Experimental and Pilot Investigation of The Impact of Drag Reducing Agents on Filter Performance

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ABSTRACT
Drag reducing agents (DRA) are commonly used chemicals in the process and pipeline industry. The unique properties of DRA allow for the reduction in friction and turbulence at the pipe wall, which reduces pumping and transportation costs for both raw crude and refined products. Most of the DRA that is injected into product pipelines is assumed to be sheared into small molecules via turbulence induced polymer chain scission by the time it reaches its destination which eventually renders it ineffective for drag reduction. Although this may sometimes be the case, often unsheared or partially sheared DRA persists in hydrocarbon products which may cause problems for end-users. DRA has been cited as the culprit for issues with clogging of fuel injectors and fuel filters. Problems of this nature have been reported by end-users of diesel and aviation fuel products. As a result, it is often in the best interest of refiners and fuel wholesalers to ensure that their products have minimal to no persisting DRA contamination prior to sale. Filtration is one viable method of lowering the DRA concentrations in fuel products, however the impacts of macro-molecular DRA on filter life and performance is not well understood. To this end, a study was conducted to investigate the impact of hydrocarbon-based DRA on the filtration systems. A method to characterize the level of DRA contamination in product fuel, the polymer filtration index (PFI), is presented and utilized to benchmark the performance of a media filter. Impacts of DRA on filter life and removal efficiency are discussed from an industrial perspective. In light of the findings, a discussion on filtration as a method for the removal of DRA from diesel fuels is presented.

1. Introduction

Drag reducing agents (DRAs) are commonly used in industry during the transportation of crude and refined product fuels. Most often, DRA is composed of long-chain polymers that are soluble in the pipeline fluid. In the case of water and sewer transmission these are often polyethylene oxide and polyacrylamide compounds, while for hydrocarbon fuels α-polyolefins are used (*1*, *2*). The molecular structure of DRA allows for expansion of the viscous sub-layer which reduces near-wall turbulence, friction, and pump energy losses (*3*).

The exact mechanics of drag reduction are still being explored. The formation of an elastic polymer layer above the viscous wall-layer is known to contribute to the

frictional reduction by providing a buffer between the main turbulent core of the flow and the wall. In fact, it is postulated that this elastic layer absorbs some of the turbulent energy that is generated by the flow, thereby reducing the overall turbulent stresses felt by the pipe wall (*4*). Lumley postulated that the polymers uncoil in the flow and are able to expand the viscous sub-layer, thereby limiting near-wall turbulence (*5*). As the turbulent energy cascades through the smallest turbulent length scales, this energy can be absorbed by the DRA molecules either through molecular movement or by chain scission in which the polymer itself is broken into smaller chains (*6*, *7*). Sher et. al. (2008) proposed a mechanistic model of needle-like polymers which absorbed energy via centrifugal motion thereby altering the velocity profile primarily in the range of $10 < y^+ < 100$ (*8*). This model was shown to predict the data of Virk (1975) with good results(*7*). Although polymeric degradation can occur via chemical attack due to oxidation or salinity, most of the degradation has been attributed to mechanical shear forces that steadily break the DRA into smaller molecules, eventually rendering the drag reduction ineffective (*9*). The time required for the chain scission process to completely degrade the polymer depends upon the turbulence level, solvent properties, and original chain length. Studies have found that the process can be described quite well by the exponential decay model which accounts for length of time and turbulence level (*6*, *10*). On a whole, the level of shear experienced by DRA is difficult to predict in practical pipeline situations. In practice, the pipeline performance curve is used to adjust dosing which may lead to higher DRA concentrations than are desired once the product reaches a terminal.

Although these molecules are critical for efficient pipeline transport, DRA has been identified as a cause of fuel filter and fuel injector fouling in automotive and aerospace applications (*11*). Some authors have also noted challenges with heat exchanger and reactor fouling when the DRA enters a plant in the crude feedstock (*12*). This fact has led to prohibitions on the presence of DRA in aviation fuels (*13*). The U.S. Air Force was one of the first to note the detrimental impacts of DRA on the fuel quality and fouling tendencies in aerospace fuels. They noted that persisting DRA in product fuels lead to increased carbon deposits and gum residue on injector and engine internals (*14*). Additionally, they noted similar effects with DRA in diesel fuels and recommended avoiding DRA in product diesel fuels.

Unfortunately, the direct removal of DRA is difficult and there is no description of methods in the open literature. Some of the DRA in pipelines may be broken down by mechanical degradation or polymer chain scission however this is entirely dependent upon the operating conditions and whether the DRA was added in appropriate quantities upstream (*6*). Media filtration is a common process for refined fuels at the terminal and is used for removal of pipe scale and particulates prior to sale. In fact, many regulating organizations require filtration to at least 15 microns to aid in extending vehicle fuel filter life and to prevent injector clogging (*15*). Given that this process is often in place at many fuel terminals, it is useful to know how the concentration and shear level of DRA impacts the filtration process and whether filtration may also be a viable means to remove the DRA. To this end, a laboratory and field case study of the impact of DRA present in product diesel fuel on filtration was undertaken. The methods and theory used for the study will be addressed first followed by the results and discussion. A summary of the major conclusions and recommendations for DRA handling and mitigation in product fuel is also provided.

2. Methods

Refined diesel, free of any DRAs, was obtained from a mid-western fuel terminal that had experienced issues with excessive DRA contamination. Prior to testing, the refined diesel was mixed with a polymeric drag reducing agent (FLO MX68C Pipeline Booster) to produce a mixture of diesel and DRA at concentrations of 100 ppmw and 10 ppmw. The drag reducing agent was an α-olefin based polymer suspended in a hexyl-alcohol solvent. The density and viscosity of the neat refined diesel and the mixtures were measured using an Anton Paar SVM 3000 Viscometer/Densitometer at room temperature (75 °F). For the remainder of this paper, the mixture of DRA and refined diesel that *did not* experience significant mixing or agitation is referred to as an unsheared DRA mixture.

Given that DRA normally experiences shear degradation due to turbulence within the pipeline, it was necessary to simulate these conditions for consequent evaluations of the impact on filter performance. To create a sheared DRA/diesel mixture, the neat refined diesel was mixed with DRA to a concentration of 10 ppmw. The mixture was allowed to rest for 1 hour to allow the polymer chains to fully extended and viscosify the mixture (*6*). A Silverson L5M-A batch shear mixer was used to mix the diesel to produce a sheared mixture.

