Reduction of Asphaltene Adsorption/Deposition on Silica

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Abstract

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During the production and processing of crude oil, asphaltenes are deposited within the porous rock from which the oil is extracted and in downstream machinery. This phenomenon has prompted numerous studies aimed at mitigating asphaltene-related issues. Easy-to-apply pre-adsorbates are sought to minimize asphaltene adsorption or deposition. Previous efforts have demonstrated some success; for instance, pre-treatment with a fluorinated silane reduced asphaltene adsorption onto silica substrates by up to 50%.

This study investigates the efficacy of Liquid Nails® LN-207 100% Silicone Adhesive (comprising 75-90% Poly(dimethyl siloxane) and 5-10% Methyltris(methylethylketoxime) silane) as a pre-treatment in Isopar™ L, a readily available, inexpensive material. It was found that treatment of the silica with a 5.0 weight percent solution of Liquid Nails® resulted in a remarkable 67% reduction in asphaltene adsorption. Wettability analysis showed a high water contact angle of 118 degrees for treated silica microscope slides, higher than that obtained for other treatments, suggesting that enhanced hydrophobicity correlated with asphaltene adsorption reduction.

This study establishes that Liquid Nails® treatment is promising for reducing asphaltene adsorption on silica gel. These findings advocate for Liquid Nails® as a surface treatment in managing asphaltene-related challenges in petroleum engineering, contributing to more efficient oil recovery processes.

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1. Introduction

There are many components in crude oil. The largest and densest molecules are bitumen, also known as asphalt. Within asphalt exists a polyaromatic core of molecules known as asphaltene. This core contains carbon, hydrogen, nitrogen, oxygen, and sulfur; as well as trace amounts of iron, nickel, and vanadium.[1] The exact structures of asphaltenes vary depending on their source, but their molecular weight averages around 750 g/mol.[2]

The traditional definition of asphaltenes is that they are soluble in aromatic solvents like toluene but not n-alkanes like tetradecane.[3] In the 1960s, Yen, Erdman, and Pollack described asphaltenes as polycyclic aromatic hydrocarbons (PAH) through powder X-ray diffraction (XRD). Asphaltenes had a crystalline structure with stacks of aromatic sheets approximately 0.85 to 1.5 nm in diameter which became known as the Yen model.[2] However, this only provided a macroscopic model of asphaltenes and did not give any insights into their chemical structure. Furthermore, Ebert's work in the 1980s suggested that it was incorrect to assume that Yen's XRD data indicated that crystalline structure "stacking" was occurring.[4] In 2010, Mullins modified Yen's model to account for nanoaggregate clusters and precipitates formed at low concentrations to create the modified Yen-Mullins model.[2]

The modified Yen-Mullins model suggests that PAHs stack can stack to form asphaltene nano aggregates with an aggregation number of about 6 (approximately 2 nm).[2] Beyond an aggregation number of 6, the critical nanoaggregate concentration (CNAC) is achieved, stopping further PAH aggregation. The steric-repelling alkanes of the PAHs align themselves in such a manner that prevents additional PAHs from attaching. However, the nanoaggregates can form nanoaggregate clusters with an aggregation number of about 8 (approximately 10 nm).[2]

In the past two decades, advances in Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) have also made it possible to determine the unique molecular elemental composition of most crude oil specimens, creating a new field of "petroleomics," the study of petroleum at a molecular level.[5] Additionally, non-contact atomic force microscopy (nc-AFM) has also been used to visualize the structure of individual asphaltene molecules.[6]

When extracting crude oil from porous sandstone, asphaltenes precipitate and adsorb onto the sandstone due to changes in pressure and temperature. This asphaltene adsorption then obstructs oil pipes and refinery catalysts, causing economic damages due to intervention costs and process downtime. Studies suggest that there are approximately 41,000 oil fields worldwide: 65% of oil fields are onshore and 35% are offshore.[7][8] Treating this asphaltene adsorption can cost approximately 0.5 million dollars for onshore fields and approximately 3 million for deepwater wells. These figures do not account for the lost production costs of approximately 1.2 million dollars per day.[9]

Currently, xylene is used to treat the asphaltene deposits in the oil fields. The United States consumes an estimated 250 million pounds each year to combat asphaltene adsorption.[10] West Texas alone consumes about 35 million pounds of xylene.[10] However, there are many problems with this treatment. If the xylene is not promptly removed, the asphaltene can redeposit on the oil fields. The xylene can also cause formation damage to the oil fields themselves.[10] Xylene has also been associated with health problems. Chronic occupational exposure has led workers to report problems of labored breathing and impaired pulmonary function.[11]

Terpenes are being considered as an alternative asphaltene treatment due to their biodegradability and higher flash point than xylene, making them safer and easier to transport. They are also as effective as xylene in dissolving asphaltenes. However, scaling the production of these terpenes has been proven to be expensive.[10]

As of 2023, oil, gas, and coal provide 82% of the world's energy.[12] Therefore, there is a great economic and environmental incentive to investigate surface modification using adsorbate barriers that might reduce or prevent asphaltene adhesion. This study serves to be a continuation of Sarsito and Berg's work where they attempted to find treatments that would reduce asphaltene and deposition on silica gel surfaces.[13] Silica gel was used as a model substrate due to its hydroxyl groups, which are similar to the features of sandstone reservoirs and pipes in crude oil processes. Three key findings were made in their study. Firstly, the results from an asphaltene particle deposition study parallel those for molecular adsorption. Secondly, a wettability study suggested that the more hydrophobic a treatment is, the better it is at reducing asphaltene adsorption. Lastly, a 1H,1H,2H,2H-Perfluorooctyltriethoxysilane fluorinated silane treatment was able to reduce asphaltene adsorption by up to 40%, in contrast to untreated silica gel.[13]

However, like the terpenes, the fluorinated silane treatment is also expensive and hard to obtain. At the time of writing, 5 grams of the fluorinated silane costs 146 dollars.[14] It was then of interest to find a more cost-effective treatment. In 2014, it was found that silica surfaces could be covalently functionalized by poly(dimethylsiloxanes).[15]

In another study done by El Khoury and Berg, a Liquid Nails® LN-207 100% Silicone Adhesive (75-90% Poly(dimethyl siloxane) and 5-10% Methyltris(methylethylketoxime) silane) adhesive was found to be a cheap and readily available treatment that was very successful in reducing adhesion onto carbon-fiber epoxy composites.[16] It was hypothesized that Liquid Nails adhesive could also be effectively used to minimize asphaltene adsorption on silica gel. It was also of interest to study how thick water films on silica could impact asphaltene adhesion. In a study by Hu et al., it was suggested that thick water films could prevent asphaltene adhesion.[17] It was then of interest to see how varying the thickness of the water films could impact asphaltene adsorption.

Therefore, the objective of this study was to treat silica gel with a Liquid Nails treatment at various concentrations to determine their effectiveness in reducing asphaltene adhesion. Afterwards, it was then of interest to treat the silica gel with different moisture levels, to see how the thickness of water films would affect asphaltene adsorption. Treated silica gel was placed into scintillation vials with asphaltene in toluene solutions, which was inspired by the studies of Alkafeef, Al-Marri, and Smith.[18-20] After some time, the supernatant solutions were pipetted into a quartz crystal cuvette. The amount of asphaltene that had adsorbed onto the sand could then be determined via UV-Vis spectroscopy analysis.

2. Methodology

2.1 Overview

In the study of El Khoury and Berg referenced earlier, it was shown that Liquid Nails® could reduce adhesion between carbon-fibers and an epoxy matrix in composite systems. Therefore, it was hypothesized that Liquid Nails® may also reduce asphaltene adsorption on silica surfaces. To determine qualitatively if Liquid Nails® adsorbed to silica gel, the mass of a given amount of silica gel was determined before and and after treatment with the Liquid Nails®, with an increase in mass suggesting significant adsorption. To investigate further, a BET (Brunauer-Emmett-Teller) analysis was done on the Liquid Nails® treated silica gels by using a FlowSorb II 2300 (Micromeritics; Norcross, GA). BET analysis measures the amount of an inert gas (usually N2) adsorbed to a given weight of the adsorbent (silica gel) at cryogenic temperatures. The amount of gas molecules adsorbed to a given mass of the solid gives its specific area from knowledge of the adsorption area of the gas molecules. Therefore, if the specific surface area of the silica gel decreased as the weight percent of the Liquid Nails® increased, there would be an indication that the Liquid Nails® was adhering onto the silica gel.

