

REMOVAL OF WATER DROPS FROM VISCOR 1487 OIL

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ABSTRACT

Water-in-oil emulsion separations are important to petrochemical industries. Water molecules of less than 100 μ m diameter are present as secondary emulsions. The presence of water reduces the efficiency of the fuel combustion, the water droplets can plug small orifices, and water can dissolve polar compounds from the fuel and form corrosive materials, such as sulfuric acid which can damage engine parts. Thus, fuel filtration extends the life of engine. Coalescence filters are efficient and effectual for the removal of secondary emulsions.

The aim of this work was to eliminate these water molecules by development of filters to suit this application. The approach to this work was to apply surface modifiers to change surface wetting characteristics. In this approach, surface wettability of the filter was varied to determine its effect on coalescence phenomena and filter performance.

It also included construction of depth filter media with specified coatings where the fibers were coated prior to forming the media, or the media were constructed and the coating was applied to the media. The difference in wettability of the filters was studied using modified Washburn's equation is presented. Filters were tested in a liquid-liquid coalescence experiment. Recommendations for future work is proposed.

Key Words: Silanes, coatings, coalescence, filtration

INTRODUCTION

The problem of separation of Liquid – Liquid emulsions is frequently encountered in the field of chemical engineering. Some of the industrial examples are Liquid- Liquid extractions, sea water conversion, which includes desalting and dewatering of crude oils, water that exists as haze in aviation fuel needs to be eliminated [1].

Today, water contamination in refinery fuels can be a bigger problem than solids contamination. Water in fuel can corrode and plug engine parts and is a significant contributor to tank bottom corrosion and

bacterial growth. In addition, water may contain corrosive materials like chlorides that will cause equipment damage. Unfortunately, it doesn't take much water to cause a problem. Water along with surfactants which lower interfacial tension, at low concentrations (100 ppm) can cause a product to be off-specification due to haze or color [2].

For the removal of water in crude oil gravity settling is often used. It depends on the size of droplets that are to be removed. Often droplets less than 100 μ m in diameter are difficult to remove and separation is dependent on the Brownian and velocity gradient – induced coalescence to produce drops large enough to settle out. This oil-water mixture is referred to as a secondary dispersion.

There are several steps that have been used to enhance the formation of large drops like alternating electrical fields, addition of chemical coagulants and coalescence by flow through porous solids.

Amongst the aforementioned pretreatments to water in oil emulsions, coalescence is attractive since it has a higher effectiveness of separation under favorable conditions. Smaller droplets are coalesced into larger drops and they are eliminated by subsequent gravity settling.

Two parameters are of basic importance for the design of fiber bed coalescers: pressure drop and separation efficiency. The separation efficiency is highly dependent on the characteristic properties of the dispersion (e.g. composition, density, viscosity, droplet diameter) and of the fiber bed (e.g. material, diameter, surface structure, porosity) [3]. The fluid velocity plays an important role in emulsion flow as it controls the capture mechanism and capture probability of droplets.

INFLUENCE OF WETTABILITY OF FIBERS ON FILTER PERFORMANCE

The effect of the chemical nature of the solid surface on coalescence media is normally considered only on the basis of two material classifications: low - surface energy and high-surface energy materials. Thus, solid surface wettability with a dispersed liquid was designated as a crucial factor in coalescence phenomena. It is known that the ratio of the critical

surface tension of a solid to the liquid surface tension which determines the character of solid wettability [4].

An intermediate wettability gives the most effective separation, thus for the best performance the filter should be sufficiently water-wetted to coalesce the water, but not so saturated as to produce excessive pressure drop by the accumulated water. It has been found that fiber contact surface area is more important than pore size. The water droplets in water-in-oil emulsions must displace the oil film from the wet fiber for the attachment to be effective. A water droplet easily displaces oil on hydrophilic surfaces. The displacement of the continuous phase by the discontinuous phase on a low energy surface, such as polyethylene or PTFE (polytetrafluoroethylene, ie. Teflon®), should be considerably less than on a high energy surface, such as glass. The wetting behaviors of the water-in-oil or oil-in-water emulsions are considered to be important in determining the performance of the coalescence efficiency.

OBJECTIVE

Efficiency of coalescer filter media made from the glass fibers is influenced by the surface property of the glass fibers. This property is related to the wettability of the surface. Organo silane coupling agents can alter the surface energy of silica and glass.

The objective of this work was to study the effect of silanes on the wettability of the glass fibers which were made into filter media and used in liquid- liquid coalescence filtration experiments. This wettability study was done using the modified Washburn's equation; the penetration weight of liquid in the filter was measured which was used to investigate the advancing contact angles of filter media.