To determine the proper shear level required for accurate testing, the polymer filtration index (PFI) method was developed and used for evaluating the neat refined diesel and for obtaining multiple data points for the DRA/diesel mixture at various shear levels. This test proved to be an excellent alternative to measuring total suspended solids (TSS) using a 0.45 μm polyvinylidene fluoride (PVDF) membrane which, in the author's experience, may be severely impacted by the presence of polymeric substances, as is the case with this test. The PFI method described in this study also is advantageous for a quick evaluation versus direct methods (such as gel permeation chromatography) which are difficult and expensive. This method has the distinct advantage of being broadly applicable to any fluid with a soft or polymeric contaminant.
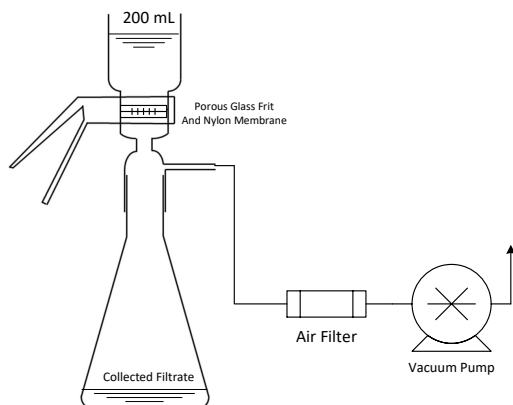

Figure 1. Vacuum flask apparatus used for measuring the polymer filtration index

The polymer filtration index is measured using a vacuum flask filtration apparatus manufactured by Millipore (Figure 1). To start the test, 200 mL of neat refined diesel fuel (no DRA) is measured using a 250 mL graduated cylinder. The neat diesel sample is then filtered through an absolute rated 5 micron nylon membrane disk (Millipore,

47 mm diameter) using the vacuum flask apparatus while measuring the total time, in whole seconds, required to filter the entire 200 mL volume. Next, a 200 mL sample containing DRA is similarly filtered through a 5 micron nylon membrane. The polymer filtration index is then calculated as the quotient of the two filtration times using Equation 1. If a clean sample (not containing DRA or polymer) is not available, one may shear a sample using a high speed mixer for an extended period of time (cf. Figure 3) or pre-filter a sample twice to 0.2 microns using an appropriate membrane disk.

$$PFI = \frac{t_{sample}}{t_{clean}} \tag{1}$$

When creating a sheared DRA/diesel mixture, the shear level achieved by the mixer was quantified using the total energy dissipated by the mixer over a given interval and normalized by the sample mass. The power number and Reynolds number of the mixer (defined by Equations 2-3) were used to determine the mixing regime and calculate the total energy transferred to the fluid (16). This information was then used to choose a shear level that was close to the PFI of the DRA contaminated product diesel that had been sampled at the terminal.

$$N_p = \frac{Pg_c}{\rho N^3 D_m^5} \tag{2}$$

$$Re = \frac{D_m^2 N \rho}{\mu} \tag{3}$$

In Equations 2-3, P is the power input to the fluid by the mixer, N is the RPM of the mixer head, D_m is the diameter of the mixer head, ρ is the fluid density, and μ is the fluid viscosity. The correlation presented by Beshay et al. (2001) (17) was used to calculate the power number of a straight 4-blade Rushton-type turbine (Equation 4).

$$N_p = 0.996 n_B^{0.682} (\frac{h}{D})^{-0.178} \tag{4}$$

Where n_B is the number of blades, h is the off-bottom clearance of the mixer, and D is the impeller diameter. The power number was then used to calculate the power input to the fluid by the mixer by Equation 2.

Based on the data obtained and presented in the results section, the PFI has proven to be a useful technique to quickly evaluate the shear level of a diesel/DRA mixture and also a quick tool to evaluate its fouling potential for filtration process. This measurement is a great alternative to measuring the total suspended solids (TSS) which can be difficult to evaluate for polymer laden fluids. The advantage of minimal time and equipment requirements means that the technique may be used in the field or a lab to quickly conduct estimates of the degree of DRA contamination.

The impact of the diesel containing the provided DRA on filtration performance was evaluated using a custom, laboratory scale filtration test apparatus. The apparatus consists of a high precision dual-piston pump (Vindum Engineering, Inc.) capable of constant flow delivery at between 0.001-97 ml/min through a test section of filter media

Table 1. Viscosity and density of unsheared diesel samples

Sample ID	Viscosity (mPa.s)	Density (g/cc)
Neat Refined Diesel (no DRA)	2.1774	0.8231
Diesel w/10 ppmw DRA	2.2667	0.8236
Diesel w/100 ppmw DRA	3.1132	0.8311
Product Diesel w/sheared DRA (from terminal)	3.0750	0.8317

which was contained in a custom flow cell. The flow cell is designed such that flow is only allowed across the media thickness and not radially along the media surface. The differential pressure, flowrate, and pumped volume were tracked using a custom data acquisition system. To conduct each test, a 47 mm diameter coupon of filter media was dried and weighed prior to placing in the high-pressure filter media flow cell of the test system. The system was then purged with clean, refined diesel fuel to remove any trapped air, which would skew the results. To start the test, the refined diesel/DRA mixture was pumped through the filter media coupon at a set flowrate while the pressure and total volume were monitored. The tests were terminated once the differential pressure reached 172 kPa (25 psid) or once a predetermined terminal volume was pumped. In addition to laboratory testing, on-site testing was conducted using a pilot filtration vessel to evaluate trends in an actual process setting.

Pilot testing was conducted at the mid-western diesel fuel terminal from which the diesel samples were obtained. The diesel blend is transported via 8-inch pipeline from a refinery located about 180 miles away from the terminal. In order to reduce pumping energy and increase product volumes, the refinery adds DRA shortly after the first pump station. The DRA is intended to be dosed at a concentration of about 10 ppmw although reportedly the DRA is intentionally over-dosed since there is no way to directly test or accurately control the injection at the pump station. The pilot tests included a filtration evaluation of the diesel product over a period of two weeks. The total flowrate, cumulative volume, and differential pressure across the pilot filter vessels were recorded over this time period and the spent filter elements were returned to the lab for post-usage autopsy and analysis.

3.   Results

3.1.   *Viscosity and Density*

The viscosity of the neat refined diesel, the DRA/diesel mixtures, and the product diesel are shown in Table 1. As expected, the DRA appeared to increase the viscosity and density of the diesel sample.

