The role played by the aging of aloe vera on its drag reduction properties in turbulent flows

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Abstract

Polymeric drag reducers have been developed over many years due to the great number of practical applications. In all of them, the molecular stability is an essential requirement. Usually, polymers break down under turbulent flows, which causes a decrease in their efficiency as drag reducers. Besides that, some specific applications, in agro and biomedical fields, impose a specific requirement that must be fulfilled, which is the use of non-toxic materials. A suitable stable material that is elected to accomplish this necessity is the mucilage of aloe vera, which is a bio-polymer that can be used as an alternative to the synthetic ones. Here, we investigate the role played by the aging of aloe vera on its capacity to reduce drag. The results obtained by $^1$H nuclear magnetic resonance indicate that the compositions of young
and mature leaves of aloe vera are different and such a difference plays an important role on their efficiency as drag reducers. Tests were performed to analyse the drag reduction in a rotating apparatus and in a pipeline system and the efficiencies of leaves of different ages were compared to their composition. The main conclusion of these experiments is that the young mucilage samples, which are richer in complex polysaccharides and exhibit lower acid contents, are more efficient drag reducers.

**Key words:** polymer degradation, drag reduction, turbulent flows, complex polysaccharides

1 Introduction

When a very small amount of polymer, fiber or surfactant, is added to a turbulent flow, the drag eventually falls. This phenomenon has been studied since the pioneering works of [24], [66] and [39]. The number of practical uses is immense, including transport of liquid in ducts, firefighting operations, irrigation and medical applications [22, 14, 31].

The main aspects of the drag reduction (DR) phenomenon, including additive’s concentration, polymer’s molecular weight, solution’s temperature and Reynolds number, have been extensively analyzed by many authors. One can find a good overview in [69], [33], [56] and [70]. Up to now, there is not a generally accepted theory for the mechanism of drag reduction, despite the fact that researchers have contributed with many significant works, most of them following two main ideas, the viscous theory, defended by [33], and the elastic one, proposed by [64]. Other efforts to further understand the main

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mechanism of DR can be found in [19, 18, 9, 73, 65, 45, 6] and [44, 47, 48].

Regarding polymeric drag reducers, a huge obstacle to their practical use is the mechanical molecular degradation. There are many experimental evidences showing that, under extensional flows, the molecules are stretched and eventually break down, reducing the molecular weight and their efficiency as drag reducers [62, 60]. A pioneering work focused on the effects of polymer degradation on drag reduction is [43]. Refs. [27] and [67] also analyzed turbulent flows throughout straight tubes and, using gel permeation chromatography (GPC) results, they proved that polymers can really be highly degraded. For sure, there are many important variables that must be taken into account to understand polymer degradation in drag reduction applications. One remarkable paper in which some important variables like polymer concentration, molecular weight and the quality of solvent were treated all together is [37]. Similar analysis with polymer solutions, but using rotating geometries, can be found in [15] and [49]. Most of the works related to polymer degradation are experimental researches; it seems that the first attempt to numerically simulate the drop of DR efficiency by mechanical scission in turbulent flows comes from [46].

One way to avoid the mechanical degradation and, consequently, to increase the molecular stability is to use rigid polymers as drag reducers. Among the different rigid polymers, xanthan gum (XG), which is a polysaccharide obtained from the fermentation of the bacteria \textit{Xanthomonas campestris}, seems to be of particular interest in food, cosmetics and oil industry [23, 71]. XG has a linear structure similar to cellulose, which is responsible for its rigidity and stability [11].
According to [68], the DR mechanisms when flexible or rigid polymers are used are distinct. The author divided the DR mechanisms into two types, A and B. The former is associated with polymers that stay coiled at rest, the flexible molecules. Such materials need a certain level of turbulence to stretch and start to reduce drag. In contrast, the second mechanism is related to polymers that stay extended at rest, the rigid polymers. The main difference between the DR mechanisms for rigid and flexible polymers can be seen in terms of the Fanning friction factor in Prandtl von Kármán coordinates, which shows a weaker dependence on the Reynolds number for the rigid polymers.

The main characteristics of XG, a very known rigid polymer, as a drag reducing agent (DRA) were studied by several researchers such as [36], [38], [20], [72], [11], [29], [62], [45], [6], [60], [55], [7] and [45], using a rotating apparatus. Ref. [60], using a pipeline system, conducted many experiments with PEO (polyethylene oxide) and PAM (polyacrylamide), which are both flexible polymers, and with XG (a rigid polymer), to show that the latter does not really degrade mechanically. The authors argue that the observed drop of efficiency is related to another phenomenon, called de-aggregation, as stated by [57]. It is believed that the rigidity observed in XG is a fingerprint of many other natural polymers, as okra mucilage, and one of their great advantages with respect to the synthetic materials [16].

