the second class focuses on elastic effects (Tabor & de Gennes [135]). A review of drag reduction by additives is available in Lumley’s work. Lumley stated that stretching random coiled polymers would increase the effective viscosity. The increase of viscosity suppresses turbulent fluctuation and therefore it leads to reduce a wall friction and a thickening of the buffer layer separating the viscous layer. For given pressure gradient, this leads to increased flow, i.e., drag reduction. Little et al. [136] examined alternative mechanisms and supported the idea of elongational viscosity as suggested by Lumley. However, Bermann [137] studied many molecular models and concluded that the stretching of individual molecules to full length was not relevant. With the aid of scaling arguments and a model polymer, Ryskin [134] formulated an expression for effective viscosity increase as a result of polymer stretching in a turbulent flow. According to the derived expression, the effective viscosity is a function of polymer concentration and the largest extensibility of a polymer. Lumley and Ryskin therefore both state that drag reduction is due to an increase in the local effective viscosity of flow during hydrodynamic interaction between polymer chains and flow.
Subsequently, Tabor & de Gennes [135] proposed a new hypothesis, however, arguing that drag reduction is caused by a polymer’s elastic properties, rather than its viscosity. This was illustrated by experiments in which polymers were active at the centre of the pipe, where viscous forces do not play a meaningful role [138]. Tabor & de Gennes assert that the elastic energy stored by the partially stretched polymers is an important variable for DR and the increase in the effective viscosity is small and inconsequential. The elastic theory postulates that the onset DR takes place once when the cumulative elastic energy stored by the partially stretched polymers becomes comparable with the kinetic energy in the buffer layer at some turbulent length scale. Experiments [138] and numerical simulations [139, 140] have demonstrated that the elastic theory is effective in terms of being useful in the prediction of DR. According to the scaling arguments and experimental data, the time criterion requires that for DR to occur. It is important that polymer possess a longer relaxation time than a representative time scale of the near-wall turbulence $T_z$. The relaxation time, $T_z$, is defined as the average time it takes for a stretched polymer to reach its initial coiled configuration. Sreenivasan and White [138] used the following this relationship for relaxation time:

$$\frac{1}{T_z} = \frac{kT}{\eta_0 R_G^3}$$

(22)

Where $\eta_0$ is the viscosity of the solution, $k$ is the Boltzman constant, $T$ is the solution temperature and $R_G$ is the radius of gyration.

For flexible linear molecules, the radius of gyration is represented by:

$$R_G \approx N^{2/5} a$$

(23)

where $N$ is the number of repeating monomers in the molecule, and $a$ is the length of a single monomer. Sreenivasan and White declare that there is a turbulent length scale $r^*$ whose time scale $\tau^*$ matches $T_z$. The length scale is defined as:

$$r^* = u_r T_z$$

(24)

where $u_r^*$ is the velocity scale, given by Kolmogorov [141] as:

$$u_r^* = (r^* \langle \varepsilon \rangle)^{1/3}$$

(25)
where $\langle \epsilon \rangle$ is the average dissipation rate of the turbulence kinetic energy. Given a certain scale range $r^+<r<r^*$, elastic theory proposes that the polymers are stretched a little amount; therefore, they do not produce a reciprocal effect on the flow. Sreenivasan and White developed this concept to explain the phenomenological process of drag reduction in terms of the elastic model.

In more recent work, L'Vov et al. [142] and Benzi et al. [143] rationalized these concepts by constructing a model for drag reduction according to Reynolds averaged momentum and energy equations. The effect of the drag reducing polymers is closely related to the effective viscosity, which was shown to be negligible at the wall and increases with wall-distance. The drag reduction of polymer is therefore the result of the suppression of the Reynolds stress in the elastic sublayer. Numerical simulations [144] have shown that a space dependent viscosity model that varies linearly from the wall indeed produces drag reduction.

In fact, the paper by Cadot et al. [128] shows that the Tabor & de Gennes theory must be wrong, since they could assess that DR in a boundary layer effect.

Although, the first publications on drag reduction by additives dealt with on surfactant solutions, these kinds of additives have obtained less attention than polymers. Mysel [79] investigated the drag reduction in turbulent pipe flow using surfactant. He studied the effect of aluminum disoaps on gasoline flow. Savins [89] found 80% drag reduction could be obtained using a 0.2% Sodium Oleate aqueous solution with KCl as the counterion.

It was long believed that the mechanism of turbulent drag reduction by surfactants should be similar to that of polymers, implying that the phenomenon is due to a high elongational viscosity. Some investigations on drag-reducing surfactants stated that there is a strong correlation of high extensional viscosity with the drag reduction [145]; however, others report that its importance is negligible. A large number of researchers have proposed that viscoelastic effects of surfactant solution could be responsible for turbulent drag reduction. However, some drag reducing solutions, like surfactant ones, are neither viscoelastic fluids nor present an elevated elongational viscosity (Zakin [103], Lu et al. [97] and Lin et al. [146]). According to Gyr and Bewersdorf’s investigation [102], the shear induced structure can be responsible for drag reduction. Therefore, other hypotheses have been examined, such as local shear thickening (Guillou and Makhloifi [147]) or wall slip (Drappier et al. [148]). Bewersdorff & Ohlendorf [93] illustrated that the micro and integral scale of turbulence axial velocity fluctuations can increase when compared to Newtonian solvent. They demonstrated that this increase in the size of eddies could be due to an
increase in local viscosity resulting from the formation of the shear induced structures. During drag reduction, when the critical shear gradient is exceeded in surfactants, the formation of the shear induced state causes suddenly increase of the shear viscosity and elasticity. At the high viscosity peak, micelles are fully aligned in the direction of flow. This is confirmed by birefringence experiments [111] and a small-angle-neutron scattering (SANS) [112]. Accordingly, in the SIS, micelles must build up larger, super-order structures. The critical shear rate for SIS takes place at the onset of drag reduction [107]. It follows that drag-reducing surfactant solutions show increased shear viscosity at the buffer zone of a turbulent velocity profile.

In spite of the large amount of research into the drag reduction with additives, the nature of the drag reduction mechanism by which this occurs is not fully understood and it still continues to be challenging subject of controversy.
Bibliography


84. R Zana, Surfactant solutions: New methods of investigations (Dekker, New York, 1987)