The viscosity of the sheared diesel was measured to obtain several data points as a function of the mixer energy dissipated into the fluid mixture. As shown in Figure 2, the viscosity slightly declined with increased shearing of the mixture. After allowing the sheared diesel/DRA sample to sit for 24 hours, the original viscosity was not recovered. Shear thinning usually is a typical phenomenon of non-Newtonian flows. Although the presence of the polymers may induce some true shear thinning, the irreversible nature of this reduction in viscosity with increased shear indicates that the phenomena in Figure 2 is more likely a result of polymer chain scission rather than classic shear thinning. Without shearing, these large polymer molecules become soluble in the diesel and change the rheology with their long chains. With increased

shearing, these large molecules begin to experience chain scission, which results in a reduction in the viscosity of the mixture fluid. The result in Figure 2 indicates the presence of DRA, even at ppm level, can change the rheology of the diesel product.
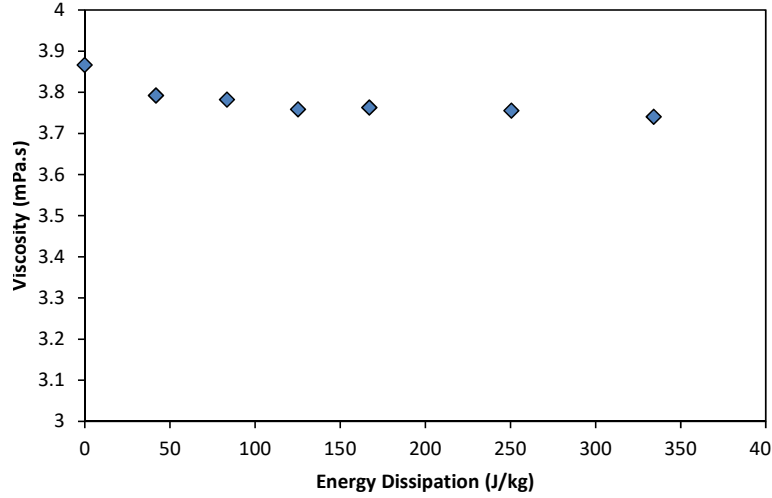

Figure 2. Viscosity of the 10 ppmw DRA/diesel mixture as a function of mixer energy dissipation.

Although a relationship between the viscosity and energy dissipation is evident from Figure 2, the sensitivity of the viscosity measurements were deemed too low to be accurately used as an analysis method to determine the concentration (or removal efficiency) of DRA polymer in the filtered and unfiltered diesel and therefore cannot be used to accurately estimate the filtration efficiency of DRA. The gravimetric total suspended solids (TSS) method was also evaluated as a potential means of measuring the DRA concentration changes. This method also failed to provide reliable, repeatable results in initial testing. This was primarily due to the fact that the DRA polymer rapidly fouled the 0.45 μm PVDF membrane and did not allow sufficient volume for a representative sample. For these reasons, the PFI was adopted as a fast and repeatable method for determining the relative level of DRA in the diesel fuel.

3.2. *Polymer Filtration Index*

The PFI was measured for several batches of diesel/DRA mixture that were prepared and sheared to different levels. The PFI was found to have a power law dependence upon the mixer energy dissipation (ϵ_m), as approximated in Equation 5 and shown in Figure 3.

$$PFI = \epsilon_m^{-0.3} \tag{5}$$

Note that Figure 3 contains several data points taken at high energy dissipation which fell slightly below 1.0. This may be attributable to the presence of natural fatty acid polymers arising from trace biodiesel constituents that were sheared, thereby reducing the filtration time below that of the original refined diesel. Also, note that the original refined diesel was received in an unsheared state and was known to not contain DRA. The general trend of Figure 3 is in agreement with previous studies

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that suggest a critical molecular weight below which chain scission ceases to occur with frequency (*6*). This is evident in the break-point of the curve in Figure 3.

The average PFI of the product diesel sampled at the fuel terminal, where the contamination issues were primarily occurring, was measured to be 1.4 by a set of three repeated PFI tests. It was desired to conduct the filter life evaluation testing at a shear level at or near the shear level of the diesel arriving at the terminal. As such, a target PFI of 1.4 was chosen for filter life evaluations with the sheared diesel. Each batch of the unsheared diesel/DRA mixture was progressively mixed and the PFI was measured until it was at or near 1.4.
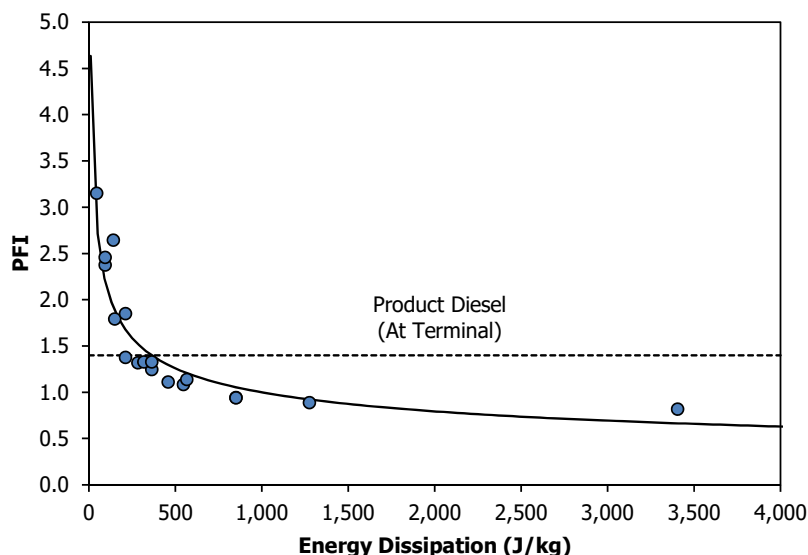

Figure 3. Polymer filtration index as a function of mixer energy dissipation. The PFI of the product diesel, as received from the terminal, is denoted by the dotted line.