A number of applications of drag reducers, such as their use in agriculture and in the biomedical field, impose some specific requirements that must be fulfilled. The prospects of such kind of use have encouraged the study of natural non-toxic materials as an alternative to the synthetic ones. In this scenario, bio-polymers appear as the most promising alternative, including the aforementioned rigid polymer XG.
Another natural polymer used as drag reducer is scleroglucan gum, which is a polysaccharide obtained from the fermentation of the filamentous fungus *Sclerotin rolfsii* [29, 28]. Ref. [28] investigated the efficiency of this polymer in a circular tube and in a concentric annulus. By the measured values of pressure drop, they verified that the polymer is efficient as DRA and its behavior is similar to that of XG and other materials such as carbomethylcellulose (CMC). Such a similarity was in fact expected, since all these polymers are rigid materials and the DR mechanism is of the type B, as described previously.

Many researches have been directed towards the use of natural drag reducers obtained from plants. The processes to obtain such materials are considerably easier than those for XG and scleroglucan and they are available in large quantities in nature, which suggests that they can also be cheaper than commercially available materials. However, these natural DRA need to be further investigated.

Ref. [58] commented on the potential applications of natural polymers. The authors used banana peel synthesized and converted to CMC as DRA. According to the authors, the material is a good drag reducer. Ref. [50] performed some tests with guar gum, aiming to improve sprinkler irrigation and percolation in the soil. They observed that the irrigation area increased in addition to the decrease in the rate of infiltration, which is useful for areas with rain deficit. Ref. [63] also conducted tests with guar gum and analyzed the role of KCl salt on the shear stability. According to [25], polysaccharides produced from marine micro-algae are also able to reduce drag. Another natural material used as DRA is *Nata de Coco* [40, 54]. Mucilage extracted from okra can also be used as a natural DRA [1, 3, 5]. More recently, [16] and [61] used a
mixture of fibers and mucilage of okra as a natural DRA. The authors also verified the role played by the biological degradation of this material on DR efficiency.

The material we are interested to investigate in the present work is the mucilage extracted from aloe vera leaves. There are only few works related to the use of such material as drag reducer and most of them are related to medical applications.

Two pioneering and interesting studies using aloe vera as drag reducer were carried out by [32] and [34]. The authors used a resuscitation fluid (which has characteristics similar to blood) as solvent and the tests were performed on guinea pigs subjected to lethal hemorrhagic shock. The increase in survival rate with the use of the additive was clear. Ref. [53] also used aloe vera as DRA in the coronary arteries in guinea pigs and also observed a significant reduction in the mortality of the animals. Ref. [31] analyzed the use of aloe vera mucilage as DRA to produce hemodynamic effects in guinea pigs and observed that an increase in tissue perfusion can be obtained without increasing blood pressure, a fact of extreme importance for cases of severe bleeding.

Concerning industrial applications of aloe vera, we can cite the work of [2] who investigated experimentally the use of aloe vera mucilage as DRA in turbulent flow of water in ducts. The authors observed satisfactory results with the use of this material and the maximum drag reduction was 63 % for the concentration of 400 ppm. The results obtained by these authors show the potential of this natural material as DRA and strongly suggest it as an alternative for synthetic DRA and other natural bio-polymers. We show in the present work that the DR efficiency of aloe vera can be improved by the simple selection of leaves.
by age.

In fact, the goal of this work is to investigate the capability of aloe vera mucilage of different ages (extracted from young, intermediate and mature leaves) to reduce the friction factor. According to [13], the aloe vera gel (mucilage), contained in the inner part of the fresh leaves, consists primarily of water (> 98%) and polysaccharides (pectins, cellulose, hemicellulose, glucomannan, acemannan and mannose derivatives). This combination of polysaccharides is probably the key factor promoting drag reduction, but their composition changes as the leaves get older. The use of $^1$H nuclear magnetic resonance (NMR) spectroscopy for the analysis of the composition of the gel of aloe vera leaves has been frequently reported [13, 17, 30, 51, 52, 35]. The $^1$H NMR spectra of these materials are generally recorded in aqueous solution and show the signals expected for the main chemical constituents, with carbohydrates and organic acids representing the dominant organic compounds in the material. Among these, the occurrence of acemannan is of particular interest, since it is the major polysaccharide present in aloe vera gel and it is considered to play a significant role in the biological activity of this material, as reported by [35]. In the $^1$H NMR spectra, the occurrence of acemannan is identified by a group of signals in the chemical shift range between 2.0 and 2.3 ppm, associated with acetyl groups, which can be considered as a fingerprint of aloe vera-derived products [13, 17, 30].