SILANES AS COUPLING AGENTS

Organofunctional silanes may be used as adhesion promoters between organic polymers and mineral substrates. They can function as a surface modifier or primer or an adhesive based on the quantity at the interface. As a surface modifier they form a mono or multimolecular layers on many materials without affecting the mechanical properties of the underneath substrate.

The coupling mechanism of the organofunctional silanes depends on a stable link between the organofunctional group (Y) and hydrolyzable groups (X) in compounds of the structure X_3SiRY . The organofunctional groups provide the reactivity with the polymer; the hydrolyzable groups are intermediates that form the silanol groups for bonding the mineral surfaces [5].

The advantages of choosing silanes to alter the wettability of the surface are: (1) the covalent bond between the organosilane molecule and the glass is relatively stable, (2) the amount of organosilane coating may be varied by duration time of treatment to provide a means of achieving different degrees of wettability, and (3) different functional organic groups of different silanes can impart different wetting properties [6].

The common hydrolysable groups (X) of organosilanes are chloro, acyloxy and amino. The byproduct of hydrolysis of chlorosilanes is hydrohalic acid. Acyloxy and amino substituted silanes are far more susceptible to hydrolysis in the presence of water; these products do not give acid on hydrolysis. Also they are more convenient to use. The silanes chosen for the experimentation work are all alkoxy based.

SURFACE FUNCTIONALIZATION OF FIBERS:

Silane coating is achieved by solution based deposition and vapor phase deposition. The glass fibers are coated with solution based deposition and are then made into filter media. Filter made from uncoated fibers are subsequently coated with vapor phase deposition. Both these techniques are explained beneath.

Solution Deposition:

The glass fibers were cleaned by immersion in a mixture of 30/70 by volume of sulfuric acid and hydrogen peroxide (technical grade) for at least 30 minutes, followed by rinsing with distilled water, dried under a stream of N_2 gas and were described subsequently as "clean" glass. The pre-treated hydrophilic glass fibers were oxidized by UV ozone for 10 minutes.

Organosilanes were deposited onto the cleaned and oxidized glass fibers using a solution deposition method. Glass fibers were placed in a solution of 3mM of organosilane in hexane (HPLC grade). The chemisorption of organosilanes was allowed to occur for 45 minutes to 1 hour. Finally, the glass fibers were removed from organosilane solution, rinsed with hexane, and dried under a stream of N_2 gas. The silanes used in experiments are listed in Table 1, [7].

Vapor Phase Deposition:

Uncoated glass fiber filters that were to be coated were cleaned under a stream of N_2 gas. They were then suspended in a desiccator above a glass dish that contained a mixture of silane solution in paraffin oil (3gm) with 200microliter of silane. The coating time was maintained to at 30 minutes.

Table 1. Summary of coatings used to alter the surface energy of the glass fibers.

Silane	MW (g/mol)	Specific Gravity
APTS (3-aminopropyltriethoxysilane)	221.37	0.951
CES (2-(carboxymethylthio)ethyltrimethylsilane)	192.35	1.0139
FTS ((heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane)	581.56	1.703

Contact Angle Measurement:

Contact angles are a measure of wettability of glass surfaces. Solution deposition was used to coat flat glass surfaces (glass slides), which we assume to have the same wettability of glass fibers used to make filter

media. This measurement was made using a Goniometer (Rame-Hart, Inc., Model 100-00 Contact Angle Goniometer) and by calculating the slope of the tangent to the drop at the liquid- solid- vapor interface line [8]. Table 2, gives the values of contact angles of silanes selected.

Table 2: Contact Angles of Flat surface.

Silane	Contact angle θ for water
APTS (3-aminopropyltriethoxysilane)	39°
CES (2-(carboxymethylthioethyltrimethylsilane)	62°
FTS ((heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane)	104°

Silane Depletion Study:

This study was conducted with the aim of studying the deterioration of silane-treated glass fibers that are immersed in water for a period of 2 hours in the slurry to make filter samples.

Glass slides were prepared using the aforementioned procedure for solution deposition technique with FTS (3mM solution in hexane) as the silane. Liquids used for this test were: Water, Water + Acrylic Binder, Water with a pH 2.75 using Sulphuric acid and finally all the three as per the recipe of slurry to make the filter media. Table 3, gives the change in values of the contact angles. All values are averages of three measurements taken on three slides for each liquid. Changes in the contact angles were insignificant in all of the solutions indicating that the 2 hour exposure to the liquid solutions when forming the filters has negligible effect on the silane coatings.

Table 3. Contact Angle using silane and testing with different liquids.