3.3. *Polymer Size Distribution*

In an effort to determine the size distribution of the DRA polymers in solution, 2,000 mL of neat refined diesel was pre-filtered through a 0.45 μm PVDF membrane in order to remove native particulates. The particle size distribution of the clean, filtered refined diesel was measured prior to mixing with 10 ppmw of DRA and allowing the mixture to viscosify for 1 hour. The particle size distribution of the DRA/pre-filtered diesel mixture was then re-measured. Finally, the mixture was sheared to reach a PFI of 1.4 (same as product diesel from the terminal) and again the particle size distribution was measured. All beakers, transfer vessels, and mixing instruments were thoroughly washed with n-hexane followed by methanol to ensure no contamination after each step of the process.
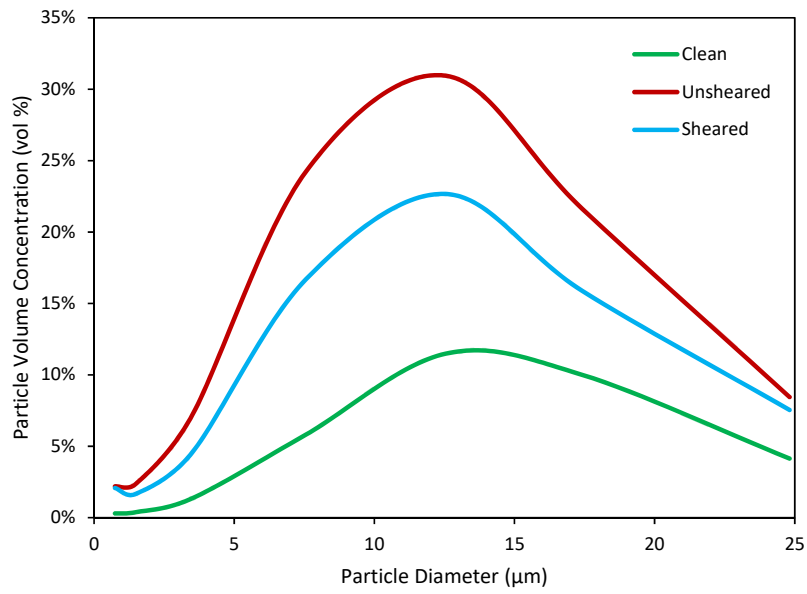
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Figure 4. Particle size distributions (by volume) for clean (pre-filtered) refined diesel (no DRA), diesel with unsheared DRA at 10 ppmw, and diesel with sheared DRA at 10 ppmw and PFI=1.4
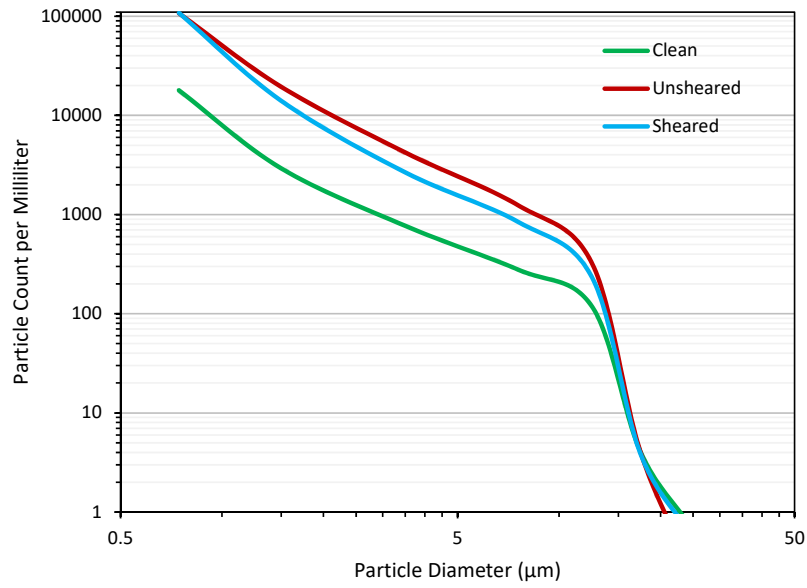

Figure 5. Particle size distributions (by particle count) for clean (pre-filtered) refined diesel (no DRA), diesel with unsheared DRA at 10 ppmw, and diesel with sheared DRA at 10 ppmw and PFI=1.4
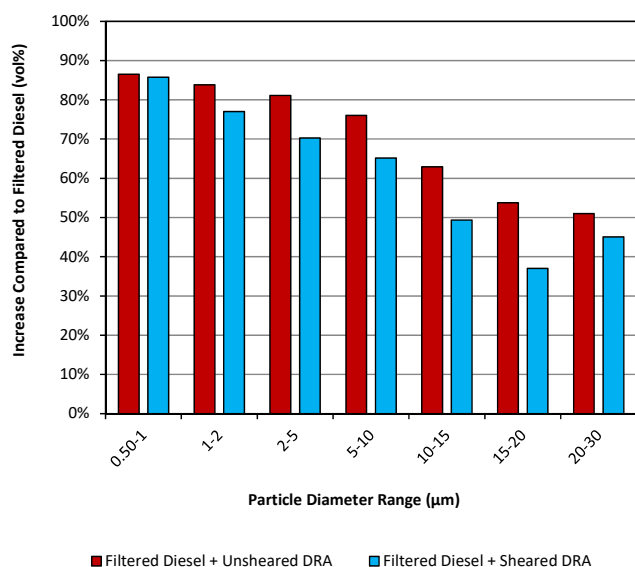
Figure 6. Percentage increase in volumetric particle concentration for mixtures of unsheared and sheared DRA relative to diesel filtered to 0.45 μm.

The results revealed that the 0.45 μm PVDF membrane was not able to remove all the native particulates from the diesel product, indicating that there were still some native soft particulates or emulsified water particles larger than 0.5 μm remaining in the diesel that were able to pass through the 0.45 μm PVDF membrane. The addition of DRA can be seen clearly from the cumulative particle size distribution change relative to the control clean filtered diesel sample. With all measurements, 99.5% of the particulate counts correlated to objects that were below 25 microns in size. The volume fraction of the particles was compared between the three measurements. The results in Figure 4 and 5 show that with the addition of the unsheared DRA the particle volume fraction and count increased in the lower size range, as would be expected. After shearing, the contribution of particle counts decreased, primarily in the 1-25 μm range. This observation is consistent with a reduction in the average polymer size (or cluster size), either through unravelling entangled molecular clusters or mechanical chain scission which separated the molecules into pieces with short chains, due to the increase in shearing energy. This process simulated in the lab has some similarity to the mechanical degradation in flow (MDF) which naturally occurs in the pipeline transportation process via turbulence over distance. MDF eventually results in the loss of the drag reduction along the transportation pipeline as the DRA polymers reach their critical minimum molecular weight. Figure 6 shows the volume percentage increase in particle concentration after the addition of the unsheared and sheared DRA relative to the original filtered diesel. Again, it is clear that shearing reduced the amount of optically visible particles primarily in the range of 1-25 μm. Based on the measurements, it may be concluded that this DRA polymer forms optically visible particle-like substances mostly in the 1-25 μm size range.

3.4. *Filtration Media Performance*

The constant flow filtration system described in the methods section was used to evaluate a 47 mm disk of 5 μm media material rated at β_{5000} (i.e. 99.98% removal

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efficiency at 5 μm as per ISO 16889:1999). The media was placed in the sample holder and initially subjected to a flow of clean, pre-filtered (to 0.45 micron) refined diesel at 25 mL/min in order to saturate the filter media prior to starting each test. A set of six tests were conducted to evaluate the life of the 5 μm media when subjected to a flow of diesel containing the DRA in both sheared and unsheared condition. The filter media life was defined as the amount of time required to reach the terminal differential pressure (25 psid) under a given flow condition with a specific fluid mixture. The flux was changed by altering the flowrate of the diesel mixture. Table 2 presents the details of the tests performed.