In this work, $^1$H nuclear magnetic resonance (NMR) was used for the analysis of gels extracted from aloe vera leaves of different ages, aiming to identify the chemical changes occurred in the material upon maturation and to access the effects of these changes on the rheological properties exhibited by the material and on its capability to reduce drag. By doing so, we expect to go further in
the attempt to find a more efficient composition to be used as a natural drag reducer.

2 Material preparation and characterization

At first, we describe the criterion used to classify the leaves of aloe vera by age and to separate them into different groups (Subsection 2.1). In the sequence, we show in details how the aloe vera mucilage is extracted from the leaves (Subsection 2.2). In Subsection 2.3 we show how the rheological and chemical characterization was performed.

2.1 Separation of aloe vera leaves by age

The leaves of aloe vera were divided into three groups by age. We used a simple criterion based on length, thickness, width, area and color of the leaves to separate them into groups: young, intermediate and mature leaves [21, 8, 41]. Naturally, the dimensions of the leaves increase with time. Their color also changes from a light green to dark green. Table 1 shows the physical characteristics corresponding to each of the three groups of leaves classified in terms of the parameters mentioned before. The youngest leaves were characterized by a mean length of 25.6 cm, comprising leaves with length ranging from 21 to 28 cm. For the second group, called intermediate, the mean length of the leaves was 36.8 cm, comprising leaves ranging from 34 to 42 cm. Finally, the mean length of the group of mature leaves was 52.2 cm, comprising leaves with length between 47 and 58 cm. The thickness and width of each leaf are proportional to its length. The area of the mature leaves and, consequently,
their volume are significantly larger than the values corresponding to the other two groups. Hence, the amount of mucilage in these leaves is also much larger. Thus, if we randomly collect leaves to extract their mucilage, the sample will probably have more material from the mature leaves. We will talk about the consequence of this fact later.

Table 1
Parameters used to separate the leaves

<table>
<thead>
<tr>
<th>Samples</th>
<th>length (cm)</th>
<th>thickness (cm)</th>
<th>width (cm)</th>
<th>leaf’s area (cm²)</th>
<th>color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young</td>
<td>25.6</td>
<td>1.1</td>
<td>2.9</td>
<td>41.3</td>
<td>light green</td>
</tr>
<tr>
<td>Intermediate</td>
<td>36.8</td>
<td>1.6</td>
<td>4.3</td>
<td>96.5</td>
<td>green</td>
</tr>
<tr>
<td>Mature</td>
<td>52.2</td>
<td>1.9</td>
<td>5.5</td>
<td>338.3</td>
<td>dark green</td>
</tr>
</tbody>
</table>

2.2 Material’s Preparation

For the aloe vera mucilage extraction, the plant was washed and the outer leaf removed. The inner leaf stores the mucilage that was used as drag reducer. The outer leaf, which was not used in the present study, is a byproduct rich in fibers and can also be used as drag reducer [59]. In order to extract the mucilage from the inner leaf, it was ground to release the gel. After that, the gel was filtered so that only the mucilage remained in the process. Fig. 1 illustrates the steps of the process: the aloe vera leaf in its integral form (A); extraction of the outer leaf (B); the inner leaf (C); the grinder used to break the gel structures (D); filtering of the solution using tissue (E); sieves used (F); last filtering of the solution (G); and the concentrated mucilage in its
Fig. 1. Aloe vera mucilage extraction process.

The gels extracted from young, intermediate and mature leaves were characterized in a rotating rheometer to obtain the shear viscosity $\eta$ as a function of the shear rate $\dot{\gamma}$ for a range of concentrations at a temperature of 25 °C. Details concerning the rheological characterization can be found in [49] and [45].

For the chemical characterization, immediately after extraction, the gels obtained from the aloe vera leaves of three different ages (young, intermediate and mature) were first diluted with deionized water to a fixed concentration of 8000 ppm (m/m). These solutions were then frozen and stored in a freezer; prior to the NMR experiments, the samples were left overnight to warm up to room temperature. From the obtained solutions, 350 µl were taken and
added to 350 μl of deuterated water into a 5 mm NMR sample tube. The $^1$H NMR experiments were performed at room temperature in a Varian-Agilent spectrometer operating at 399.73 MHz (9.4 T magnetic field), equipped with a 5 mm broadband probe. The pulse sequence consisted in a 2 s long, low-power pre-saturation pulse in order to suppress the water signal [26], followed by a $\pi/2$ excitation pulse with duration of 11.8 μs, the recording of the free induction decay (FID) for an acquisition time of 1.2 s and a recycle delay of 3.8 s. The spectral window was set to 6410 Hz and the number of transients was 128. The spectra were obtained by Fourier transform of the FID, with all chemical shifts referenced to tetramethylsilane (TMS).

