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IMPACT OF CLAY TREATMENT ON AVIATION FUEL THERMAL STABILITY

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This report examines the impact of clay treatment to improve the thermal stability of aviation fuel. Experiments were conducted at pilot and bench scales, demonstrating the ability of clay treatment to improve thermal stability. Analytical measurement of fuel composition were also made in order to determine which heteroatomic compound classes are most effected by clay treatment enabling further examinations of the relationships between fuel composition and thermal stability.

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1.0 EXECUTIVE SUMMARY

Recent years have seen an increase in jet fuels exhibiting poor/failing thermal stability behavior. Clay treatment is a process typically used to remove surfactants and other polar compounds from jet fuels to prohibit the formation of fuel-water emulsions and allow for proper filter-coalescer performance. However, the clay treating process can also remove polar compounds that are deleterious to fuel thermal stability. Because of the availability of clay treatment within the distribution system and its ability to remove chemical contaminants, clay treatment has been suggested as a possible solution to jet fuel thermal stability problems in the field. The purpose of this project, funded by DLA-Energy, is to examine the effect of clay treatment (using drum quantity, clay treating equipment) on the chemical composition of thermally unstable (or marginal) fuels and to track the ability of clay to improve thermal stability. The adsorptive capacity of clay used in the treatment process will also be evaluated.

A poor thermal stability fuel from the Puget Sound area was used for initial clay filtration experiments. The fuel failed the minimum thermal stability test (ASTM D3241) with a breakpoint requirement of 260 °C by exhibiting a breakpoint of about 235 °C. This fuel was clay treated, using a commercially available clay cartridge, in a single pass configuration at the manufacturer-specified flow rate of 6 gallons per minute (GPM). Chemical analysis indicated that certain polar compounds (quinolines, indoles, anilines, phenols, polar nitrogen, and others) were dramatically reduced during clay treatment. While clay treatment could clearly improve thermal stability, the capacity to perform systematic studies of clay using drum level volumes of fuel was unrealistic. Preliminary results also indicated that the flow rate of fuel through the clay had to be ~6 times lower than typical operating conditions to effectively adsorb the polars that cause instability. Laboratory scale studies using chemical analysis of the filtered fuel and Quartz Crystal Microbalance (QCM) studies also verified the larger scale findings that 1) polar components are implicated in fuel thermal instability; 2) only low flow rates of fuel through clay treatment could effectively improve problems; and 3) the ability of clay to treat fuel is limited to a fuel volume of ~250 times the clay volume for the testing performed – a limited capacity.

Several experiments were also conducted to examine how to monitor fuel or clay to ascertain when the clay was no longer removing enough fuel components to sufficiently improve thermal stability. Two measurements, total nitrogen content and interfacial tension (IFT), were examined. While IFT did increase as clay was treated, it continued to increase even as the clay treating effectiveness to improve thermal stability started to decline. A measurement of total nitrogen in the fuel was able to gauge clay effectiveness for predicting the thermal stability of a fuel.

Based on the data highlighted in this report, it is recommended that if field practitioners wish to use clay treatment to improve the thermal stability of a fuel, that careful and judicious monitoring of the thermal stability (via D3241) of the treated fuel be conducted regularly throughout the process. Practitioners should understand that fresh clay should be used to achieve maximum effectiveness and that there is a limited capacity of the clay for treating poor thermal stability fuel.

2.0 INTRODUCTION

Recent years have seen an increase in jet fuels exhibiting poor/failing thermal stability behavior. Some of these unstable fuels are located in large stores and involve millions of gallons of product. Due to the inability to pass specification, these fuels cannot be issued, and therefore, sequester until proper dispositioning can be obtained.

Clay treatment is a process used to remove surfactants from jet fuels to prohibit the formation of fuel-water emulsions and allow for proper filter-coalescer performance. This process is used both at the refinery and throughout the jet fuel distribution system, e.g., airfield terminals. Because of the availability of clay treatment within the distribution system, and its ability to remove chemical contaminants, clay treatment has been suggested as a possible solution to mediate jet fuel thermal stability problems in the field. In short, if a batch of fuel fails thermal stability by ASTM D3241, clay treatment has been suggested to remove those components believed to cause the failure and remediate the fuel to an acceptable level of thermal stability.

Fuel born surfactants are removed during clay treatment by an adsorption mechanism. Surfactant molecules, by their nature, are polar—as opposed to the non-polar hydrocarbon fuel molecules—and will often contain compounds with sulfur, oxygen, and/or nitrogen atoms. Some examples of surfactant molecules include naphthenic acids, sulfonic acids, sodium salts of these acids, and phenols [1]. These examples of surfactants are similar to the heteroatomic compounds often implicated with fuel thermal stability issues [2-4], thus the desire to use clay treatment as a possible mitigation strategy.

Very little work has been reported in the literature about using clay treatment to improve jet fuel thermal stability. A series of articles by Pillon [5-7] provide the most complete set of information to date regarding the effects of clay treatment on fuels with respect to jet fuel thermal stability. While clay treatment is reported to improve jet fuel thermal stability (as measured by ASTM D3241) in some cases, Pillon also points out that clay treatment quickly loses effectiveness as target species saturate the clay and breakthrough occurs [6]. This breakthrough effect occurs more readily in the presence of water [7]. While the efforts of Pillon were extensive, there are knowledge gaps related to clay efficacy, especially under more representative conditions used in field clay treatment applications.

The purpose of this project is to examine the effect of clay treatment (using drum quantity, clay treating equipment) on the chemical composition of thermally unstable (or marginal) fuels and track the ability of clay to improve thermal stability. The capacity of clay used in the clay treatment process to adsorb polar compounds will also be evaluated.

3.0 METHODS, ASSUMPTIONS AND PROCEDURES

3.1 Fuel Sample

Two poor/marginal thermal stability jet fuel samples—Jet A fuel sample number F13385 and F-24 sample number F12843—were used during this study. Table 1 and Table 2 list specification and non-specification measurements, respectively, for the two fuel samples. Most testing was conducted using the poor thermal stability fuel sample (F13385), which has an ASTM D3241 breakpoint temperature of 235 °C.

Table 1. Select Specification Properties of Jet Fuel Samples

ASTM Method	**POSF ID** / **Fuel Type**	12843 F-24	13385 Jet A
D3242	TAN (mg KOH/g)	0.005	0.010
D1319	Aromatics (%vol)	18.6	15.6
D3227	Mercaptan Sulfur (%wt)	0.001	0.002
D2622	Total Sulfur (%wt)	0.14	0.07
D4052	Density at 15 °C (kg/L)	816	804
	Thermal Stability at 260 ℃		
	VTR	<2	n/a
D3241	ETR (nm)	35	n/a
	ΔP (mmHg)	0	n/a
	Breakpoint Temperature (℃)	265	235

Table 2. Trace Chemical Compositions of Jet Fuel Samples

		Sample ID:	12843	13385
Speciated Polars (mg/L)	Nitrogen Compounds	Anilines (C6-C10)	9	6
		Indoles (C8-C12)	3	4
		Quinolines (C9-C15)	18	23
		Tetrahydro- quinolines (C9-C14)	7	3
		Pyridines (C7-C10)	3	2
		Carbazoles (C12-C16)	2	2
		Indolines (C8-C9)	<1	<1
	Aromatic Oxygenates	Phenols (C6-C14)	273	188
		Ketones (C8-C11)	<1	1
		Alcohols (C7-C11)	59	26
		Aldehydes (C7-C10)	1	1
		Di-esters or Phthalates (C16-C24+)	1	<1
	Aliphatic oxygenates	Ketones (C7-C14)	7	59
		Cycloketones (C7-C14)	8	16
		Alcohols (C6-C13)	7	30
		Aldehydes (C7-C13)	2	7
		Esters (C8-C12)	<1	1
		FAME Esters (C17-C18)	<1	<1
		Di-esters or Adipates (C16-C26)	<1	<1
		Other Polars (mg/L)	109	110
		Total Polars (mg/L)	511	478
		Total Nitrogen (mg N/kg)	9.3	7.6

3.2 Drum Scale Experiments

Initial experiments were conducted at drum scale volumes to be more representative of fielded clay treatment conditions. Jet fuel was pumped through a Velcon Systems model MP5E-10 single-element filter vessel outfitted with either a Parker-Velcon model CO-718CE (Attapulgus clay (AC)) or LA-71801B (Fuller's Earth (FE)) clay canister. The filter vessel was flushed with the sample fuel prior to installation of the clay canister. After installation of the new clay canister, fuel was pumped at the desired flow rate (e.g., 1 or 6 GPM) and vendor recommended pressure through the test cartridge. Fuel treatment was a single pass from the upstream drum into a clean downstream drum. Two 1 L grab samples were collected after 21 gal and 42 gal had passed through the filter vessel.