Table 2. Test details for DRA filtration performance evaluation

Flowrate (mL/min)	Flux (GPM/ft^2)	DRA Conc. (ppmw)	Polymer Filtration Index
10.0	0.26	10.0	>7
20.0	0.51	10.0	>7
50.0	1.28	10.0	>7
20.0	0.51	100.0	>7
50.0	1.28	10.0	1.4
20.0	0.51	10.0	1.4

3.4.1. Unsheared DRA

After each test with the unsheared DRA mixture, the formation of a stable gel layer was noted on the media surface. The differential pressure trends for the three tests conducted at 10 ppmw DRA concentration are shown in Figure 7. The trends confirm that flux exerts a significant impact on filter life. Lowering flux can significantly extend filter life by increasing the dirt holding capacity, a phenomenon which is exhibited by other non-polymer particulates in the filtration process. Relative to the filter life at a flux (media face velocity) of 1.28 GPM/ft^2, lowering the flux to 0.51 GPM/ft^2 produced an increase in filter life by 3.2 times and further reduction to 0.26 GPM/ft^2 was able to increase filter life by 5 times.

Qualitatively, it appears that a large amount of polymer molecules and particles were able to be retained on the 5 μm media surface. Under these conditions, the DRA polymers initially formed a concentration polarization (CP) layer as filtration proceeded. As more and more large molecules accumulated and concentrated on the media surface, either through mechanical retention or adsorption to media fibers, the viscosity of the CP layer increased gradually as a function of concentration, as described previously. When the concentration reached a certain level, these large polymers could deposit and eventually formed a low porosity gel layer that exhibited a low permeability, thereby limiting the ability of the fluid to flow. The formation of the CP layer and gel layer was a gradual process. This is reflected in the gradual change in the differential pressure curve as indicated in Figure 7. The distinct change in the rate of pressure loss increase across the filter media can be noted in the curves and may indicate the point at which the CP layer formed a continuous low porosity gel layer. Increasing flux simply expedited the formation of this gel layer thus shortening the filter life.

Figure 8 presents the total filtered volume (normalized by media area) as a function of the test flux. All points represent the volume filtered at the terminal differential pressure of 25 psid. As expected, lower flux resulted in higher total filtered volume and thus longer filter life.

The impact of DRA concentration was also investigated. The single test conducted at 100 ppmw DRA concentration indicated that the filter life is linearly related to
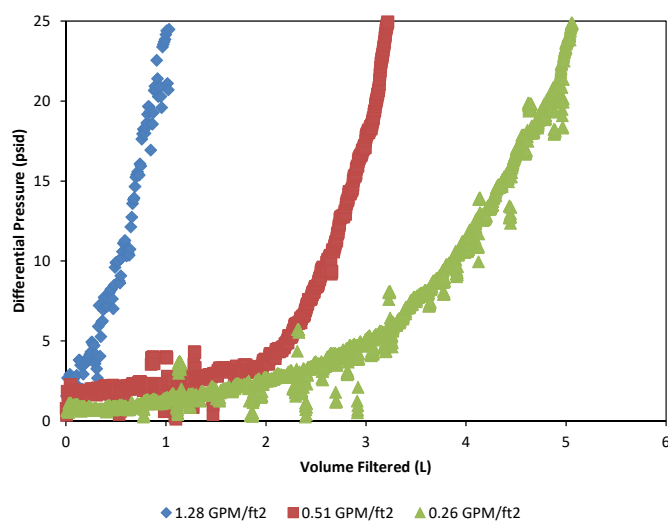
Figure 7. Differential pressure versus filtered volume for the three tests at 10 ppmw DRA concentration

the DRA concentration. The total filtered volume of 100 ppmw solution was almost exactly 10 times less than the total filtered volume achieved at a concentration of 10 ppmw. This indicates that the DRA concentration did not affect the dirt holding capacity of the filter within the range investigated in this study. This finding is also consistent with trends observed in flux decline with the filtration of standard solid particles, for example, silica test dust. It is also expected that the trend in Figure 8 is roughly hyperbolic such that a reduction in flux results in a significant gain in filter life. This implies the unsheared polymeric DRA molecules show some similar behaviors to rigid particles during filtration, except that these molecules may be able to cause higher resistance per unit mass, once retained on the media, compared to rigid particles. This explains why the soft polymers can cause more significant fouling during filtration operations, even at a very low concentrations. These the results show that unsheared DRA presents a significant removal challenge in product fuels.

3.4.2. Sheared DRA

Filter life evaluations were also conducted with the 10 ppmw diesel/DRA mixture that had been sheared to reach a measured PFI of 1.4. With the available volume of diesel, testing at a flux of 1.28 and 0.51 $\mathrm{GPM/ft^2}$ was able to be conducted. The shearing of the DRA significantly aided in extending filter life as shown in Figure 9. The shearing of the DRA resulted in an increase in filter life at a flux of 1.28 $\mathrm{GPM/ft^2}$ as compared to the unsheared mixture by a factor of 17. This is a result of the mechanical degradation of the DRA polymers due to the shearing process. Increasing shearing rate also reduced the fluid viscosity, which is proportional to the differential pressure drop across a porous medium as in the Poiseuille law. In addition, the smaller polymers after shearing may also be able to slow down the formation of gel layer on media surface due to increased entropy and the ability to rearrange and shift on the surface, therefore extending filter life (*18*).

Although the test at 0.51 $\mathrm{GPM/ft^2}$ was not able to reach 25 psid differential pressure
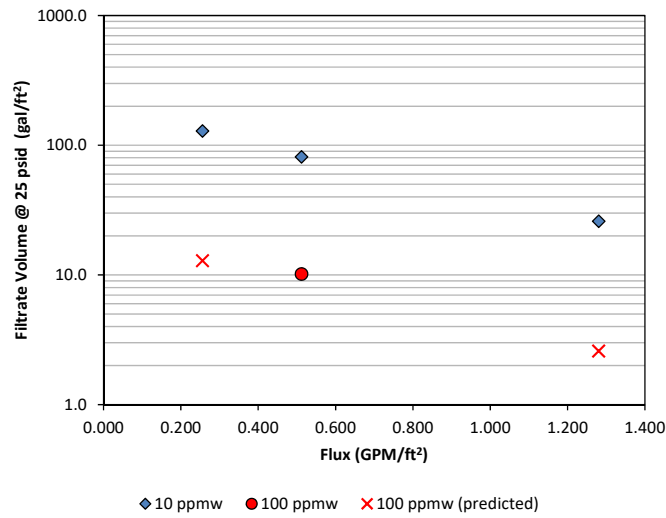
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Figure 8. Total volume filtered at 25 psid vs. flux for the four tests conducted. The results for a single 100 ppmw test were used to predict performance at other flux points
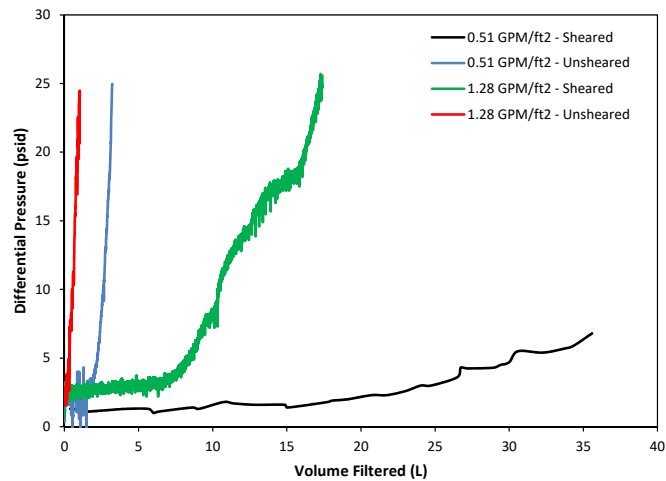