It was next needed to determine the relationship between the amount of adsorption of Liquid Nails® to the silica and its concentration in the treatment solution. Scanning electron microscopy (SEM) images were obtained to confirm that increasing the concentration of Liquid Nails® led to a higher extent of Liquid Nails® deposition. SEM images of treated silica slides were taken using an Apreo Scanning Electron Microscope (SEM) (ThermoFisher Scientific; Waltham, MA) at 1500x magnification. SEM was used since it can achieve magnifications that far exceed the capability of normal microscopes. With such high magnification, the morphology (spatial distribution) of the Liquid Nails® deposition could also be studied.

After determining that Liquid Nails® was adhering to the silica gel, there was a need to quantify the extent of adsorption and ultimately relate it to its effectiveness in reducing asphaltene adsorption. The amount adsorbed in each treatment is determined stoichiometrically by measuring the change in concentration of the Liquid Nails® in the supernatant after it is used to treat silica gel. The Beer-Lambert law, as shown in Eq. 1, states that absorbance is proportional to the concentration of chemical species that absorb light.

$$A = \varepsilon b C \tag{1}$$

where A is the absorbance, ε is the molar absorptivity, b is the cell depth, and C is the concentration. Therefore, if Liquid Nails® is a chemical species that absorbs light, a BioTek Synergy H1 Microplate Reader (Agilent; Santa Clara, CA) could be used to observe changes in concentration of an used Liquid Nails® treatment by measuring its absorbance. A microplate reader is an instrument that can measure absorbance of samples that are pipetted onto a 96 well plate made of polystyrene.

The next objective was to investigate the extent of effectiveness of the Liquid Nails® treatment in reducing asphaltene adsorption on silica gel via jar tests. Jar tests of treated silica gel and asphaltene in toluene solution were made and let to rest at certain time intervals. The change in asphaltene concentration of the solutions could be measured as a function of time and be used to determine the extent of asphaltene adsorption. Since toluene dissolves polystyrene, a Cary 60 UV-Vis Spectrophotometer (Agilent; Santa Clara, CA) was used instead to measure the absorbance of the solutions, as they could be pipetted into a quartz cuvette that was resistant to toluene.

In the study of Sarsito and Berg [13], it was suggested that the more hydrophobic a treatment is, the better it is at reducing asphaltene adsorption. Thus it was of interest to see how hydrophobic the Liquid Nails® treatment was by measuring the contact angle, the angle formed at the interface of a water drop and the treated microscope slide. Water drops were dispersed onto the microscope slide by using a FTÅ200 (FTÅ Instruments; Portsmouth, VA). A schematic of the FTÅ200 is shown below in Fig. 1.

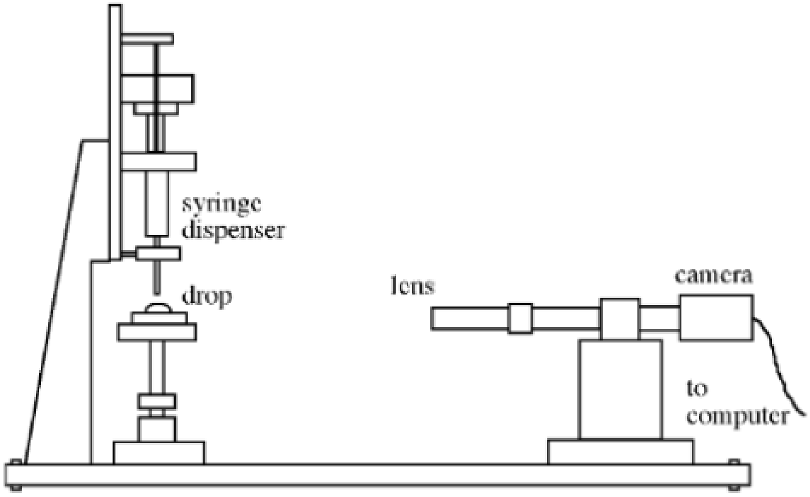

Fig. 1: FTÅ200 Analysis Instrument

The syringe dispenser is computer controlled and dispenses water drops onto the treated microscope slide. A high-resolution camera connected to the computer then captures an image, allowing for detailed observation of the water drop. These images are processed by specialized FTÅ software, which analyzes the drop profile to calculate contact angles.

Finally, it was sought to determine the effect, if any, of a pre-existing film of water on the silica surface. In Hu et al.'s study [17], it was proposed that water films could reduce asphaltene adsorption. Thus it was of interest to reintroduce water moisture into the silica gel and redo the jar tests with the moistened silica gel. Furthermore, some of the jar tests are also sonicated to consider effects of breaking the water films.

2.2 Material Preparation

Silica Gel:

200-400 mesh high-purity grade Silica Gel (Sigma Aldrich; Burlington, MA) was used as the model substrate of this study. Approximately 200 grams of silica gel was weighed via weighing trays and a Scout Pro SP2001 Portable Balance (Ohaus; PineBrook, NJ). The silica gel was then spread evenly in a 9 x 13" Rectangular Glass Baking Dishes (Pyrex; Corning, NY) and heated overnight (approximately 18 hours) in an Isotemp 725F Oven (Fisher Scientific; Pittsburgh, PA) at 200 degrees Celsius. After the heating process, the silica gel was carefully moved into a 1 L Reusable Glass Media Bottle (Fisherbrand;

Pittsburgh, PA) using a glass funnel and thermal work gloves. Finally, the media bottle was capped and placed into a 1400E Vacuum Oven (VWR; Radnor, PA) until the silica gel had sufficiently cooled down and could be used, which took approximately 1 hour. The silica gel was now effectively free of moisture and attempts to reintroduce moisture in later studies could be accurately quantified.

Steamed Silica Gel:

24 grams of silica gel was weighed using weighing trays and a portable balance before being transferred into a coffee filter. The coffee filter was then positioned over a piece of perforated plastic, which was the upper half of a Buchner funnel in this case. The setup was lightly shaken to ensure that the silica gel was evenly distributed across the coffee filter. Next, the perforated plastic was secured onto a ring stand, with the bottom of the mesh strainer elevated 20 cm above the lab bench to facilitate proper airflow. A hot plate was arranged beneath the ring stand, supporting a Pyrex crystallizing dish measuring 150 x 75 mm, which contained 500 mL of deionized (DI) water. The hot plate was set to its maximum temperature and left to operate for 30 minutes, allowing the silica gel to be adequately steamed. This duration was to ensure that the entire amount of silica gel was thoroughly soaked. After the 30 minutes elapsed, the silica gel was carefully transferred into a 250 mL media bottle using a glass funnel. The media bottle was then capped.

Soaked Silica Gel:

To determine the maximum amount of water that silica gel could hold, an initial mass of 24 grams was weighed using weighing trays and a portable balance before being transferred into a coffee filter. The coffee filter was then placed over a piece of perforated plastic. The setup was lightly shaken to ensure that the silica gel was evenly distributed across the coffee filter. DI water was subsequently poured over the top of the coffee filter until all the silica gel was visibly soaked. Afterward, excess water was squeezed out, and the soaked silica gel was weighed. However, transferring the soaked silica gel into scintillation vials proved challenging due to clumping. To address this issue, it was decided to first determine the amount of DI water that the silica gel had adsorbed. The mass of the silica gel was recorded before it was placed into a Pyrex dish and heated in an oven overnight at 200°C. After the heating process, the silica gel was weighed again, revealing that 67% of its weight was attributed to water. Consequently, when preparing soaked silica gel samples for scintillation vials, a precise method was established: 0.67 mL of DI water was added via pipetting to 0.33 grams of silica gel in a scintillation vial, resulting in a total sample weight of 1 gram of soaked silica gel. This method ensured accurate and effective preparation of the samples for further experimentation.

Liquid Nails® Solution:

A stock solution of 10 weight percent Liquid Nails® LN-207 Clear 100% Silicone Adhesive (PPG; Cranberry Township, PA) in Isopar™ L isoparaffinic hydrocarbon solvent (CORECHEM; Knoxville, TN) solution was prepared and subsequently diluted to achieve specific weight percentages of interest. Approximately 100 grams of Liquid Nails® were squeezed into a pre-tared 1 L media bottle. To achieve the desired concentration of Liquid Nails®, an appropriate amount of Isopar™ L was added to the media bottle. It was noted that accurately squeezing the exact amount of Liquid Nails® was challenging, so it was easier to adjust the concentration using the mass of Isopar™ L. For instance, if the actual amount of Liquid Nails® squeezed was 102.3 grams, then 920.7 grams of Isopar™ L would be added to the media bottle to create the 10 weight percent solution. This 10 weight percent solution was then diluted in new 1 L media bottles to produce solutions with weight percentages of 0.1, 0.5, 1.0, 2.5, and 5.0.

Silica Gel Liquid Nails® Treatment:

A Pyrex dish was first wrapped in aluminum foil to prepare for the treatment process. Subsequently, 24 grams of dried silica gel were removed from the 1 L media bottle and placed into a coffee filter, which was then positioned on top of the Pyrex dish. To avoid displacing the silica gel from the coffee filter, 300 mL of the Liquid Nails® in Isopar™ L treatment was gently poured into the Pyrex dish. The dish was then covered with a lid and allowed to rest overnight for approximately 16 hours.