3.3 Bench Scale Experiments

Jet fuel was pumped through a small volume of clay (e.g., 10 or 25 mL) housed in an Omnifit EZSOLV column (model 006EZS-25-10-AF) using an Isco model 500D syringe pump. The column length was adjustable up to 100 mm (depending on the clay loading), with a fixed diameter of 25 mm. The clay was packed efficiently into the column without significant void spaces, similar to the packing of the clay cannisters used in full scale and pilot scale clay treaters.

Clay was extracted from new Parker-Velcon CO-718CE or LA-71801B clay canisters and fresh clay was loaded into the column for each experiment. Similar to the drum scale experiments, the cartridge was rinsed prior to use and fuel was treated with a single pass. Sample fractions were collected as aliquots post-clay treatment. Flow rates and clay volumes used in the bench scale experiments were designed to simulate drum scale flow rates by matching the fuel-clay contact times experienced in the drum scale experiments; values are listed in Table 3. Bench scale values were calculated using the following method: the volume of clay in the Parker-Velcon canisters is about 2.55 gal based on the canister dimensions. If a 6 GPM fuel flow rate was used, then the fuel-clay contact time was approximately 0.425 min since $2.55\ Gal \div 6\ GPM = 0.425\ min$. If a 10 mL load of clay was used in the bench scale column, then a flow rate of 23.5 mL/min would be required to match the contact time of 0.425 min, that is: $10\ mL \times (6\ Gal/min) \div 2.55\ Gal = 23.5\ mL/min$.

Table 3. Flow Rates and Volumes Used in Bench Scale Experiments

Drum Scale Flow Rate, *to simulate* (GPM)	Approx. Contact Time (min)	Bench Scale Clay Volume Used (mL)	Bench Scale Flow Rate (mL/min)
6	0.425	10	23.5
1	2.55	25	9.8

4.0 RESULTS AND DISCUSSION

4.1 Drum Scale Clay Treating Results

A poor thermal stability fuel, sample 13208 from the Puget Sound area, was used for initial clay filtration experiments. The fuel gave an ASTM D3241 max spot thickness value of 179 nm via ETR when tested at 260 °C; a thickness value of 85 nm is considered a failure. A drum (~42 gal) of this fuel was clay treated using a single canister clay treater, with a single fuel pass at a flow rate of 6 GPM, which is a typical full scale flow rate per clay cartridge. The treated fuel passed D3241 with an ETR value of 14 nm. The clay used in this case was FE (manufacturer: Parker-Velcon, model: LA71801B). Chemical analysis was conducted to understand what may have changed in the fuel during clay treating to improve the thermal stability result. The results, shown in Table 4, indicate that certain polars (quinolines, indoles, anilines, phenols, polar nitrogen, and others) were reduced during clay treatment. This result points to the importance of these components in fuels with poor thermal stability.

Table 4. Initial Drum-Scale Clay Treating Results

Fuel Sample POSF ID:	**13208**	**13550**
Sample Description:	Jet A	6 GPM (2^{nd} 21 Gal)
Clay Filter Element:	n/a	LA-71801B
Polars (mg/L)		
Phenols	213	202
Anilines	8	6
Indoles	9	6
Quinolines (C9-C14)	16	5
Tetrahydroquinolines	1	2
Pyridines	2	1
Carbazoles	5	4
Ketones	89	98
Cycloketones	16	16
Alcohols	28	25
Aldehydes	4	4
Ethers	<5	<5
Esters	3	2
Phthalates	3	4
Other	158	112
Total	556	486
GC-SCD/NCD		
Sulfur-polar (mg/kg)	6	3
Nitrogen-polar (mg/kg)	7	3
JFTOT @260C-ETR (nm)	179[a]	14

[a]Fuel sample 13208 breakpoint is 240 °C.

In a similar experiment, a separate batch sampling of the poor thermal stability Puget Sound fuel (POSF 13385) was used. Fuel 13385 was clay treated with the same drum scale clay treater at 6 GPM, however, a model CO-718 clay canister (Parker-Velcon) was used (this clay is marketed for jet fuel usage). Filtration of 42 gal of fuel through the single-pass, single-element clay treater resulted in fuel that still failed D3241 surface deposits. Therefore, a slower flow rate of 1 GPM was attempted. The fuel collected from the 1 GPM rate passed D3241. Results of this experiment are shown in Table 5. It can be seen that many of the polar species classes were reduced at 6 GPM, however, the reductions were insufficient to provide adequate improvement to the fuel thermal stability (as assessed using D3241). The slower flow rate (1 GPM), and therefore greater residence time, did provide improvement in D3241 results. However, the total amount of fuel treated by the single clay cartridge was unrealistically low. Field implementation of clay filtration is expected to use hundreds to thousands of gallons of fuel per clay canister. Additional

studies are required to examine when potential breakthrough, or reduction in treatment efficacy, might occur.

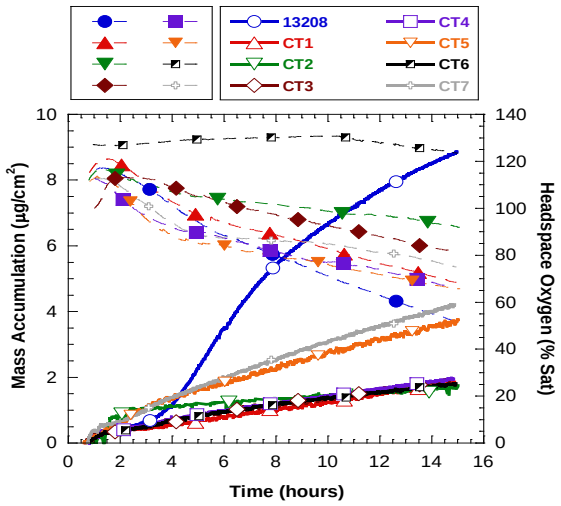
Table 5. Drum-Scale Clay Treating Results at Two Flow Rates

Fuel Sample POSF ID: Sample Description: Clay Filter Element: **Polars (mg/L)**	**13385** Jet A n/a	**13570** 6 GPM (2nd 21 Gal) CO-718	**13575** 1 GPM (2nd 21 Gal) CO-718
Phenols	197	145	168
Anilines	9	5	2
Indoles	8	5	2
Quinolines (C9-C14)	14	9	4
Tetrahydroquinolines	1	3	1
Pyridines	1	1	1
Carbazoles	5	3	3
Ketones	80	55	72
Cycloketones	14	10	12
Alcohols	26	20	26
Aldehydes	3	3	4
Ethers	<5	<5	<5
Esters	2	2	2
Phthalates	1	1	1
Other	141	98	98
Total	502	359	397
GC-SCD/NCD			
Sulfur-polar (mg/kg)	5	4	3
Nitrogen-polar (mg/kg)	6	4	1
JFTOT @260C-ETR (nm)	off-scale[a]	117	13

4.2 Lab Scale Clay Treatment Results

The experiences with the treatment of drum quantities of fuel quickly lead to the realization that it would be important to conduct bench scale clay treatment experiments to increase the number of independent variables that could be examined. Some feasibility/proof-of-concept work conducted early on involved clay treating aliquots of fuel with small amounts of clay. The resulting fuel samples were characterized with chemical analysis and thermal stability assessment using ASTM D7739, the Quartz Crystal Microbalance (QCM) apparatus, due to the limiting volumes of fuel sample. Figure 1 shows both the QCM profiles and tabulated chemical analysis of the initial experiment of clay treating fuel 13208 with FE. The flow rate, e.g., the contact time, was not controlled in this initial work. Sample aliquots were collected every 100 mL after passing through the same bed of clay. The baseline fuel exhibited poor thermal stability

characteristics on the QCM, giving about 9 µg/cm^2 of surface deposits. Clay treatment of this fuel showed an initial improvement in the thermal stability characteristics by decreasing the surface deposits; however, as more fuel was passed through the clay an increase in the polar concentration and, to a lesser degree, the amount of deposits was observed. This data prompted more controlled studies.