Figure 9. Differential pressure versus filtered volume for the two tests at 10 ppmw DRA concentration with sheared and unsheared diesel. All tests were conducted with 5 micron β-5000 rated media

due to limited diesel volume available, the proportionality between the two sheared DRA tests was very similar to the tests with the unsheared DRA mixture. This was confirmed by comparing the power-law fit of the differential pressure data between the sheared and unsheared DRA tests. As a result and based on this proportionality, the total volume filtered for the 0.51 GPM/ft^2 test and for 0.26 GPM/ft^2 was able to be predicted in Figure 10.

The pilot testing was conducted at an average flux of 0.32 GPM/ft^2. Figure 11 shows the pilot data plotted along with the laboratory test data for sheared DRA at 0.51 GPM/ft^2. Interestingly, the pilot test appears to have an uncharacteristically rapid rise in differential pressure considering the low reported solids concentration ($\sim$1
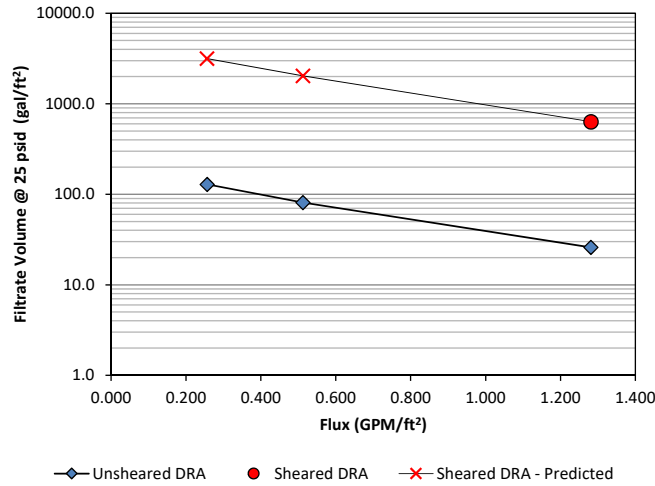
Figure 10. Total volume filtered at 25 psid vs. flux for the tests conducted with sheared and unsheared diesel/DRA mixtures. Based on the proportionality relationships, several points were predicted

mg/L). The filter autopsy results, to be presented later, suggested that DRA polymers likely played a significant role in blocking the filter media pores and causing the shorter filter life.

This trend is qualitatively consistent with the laboratory testing at a similar flux rate and PFI (PFI=1.4), as indicated in Figure 11.
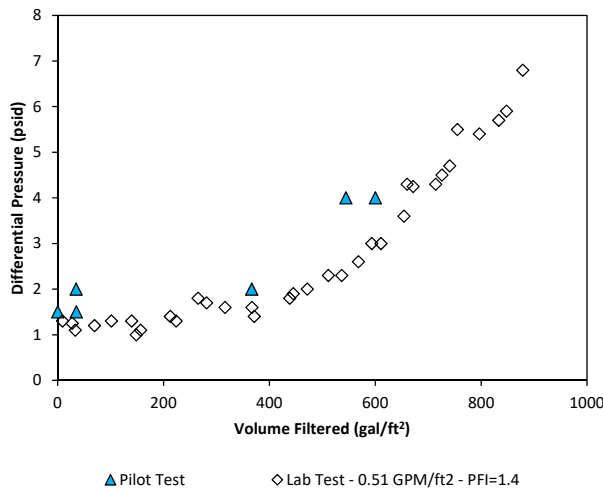

Figure 11. Differential pressure vs. total volume filtered for the pilot tests compared with the laboratory testing with sheared diesel/DRA mixture at a similar flux rate of 0.51 GPM/ft^2.

3.5. *Filter Media Efficiency*

Initially, a 1000 mL batch of refined diesel was filtered through a 0.45 micron PVDF membrane prior to gently mixing with DRA (10 ppmw) to create a mixture which was allowed to viscosify for 1 hour. The batch was then sheared to reach a measured PFI of

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1.4. After shearing, 200 mL of the mixture was passed through a sample of 5 micron and 10 micron filter media rated at β_{5000} using the same vacuum filtration apparatus. The 200 mL of effluent was collected separately from both tests and passed through clean 5 micron nylon membranes, in accordance with the PFI testing procedure presented in the methods section. The reduction in the PFI after filtering through the filter media was noted and is presented in Figure 12.

As can be seen from Figure 12, both the 10 micron and 5 micron media were able to reduce the PFI of the sheared diesel mixture. This implies both 10 micron and 5 micron media were able to remove some of the sheared DRA polymers, while the 5 micron media was able to remove more. The 5 micron media was able to reduce the PFI to a value close to 1.0; near the value of the clean and filtered diesel *without* DRA. This result suggests that the 5 μm media was able to remove a significant portion of the polymers, even in the absence of native solid particulates. This is consistent with the observation of scanning electron microscopy (SEM) imaging and energy-dispersive X-ray spectroscopy (EDS) analysis of a spent element and membrane samples collected from the pilot testing which showed a gel-like layer on the spent filter media surface.
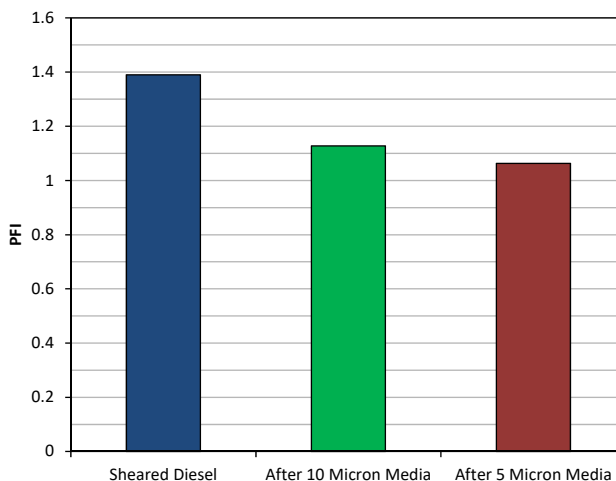

Figure 12.   Polymer filtration index of sheared diesel and after filtering through 5 and 10 micron β-5000 rated media.