After the resting period, the coffee filter was carefully removed from the Pyrex dish and placed onto paper towels to soak up any excess treatment solution. For the 5.0 weight percent solution, five 200 mL aliquots of the treatment solution from the Pyrex dish were pipetted into a 96-well plate for later analysis, while the remaining treatment solution was disposed of in a waste bottle. The Pyrex dish was cleaned with alcohol wipes, rewrapped in aluminum foil, and the coffee filter along with the paper towels were placed back onto the dish.

The Pyrex dish was then heated overnight in an Isotemp oven at 200 degrees Celsius for another 16 hours. Once the heating was complete, the treated silica gel was transferred into a 1 L media bottle using a glass funnel and thermal work gloves. The media bottle was capped and placed into a vacuum oven until the silica gel had sufficiently cooled down and was ready for use, which took about 1 hour. This entire process was repeated to produce treated silica gel corresponding to all the weight percent solutions of interest: 0.1, 0.5, 1.0, 2.5, and 5.0 weight percent.

Asphaltene in Toluene Solution:

10 grams of asphaltene from the West Kuwait Marrat Oil Formation was crushed into a fine powder using a ceramic mortar and pestle set. Subsequently, 750 mg of the crushed asphaltene was mixed with 1 L of toluene in a 1 L media bottle to create a solution with a concentration of 750 mg/L asphaltene in toluene. This mixture was stirred overnight for approximately 16 hours using a magnetic stirrer to ensure thorough mixing. After the stirring period, the solution was placed in a 5510R-MT Ultrasonicator (Branson; Brookfield, CT) for one hour to guarantee that the asphaltene was well dissolved.

2.3 Experimental Procedure:

BET Analysis Procedure:

Before beginning the BET analysis, two preliminary steps were taken. The night prior to the analysis, all silica gels of interest were reheated in the Isotemp oven at 200 degrees Celsius to eliminate any measurement inaccuracies from moisture interference. Two hours before the analysis, the Flowsorb was turned on to allow sufficient time for the air within the Flowsorb to be purged with Nitrogen gas, the medium that would be used to determine the surface area of the silica gel.

After purging the system, the FlowSorb was calibrated using nitrogen gas. Following calibration, the "DEGAS" sample holder was removed and tared on a HR-250AZ Standard-Level Analytical Balance

(A&D; Tokyo, JP). Approximately 0.1 (+/- 0.005) grams of silica gel was weighed using weighing trays and the analytical balance. The exact mass was recorded, and the silica gel was gently transferred into the Flowsorb's sample holder. The sample holder was then placed into the Flowsorb's "DEGAS" chamber at 200 degrees Celsius to remove any new moisture introduced during the weighing process, which usually took about 20 minutes.

Next, the sample holder was moved into the "TEST" chamber to obtain the nitrogen gas adsorption/desorption surface area values. If the two values were within 1% of each other, the measurement was considered valid. To ensure accuracy, three measurements were taken for each sample to obtain an average surface area for the silica gel. The surface area was then divided by the mass of the silica gel to obtain the specific surface area. This entire process was repeated until specific surface area measurements were obtained for all the silica gels of interest.

SEM Imaging Analysis Procedure:

Silica slides were functionalized with a treatment of a 5.0 weight percent Liquid Nails® stock solution by pipetting a layer of the solution onto each slide. Silica slides were also functionalized with a 1/1000 dilution of the 5.0 weight percent solution. The slides were then left in a fume hood overnight for approximately 16 hours to allow the treatment to cure properly. The slides were placed onto the stage of the SEM. After pumping the chamber of the stage, the electron beam can be turned on. The voltage of the electron beam and magnification are adjusted until a sufficient image is produced. If more Liquid Nails® was visually present in the slides functionalized with the stock solution, there would be sufficient visual proof.

Microplate Reader Analysis Procedure:

As previously mentioned, for the 5.0 weight percent solution, five 200 mL aliquots of the used treatment solution from the Pyrex dish were pipetted into a 96-well plate for later analysis. Additionally, five 200 mL aliquots of the original 10.0 and 5.0 weight percentage treatments, along with pure Isopar™ L (0 weight percent), were also pipetted into the 96-well plate. This was done to determine that Liquid Nails® was a chemical species that could absorb light and create a calibration curve that would correlate absorbance to Liquid Nails® concentration.

To facilitate the analysis, a Microplate reader procedure was developed using the Gen5 3.09 software, which operates the Microplate reader. The procedure was configured to measure absorbance at 300 nm, a wavelength that was experimentally determined to be capable of detecting Liquid Nails®. Once the 96-well plate was read using this procedure, a calibration curve was constructed to determine the change in concentration of the used 5.0 weight percent Liquid Nails® treatment.

Given that the total amount of treatment used was 300 mL, the exact mass of Liquid Nails® that adsorbed onto the silica gel could then be accurately determined based on the absorbance values obtained from the calibration curve.

UV-Vis Spectroscopy Analysis Procedure:

20 Metal Foil / Pulp Borosilicate Glass Scintillation Vials (DWK LIFE SCIENCES; Millville, NJ) were filled with 1.00 (+/- 0.005) gram aliquots for each treated silica gel. This process was carried out using weighing trays and an analytical balance to ensure precise measurements. Through trial and error, it was determined that asphaltene adsorption generally reaches equilibrium after approximately two weeks. Therefore, having 20 samples for each silica gel type would provide sufficient data points to obtain conclusive results.

Following the addition of the silica gel, 10 mL of the 750 mg/L asphaltene in toluene solution was pipetted into a scintillation vial each day. Each vial was labeled with the corresponding pipetting date. After two weeks, the samples were ready for analysis using a spectrophotometer to determine the extent of asphaltene adsorption onto the various silica gel surfaces.

A calibration curve was established using calibration solutions of asphaltene in toluene at concentrations of 0, 15, 30, 45, 60, and 75 mg/L to correlate absorbance with asphaltene concentration. This was accomplished by pipetting 3 mL of each calibration solution into a quartz crystal cuvette. After transferring the solution, the cuvette was cleaned with a Kimwipe to ensure there was no external contamination before it was placed into a Cary 60 UV-Vis spectrophotometer.

The spectrophotometer was connected to a computer equipped with Cary WinUV Simple Reads software, which facilitated individual UV-Vis absorbance measurements. For each calibration solution, five measurements were taken at a wavelength of 600 nm to calculate an average absorbance. After completing the measurements for each solution, the calibration solution was disposed of, and the cuvette was rinsed with toluene to remove any residual asphaltene.

To verify that the cuvette was properly cleaned, it was filled with pure toluene, and an additional measurement was taken and compared to the original pure toluene measurement. Once all calibration solutions were analyzed, the same procedure was repeated for the supernatant solutions in the scintillation vials. From there, an adsorption curve could be created for each treated silica gel and the effectiveness of the Liquid Nails® treatments could be quantified. The supernatant solutions were placed back into their respective scintillation vials for potential future studies, ensuring that the data collected would be reliable for subsequent analyses.

FTA Wettability Analysis Procedure:

Microscope slides were functionalized with a treatment of 5.0 weight percent Liquid Nails® by pipetting a layer of the solution onto each slide. The slides were then left in a fume hood overnight for approximately 16 hours to allow the treatment to cure properly. A total of three slides were treated in this manner.

After the curing period, the slides were placed on the specimen stage of the FTÅ, where three water contact angle measurements were taken for each slide using the FTÅ32 software. The contact angles were then averaged to obtain a final contact angle value for each slide.

Water Thickness Analysis Procedure:

The procedure is similar to the UV-Vis Spectroscopy Analysis Procedure. However, the steamed and soaked silica gels were used instead, and the study was confined to using the 5.0 weight percent Liquid Nails® treatment. Afterward, some of the jar tests were sonicated for 2 hours to break the water films. The UV-Vis Spectroscopy Analysis was then done on these jar tests as well.

3. Results

3.1 BET Analysis:

As stated earlier, silica gels were treated with Liquid Nails at different weight percentages. BET analysis was performed three times on each silica gel and the average specific surface area was recorded. The averaged values were then plotted, as shown in Fig. 2.