Sample Description	LHS	RHS
No Liquid	76.63°	77.71°
Water	73.23°	73.26°
Water + Sulphuric Acid	77.90°	74.86°
Water + Carboset- 560	73.26°	72.37°
Water + Sulphuric Acid+ Carboset- 560	74.95°	74.51°

FILTRATION

The aim of this research work is to determine the effect of surface wettability of filter media on coalescence performance for filtration of water in oil emulsion. The direct approach of characterizing the wettability of a solid material surface using contact angle cannot be used for filter media. Instead, the liquid penetration approach is used to measure the contact angles of filter media treating the pores as a bundle of uniform capillaries. This method of the liquid penetration is based on the equilibrium capillary pressure and Washburn's equation. Washburn's equation is based on the capillary driving force of a liquid that penetrates a compact vertical bed of particles with small pores and the viscous drag:

$$h^2 = \frac{r_{eff} \cos \theta_a \gamma_{lv} t}{2\eta} \quad (1)$$

where η is viscosity of the penetration liquid, γ_{lv} the surface tension of the penetrating liquid, r_{eff} the effective capillary radius, h the height of penetrating liquid in the bed in time t , and θ_a is the advancing particle contact angle, measured through the liquid phase [9].

In filter media, r_{eff} is very difficult to determine precisely and thus leads to significant error in the penetrating rates of liquid. To overcome shortcomings and errors prone to visual penetration rate, liquid weight gain measurements are used instead.

The weight, w , is related to the height in the capillary by

$$w = \varepsilon \cdot \rho \cdot \pi \cdot R^2 \cdot h \quad (2)$$

where ε is the porosity of the packed filter column, ρ the density of the liquid, and R the inner radius of the capillary.

Finally when we combine equations 1 & 2 by substituting for h , we get

$$w^2 = r_{eff}^2 \varepsilon^2 (\pi R^2)^2 \frac{\rho^2 \gamma_{lv} \cos^2 \theta_a t}{2\eta} \quad (3)$$

this gives a value

$$w^2 = \frac{c \rho^2 \gamma_{lv} \cos^2 \theta_a t}{\eta} \quad (4)$$

To determine the value of $c = r_{eff}^2 \varepsilon^2 (\pi R^2)^2 / 2$, one total wetting liquid must be used for which the contact angle is assumed to be zero. From the measurement of slope $\Delta w^2 / \Delta t$ and knowing liquid characteristics the value of c is computed.

Once the contact angle is found for a total wetting liquid, it can be used for another liquid from the slope of the curve.

$$S = \frac{c\rho^2\gamma_{lv}\cos\theta_o}{\eta} \quad (5)$$

S is the measurement of the curve slope $\Delta w^2 / \Delta t$ [10].

A concept called the Lipophilic / Hydrophilic Ratio (L/H) which was defined in [11] is used in this work. In this approach the contact angles of an apolar liquid (representative of oil phase) and a polar liquid (representative of water phase) for a filter medium are tested. The L/H ratio is related to the contact angles by

$$\frac{L}{H} = \frac{\cos\theta_o}{\cos\theta_w} \quad (6)$$

Using Eq.(5) to eliminate $\cos\theta_o$ from the equation we get

$$\frac{L}{H} = \frac{S_o\eta_o.c_w\rho_w^2\gamma_w}{S_w\eta_w.c_o\rho_o^2\gamma_o} \quad (7)$$

Both c_w and c_o are the same for a filter medium, thus L/H value reflects the wettability of the filter medium. L/H values when less than 1 indicates the surface is hydrophilic and values greater than 1 indicate the surface is lipophilic, L/H equal to 1 means equal wettability.

EXPERIMENTAL WORK

PREPARATION OF FILTER SAMPLES

The filter samples were made of glass fibers supplied by Hollingsworth and Vose with no further treatment. 0.5 gm of glass fibers were dispersed in a dilute aqueous solution of sulfuric acid (pH 2.5-2.75) and 0.5 ml of acrylic binder solution (Carboset 560, BF Goodrich). The slurry was stirred for 2 to 3 hours.

The slurry was vacuum filtered onto a fine mesh screen in a mold with five holes with an inside diameter 2.54 cm to form five filter samples. The applied vacuum pressure was from 100 to 160 kPa [12]. The filter samples were then dried and heated in an oven for 2 hours at 120°C.

EXPERIMENTAL SET UP FOR WETTABILITY STUDY

The experimental setup for this work is illustrated in Figure 1. Filters made from the above procedure were characterized prior to wettability studies. Filter samples were weighed using a microbalance, thickness was measured using Vernier Caliper. The thickness was maintained uniform throughout the experiment. They were then tested for their porosity using a Pycnometer.