3.6.   *Filter Media Fouling*

The pilot filter elements tested at the diesel terminal contained β_{5000} rated 5 μm fiberglass filter media which was identical to the media utilized for lab testing. Figure 13 shows the pilot vessel setup utilized for field testing of the filter elements at the diesel terminal. The filter elements used for pilot testing were autopsied for examination of the filter media layers.

SEM-EDS imaging indicated that the media pore space was blocked with a carbon based polymeric material which was attributed to DRA build-up. Figure 14 shows the SEM images from the post-pilot testing autopsy compared with clean, unused media. It is immediately apparent from the images and EDS results that the polymeric contaminant is carbon based which is consistent with the α-olefin DRA.

The SEM image in Figure 14 indicates the media was able to remove some of these
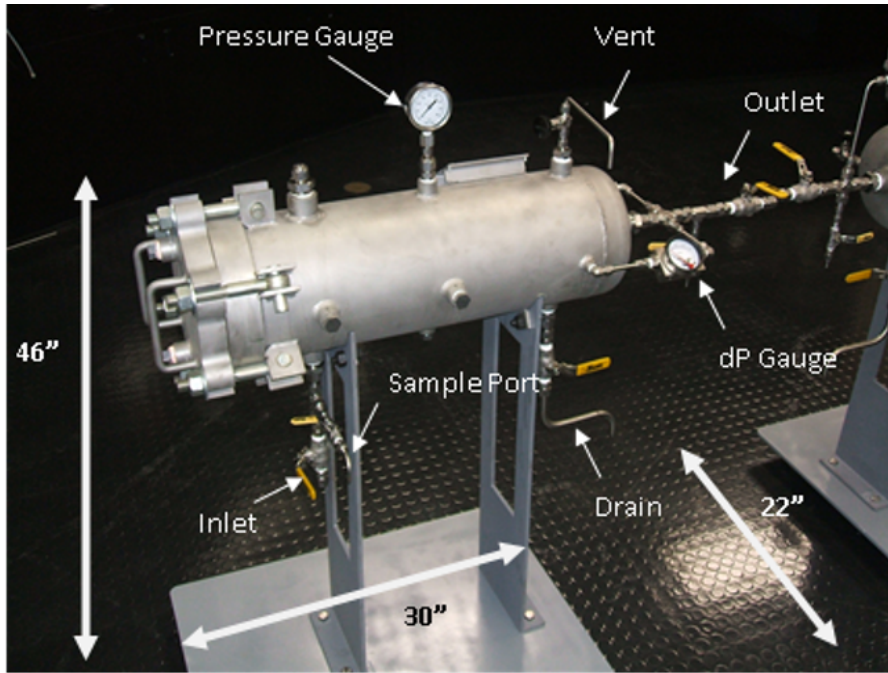
Figure 13. Pilot vessel utilized for field testing of filter elements at diesel terminal
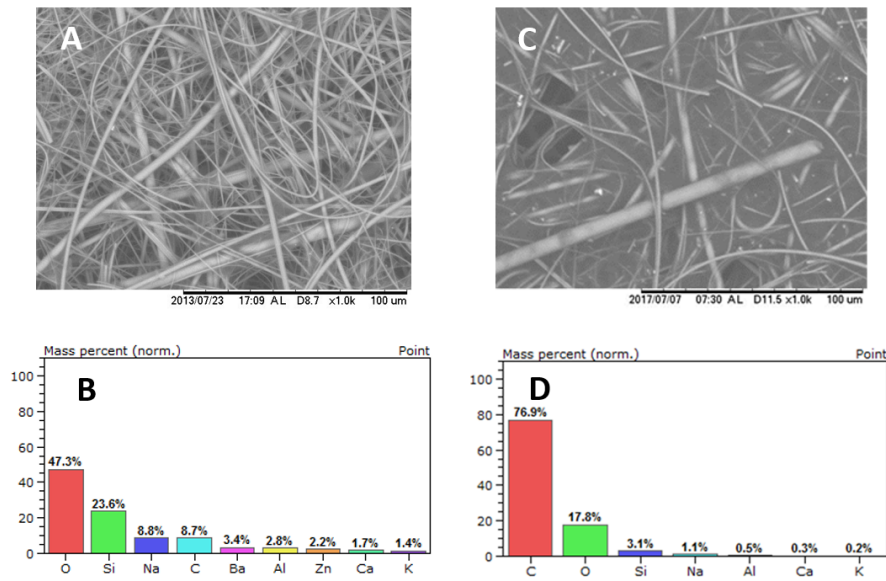

Figure 14. SEM-EDS results for clean media (A-B) and media from pilot testing at the terminal (C-D)

DRA polymers. During on-site pilot testing, gravimetric measurements of the total suspended solids were conducted by passing fluid through a 0.45 μm PVDF membrane disks. Total suspended solids were measured at the inlet and outlet of the pilot vessel containing the 5 μm filter during the testing. The average inlet solids concentration was 0.94 mg/L while the outlet averaged 0.22 mg/L.

The SEM images and EDS imaging of the inlet and outlet gravimetric membrane samples were able to provide more qualitative information to further answer the question regarding DRA removal efficiency of the filter. Although both membranes appear

relatively clear of particulates visually, a contaminant primarily composed of carbon was coating the inlet membrane (Figures 16). Again, this carbon based material is likely attributable to the DRA polymers. An outlet membrane was also examined, but the membrane did not have the additional carbon-based build-up observed on the inlet membrane EDS spectra. This observation also implies that the 5 μm filter media element was able to remove a majority of the DRA from the diesel. This result supports the conclusions of the PFI results presented in Figure 12.
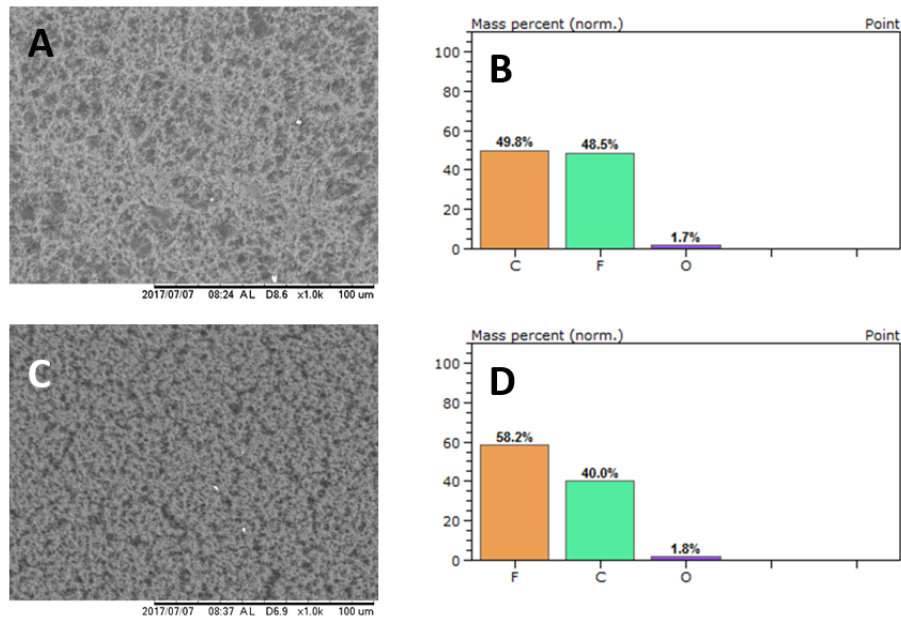