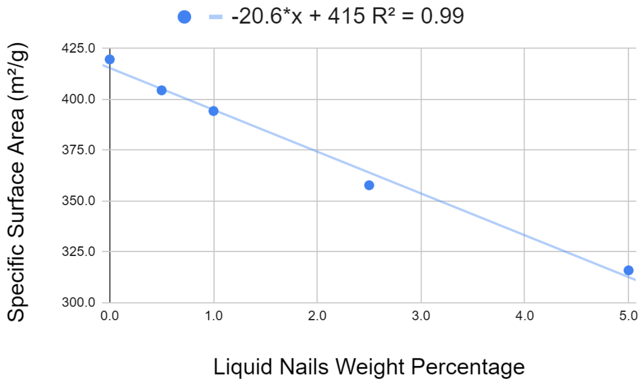

Fig. 2: Average specific surface area of silica gel treated with Liquid Nails for a weight percentage range of 0 to 5.0.

The specific surface area appears to decrease linearly by about 21 m^2/g for every additional weight percentage of Liquid Nails. This result is in accord with el Khoury and Berg's findings [16], where increasing the weight percentage of Liquid Nails led to more deposition on the soaked carbon fibers.

3.2 SEM Imaging Analysis:

Scanning electron micrographs (SEMs) taken of the treatment also verified that increasing the weight percentage of Liquid Nails led to more deposition. Another interesting observation to note is that the Liquid Nails does not deposit uniformly, instead it appears to cover the silicon slides in a "patch-like" manner, as shown below in Fig. 3.

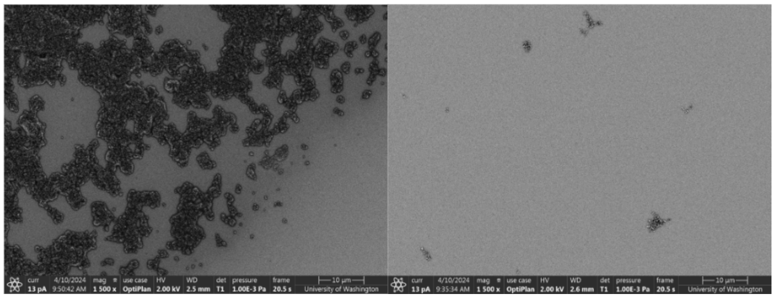

Fig. 3: Scanning electron micrographs of a 5.0 weight percentage Liquid Nails treatment microscope slide (left) and a 1/1000 dilution 5.0 weight percentage Liquid Nails treatment microscope slide (right). Images were acquired using an Apreo SEM, courtesy of the University of Washington Molecular Engineering & Science Institute's Molecular Analysis Facility.

This patch-like deposition can be explained by PMDS, a key component of Liquid Nails, being inherently hydrophobic. Since it has a high contact angle on a variety of substrates[21], its hydrophobic nature makes it difficult to spread evenly across a surface.

3.3 Microplate Reader Analysis:

Next, it was needed to quantify how much Liquid Nails had adsorbed onto the silica gel. To simplify the following analysis, only the 5.0 weight percentage Liquid Nails treatment was considered. To begin, a calibration curve was established, relating absorbance to different Liquid Nail weight percentage solutions, as shown below.

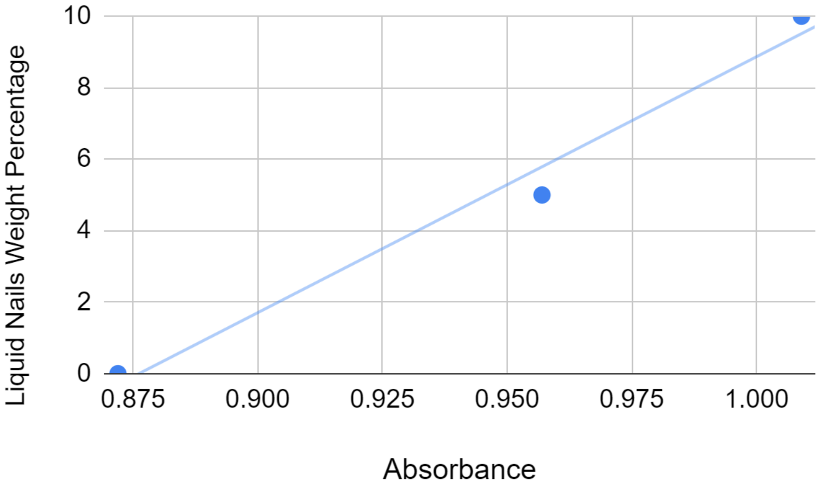

Fig. 4: Calibration curve of relating absorbance to Liquid Nails weight percentage.

This calibration curve effectively confirmed that Liquid Nails absorbs light. Therefore, the Microplate Reader can be used to measure the change in concentration. This method raises the question of why the amount of Liquid Nails adsorbed onto the silica gel could not be determined by a change in mass. However, when attempting to weigh the silica gel, it was inevitable that some would stick to the beakers or scatter while being weighed, causing non-negligible errors.

As seen in Fig. 4, the following relationship was established in Eq. 2.

$$Liquid\ Nails\ Weight\ Percentage\ = 71.6\ *\ Absorbance\ -\ 62.7 \tag{2}$$

It was experimentally determined that a 300 mL aliquot of 5.0 weight percent Liquid Nails solution had an average absorbance of 0.931. The relationship in Eq. 2 was used to find the corresponding weight percent, which was 3.96. Therefore, 1.04 weight percent of the 300 mL was used, which is 3.12 mL of Liquid Nails. Liquid Nails has a density of 1.04 g/mL, so a total of 3.25 grams of Liquid Nails was used to treat 24 grams of silica gel (an amount outlined in the Methodology section). Thus, 0.14 grams of Liquid Nails were deposited per gram of silica gel from the 5.0 weight percent Liquid Nails solution.

3.4 UV-Vis Spectroscopy Analysis:

After determining the Liquid Nails had been successfully applied onto the silica gel, it was then needed to see the effectiveness of the treatment. Jar tests were created using the scintillation vial test creation outlined in the Methodology section and then the supernatant solution was analyzed using UV-Vis spectroscopy. Similar to the Microplate Reader Analysis, a calibration curve was established, relating absorbance to asphaltene concentration, as shown in Fig. 5 below.

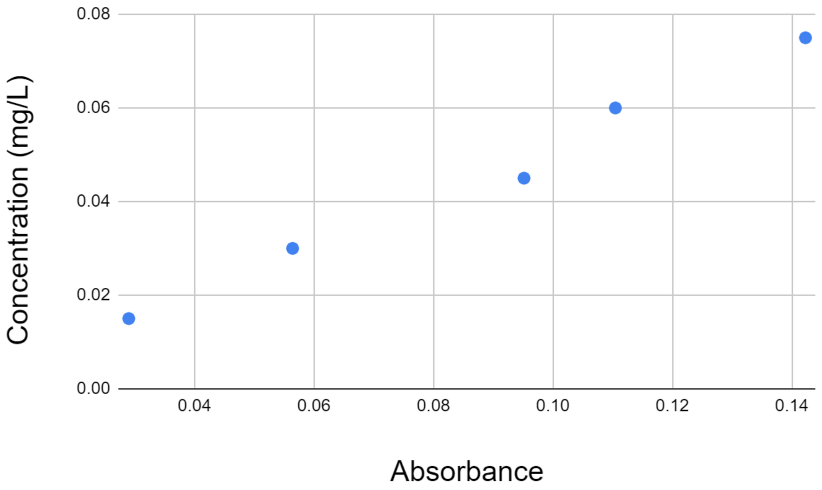

Fig. 5: Calibration curve of relating absorbance to asphaltene concentration.

The initial test considered three silica gels, an untreated gel, a treated 0.1 weight percent, and a treated 0.5 weight percent. The results are shown in Fig. 6.

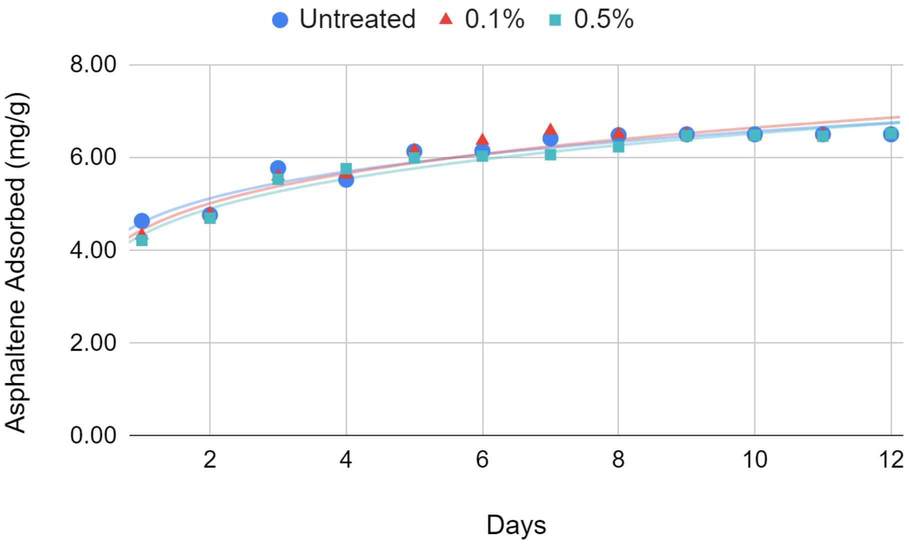

Fig. 6: Amount of asphaltene adsorption on a gram of silica gel for an untreated gel, 0.1 weight percent, and 0.5 weight percent.