In Figure 1, a glass tube was suspended from a wooden plank that was attached to a scissors stand which could be raised and lowered using a knob. This tube has a tapered diameter which was the same as that of the filter. The filter medium under test was cleaned

using nitrogen gas and was placed inside the tapered end of the tube.

A glass beaker with reference liquid, with temperature maintained around 23^o-25^oC was placed on the plate of an electronic balance. A stop watch was placed in front of the electronic balance along with a video camera facing both balance and stop watch. The cylinder descended slowly with a low speed of 1.0 mm/sec it was carefully done with several manual practices in order to get reproducible results. It was done with the extremity of the tube just touching the reference liquids. The video camera and stop watch were turned on when the filter medium touched the reference liquid to record the change in weight with time. The decline of the glass tube was ended and the liquid rose through the filter until it reached the top of the medium, causing an increase in weight of the cylinder. The video recording was stopped when liquid reached top of the filter medium.

The increase in weight of the cylinder was equal to the decrease in weight of the reference liquid placed on the balance. The evaporation rate of the liquids was measured and accounted for in decrease in weight of reference liquids. The experimental data were obtained from the video camera for every 5 seconds until the liquid reached top of filter.

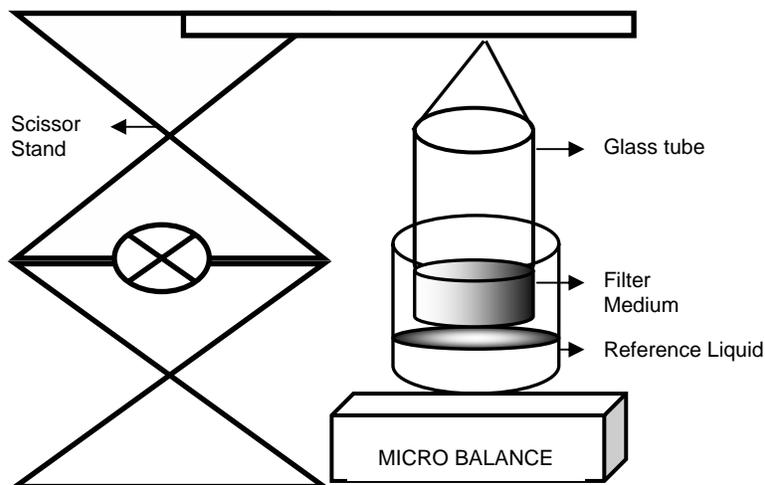


Figure 1. Schematic representation of experimental set up for measuring filter media wettability.

Materials and Methods

B-Glass fibers obtained from Hollingsworth and Vose were made into filters using the procedure described above. These filters were coated with silane using a solution 0.4 to 0.8 % (vol/vol) silane in water sprayed with 2 nozzles at the fibers. Filter samples made with a vapor deposition of CES, FTS and APTS on glass based filter media were tested.

The oil used for both filtration and wettability test is a calibration fluid. Calibration fluids have very similar properties to that of diesel fuel and gasoline. As stated by the manufacturer they have specifically controlled specific gravity and viscosity, higher and safer flash points as well as lower hydrocarbon content. The Viscor

oil 1487 that was used met requirements of SAE J-967 and ISO 4113 specifications.

Physical properties of water and Viscor Oil 1487 are presented in Table 4. Surface Tension was measured using a tensiometer at 25°C.

Table 4. Characteristics of reference liquids at 25°C.

Reference Liquid	γ (N/m)	ρ (Kg/m ³)	η
Viscor Oil 1487	0.0285	832	2.49(ASTM) D 445
Water	0.072	998	0.001(Ns.m ⁻²)

Table 5. Filter Sample Physical Characteristics (All values are averaged over three samples).

Filter Sample	Technique	Reference	Mass (g)	Height (mm)	Porosity
		Liquid			
Glass	Uncoated	Water	0.5444	9.474	0.914
Glass	Uncoated	Viscor Oil 1487	0.5397	10.414	0.917
APTS	SD	Water	0.4006	9.525	0.892
APTS	SD	Viscor Oil 1487	0.4488	9.448	0.85
APTS	VPD	Water	0.4332	9.443	0.93
APTS	VPD	Viscor Oil 1487	0.4107	9.886	0.936
FTS	VPD	Water	0.421	10.212	0.924
FTS	VPD	Viscor Oil 1487	0.4132	9.93	0.91
CES	VPD	Water	0.4671	9.556	0.942
CES	VPD	Viscor Oil 1487	0.4237	9.446	0.932

SD: Solution Deposition

VPD: Vapor Phase Deposition

RESULTS AND DISCUSSION

Wettability has a considerable influence on the performance of coalescence filters. Intermediate wettability is reported to give the best results. This study is done to evaluate the effect of silane coats on filter fibers and also best technique to coat filter. The silane depletion study indicated negligible change in the contact angle values after the treated fibers were submerged in the slurry to make filters. Some of the wetting kinetics results are illustrated in Figures 2- 6.