3 Experimental setup

The tests of drag reduction were carried out in two distinct experimental apparatus: a) a system with rotating geometry and b) a pipe system. In the first one, the amount of material is very small and the measurements are very precise and fast, but the Reynolds number is not very high, much lower than the value found in practical applications. Such an unfavorable circumstance is surpassed when we use our second approach, a pipe system. In fact, we used the rotating apparatus for preliminary tests before producing a large amount of material to be tested in our pipe system. It is worth noticing that our tests were carried out at fixed Reynolds number, $Re$, and temperature. Hence, the values of viscosity used to determine $Re$ are those corresponding to the same temperature of the test.
The DR values were calculated by Eq. (1),

$$DR = 1 - f_p/f_0.$$  \hspace{1cm} (1)

Where $f_p$ and $f_0$ are the friction factor of the polymeric solution and solvent, respectively. The two approaches are described in the sequence and the definition of each parameter will be given properly with respect to each geometry.

3.1 Rotating apparatus

The rotational rheometer has a cylindrical double gap device. The main details concerning this geometry and procedure were discussed in [49] and [45] (see Fig. 1 A in [49]). Hence, we will describe here only the essential details for the understanding of the present work.

The Reynolds number, $Re$, and the friction factor, $f$, are defined by Eqs. (2) and (3), respectively,

$$Re = \frac{\bar{h}u}{\eta} = \frac{\rho \left( \bar{h} \right) \left( \omega \bar{R} \right)}{\eta},$$  \hspace{1cm} (2)

$$f = \frac{2\tau}{\rho u^2} = \frac{2\tau}{\rho \left( \omega \bar{R} \right)^2}.  \hspace{1cm} (3)$$

Where $\eta$ is the solution’s viscosity, $\omega \bar{R}$ is a characteristic velocity, $\omega$ is the rotor angular velocity, $\bar{R} = (R_2 + R_3)/2$ is the mean radius and $\bar{h}$ is the average gap given by $\left( (R_2 - R_1) + (R_4 - R_3) \right)/2$. Since the bio-polymer solutions exhibit shear thinning behavior, even for low concentrations, $\eta$ is the Newtonian plateau at high shear-rate, $\eta_{\infty}$. 

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3.2 Pipe system

The pipe system was the same used in [60, 55, 16] (see Fig. 1 in [60]). The mucilage is deposited in the storage tank and after 3 h of mixing the solution goes directly to a vessel. The vessel is connected to a centrifugal pump, which works at a constant flow rate. The path from the vessel to the test section was constructed to minimize any local material degradation or de-aggregation [60]. A magnetic flowmeter was placed at a point where the turbulent flow was fully developed. Static pressure transducers were placed on the right side of the flowmeter in a polished stainless steel tube with well controlled internal diameter. After all the solution, initially in the pressure vessel, has passed through the pipeline, with total length of 13.5 m, it is sent to the storage tank. The main section of test \( A - A' \) has 593 diameters. The tubes were thermally insulated to minimize heat transfer, and the test temperature was kept constant at 25 °C. The flow rates, the values of the static pressures at the test section and the temperatures, at different points of the experiment, were collected simultaneously by a data acquisition system (using the LabVIEW platform, from National Instruments).

When the total amount of solution, initially in the pressure vessel, had passed through the pipeline, one round was finished. After that, the solution, now partially de-aggregated, returns to the pressure vessel from the storage tank by gravity, in a very slow motion, to avoid any uncontrolled polymer degradation or de-aggregation (here mainly de-aggregation), and, finally, one cycle has been completed and the same solution is then used for the next cycle. The value of the solution’s friction factor was calculated at each step and the test continued until no significant change in \( f \) was observed. In most cases, less
than 30 steps were necessary to reach the steady state.

For a given flow rate, the Darcy friction factor is calculated by

\[ f = \frac{2D}{\rho \bar{u}^2} \left( \frac{\Delta P}{L} \right). \tag{4} \]

Here, \( \Delta P \) is the pressure drop between a pair of pressure transducers placed in the test section and \( L \) is the distance between them. \( D \) is the tube diameter, \( \rho \) is the density of the solution and \( \bar{u} \) is its mean velocity over the test section. The Reynolds number is defined, as usual, as

\[ Re = \frac{\rho \bar{u} D}{\eta}. \tag{5} \]

Here, as previously pointed, \( \eta \) is the solvent’s viscosity at high shear rate.