With such low weight percentages, there seems to be no noticeable reduction in asphaltene adsorption. Jar tests were then made for a 1.0 and 2.5 weight percent. The results are shown in Fig. 7.

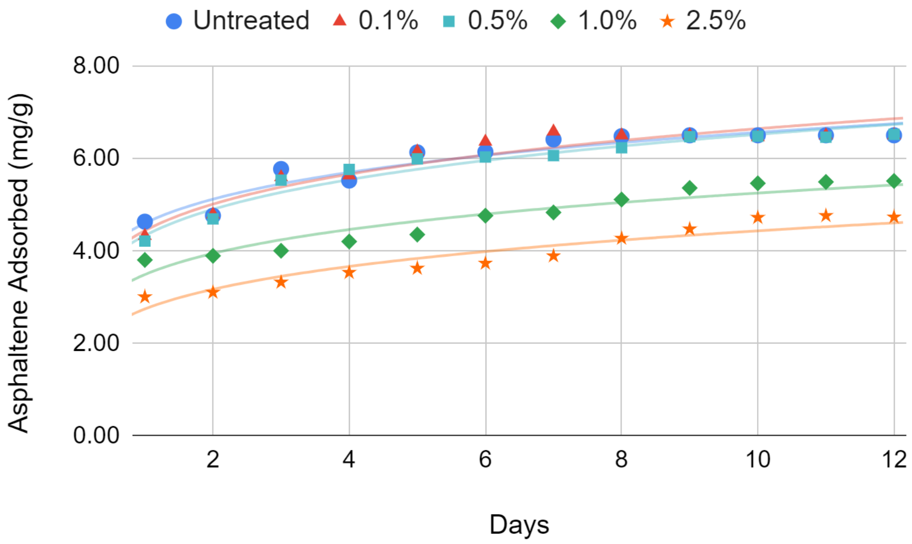

Fig. 7: Amount of asphaltene deposition on a gram of treated silica gel from weight percentages of 0 to 2.5 weight percent.

The 1.0 weight percent treated silica gel started showing signs of reducing asphaltene adsorption. The effect was even more noticeable in the 2.5 weight percent treatment. It was then of interest to see if increasing the weight percent of Liquid Nails led to further reduction in asphaltene adsorption. A 5.0 weight percent treatment was then used on the silica gel. Attempts were made to increase the weight percentage beyond 5.0 percent, however, this proved to be difficult as the silica gel started clumping together. The results are shown in Fig. 8.

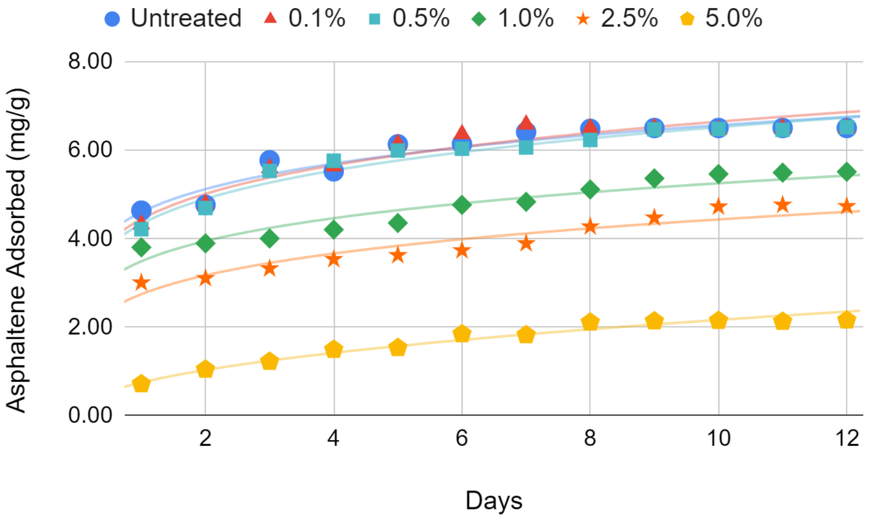

Fig. 8: Amount of asphaltene adsorption on a gram of treated silica gel from weight percentages of 0 to 5.0 weight percent.

There was a significant decrease in adsorption by the end of the experiment for the 5.0 weight percent. It was found that, by Day 12, the 5.0 weight percent silica gel had only adsorbed 2.16 mg of asphaltene, compared to 6.51 mg for the untreated silica gel. The 5.0 weight percent treatment effectively reduced asphaltene adsorption by 67%. A picture of the scintillation vials was taken at the end of the test shown in Fig. 9. As seen, there was significantly more asphaltene adsorption for the untreated and 0.1 weight percent treated silica gel.

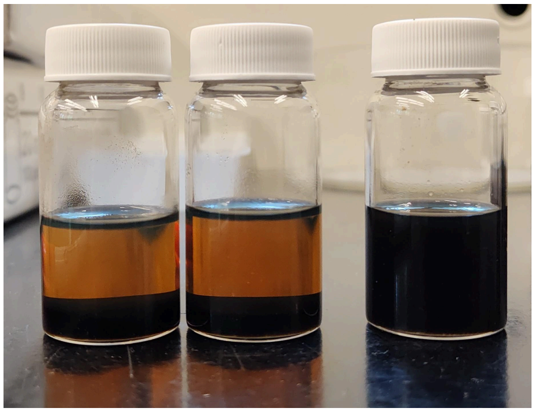

Fig. 9: Amount of asphaltene adsorption after 12 days for an untreated gel, 0.1 weight percent, and 5.0 weight percent (left to right).

The whole spectrum of solutions are also shown in Fig. 10.

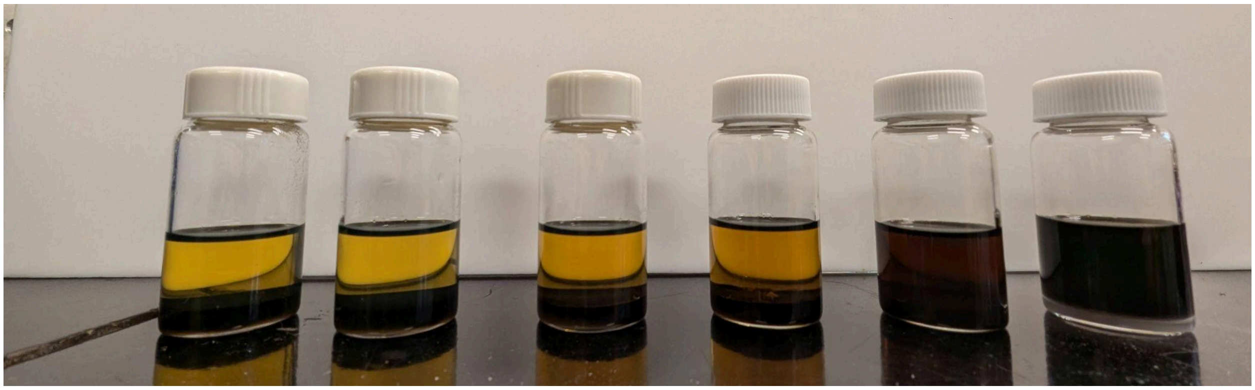

Fig. 10: Amount of asphaltene deposition after 12 days for an untreated gel, 0.1, 0.5, 1.0, 2.5, and 5.0 weight percent (left to right).

3.5 FTA Wettability Analysis:

A water wettability study was also done on the Liquid Nails treatment. One of the measurements is shown in Fig. 11. The water contact angle was found, on average, to be 118 degrees. This value confirms that Liquid Nails is highly hydrophobic. This value was also drastically higher than the 99.2 degree contact angle of the fluorinated silane in Sarsito and Berg's work [13], showing promise that Liquid Nails could be a more effective treatment in reducing asphaltene adsorption.