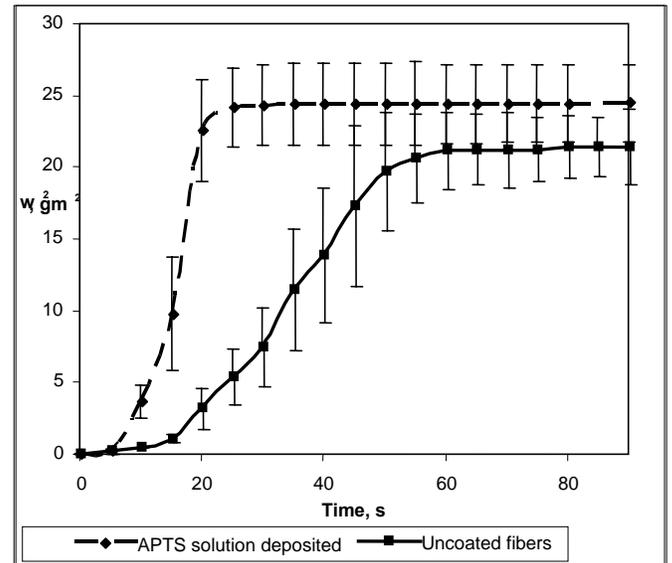


Figure 2: Wetting kinetics for different filter media with water as reference liquid.

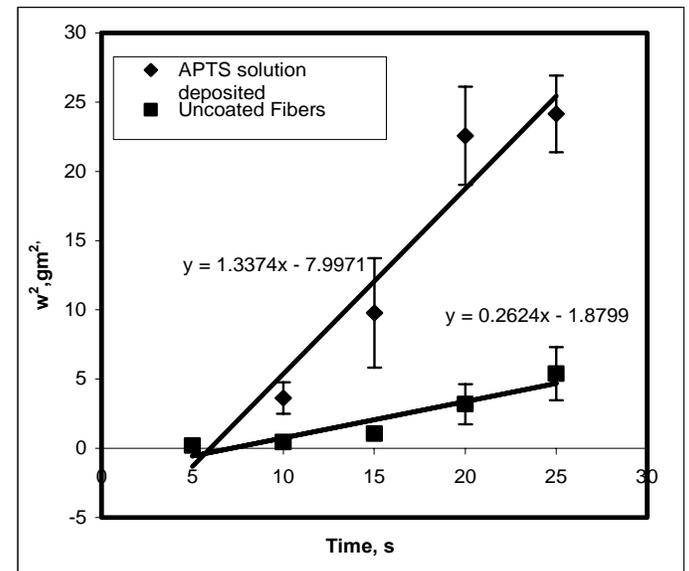


Figure 3: Wetting kinetics of filter media using water as reference liquid.

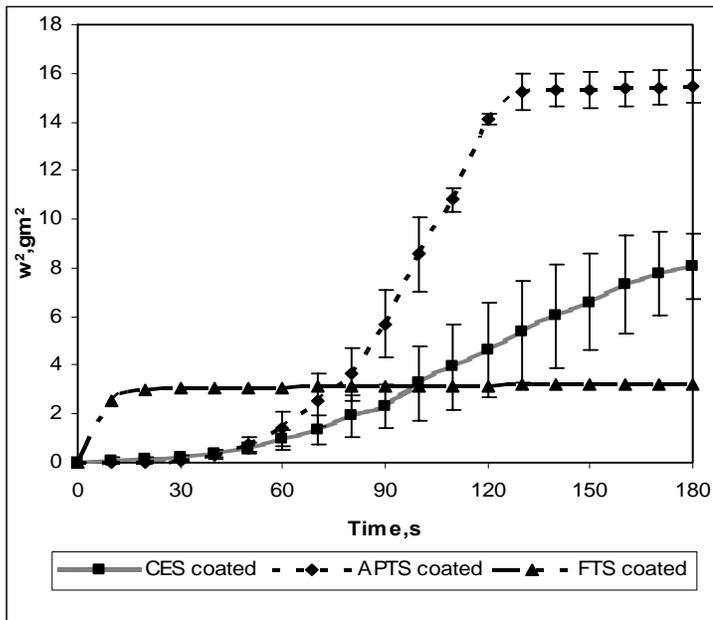


Figure 4: Wetting kinetics of vapor deposited silane based filter media using water as reference liquid.