Polar Species (mg/L)	Neat	Clay Treatment Aliquot 1	2	3	5	7
Phenols	407	127	212	302	343	362
Anilines	9	2	5	5	10	11
Indoles	20	4	7	11	14	15
Quinolines	20	2	4	6	9	13
Tetrahydroquinolines	4	3	3	3	3	4
Pyridines	4	2	2	2	3	3
Carbazoles	7	3	4	5	5	5
Ketones	120	45	77	107	111	113
Cycloketones	26	8	15	20	22	23
Alcohols	42	17	29	32	38	37
Aldehydes	7	4	6	8	8	7
Ethers	<1	<1	<1	<1	<1	<1
Adipates	<1	<1	1	1	1	1
Other Esters	2	1	2	2	2	2
Other Aromatic oxygenates	30	3	7	14	15	21
Phthalates	1	<1	<1	1	1	1
Other	196	61	95	144	144	154
Total Polars	896	282	469	664	729	772

Figure 1. QCM (left) Profiles of Fuel 13208 before and after Clay Treated, CT# Represents Aliquot Sequence, 1 through 7; Chemical Analysis (right) by SPE-GC×GC-MS/FID

More controlled bench scale experiments used a measured amount of clay in a glass chromatography column, a diagram of which is shown in Figure 2. A syringe pump was used to flow a metered rate of fuel through the clay bed. Both FE and AC were used from commercially available clay canisters manufactured by Parker-Velcon (LA-71801B and CO-718, respectively). Aliquots of fuel were collected, e.g., 5x 100 mL samples then 4x 500 mL samples, and subsequently examined for trace chemical content as well as thermal stability. Bench scale flow rates were scaled to that of a full sized single clay canister by maintaining equivalent residence times as reported in the Experimental section (see Table 3). All of the experiments were conducted with a fresh volume of clay, as was also the case in the drum scale clay experiments.

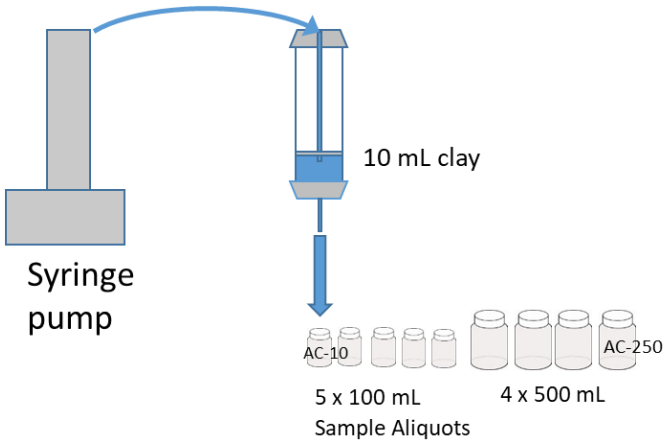


Figure 2. Small Scale Laboratory Clay Treatment Process for 2,500 mL of Fuel

Fuel sample F13385 was filtered using the bench scale apparatus shown in Figure 2 using AC and FE, separately, at a simulated flow rate of 5 GPM. Aliquots of fuel were sampled throughout the runs and total nitrogen was determined on each sample, with the results shown in Figure 3. As the data show, both AC and FE remove a significant amount of nitrogen at low fuel/clay (F/C) volume ratios (less than ~40 (F/C) ratio), however, as more fuel is treated by the clay, the concentration of total nitrogen returns to initial levels. The initial and final clay treated samples, at (F/C)ratios of 10 and 250, respectively, were tested on the QCM (see Figure 4) to evaluate thermal stability performance. These results show a significant decrease in surface deposits (that is, a significant improvement in thermal stability) for when either AC or FE is used to treat the fuel at a (F/C) ratio of 10. However, only a modest decrease in deposits is observed at the larger (F/C) ratio of 250. It should be noted that within our knowledgebase of fuels, a QCM level of surface deposit 6 $\mu g/cm^2$ or greater is considered to be poor thermal stability. Regardless, the trend is clear: *clay treatment can be used as a way to improve the thermal stability of poor quality jet fuel, but the capacity of the clay to improve thermal stability is limited.*

In addition to the 5 GPM simulated flow rate, both 1 and 6 GPM flow rates were simulated using the bench scale apparatus. Fuel 13385 was clay filtered at these additional flow rates using both AC and FE clay, with similar sampling and analysis procedures. Figure 5 shows the total nitrogen profiles of all three flow rates conducted on the bench scale along with the drum scale data.[1] Similar trends are observed with these data regardless of clay type; method of filtration, and to a lesser degree flow rate, i.e., clay filtration removes a significant fraction of the total nitrogen components at low (F/C) ratios, however, as more fuel is treated, less nitrogen is removed. In general, there appears to be no removal of nitrogen containing species via GC-NCD with (F/C) ratios of about ≥150, although selective adsorption/desorption may still occur. A more detailed chemical analysis (such as GCxGC) could be performed with more nitrogen component speciation to determine which of the nitrogen compounds may be more affected by the clay. Regardless, the thermal stability performance of some low (≤10) and high (≥100) (F/C)ratio samples was tested in the QCM and results are shown in Figure 6. As these data show, the initial fuel has very poor thermal stability. giving 13 to 14 $\mu g/cm^2$ of mass accumulation after 15 hours of thermal stress duration. Clay filtration with either AC or FE clay at 1 GPM and/or 6 GPM simulated flow rates greatly improves the thermal stability characteristics of these samples by reducing deposition values to <5 $\mu g/cm^2$ when (F/C) ratios of ≤10 are observed. However, when (F/C) ratios become ≥100 the fuel samples trend toward the original poor/very poor thermal stability performance.

[1] Additional, detailed polars data is available for many of the tested samples and is reported in Appendix A. We have chosen to focus our discussion of chemical composition on total nitrogen content as a harbinger of the many polar heteroatomics in these fuel samples. However, it is acknowledged that this is an oversimplification since some sub-classes of compounds can be retained more efficiently than others. Thus the reader is suggested to review the complete detailed polars data as well.