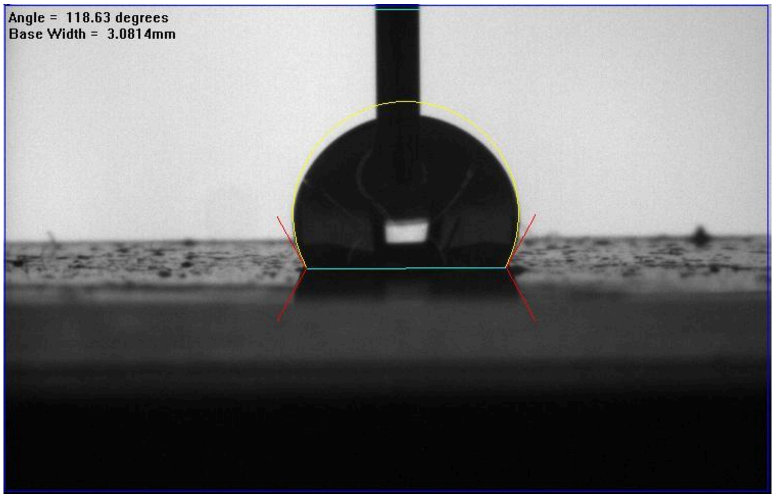

Fig. 11: Contact angle of a microscope slide functionalized with a 5.0 weight percent.

3.6 Water Thickness Analysis

After determining the Liquid Nails had been successfully applied onto the silica gel, the next objective was to understand the effects of moisture on the silica gel and how that would impact asphaltene adsorption. Steamed and soaked silica gels were created through the described methods in the methodology section. Afterward, the silica gels were heated in the Isotemp oven overnight at 200 C and then the mass change was recorded.

In the case of the steamed silica gel, the mass change was 0.70 grams. The mass change was divided by the original mass of the steamed silica gel to obtain the water content of the sand. The average water content of the steamed silica gel was found to be 12.67% of the system mass. Therefore, for 1 g of soaked silica gel, 0.1267 grams is water. The volume of 0.1267 grams of water would then be $12.67*10^{-7}$ m^3 of water. As seen in Fig. 2, 1 gram of silica gel has a specific surface area of 419.7 m^2. Thus, the thickness of water could be calculated by dividing the volume of water by the specific surface area to obtain a thickness of $3.02*10^{-10}$ m, equivalent to 3.02 Ångstroms. Using a literature value [22] of 2.5 Ångstroms as the thickness one monolayer of water, the number of water monolayers adsorbed on the silica gel was realized by dividing the two values, suggesting steamed silica gel has an average of 1.20 monolayers of water on its surface. The process was repeated for the soaked silica gel, and the values are tabulated in Table 1.

Table 1: The number of monolayers for each silica gel.

Silica Gel Moisture Level	Monolayers
Dry	0.00
Steamed	1.20
Soaked	6.33

Afterward, jar tests were performed with the silica gels as described earlier. The results are shown in Fig. 12. The adsorption of asphaltene is seen to be strongly affected by the presence of moisture at the silica surface, both in the absence and the presence of Liquid Nails surface pre-treatment. The results for the case in the absence of Liquid Nails are in agreement with the work of Hu et al [17].

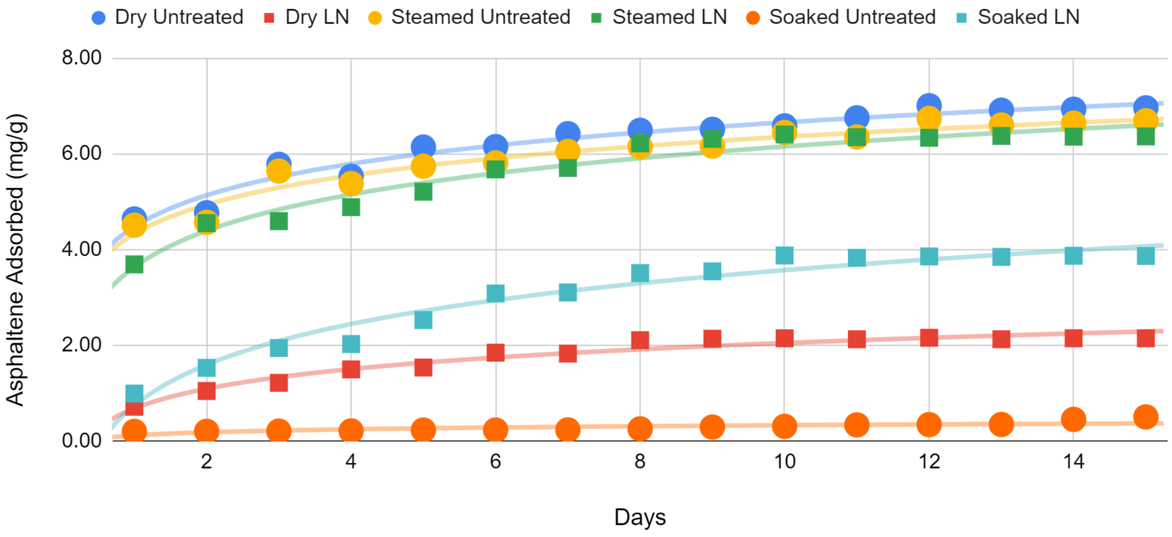

Fig. 12: Amount of asphaltene adsorption on silica gels with varying water thickness. Silica gels with the LN abbreviation were treated with a 5.0 weight percentage treatment.

The soaked silica gel had the lowest amount of asphaltene adsorption, suggesting that water films do retard asphaltene adhesion. In fact, there was barely any adsorption, even after 15 days. A subset of this data taken at two hours for comparison in a later study, shown in Fig. 13a.

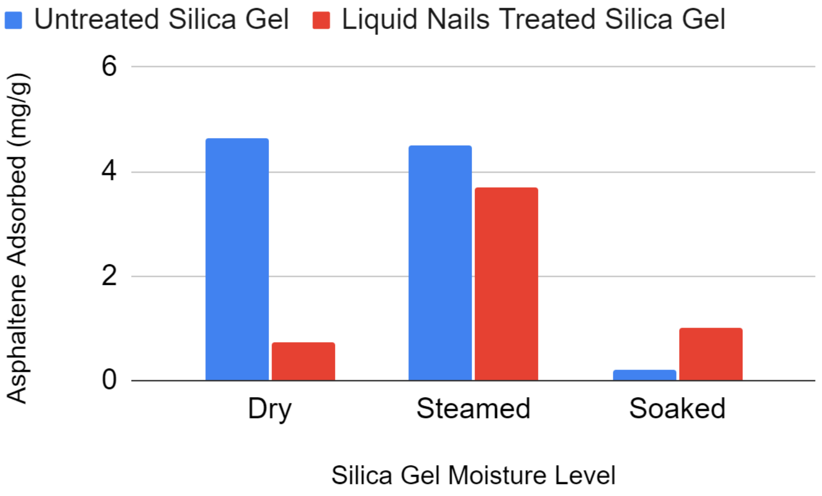

Fig. 13a: Amount of asphaltene adsorbed onto silica gels of various moisture levels in stagnant conditions.

However, these results are under the assumption that the water films are stagnant. It was then needed to see how the results would differ if the contents of the jar tests were undergoing stirring. A new study was conducted, where the jars were placed into an ultra sonicator for two hours, and then the amount of asphaltene adsorbed was recorded, as shown in Fig. 13b.

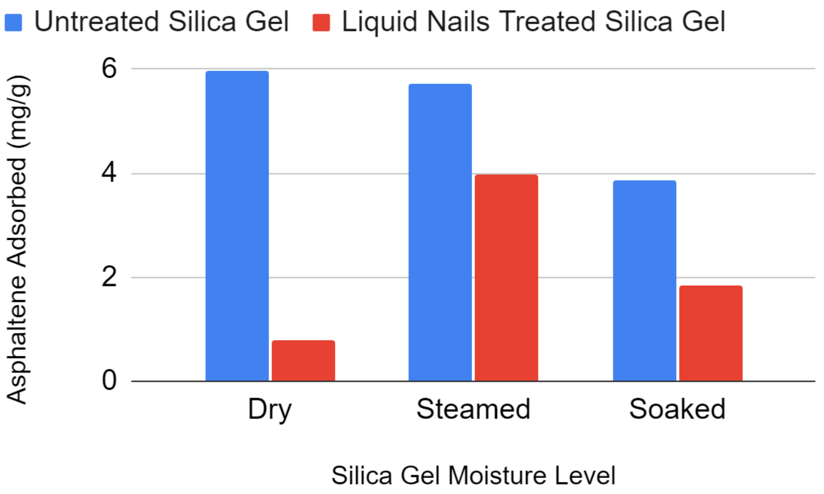

Fig. 13b: Amount of asphaltene adsorbed onto silica gels of various moisture levels after the jars were placed into an ultra sonicator for two hours.

Comparing Fig. 13a and Fig. 13b, it is observed that the amount of asphaltene adsorbed increased for all silica gels when the jars were sonicated. This result is visualized in Fig. 14.