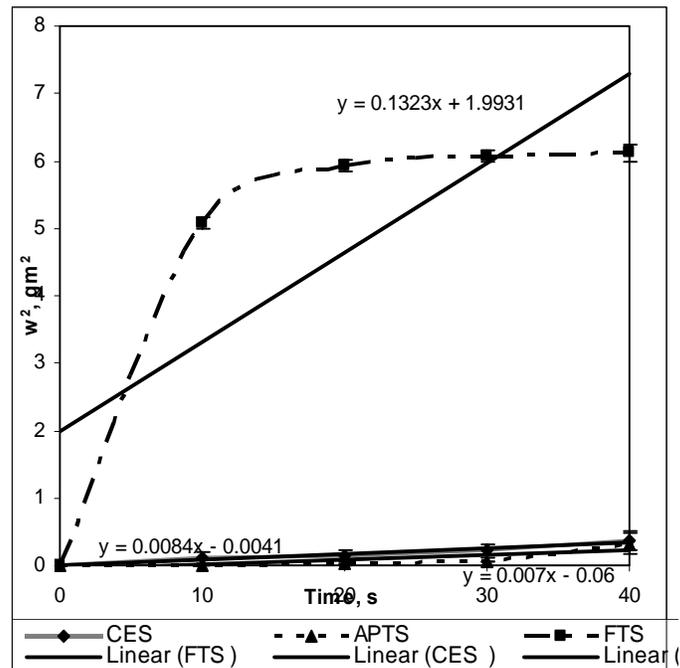


Figure 6: Initial Wetting Kinetics of filter media using water as a reference liquid.

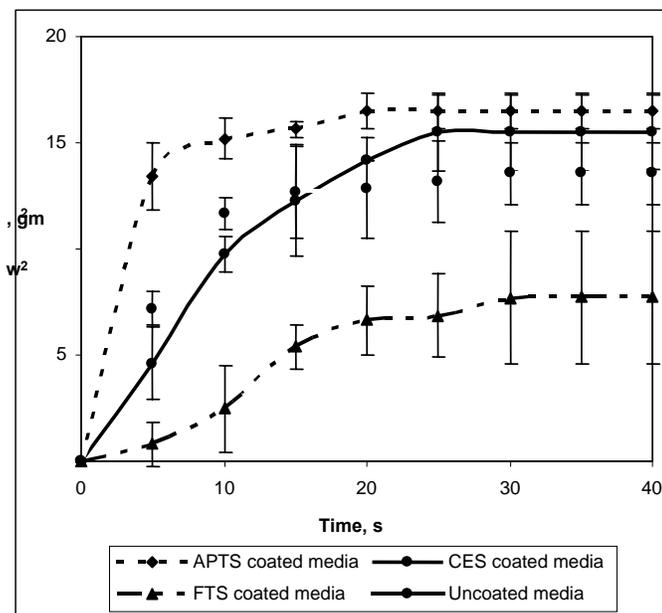


Figure 5: Wetting Kinetics of filter media using Viscor oil 1487.

*All values reported are average values of three filters.

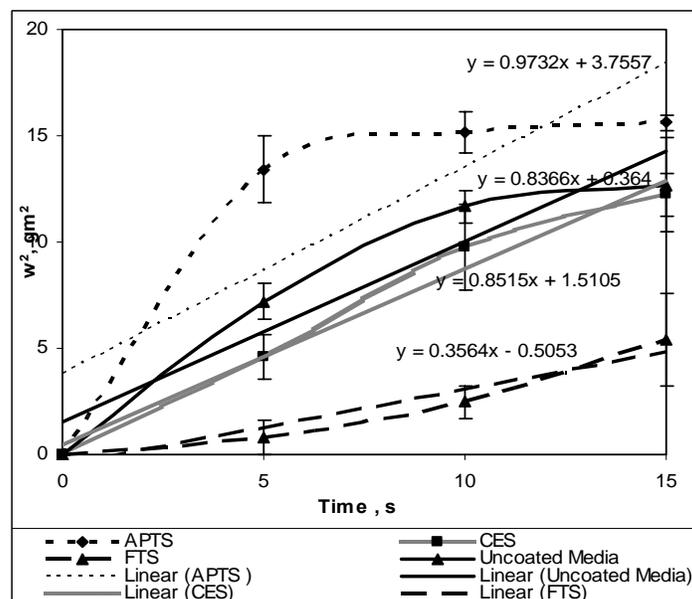


Figure 7: Initial wetting kinetics of filter media using Viscor oil 1487.