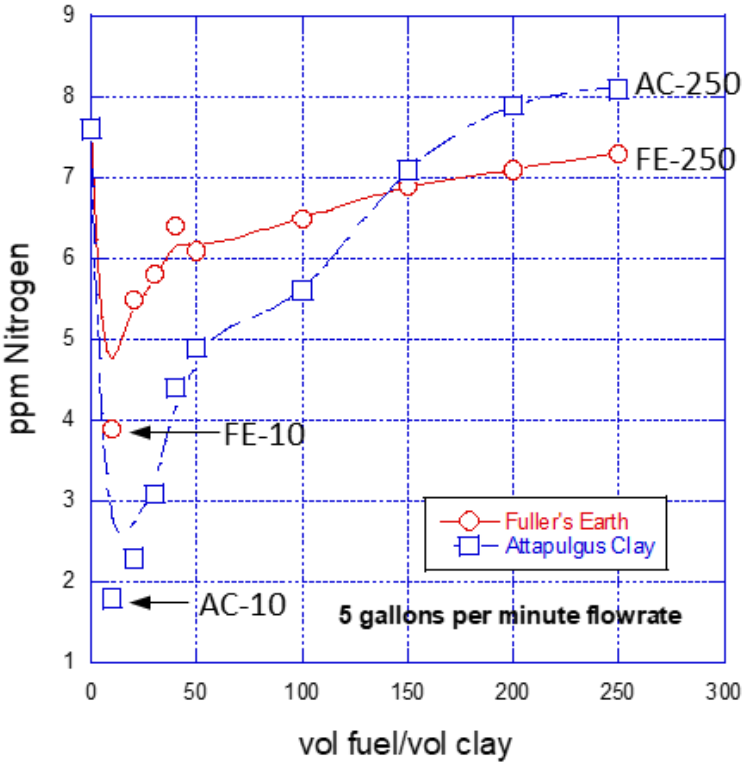


Figure 3. Total Nitrogen Content of Bench Scale, Clay Treated Fuel Samples; Simulated 5 GPM Fuel Flow Rate

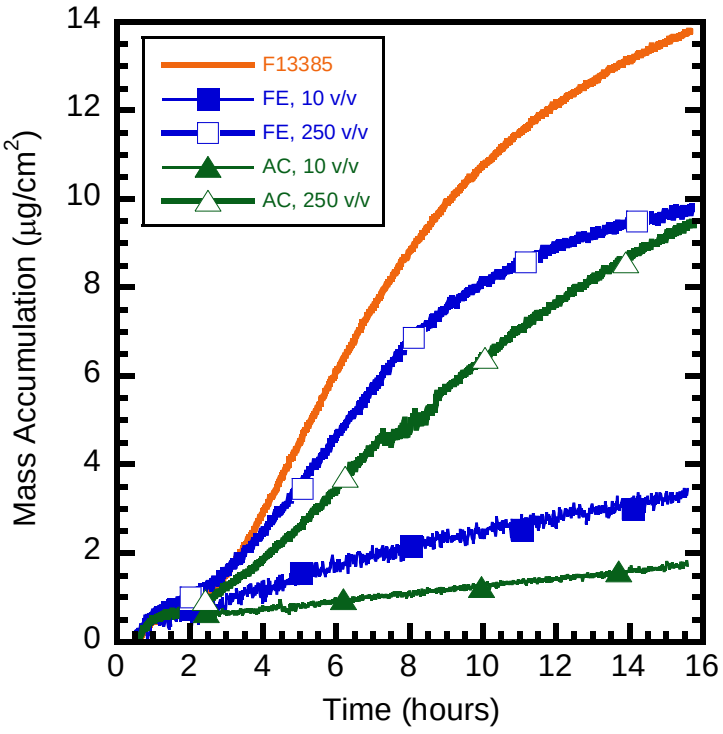


Figure 4. QCM Mass Accumulation Profiles at 140 °C; Neat Fuel Sample F13385 Filtered with FE or AC at a F/C Volume Ratio of 10 or 250

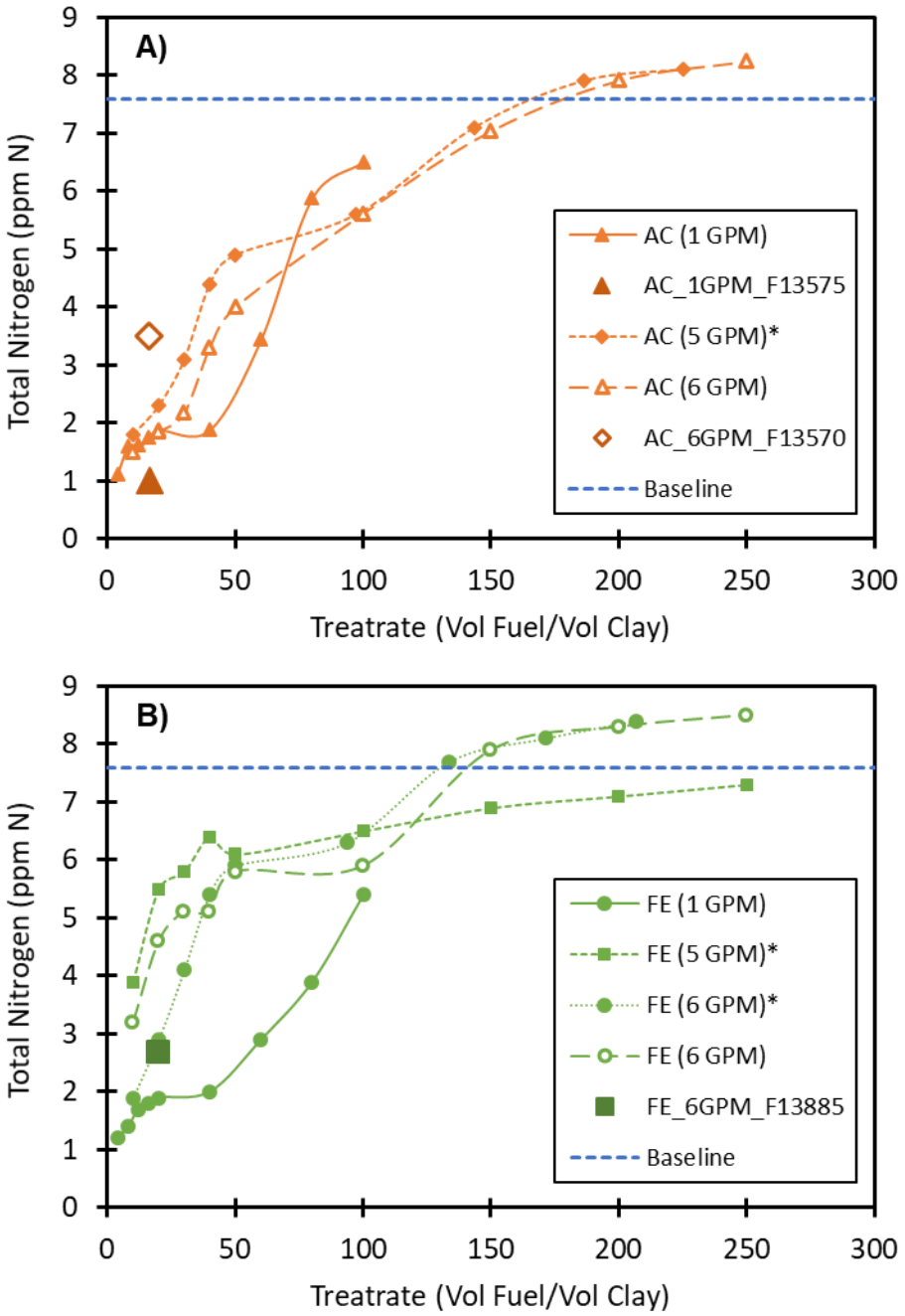


Figure 5. Total Nitrogen Profiles of Bench Scale (Lines and Markers) and Drum Scale (Only Markers) Fuel Samples after Clay Filtration using (A) AC or (B) FE; Nitrogen Level of Untreated Fuel Shown with Dashed Blue Line (*Data Generated Using HPLC Pump)