4 Main results

Before running the tests to evaluate the DR efficiency of the solutions prepared with aloe vera leaves of different ages, the rheometric and chemical characterization of the material was carried out. The flow curves for the young, intermediate and mature leaves mucilage solutions are displayed in Fig. 2 A, B and C. The mucilage clearly exhibits shear thinning behavior even for the least concentrated solution of 50 ppm. The viscosity \( \eta \) strongly drops as \( \dot{\gamma} \) increases, but reaches an asymptotic value, a Newtonian plateau \( \eta_\infty \), when the shear rate is high enough. It is important to note that the flow curves \((\eta \times \dot{\gamma})\) do not significantly change as the leaves get older. In fact, \( \eta_\infty \) is quite the same for all tested samples. Solutions with concentrations equal to or below 500 ppm have \( \eta_\infty \) close to the water’s viscosity, 0.001 Pa.s, which is
Fig. 2. Shear viscosity as a function of shear rate: (A) young leaves; (B) intermediate leaves; (C) mature leaves.

quite good. Hence, despite the clear changes in the gel composition by aging, the value of its viscosity at high shear rates was almost the same. In fact, for practical applications, it is very desirable to have a concentrated solution with low viscosity, which will obviously facilitate the process of injection of the concentrated solution into the pipelines, since it is the most common way
Fig. 3. $^1$H NMR spectra obtained for Aloe vera gels extracted from leaves of different ages. The spectral regions indicated as I and II correspond to signals attributed to acetyl groups in acemannan and to groups belonging to several organic acids (e.g., malic acid, succinic acid, citric acid, pyruvic acid), respectively.

to apply drag reducers in industry.

Concerning the chemical characterization, Fig. 3 shows the $^1$H NMR spectra recorded for the gels extracted from aloe vera leaves of different ages. Even after using a pulse sequence with a pre-saturation pulse, all spectra were dominated by a strong peak associated with water (4.6 ppm). Signals due to common carbohydrate groups are observed in the region from ca. 3.1 to 4.2 ppm, besides an isolated signal attributed to glucose at 5.2 ppm. The characteristic signals associated with acetyl groups in acemannan are in the range from 2.00 to 2.22 ppm; this spectral region is indicated as I in Fig. 3. A number of organic acids (e.g., malic acid, succinic acid, citric acid, pyruvic acid) give
signals in the region from ca. 2.3 to 3.0 ppm (region indicated as II in Fig. 3); malic acid also has a signal at 4.3 ppm, whereas acetic acid and lactic acid have signals at 1.9 and 1.3 ppm, respectively. The relative intensities corresponding to spectral regions I and II in the $^1$H NMR spectra displayed in Fig. 3 change slightly with the leaf age. As it can be observed, there is an increase in the relative contribution of II (i.e., organic acids) in detriment of the contribution of I (i.e., acemannan); this is especially clear in the case of the mature leaves, where the contribution of II is clearly higher than in the other spectra. Thus, the $^1$H NMR results suggest that the aging process causes a reduction in the relative amount of acemannan and other carbohydrates present in the aloe vera gels. This finding is similar to the previously reported changes in the amount of acemannan present in aloe vera gels submitted to different drying procedures or derived from plants with different ages or collected at different seasons [51, 35]. Also, the detection of organic acids such as succinic acid and lactic acid has been previously considered an indication of the degradation of polysaccharides present in aloe vera gels [13]. This observation is especially relevant considering that the presence of polysaccharides such as glucomannans and galactomannans has been associated with the viscoelastic properties of plant-derived gels, which is essential for the drag reduction properties of the polymers [42, 12]. Hence, as the amount of organic acids increases, a decrease in the drag reduction efficiency is expected, as it will be discussed in Section 4.

In order to certified that the solutions used to carry the tests were homogeneous, the first analysis, conducted in our rotating apparatus, was an attempt to determine the period of time necessary to have a completely diluted solution and it is displayed in Fig. 4, where the nominal shear viscosity (mPa.s)
Fig. 4. Shear viscosity as a function of rotor angular velocity: a procedure to determine the required time to have the total homogenization of the sample.

is plotted as a function of the rotation speed (rpm). Below 500 rpm, the flow is laminar and we see \( \eta \) falling with the increase in the rotor’s velocity, until reaching an asymptotic value, which characterizes the shear thinning behavior. Above such value of rotation speed, the flow becomes unstable and eventually turbulent and the apparent viscosity increases on account of turbulence. We tested many different resting times for the 460 ppm solution at 25 °C and it seems that 90 min (blue circles) is a period long enough for the complete homogenization. Most of our tests were carried out with less concentrated solutions, which typically have a faster dilution. Hence, we waited always 90 min before starting each test.