From the Figures 3, 6 and 7 we obtain values of slopes for $\Delta w^2 / \Delta t$ which was incorporated into Eq. 7 to obtain values for wettability of the filter media. Uncoated glass fiber based media have a value of $L/H = 0.89$ and coated fibers received from the industry have a $L/H = 0.163$. This indicates the media uncoated media doesn't have any preferential wetting. The difference in values of L/H indicates the wettability of the media for both oil and water.

Table 4. L/H ratios for Vapor deposited Silanes

Silane	L/H
FTS	<1
CES	>1
APTS	>1

Shin measured the contact angle of glass slides coated with silanes. It was found that both silanes CES and APTS had a contact angle less than 1° and FTS showed a higher contact angle. These results are in agreement with [12], FTS based silanes contain the CF_3 group which makes the media a low surface energy material and thus the uptake of both liquids is less. Hence the L/H value is less than 1.

CES and APTS silanes have a higher surface energy but not as high as untreated glass, it has been found that the L/H value is more than 1 which indicates the media are more lipophilic.

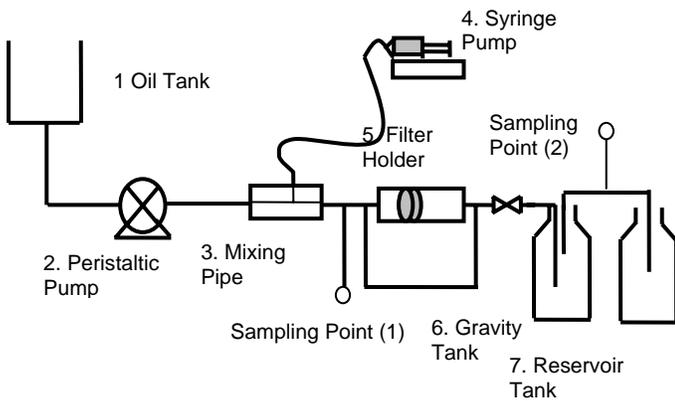


Figure 8. Schematic diagram of experimental set up for Liquid-Liquid Coalescence Filtration.

Intermediate wettability enhances coalescence filtration. Subsequent to this study filters with silane coatings are being tested for their performance in liquid-liquid filtration. Figure 8 gives a schematic of the filtration set up used for the tests [12].

The oil that is used for the tests is VISCOR 1487. It is pumped through the system using a peristaltic pump (2) (Master flex, model L/S EW-07543-60) at a flow rate of 150 ml/min to 175ml/min. At the mixing pipe (3) water droplets are introduced to make the water-in-oil emulsion using a syringe pump (WPI, Model sp101i) at a flowrate of 60 μ l/min(4). The droplet concentration is measured at sampling point (1) to obtain the inlet concentration at interval of 10 minutes. Filter media are placed in the filter holder (5) and the water in oil emulsion is pumped through it. Smaller droplets coalesce into larger drops. The pressure drop over the filter is measured as a function of time. A gravity settling tank (6) is used to remove the enlarged drops. The smaller drops are carried into the reservoir tank (7). The concentration of the flow going into the reservoir tank is measured at sampling point (2).

Sampling at points (1) and (2) is done to achieve particle size distribution using particle size analyzer (Particle Sizing systems, Model 780 Accusizer, sensor for 0.5 μ to 500 μ).

Filtration results include only settling tank and APTS vapor deposited.

Upstream particle size distribution of water droplets in the emulsion after steady state was achieved is shown in figure 9. Figure 9 shows the number of particles vs particle diameter.

The downstream particle size of water droplets at sampling point (2) for the two aforementioned cases is shown in figures 10 and 11.

Comparing the figures 9, 10 and 11 we can see that using a filter media with a coating significantly enhances the elimination of the water droplets of particle size greater than 10 micron in comparison with using only the settling tank.

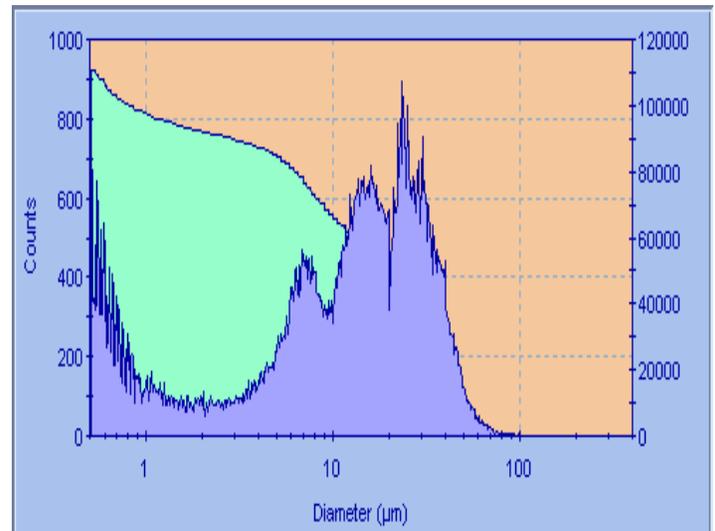


Figure 9. Particle size distribution of upstream at sampling point (1) after steady state is achieved.