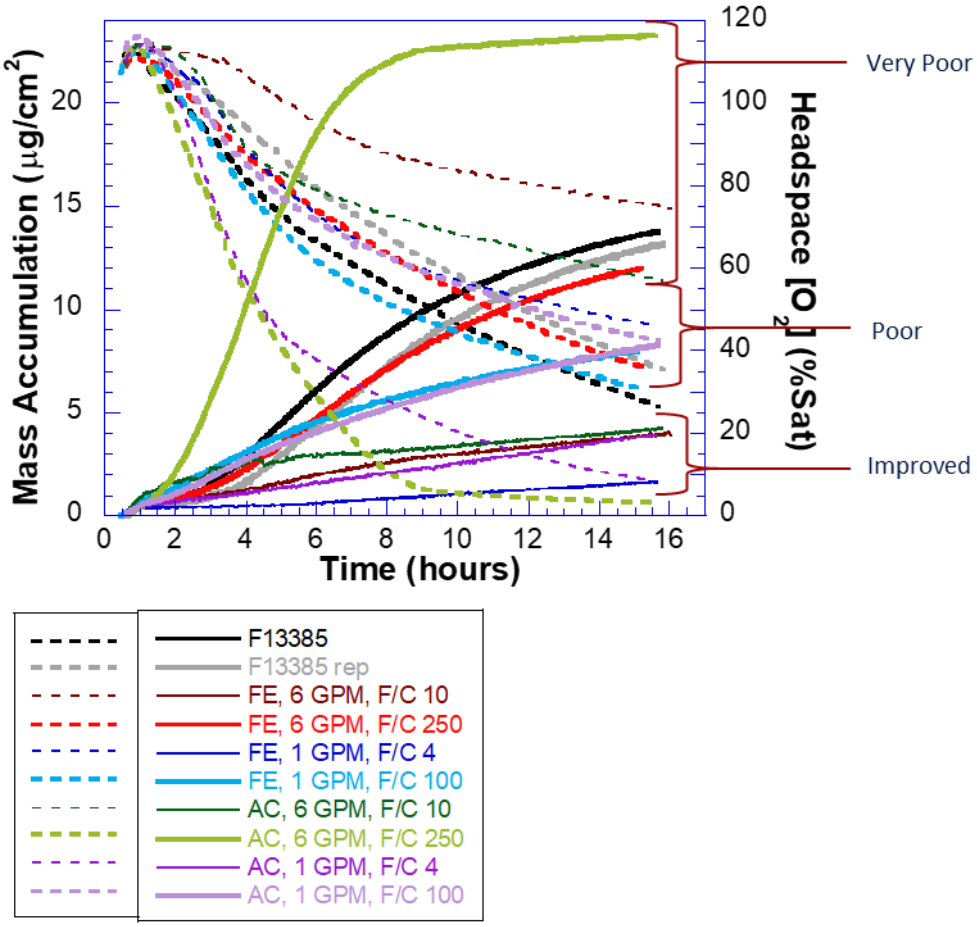


Figure 6. QCM Mass Accumulation (Solid Curves) and Headspace Oxygen (Dashed Curves) Profiles Generated at 140 °C; Bench Scale Simulated Sample Flow Rates of 1 and 6 GPM Using AC or FE at Various F/C Volume Ratios

4.2.1 High (F/C) Ratios and Other Fuels

From a practical standpoint, it is desirable to operate at high (F/C) ratios to maximize the amount of fuel treated while minimizing the amount of clay required. For instance, a typical clay tower may contain around 120 canisters (at about 2.55 gal of clay per canister) which is just over 300 gal of clay. Therefore, passing 120,000 gal of fuel through this hypothetical clay tower would give a (F/C) volume ratio (F/C ratio) of about 400. It is conceivable that F/C ratios of ≥500 would be desirable for field operations, e.g., air fields, terminals, and DFSPs. Data in the preceding sections (e.g., Figure 3 through Figure 6) is shown for F/C ratios of ≤250. Thus additional bench scale clay treatment experiments were conducted on fuels F13385 and F12843 as before, except sample aliquots were about 1 L in volume (rather than 100 mL or 500 mL), allowing F/C ratios up to about 1000. Results for each fuel are shown in Figure 7 and Figure 8, respectively.

Figure 7 shows the total nitrogen profiles of fuel F13385 for the higher F/C run (solid, diamond markers) along with comparison data from Figure 5. As these data show, the overall trends are similar with the total nitrogen level of the treated fuel returning to the original, untreated level at F/C of about ≥300 regardless of the specific experimental conditions. That is to say there appears

to be a specific saturation point of the clay with this fuel,where the clay is no longer able to adsorb additional nitrogen-containing compounds. A similar trend can be seen with the second fuel (F12843) in Figure 8, whereby the total nitrogen content of the fuel is initially reduced, however, the original nitrogen level of the fuel is quickly approached asymptotically as F/C ratio increases. The total nitrogen level can be considered a harbinger of poor fuel thermal stability.

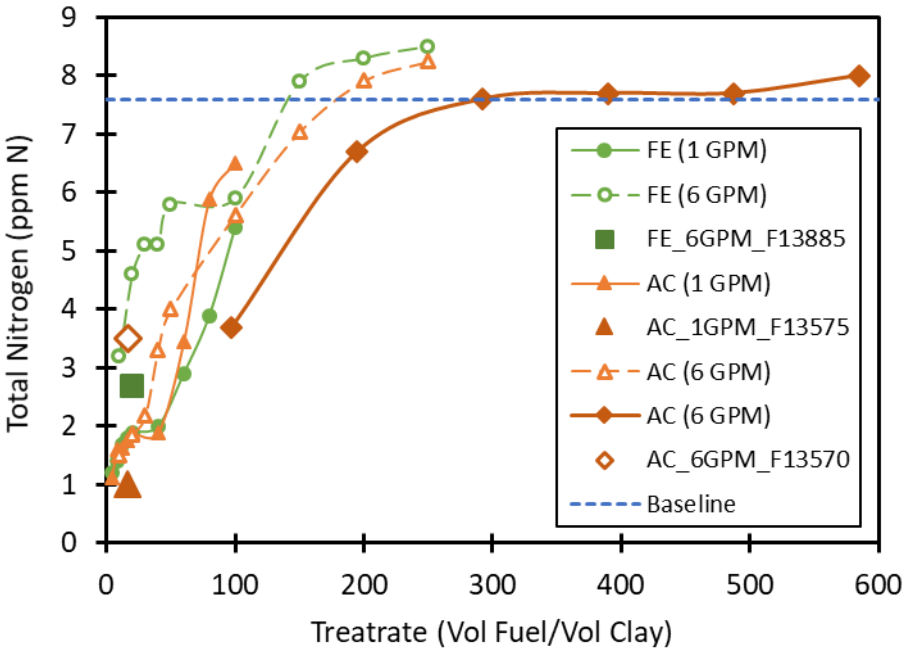


Figure 7. Total Nitrogen Profiles of Fuel F13385 at High F/C Ratios (Solid Diamond Markers); All Other Data Reproduced from Figure 5

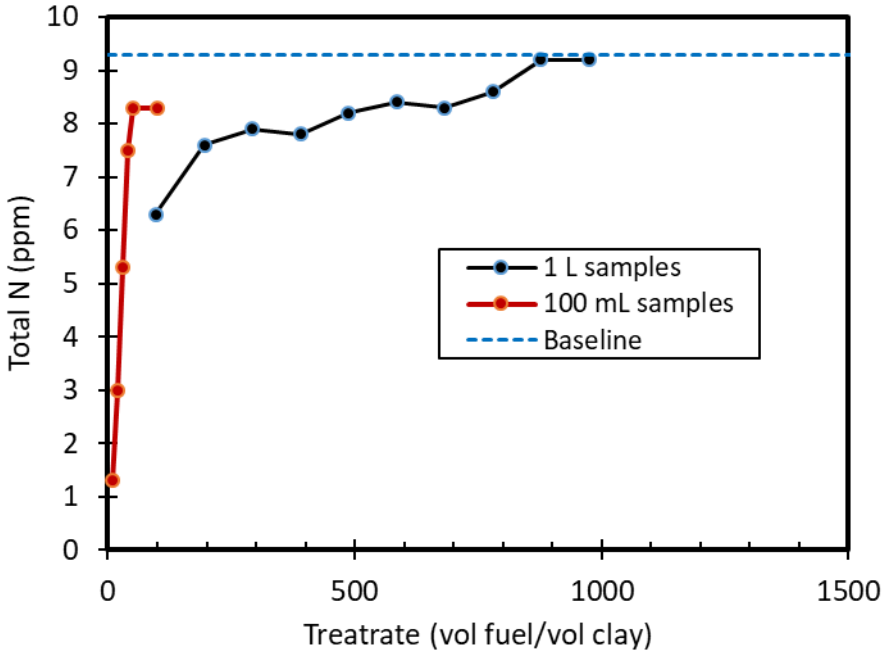


Figure 8. Total Nitrogen Profiles of Fuel F12843 at High (Dark Blue) and Low (Red) F/C Ratios