Concerning the pipe system, we undertook preliminary tests in order to verify the instrument accuracy (mainly regarding the flowmeter and the pressure transducers), at the same way we have done in [60, 55, 16]. The Darcy friction
factor for pure water as a function of Reynolds number fits quite well with Blasius correlation, in which \( f = 0.316Re^{-0.25} \). The errors are smaller than 3\%, which is satisfactory for our task. These tests are not shown here (please see Fig. 2 in [60]).

Fig. 5. DR as a function of the number of passes in the pipeline for a range of concentrations of mucilage of aloe vera. Here the leaves were not divided according to their ages.

In Fig. 5 we show our first DR test for aloe vera gel randomly extracted from young, intermediate and mature leaves, as commonly done by other researchers. By doing so, the total amount of such a sample is mainly composed of gel from mature leaves, since their area and, consequently, their volume is much larger than that of the other groups of leaves (as described in Table 1). As expected, the drag reduction increases as the concentration of DRA in the solution is increased. This aspect of the DR effect of polymers is widely known and has already been reported by many authors such as [33] and [69].
Especially for studies of natural polymer drag reducers extracted from aloe vera plants, many authors also reported the increase in DR with the increase of concentration [32, 2, 31]. From the results presented in Fig. 5, the drag reduction reaches a maximum value $DR_{\text{max}}$ in the first pass (one round throughout the pipe system, as described in Subsection 3.2) and decreases with the number of passes until reaching the asymptotic drag reduction value $DR_{\text{asy}}$. As the concentration increases, the value of $DR_{\text{max}}$ tends to be closer to the maximum drag reduction asymptote (MDR), Virk’s asymptote, which in this case assumes a value close to 80% of drag reduction. The maximum DR observed was approximately 71% for the 1600 ppm concentration.

Still referring to Fig. 5, for 200 ppm (we will use this concentration to test our three different samples, i.e., the samples obtained from young, intermediate and mature leaves), DR starts from 30% and reaches 20% after 30 passes. A fact that was not sufficiently pointed out yet is concerned to the aloe vera stability and it is worth noting here. The loss of DR is not very accentuated as commonly seen in flexible polymers such as PEO and PAM, in which the breakdown of the molecular chains plays an important role on the process, see [45]. The aloe vera mucilage, like xanthan gum, guar gum and okra, is a rigid material and does not degrade mechanically. It is believed that the loss of efficiency is caused by the de-aggregation and not by the degradation of the molecules, an aspect that has already been reported by [60] in their studies with xanthan gum. In addition, even the loss of efficiency by de-aggregation is very small for the aloe vera solutions, much smaller than the loss that occurs for xanthan gum and okra solutions, reported, respectively, by [60] and [16]. A maximum variation $\left(\frac{DR_{\text{max}} - DR_{\text{asy}}}{DR_{\text{max}}}\right)$ of 7% was verified for the concentration of 800 ppm. This shows once again that the loss of efficiency
of the material due to the de-aggregation mechanism is really low. As stated before, the low loss of efficiency is a fingerprint of natural polymers, but in the case of the gel from the aloe vera studied here, this is really remarkable.

One final comment on Fig. 5 is concerned to the DR value for the 1600 ppm solution, which shows a quite negligible drop with the increase in the number of passes. Such behaviour is a great advantage of the DRA studied here, in comparison with flexible polymers and other commonly used bio-polymers, mainly when we deal with transport of liquids through long distances.

We will show in the next figures our main goal. Precisely, we verify the drag reduction ability of our three groups of leaves, called young, intermediate and mature. We will show that the efficiency of the mucilage can be substantially increased by carefully selecting the leaves of aloe vera. More than that, since we have the main composition of the gel, we can identify, or at least, have an idea about the components that play the most important role on drag reduction process. We believe that could be a method to find a more efficient natural drag reducer and it can be applied to any kind of bio-polymer.