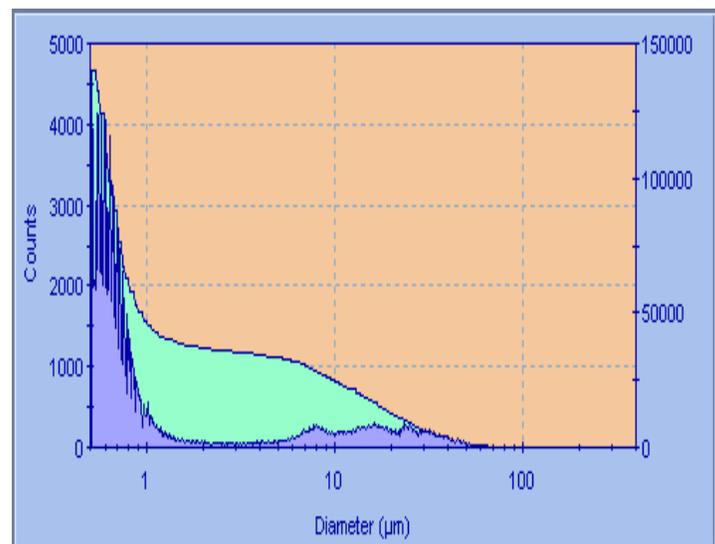


Figure 10. Downstream particle size distribution at sampling point (2) with using only settling tank.

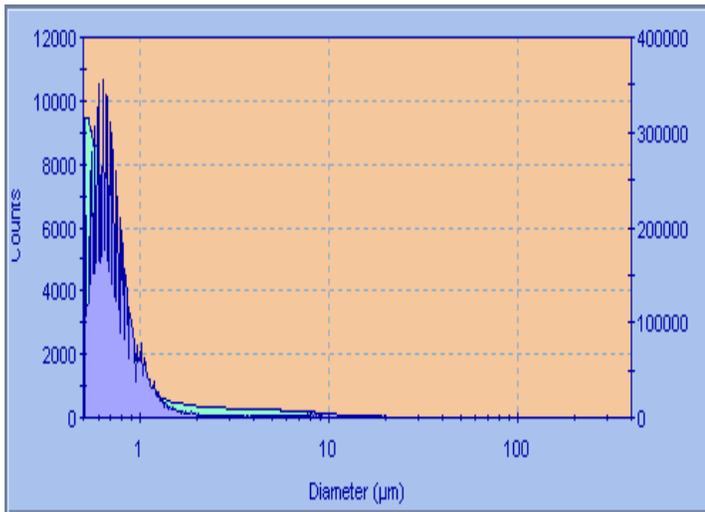


Figure 11. Steady state downstream particle size distribution for APTS coated filter media.

The separation efficiency, E, of a filter media is defined by

$$E = 1 - \frac{\sum_d \rho N_d \frac{\pi}{6} d_d^3}{\sum_u \rho N_u \frac{\pi}{6} d_u^3} \quad (8)$$

It was calculated for water particle size distributions upstream and downstream. N_u is the number of water droplets upstream of size d_u and N_d is the number of water droplets downstream of size d_d .

Table 5. Properties of filter and efficiency

Sample	Porosity	Permeability (m ²)	E
No Filter	*	*	0.486
APTS (vpd)	0.92	2.11*10 ⁻¹²	0.975

The significant difference in the values of E shows the enhancement of removal of water using the filter media coated with silane.

FUTURE WORK

The filtration results show that inclusion of a coalescing media along with settling tank significantly increases the system performance in removal of water from water in oil emulsion. Filter media with other silane coating are being tested to understand the effect of wettability on liquid-liquid filtration. This work is in progress and future results will include performance results of liquid-liquid filtration tests with the silane coated filters.

CONCLUSIONS

The difference in wettability of the filter media can be measured using the Washburn's modified equation. The experimental data show a significant difference in liquid uptake due to silane coatings. The preliminary filtration results show the significant increase

in overall efficiency for removal of water with filter and settling tank.

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