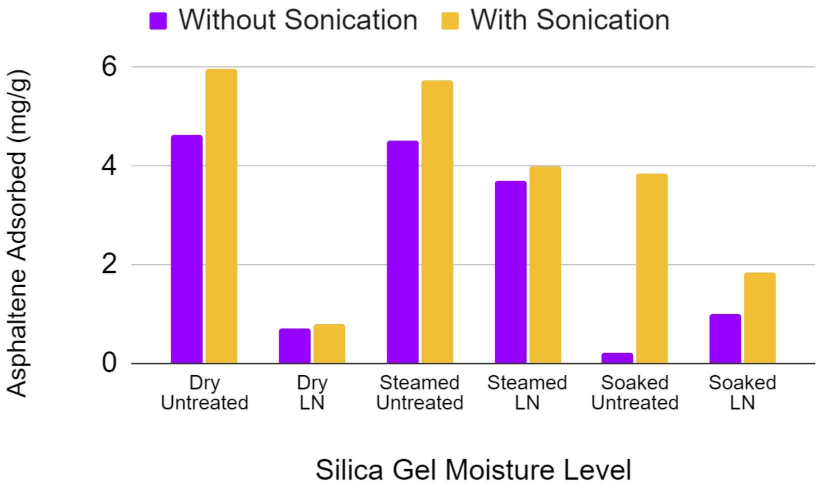

Fig. 14: Asphaltene adsorption after two hours, without and with sonication. Silica gels with the LN abbreviation were treated with Liquid Nails.

The percentage increase of asphaltene adsorption after sonication of the jars is tabulated in Table 2.

Table 2: The asphaltene adsorption percent increase upon sonication of the silica gels.

Silica Gel Moisture Level	Monolayers of Water	Asphaltene Adsorption Percent Increase
Dry Untreated	0.00	28.4%
Dry LN	0.00	9.7%
Steamed Untreated	1.20	27.1%
Steamed LN	1.20	7.8%
Soaked Untreated	6.33	1776.9%
Soaked LN	6.33	85.8%

As seen in Table 2, the amount of adsorbed asphaltene significantly increased for the untreated silica gels when the jars were sonicated. These results suggest that, while water layers may decrease the amount of asphaltene adsorption to a greater extent than Liquid Nails treatment, this is only valid for stagnant conditions. Once the water layers are disrupted, asphaltene adsorption starts to occur at a greater extent when the silica gel is untreated. As such, Liquid Nails is an effective treatment, even when in the presence of water layers.

4. Conclusions

The results of this study suggest Liquid Nails® LN-207 100% Silicone Adhesive is an effective treatment for reducing asphaltene adsorption on silica gel. A comprehensive analysis was conducted using BET analysis, SEM imaging, microplate reader assessment, UV-Vis spectroscopy, wettability studies, and water thickness evaluations to evaluate Liquid Nails® as a surface treatment.

The BET analysis revealed a consistent decrease in the specific surface area of silica gel as the weight percentage of Liquid Nails® increased. This linear relationship aligns with previous research and highlights the impact of Liquid Nails® deposition on the substrate. SEM imaging further elucidated the nature of Liquid Nails® deposition, showing a patch-like coverage on silica gel surfaces. This non-uniform distribution is attributed to the hydrophobic characteristics of PMDS, a key component in Liquid Nails®.

Quantitative assessments using a microplate reader and UV-Vis spectroscopy confirmed that the Liquid Nails® treatment deposits onto silica gel and significantly reduces asphaltene adsorption. Notably, a 5.0 weight percent treatment resulted in a remarkable 67% reduction in asphaltene adsorption compared to untreated silica gel. This substantial decrease emphasizes the potential for Liquid Nails® to serve as an effective barrier against asphaltene accumulation, which is crucial for enhancing oil recovery processes.

The wettability analysis, which indicated a high water contact angle of 118 degrees for treated silica gel, suggests that the Liquid Nails® treatment imparts strong hydrophobic properties. This finding is particularly relevant when considering other treatments such as fluorinated silanes. It indicates that Liquid Nails® may offer superior performance and cost-effectiveness in reducing asphaltene adhesion due to its enhanced hydrophobicity.

The water thickness analysis revealed that moisture levels significantly influence asphaltene adsorption dynamics. While water-soaked silica gels exhibited minimal adsorption under stagnant conditions, sonication disrupted water layers and drastically increased asphaltene adhesion on silica gels not treated by Liquid Nails®. This result highlights a critical consideration for practical applications: while moisture can act as a barrier to asphaltene attachment, its effectiveness is contingent upon environmental conditions and fluid dynamics.

In conclusion, this study establishes that Liquid Nails® treatment is promising for reducing asphaltene adsorption on silica gel. The findings advocate Liquid Nails® as a surface treatment. In doing so, advancements can be made in managing asphaltene-related challenges in petroleum engineering and contribute to more efficient oil recovery techniques.

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6. Appendix: Miscellaneous Studies

6.1 Asphaltene Deposition via a Flow System

An experimental setup as shown and labeled in Fig. A1 was used to determine how asphaltene deposits in a flow system. It should be noted, term deposition is used here because the solvent is an equimolar toluene-tetradecane solution, i.e. a poor solvent. The setup was inspired by the one used by Alkafeef et al. in their study of the electrokinetic potential at reservoir rock surfaces.[20] At Stage 1, a positive displacement pumps an asphaltene in toluene-tetradecane solution at a flow rate of 1 mL/min for 500 minutes. At Stage 2, the solution enters a steel column. Silica gel was packed into an Extreme-Temp Teflon® PTFE Semi-Clear tubing so the asphaltene deposition could be visually observed. The tubing then inserted into the steel column and the ends were plugged with steel mesh. Stage 3 is a back-pressure regulator set to 100 psi using nitrogen gas. The system pressure is maintained at 100 psi using a back-pressure regulator to prevent the formation of any air bubbles. At Stage 4, the exiting asphaltene solution is fed into the spectrophotometer so the concentration change of solution can be monitored. Initial attempts at the study were done with a 1 g/L solution but there was not noticeable concentration change so the concentration of the solution was increased to 4 g/L.

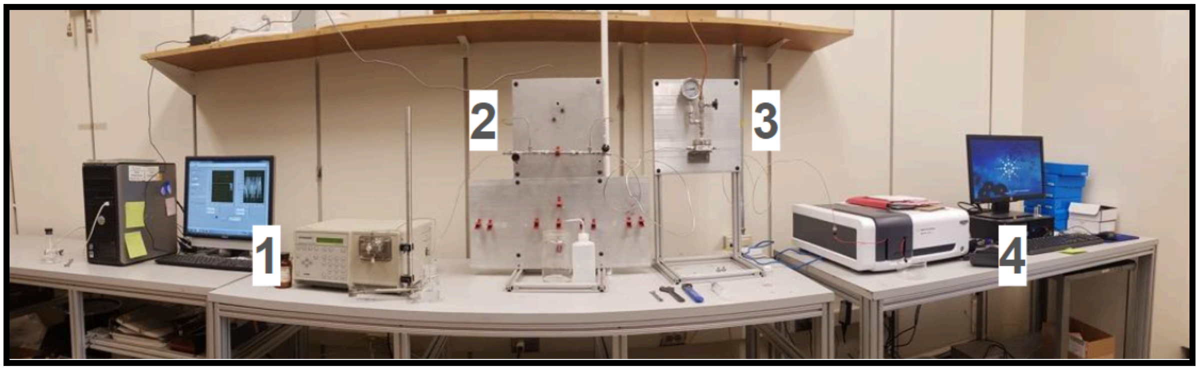

Fig. A1: Experimental setup of the flow system.

After 500 mL of solution flowed through the steel column, the setup was disassembled so the Semi-Clear tubing could be extracted as shown in Fig. A2.

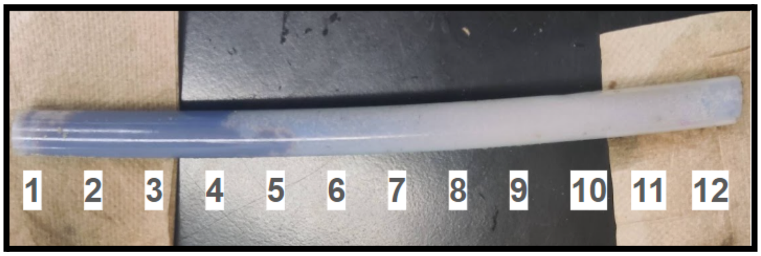

Fig. A2: Semi-Clear tubing packed with silica gel with asphaltene deposition present. The numbering represents the order in which the samples were extracted.

Fig. A2 highlights an important result. The asphaltene deposition is non-uniform. There is significantly more asphaltene deposition at the beginning of the tubing. Therefore, only the average deposition of the tube could be ascertained from spectroscopy, not the deposition at different axial positions. An alternative method of measuring local deposition was needed.