Figure 15. SEM-EDS results for membrane samples collected before (A-B) and after (C-D) the pilot vessel with the 5 μm filter. NOTE: Fluorine and most of the carbon signature is attributable to the PVDF membrane background signal (Figure 16)
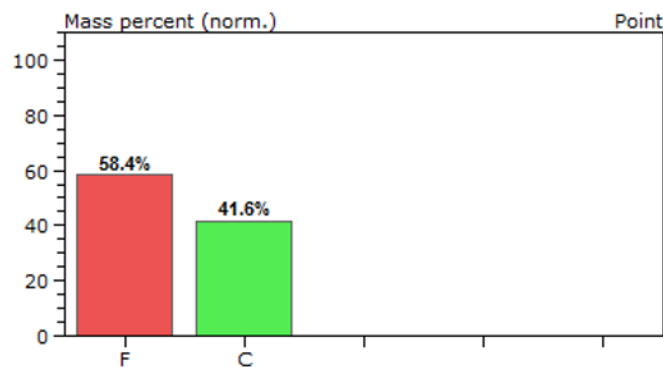

Figure 16. Elemental composition of clean 0.45 μm PVDF membrane

4. Conclusion

Overall, the laboratory and pilot testing indicates that the 5 μm filter media is capable of removing a majority of the DRA contained in the pipeline diesel product at the terminal. Removal of excess DRA is critical to prevent fuel filter and injector plugging

and excessive gum buildup in vehicles and aircraft. The exact efficiency of the media was difficult to quantify due to the very low concentration of the DRA, varying shear levels, presence of other trace particle contaminants, and lack of efficient analytical methods for quantifying DRA concentration. Particle size distribution measurements indicate that the DRA formed optically detectable particle-like substances in the 1-25 μm size range. Shearing the mixture of DRA and filtered diesel produced distributions weighted towards smaller particle sizes and reduced the overall particle counts. This indicates that the shear degradation of DRA is indeed observable on the micron scale and hence filtration is viable option to remove these substances.

A new analytical method for rapid determination of the level of DRA in a diesel feed was developed. The lab tests utilizing the developed polymer filtration index (PFI) with the sheared DRA mixture created from pre-filtered refined diesel indicate that the 5 μm filter media was able to reduce the PFI and to nearly the same level as clean refined diesel (with no DRA or particulates). Although the PFI does not directly translate to efficiency, this test does indicate that the fouling tendency of the sheared diesel, which can be considered as an alternative indication of the contaminant level, was able to be greatly reduced by single-pass filtration through the 5 μm media. SEM images and EDS results from pilot testing in the field support this conclusion.

Similar to other non-polymeric particle filtration processes, the lab testing results indicate flux impacts the filter life to a significant degree, as expected. Lowering the flux resulted in significantly extended filter life by delaying the formation of gel layer on media surface. Relative to the filter life at a flux of 1.28 GPM/ft^2, lowering the flux to 0.51 GPM/ft^2 increased filter life by 3.2 times and further reduction to 0.26 GPM/ft^2 was able to increase filter life by 5 times.

The filter life was significantly impacted by the DRA concentration and shear level. Increase in DRA concentration negatively impacts filter life. The correlation between filter life and DRA concentration was linear, as expected.

The established relationship between PFI and the mixer energy dissipation (Figure 3) shows a distinct break-point around $\epsilon_m = 350$ J/kg. This point aligns fairly well with the measured PFI of the product diesel provided by the terminal. If the DRA is sheared below this point, the impact to filter life will likely be less significant compared to an unsheared mixture. However if off-specification amounts of DRA are injected or the pipeline turbulence is significantly reduced due to turndown, the DRA may not become fully sheared. Injection of DRA into the pipeline at additional locations also increases the probability of unsheared DRA reaching the terminal. In these cases, the unsheared DRA would likely present a more significant challenge at the terminal and add unpredictability to filtration operations.

Ideally, the pipeline design should provide enough energy dissipation to significantly shear the DRA prior to reaching the terminal. The energy dissipation rate in a pipeline (i.e. W/kg) can be estimated using Equation 6.

$$E = \frac{2fv^3}{D_{pipe}} \tag{6}$$

Where v is the average fluid velocity in the pipeline, f is the friction factor, D_{pipe} is the internal pipe diameter. The friction factor is significantly reduced by the DRA which means that a much longer pipeline transit is necessary to achieve significant energy dissipation. Virk (1975) suggested that Equation 7 be used for estimating the friction factor at maximum drag reduction (7).

$$\frac{1}{\sqrt{f}} = 19log(Re\sqrt{f}) - 32 \tag{7}$$

Unfortunately, the energy dissipation rate approximation is highly dependent upon the accurate determination of the friction factor which will change along the pipeline as a function of the chain scission rate of the DRA.

In summary, the major conclusions of this study are

- Filter life is adversely affected by the presence of DRA in product fuels
- Filtration proved to be an effective technology to remove DRA polymers from diesel product at the terminal. A 5 μm filter rated at β_{5000} appears to be able to remove a majority of these polymers effectively. Choice of a proper β_{5000} media (as opposed to nominally rated media, which is common in industry) is critical for removal performance.
- The developed polymer filtration index (PFI) method is a useful tool for quickly evaluating the level of DRA contamination in product fuels and other liquid containing long-chain polymeric contaminants.

CRediT Author Statement

Evan Lowry: Conceptualization, Investigation, Formal Analysis, Writing - Original Draft; **Robert D. Barnum**: Writing - Review & Editing, Visualization; **Yanxiao Yuan**: Resources, Writing - Review & Editing, Supervision; **Eric Rodano**: Investigation; **Jared Lusk**: Conceptualization.

Disclosure Statement

At the time of writing, the authors were employed by Pentair Filtration Solutions, LLC and completed this research using the company laboratories and equipment. Pentair Filtration Solutions, LLC produces products related to the research in the study.

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