Since clay adsorbents eventually saturate and allow compound breakthrough of total nitrogen species at high enough F/C ratios, the question then becomes what is the impact on fuel thermal stability after clay treatment at high F/C ratios. To test this question, we analyzed clay treated fuel samples using both QCM and D3241 as a function of F/C ratio. Figure 9 shows QCM mass accumulation (solid curves) and headspace oxygen (dashed curves) for fuel sample F12843. As these data show, the neat fuel gives very high levels of deposition, 14.7 μg/cm^2, after 15 hours of thermal stress duration at 140 °C. Clay treating the fuel at low F/C ratios (97 and 100) provides very little improvement in deposition under these conditions, and high F/C ratios (682 and 974) also provide little to no overall improvement to the fuel thermal stability as assessed using the QCM. The QCM results for clay treated F12843 are in slight contrast to the results exhibited by sample F13385 (see Figure 4 and Figure 6), whereby an initial improvement was observed at low F/C ratios with gradual return towards the original poor thermal stability behavior. This demonstrates that not all poor thermal stability fuels are uniformly improved using clay treatment.

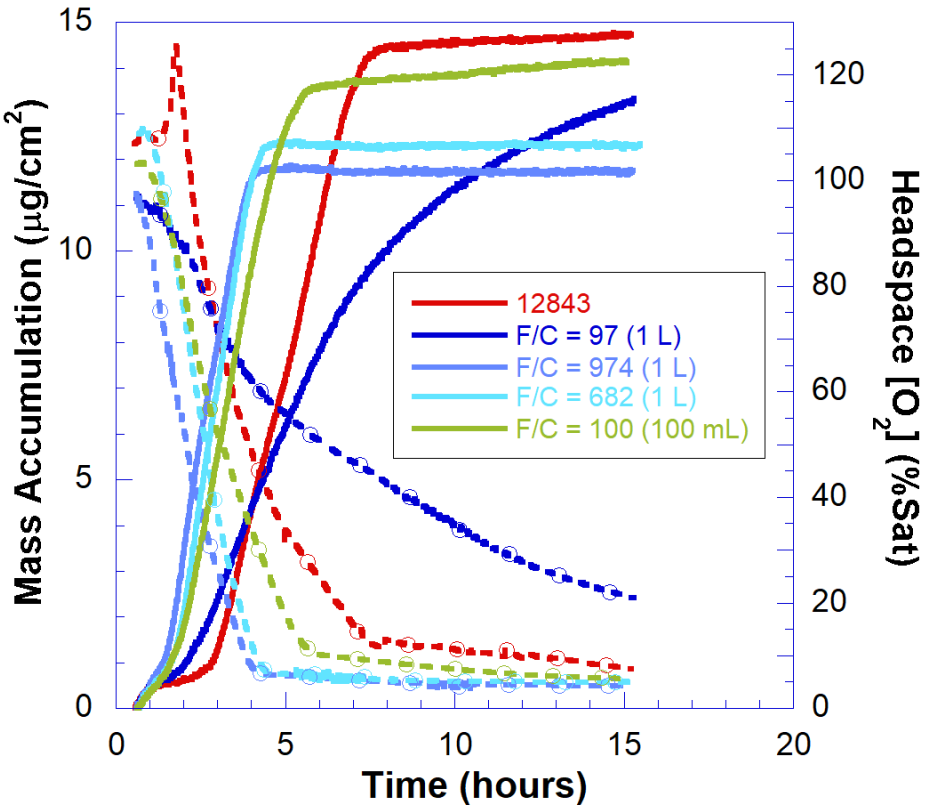


Figure 9. QCM Profiles of Mass Accumulation (Solid Curves) and Headspace Oxygen (Dashed Curves) at 140 °C for Fuel Sample F12843

Even though sample F12843 seemed less responsive to clay treatment under QCM conditions, sample F13385 did respond positively to clay treatment (see Figure 4 and Figure 6). Figure 10 shows aggregate QCM deposition data for sample F13385 as a function of F/C ratio. These data again demonstrate that significant improvement in sample deposition tendency (compared to the starting deposition level of 13.5 μg/cm^2) is observed at low F/C ratios (about <250) for this fuel sample. However, samples taken near or above the saturation F/C ratio give deposition values

greater than the initial value. It is possible that some deposit instigating compounds are being selectively removed and concentrated in the effluent fuel sample, thus actually decreasing the treated fuel thermal stability. However, it is not completely clear for these data if this hypothesis is correct, therefore, more research is suggested.

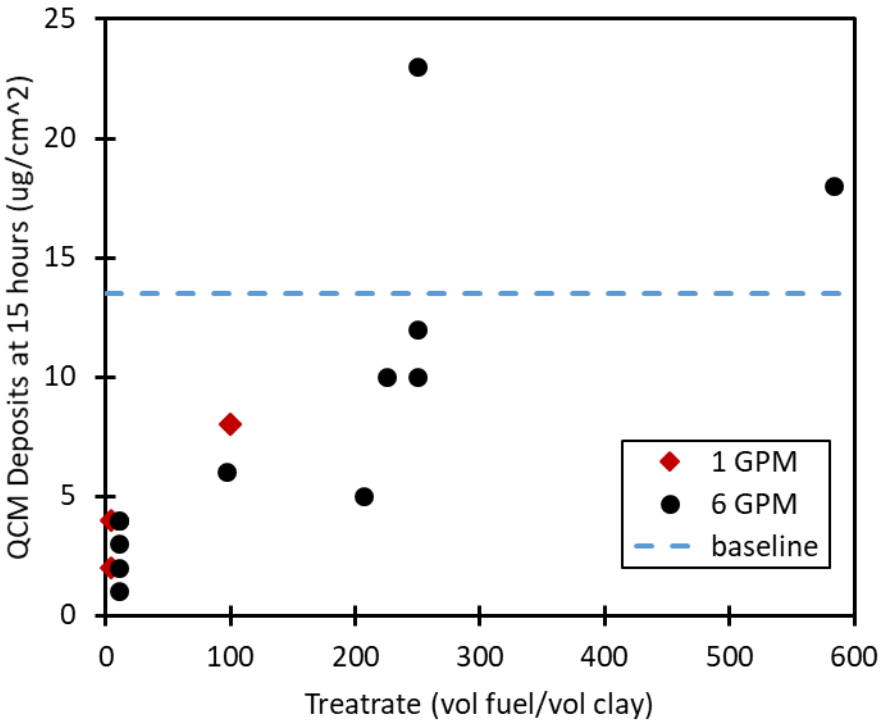


Figure 10. Aggregate QCM Deposition Data for Sample F13385 as a Function of F/C ratio; Dashed Line Indicates Neat Fuel Deposition Level