For the purpose of saving material, we initially conduct tests using a rotating apparatus, in which DR is displayed as a function of time. The data for the concentrations of 200 ppm and 460 ppm are shown in Fig. 6 (A) and (B). The tests were carried out at fixed Reynolds number, Re = 1360, and temperature, T = 25 °C. In both cases, DR increases with time until reaching a maximum value, which is maintained over most of the remaining part of the test. Such a transient behavior of DR is very quick, taking less than 5 s, and, hence, it is very difficult to be captured in pipe systems. The time to reach the steady state, the developing time, was experimentally analyzed in details by [6] and [7]
Fig. 6. DR as function time for Re fixed in 1360. In (A) the concentration is 200 ppm and in (B) the concentration is 460 ppm. The sample is divided into three types: mature; young and intermediate.

and this effect was also numerically studied using direct numerical simulation by [44]. The developing time observed here is of the same order of magnitude of that observed for xantham gum reported by [7], less than 5 s. It seems that
a quick developing time is another fingerprint of rigid drag reducers, like the bio-polymers from aloe vera gel. No significant loss of efficiency was observed, in contrast with the results previously shown in Fig. 5. This is probably due to the level of turbulence, which is much smaller in our rotating apparatus than in our pipe system.

It is worth noting the clear difference in efficiency obtained with mucilage from young and intermediate leaves in comparison to that from the mature leaves. The DR values for 200 ppm concentration solutions, Fig. 6 A, for young and intermediate leaves (black squares and blue circles) were around 8.5 % while for the mature leaves it was below 5 %. The young group was 60 % more efficient than the mature one, which is a significant improvement on DR. Similarly, for 460 ppm, Fig. 6 B, the DR for the group of young and intermediate leaves was around 12 % and for the group of mature leaves it was 9 %. For such a concentration, the improvement of efficiency was around 30 %. It is important to observe that the absolute values of DR obtained here are not expressive because the maximum drag reduction for this geometry is around 22 %, as reported by [49]. The authors tested different polymers, Reynolds number, concentration, molecular weight and temperature before reaching a MDR law for this geometry.

Figure 7 shows the results obtained with our pipeline system, in which the level of turbulence, expressed in terms of Reynolds number, is much more pronounced. The tests were conducted at a fixed Reynolds number (Re = 91,113) and concentration of 200 ppm. The de-aggregation now plays a role and DR falls in the first 10 passes. Again, the mucilage samples obtained from the young (green circles and gray crosses) and intermediate leaves (gray triangle
Fig. 7. DR as a function of the number of passes in the pipeline for 200 ppm of mucilage. The sample is divided into three types: mature; young and intermediate. and blue circles) are clearly more efficient, with DR above 30 %, in comparison to the samples obtained from the mature leaves, with DR around 20 % (black squares and red diamonds). In fact, the young group was 70 % more efficient than the mature group, which is worth noting. As expected, since the chemical compositions of the young and intermediate groups are similar, their ability to reduce drag is not significantly different. The $^1$H NMR spectra show that the amount of organic acids present in mature leaves is clearly more pronounced than in the other groups, in detriment of the amount of acemannan (region I in Fig. 3) and other common carbohydrates. Hence, there is an apparent correlation between the relative amount of acemannan (corresponding to spectral region I the spectra shown in Fig. 3) and other polysaccharides with the efficiency of drag reduction. The decrease in the amount of polysaccharides in the mature group is apparently associated with the corresponding reduced DR efficiency; this finding can be understood considering that the polymers with
Fig. 8. DR as a function of the number of passes in the pipeline for 200 ppm of mucilage: comparison between different bio-polymers.

High molecular weights are responsible for drag reduction in turbulent flows. The detailed understanding about which component plays the most important role in the DR mechanism is beyond the scope of the present investigation and is deferred to future work. A first candidate to be further investigated is ace-mannan, since it is one of the main components of the aloe vera gel and its amount is apparently reduced in the mature group, as discussed before.

Fig. 8 shows a comparison between the mucilage from young leaves (blue circles) and other bio-polymers, okra and xantham gum. The data for these two materials come from [16]. The final value of DR for the sample obtained from the young group of aloe vera leaves with 200 ppm concentration was close to 34 %, three times larger than that for okra, which was around 10 %. The young group is substantially more efficient than the mixed group (red diamonds), which is, in fact, predominantly composed by mature leaves. As pointed out...
before in Subsection 2.1, the size of the mature leaves is much larger than that of the other groups and, consequently, the amount of gel from this group is predominant when leaves are randomly selected. It is interesting to note that we obtained, with 200 ppm of mucilage from young leaves, the same value of DR obtained with 400 ppm of mucilage from mature leaves (in fact mixed leaves in this case). Now it is really remarkable that the efficiency obtained with our youngest group was quite close to that obtained with XG, a bio-polymer greatly used in many industrial applications. In fact, the asymptotic DR value obtained with young aloe vera was 89 % of that obtained with XG. With such a large efficiency, quite close to that of XG, the selected gel of young aloe vera leaves (which are richer in acemannan) appears indeed as a good alternative for practical applications. Moreover, we clearly see in Fig. 8 that XG (purple triangles) is less stable than the aloe vera (blue circles). In other words, the drop of efficiency by de-aggregation is more pronounced for XG. It value of DR falls from around 60 % to 40 %, which corresponds to a relative drop of efficiency $DR' = DR_{asy}/DR_{max} = 0.66$. At the same time, for 200 ppm of aloe vera $DR'$ was 0.77.

As mentioned before, studies of drag reduction using mucilage of aloe vera are quite scarce. Among the few available data are those reported by [4]. The authors investigate the efficiency of this natural bio-polymer to reduce drag in turbulent flows at high Reynolds number. In Table 2 we draw an analogy between their data and our own. The maximum drag reduction obtained by [4] was close to our DR for the mature group, around 27 %. Supposedly, the authors have used randomly selected leaves and, as stated before, the amount of gel is expected to come mostly from the mature leaves, which is once again a further evidence that the young leaves are more efficient. It is
Fig. 9. DR as a function of time in the rotating apparatus for 200 ppm of mucilage: biological degradation.

It is worth noting that the Reynolds number and tube diameter used in this work are different from those used by [4]. Hence, a direct comparison is not possible in this case. However, if we consider that aloe vera is a rigid material, in which the mechanism of DR is classified as Type B, we could say that the Reynolds number is not expected to play a significant role, as reported by [11, 10, 29, 45].

Table 2

An analogy between our data and those reported by [4]

<table>
<thead>
<tr>
<th>This work</th>
<th>Abdulbari et al. (2011)</th>
</tr>
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<tbody>
<tr>
<td>Re=91,000; d=1.63 cm</td>
<td>Re=38642; d=2.4 cm</td>
</tr>
<tr>
<td>Mature intermediate young mixed</td>
<td></td>
</tr>
<tr>
<td>28.4 % 39.3 % 43.4 % 27 %</td>
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Natural polymers are quite susceptible to bio-degradation. In Fig. 9 we see how such a degradation works in the different group of leaves. The tests were carried out with gels of 200 ppm from young and mature leaves in the rotating apparatus at Re and temperature fixed at 1360 and 25 °C, respectively. Samples of the two groups of leaves were left at room temperature and the tests were carried out in each of the three (or more) consecutive days. In three days the DR of the young group dropped from 0.0875 (blue circles) to 0.065 (green crosses), 25 %, while the DR value of mature leaves dropped from 0.05 (red diamonds) to almost zero (black squares). Thus, the mature group totally degrades in three days. In six days, the DR of the young leaves mucilage was around 0.03. Only after 9 days this group was totally biologically degraded (orange full circles). The accelerated bio-degradation of the gel from mature leaves is probably related to the relative amount of acids already present in the samples of this group.

Finally, it is worth emphasizing that the main reason for the young and intermediate leaves to be more efficient is apparently related to the relative amount of complex polysaccharides present in these two groups, as indicated by the $^1$H NMR spectra in Fig. 3. The relative intensity of signals due to organic acids (malic, succinic, citric and pyruvic acid) clearly increases with the leaf age. At the same time, the intensity of the signals due to common carbohydrate groups and specially acemannan falls. Hence, the more efficient group, the young one, has less acids and, consequently, is richer in complex polysaccharides, including the acemannan.
5 Concluding remarks

The role played by the aging of aloe vera gel on drag reduction in turbulent flows of water in a pipe system and in a rotating apparatus was analyzed in the present work. The $^1$H NMR spectra shows that the aloe vera composition changes with the leaves age. The amount of organic acids is significantly more pronounced in the mature group of leaves in detriment of the amount of complex polysaccharides, including the acemannan. Tests of drag reduction in both apparatus reveal that the gel from the group of leaves richer in acemannan, the young group, is more efficient than the gel from the other groups. Precisely, the asymptotic drag reduction of the young group with concentration of 200 ppm in the pipe system is considerably more efficient than that of mature group for the same concentration, $DR_{asy}^{young} = 1.5 DR_{asy}^{mature}$. To achieve the same level of DR with gel from mature leaves one must double the concentration. Such high efficiency reached with the gel richer in acemannan is comparable to that obtained with xanthan gum, a very popular natural drag reducer. We believe we can accomplish a natural drag reducer even more efficient and stable isolating some polysaccharides present in the aloe vera gel, with acemannan being the most suitable candidate to play such a role.

Acknowledgements

This research was partially funded by grants from CNPq (Brazilian Research Council) and FAPES (Espírito Santo State Research Foundation). The authors are also grateful to the Laboratory for Research and Development of Methodologies for Crude Oil Analysis (LabPetro), Federal University of Espírito Santo.
(UFES), for the use of experimental facilities.

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