Regardless of the fuel thermal stability as assessed by the QCM, current fuel specifications rely on D3241 for evaluating sample thermal stability. Most commonly, aviation fuels must have a D3241 breakpoint of at least 260 °C. The D3241 breakpoint temperatures for fuel samples F12843 and F13385 are 265 °C and 235 °C, respectively (see Table 1), i.e., F12843 just passes while F13385 fails significantly. In an effort to determine the effect of clay treatment to improve D3241 performance, it was decided to test both fuels +10 °C greater than the respective breakpoint temperature, thus sample F12843 was tested at 275 °C and sample F13385 was tested at 245 °C and the results are shown in Table 6. (The decision to test samples at a single temperature, rather than to determine the new breakpoint temperature, was due to limited sample availability.) As these data show, the neat fuel samples fail D3241 at BP+10 since they are higher than the fuel breakpoint. Clay treatment decreases the measured deposition (via ETR) for both fuels, however, the ETR deposit is seen to increase at the highest F/C ratio for F12843. Interestingly, sample F12843 experiences ΔP failures after clay treatment, which is not the original failure mode for this fuel. These D3241 data corroborate the QCM results, that is these data show that clay treatment appears to have minimal effect on improving the thermal stability characteristics of sample F12843 (even though some of the heteroatomic content of the fuel is being removed at low F/C ratios). Conversely, sample F13385 demonstrates improved thermal stability via D3241 after clay treatment up to a F/C ratio of 584. Higher F/C ratios were not examined for this fuel, therefore, it is unclear when/if the D3241 deposit values would begin to

worsen. However, the QCM does show an increase in deposit at F/C = 584. While limited in scope, these data should be cautionary to those who wish to use clay treatment as a thermal stability mitigation strategy, i.e., efficacy of clay treatment to improve thermal stability is mixed.

Table 6. Thermal Stability Results for Two Clay Treated Fuels

Fuel POSF	F/C Ratio	ASTM D3241			QCM Deposit at 15 hr ($\mu g/cm^2$)
		Test T, BP+10 (°C)	ETR (nm)	Max ΔP (mmHg)	
12843	-	275	Fail (off-scale)	1.5	15
	97		12.9	101.1	13
	584		18.3	0.9	12
	974		40.6	108.8	12
13385	-	245	98.9	0.0	13.5
	97		14.7	0.0	6
	584		19.2	0.0	18

4.3 Feasibility of IFT to Determine Clay Lifetime

Clay treatment is designed to remove surfactant molecules from jet fuel. Surfactant compounds have both hydrophobic and hydrophilic characteristics (see Figure 11 for examples) and are highly retained by the clay. As demonstrated above, clay treating can be used to remove polar, heteroatomic components that may improve fuel stability. Some of these deposit instigating compounds also have surfactant-like qualities, but the capacity of the clay to adsorb these compounds is believed to be limited to a finite number of active sites on the clay surface. After the capacity has been reached for removing polar compounds, our hypothesis is that the bed will only remove compounds more polar than the compounds already adsorbed. We suspect that a competitive exchange of polar components will occur with the clay material, which could adsorb the most polar compounds and release the less polar compounds as molecules compete for active sites on the clay surface. Regardless, many of the removed materials can reduce the interfacial tension (IFT) between fuel and water, therefore, we explore the question if IFT could be used to monitor the clay bed capacity/lifetime.

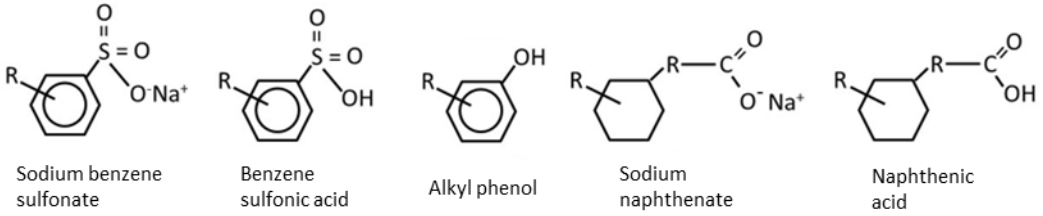


Figure 11. Surface Active Agents Which Can Be Found in Jet Fuel [1]

IFT was measured for fuel samples in contact with distilled water using the pendant drop method as described previously [8]. The absolute value of IFT varies between fuels, therefore the change in IFT (ΔIFT) of a single fuel will be used as our metric for comparison. The ΔIFT is determined by subtracting the clay filter value from the baseline fuel/unfiltered value: $\Delta IFT = IFT_{filtered} - IFT_{unfiltered}$. Results of this analysis are shown in Figure 12. As these data show, the ΔIFT value was always positive, indicating that the clay always removed some surfactant species and

therefore increased the energy at the fuel/water interface. Even though the IFT was always greater after clay treatment, the results do not indicate any trends with respect to clay bed life or ability to remove species that influence thermal stability. For example, significant increases in IFT are observed for fuel samples with high (F/C) ratios, however, these same samples indicate no improvement in thermal stability (see Figure 4).

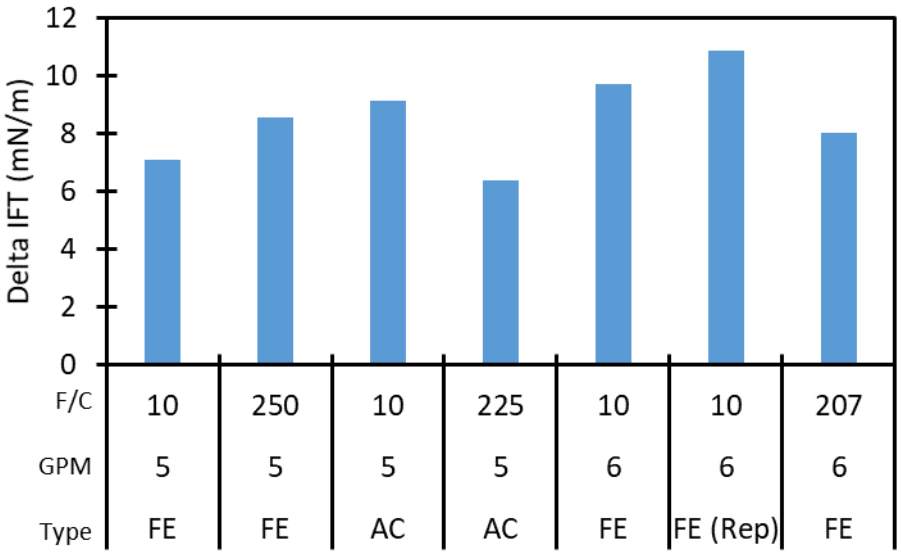


Figure 12. ΔIFT of Fuel Due to Clay Treating for Diatomaceous Earth (DE), FE, AC; Flow Rates; and F/C Ratios

These more fundamental measurements of IFT can be enlightening, however typical field assessment of surfactants is conducted using test method D7224. Thus four fuel samples were examined using both D7224 and the pendant drop method, the results are listed in Table 7. As these data show, an increase in the D7224 value is seen for all clay treated samples. Likewise, the IFT value increases for all clay treated samples. Both values indicate the removal of surfactant species for clay treated samples. Based on these data, and on fundamental principles, it is highly probable that a correlation exists between D7224 values and IFT; however, a more complete study should be conducted to determine the correlation. Regardless, these data again demonstrate that values relating to surfactant content, i.e., D7224 and IFT, do not adequately identify when breakthrough occurs on the clay and thus do not appear to be good indicators of clay lifetime with respect to thermal stability mitigation.

Table 7. Characterization of Surfactant Removal Due to Clay Filtration

Sample POSF	Description	F/C Ratio	Total N (ppm)	MSEP (D7224)	IFT (mN/m)
13385	Baseline	n/a	7.6	85.5	35.2
14017	AC, 6 GPM	195	6.7	99	45.0
13391	AC, 6 GPM	250	8.2	99	42.5
14018	AC, 6 GPM	487	7.7	99	45.4

5.0 CONCLUSIONS AND RECOMMENDATIONS

Jet fuel (F13208 and F13385) that failed D3241 was clay treated using drum scale quantities, flows, and a real clay filter cartridge. Results show a significant decrease in the fuel heteroatomic content and an improvement in fuel thermal stability at a low operational flow rate (1 GPM) and mixed results at a typical operational flow rate (6 GPM). The volume of fuel to volume of clay ratio used for the drum scale experiments was low, F/C $\leq$ 20, therefore bench scale experiments were conducted to increase the number of variables that could be reasonably explored in this study.

Bench scale testing of the failing fuel sample F13385 again shows that fresh clay removes a significant amount of heteroatomic species at low F/C ratios, however, the heteroatomic content quickly returns to untreated fuel levels at F/C of around $\geq$250. Similarly, the thermal stability of these treated fuel samples (assessed using the QCM) improves initially, with subsequent decrease back to the initial poor thermal stability level. Clay treatment of a second, moderate thermal stability fuel (F12843) shows little to no improvement in the thermal stability characteristics assessed using both the QCM and D3241.

Throughout these experiments trace, polar heteroatomic content was monitored along with fuel thermal stability (via QCM and/or D3241); the known correlation between heteroatomic content and thermal stability was re-emphasized in this work. Additional measurements were conducted for IFT and surfactant ability. Both D7224 and IFT measurements show that clay removes fuel surfactants, however there does not appear to be a correlation to clay lifetime/saturation with respect to thermal stability improvement.

Based on these data it is recommended that if field practitioners wish to use clay treatment to improve the thermal stability of a fuel that careful and judicious monitoring of the thermal stability (via D3241) of the treated fuel be conducted regularly throughout the process.

Finally, we recommend additional study in the following areas: what are the relative compound affinities for retention on the clay, is there competition for compound retention (and thus potential selective extraction from the clay), what are the implications for treating multiple fuels using the same clay, and expanding the breadth of saturation curves for different fuels.

6.0 ACKNOWLEDGEMENTS

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REFERENCES

1) Chevron Products Company. (2006). *Aviation fuels technical review* (FTR-3). Houston, TX: Chevron Corporation.
2) Zabarnick, S.; West, Z.J.; Shafer, L.M.; Mueller, S.S.; Striebich, R.C.; Wrzesinski, P.J. *Energy & Fuels* **2019,** *33*, 8557–8565.
3) Kuprowicz, N.J.; Zabarnick, S.; West, Z.J.; Ervin, J.S. *Energy & Fuels* **2007,** *21*, 530–544.
4) Mushrush, G. W.; Beal, E. J.; Hardy, D. R.; Hazlett, R. N.; Mose, D. G. *Fuel.* **1994,** *73*(9), 1481–1485.
5) Pillon, L.Z. *Petro. Sci. & Tech.* **2001,** *19*(7&8), 875–884.
6) Pillon, L.Z. *Petro. Sci. & Tech.* **2001,** *19*(7&8), 961–970.
7) Pillon, L.Z. *Petro. Sci. & Tech.* **2001,** *19*(9&10), 1109–1118.
8) West, Z.J.; Yamada, T.; Bruening, C.R.; Cook, R.L.; Mueller, S.S.; Shafer, L.M.; DeWitt, M.J.; Zabarnick, S. *Energy & Fuels.* **2018,** *32*, 1166−1178. DOI: 10.1021/acs.energyfuels.7b02844

APPENDIX A: DETAILED TRACE POLARS RESULTS

		POSF No.	13385	13570	13575	13885	13939	13940	13941	13942	13944	13945	13983	13984	13985	13986	13990	13991	13992	13993	14021	14022
Sample Information		Simulated Flow Rate (GPM)	n/a	6*	1*	6*	5	5	5	5	6	6	6	6	1	1	6	6	1	1	6	6
		Clay Type	n/a	AC	AC	FE	FE	FE	AC	AC	FE	FE	FE	FE	FE	FE	AC	AC	AC	AC	AC	AC
		Sample Volume	n/a	42 gal	42 gal	50 gal	100 mL	500 mL	100 mL	390 mL	100 mL	355 mL	100 mL	500 mL	100 mL	500 mL	100 mL	500 mL	100 mL	500 mL	974 mL	974 mL
		F/C	n/a	16	16	20	10	250	10	225	10	207	10	250	4	100	10	250	4	100	97	584
Polars (via SPE-GCxGC-FID/MS)	Nitrogen Compounds	Anilines	6.3	2.7	0.8	2.0	4.9	6.5	1.2	5.6	1.7	7.4	4.0	6.0	0.0	7.0	1.0	6.0	0.0	6.0	4	5
		Indoles	4.1	3.0	1.3	2.8	2.7	4.9	1.6	3.8	1.8	4.8	2.0	5.0	1.0	3.0	2.0	5.0	1.0	4.0	3	4
		Quinolines	22.9	13.0	5.0	9.2	11.7	26.5	5.5	22.5	5.4	24.0	9.0	30.0	1.0	12.0	3.0	31.0	1.0	17.0	13	24
		4H-Quinolines	3.2	1.9	2.5	2.2	2.4	1.9	1.6	1.8	2.0	3.1	3.0	2.0	0.0	3.0	1.0	2.0	0.0	3.0	3	2
		Pyridines	2.5	2.1	1.6	1.9	1.5	3.4	1.2	1.5	2.1	2.5	2.0	2.0	0.0	3.0	2.0	3.0	0.0	2.0	1	2
		Carbazoles	1.7	2.2	2.2	1.4	1.6	2.3	1.2	1.7	1.4	2.6	1.0	3.0	1.0	2.0	1.0	3.0	1.0	3.0	2	3
		Indolines	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Aromatic Oxygenates	Phenols	188	139	181	145	177	192	162	181	176	194	160	169	14	179	72	190	20	188	180	175
		Ar-Ketones	1	0	0	0	1	1	0	1	0	1	1	1	0	1	0	1	0	1	1	1
		Ar-Alcohols	26	15	18	17	25	27	28	27	21	28	22	27	1	31	7	33	1	30	26	27
		Ar-Aldehydes	1	0	0	0	1	1	0	1	0	1	1	1	0	1	0	1	0	1	1	1
		Ar-Esters	0	1	1	3	0	0	0	0	0	1	1	3	0	1	0	1	0	1	1	7
	Aliphatic oxygenates	Ketones	59	39	56	52	59	61	67	58	68	62	72	81	8	75	49	82	11	90	76	67
		Cycloketones	16	10	11	10	17	16	16	17	17	18	25	24	6	30	17	33	8	25	20	16
		Alcohols	30	25	36	28	28	29	28	27	33	31	27	32	6	29	18	34	10	32	32	30
		Aldehydes	7	3	6	4	7	7	6	6	4	7	4	5	1	6	3	5	1	5	5	5
		Esters	1	2	1	3	1	1	1	0	2	1	2	3	0	2	1	4	1	4	3	3
	Other		110	69	72	68	103	107	72	114	77	117	86	131	10	119	41	135	15	131	106	117
	Total		478	329	396	350	443	487	384	471	415	504	421	524	49	503	217	569	72	544	477	489
Nitrogen (mg N/kg)		Total	7.6	3.5	1.0	2.7	3.9	7.3	1.8	8.1	1.9	8.4	3.2	8.5	1.2	5.4	1.5	8.2	1.1	6.5	3.7	8.0
		Polar	6	3	1	2	3	5	1	5	1	6	2	7	0	4	1	7	0	5		
Sulfur (mg S/kg)		Total	801								758	768									3	5
		Polar	5	3	2	2	3	5	2	5	2	6	3	7	3	4	2	7	3	4		
QCM Deposit at 15hrs (ug/cm2)			13.5				3	10	2	10	1	5	4	12	2	8	4	23	4	8	6	18

*Indicates actual (not simulated) flow rate; experiment conducted on single canister system rather than smaller laboratory-scale system.