6.2 Alternative Method of Measuring Asphaltene Deposition

It was then of interest to explore another technique for measuring the extent of asphaltene deposition, viz., thermogravimetric analysis (TGA). TGA is a technique that measures the mass of a sample as it is subjected to controlled temperature changes over time. During the process, the sample is heated, allowing for the observation of mass loss due to vaporization. Initially, the sample's mass is recorded at ambient conditions, and as the temperature increases, changes in mass are continuously monitored. These data are plotted as a weight/ weight percentage curve, which illustrates mass loss as a function of temperature. Distinct peaks on this curve can provide insights into the material's local composition. In this case, the peaks could be used to infer the amount of asphaltene that was deposited.

To prepare the samples, the packed silica gel was carefully extracted from the tubing, separated into 12 aliquots, and stored in Falcon Test Tubes, as seen in Fig. A3.

Fig. A3: One of the silica samples extracted into a Falcon test tube

The samples were numbered in the order they were extracted, as shown in Fig. A2 (Sample 1 was the front of the tube, Sample 12 was the end of the tube). After extracting the silica samples into Falcon Test Tubes, a subsample of approximately 50 mg was placed into an alumina crucible and heated via a Q50 TGA (TA Instruments; New Castle, DE) from room temperature to 800°C, increasing the temperature at 10°C per minute. Fig. A4 is a weight percentage curve for Sample 3.

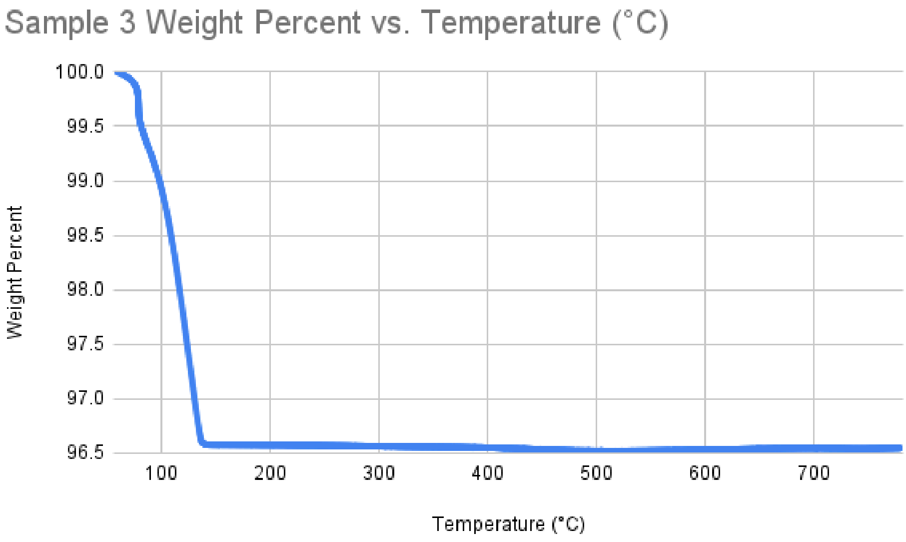

Fig. A4: Weight percentage of Sample 3 as a function of temperature.

As seen in Fig. A4, weight loss occurs quite drastically until it reaches approximately 150°C. However, it was realized that this initial weight loss was actually the evaporation of the toluene-tetradecane in the asphaltene solution. This realization was confirmed by doing a TGA analysis on a toluene-tetradecane solution with no asphaltene present. It was found that the toluene-tetradecane solution evaporates around 180°C. Thus, to find the amount of asphaltene deposition, the temperature range of 180°C to 800°C should be investigated. A TGA analysis was done on Sample 3 again with the temperature range of 180°C to 800°C.

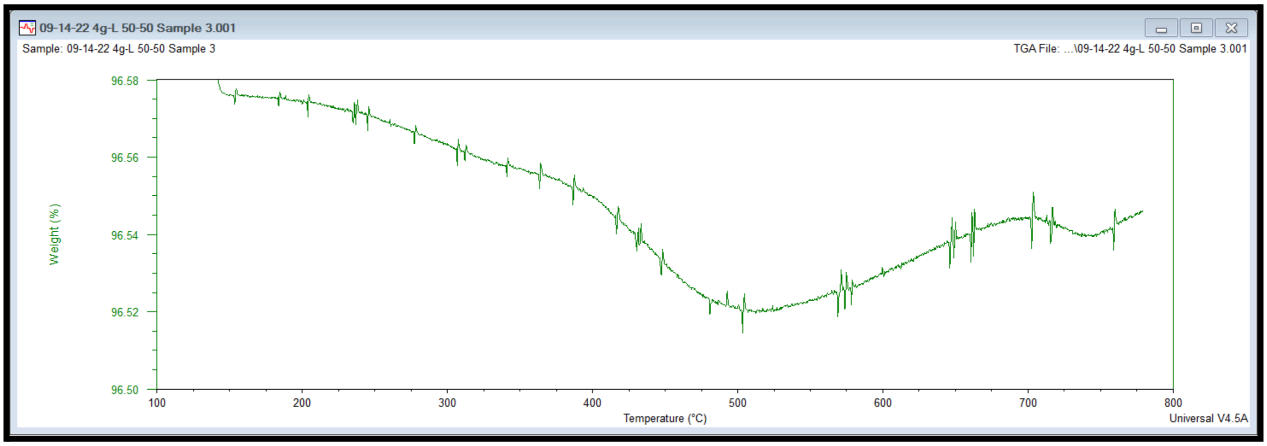

Fig. A5: Weight percentage of asphaltene from 180°C to 800°C of Sample 3

As seen in Fig. A5, there is a slight weight loss until 500°C, when a weight increase starts to occur. As a weight increase makes no logical sense, it seems wise to assume the TGA has weight drift that occurs in minuscule amounts. Thus, a TGA analysis with an empty crucible was done to test this theory, as shown in Fig. A6.

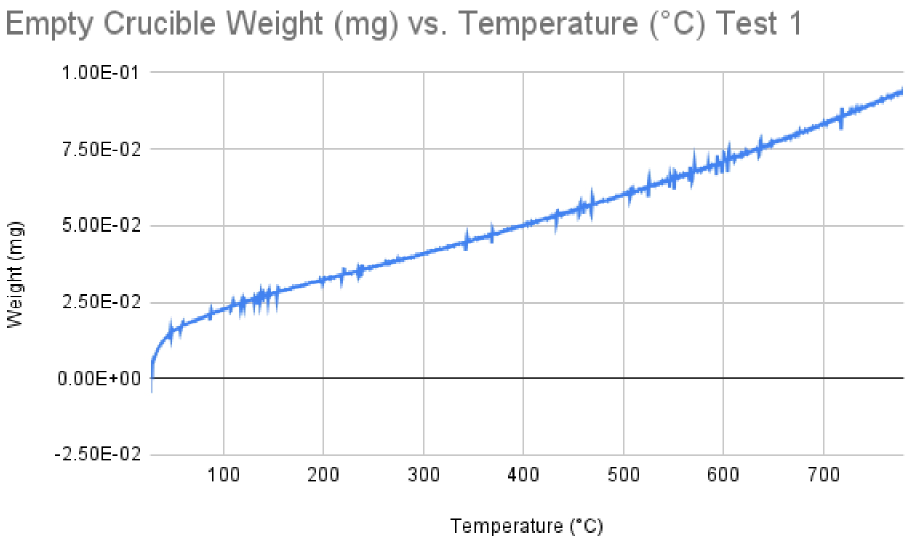

Fig. A6: Apparent weight percentage as temperature increases for an Empty Crucible

As seen in Fig. A6, there is a slight apparent weight increase as the empty crucible is heated to higher temperatures. This test was repeated five times. For each test, the weight curve was fitted with a second-degree polynomial trendline. The coefficients of the second-degree polynomial were tabulated and averaged as shown in Table A1.

Table A1: The values of each degree from the second-degree polynomial trendline of the 5 TGA empty crucible trials. 8 significant digits were recorded, the maximum accuracy of the TGA instrument.

	T^2	T	Constant
Test 1	0.00000005	0.00005941	0.01859075
Test 2	0.00000007	0.00002189	0.00867681
Test 3	0.00000009	-0.0000003	-0.00063944
Test 4	0.00000004	0.0000708	0.01696482
Test 5	0.00000008	0.00000174	-0.00625992
Average	0.000000066	0.000030708	0.007466604

Using Table A1, the polynomial trendlines were averaged to get the resulting polynomial, as shown in Eq. A1:

$$W = 0.000000066T^2 + 0.000030708T + 0.007466604 \tag{A1}$$

where W is weight in mg and T is the temperature in °C. This resulting polynomial could then serve as a correction factor to the weight drift.

Incorporating this correction factor into the TGA Analysis from Fig. A5, the weight drift was subtracted from the original weight curve and the resulting data was plotted again.

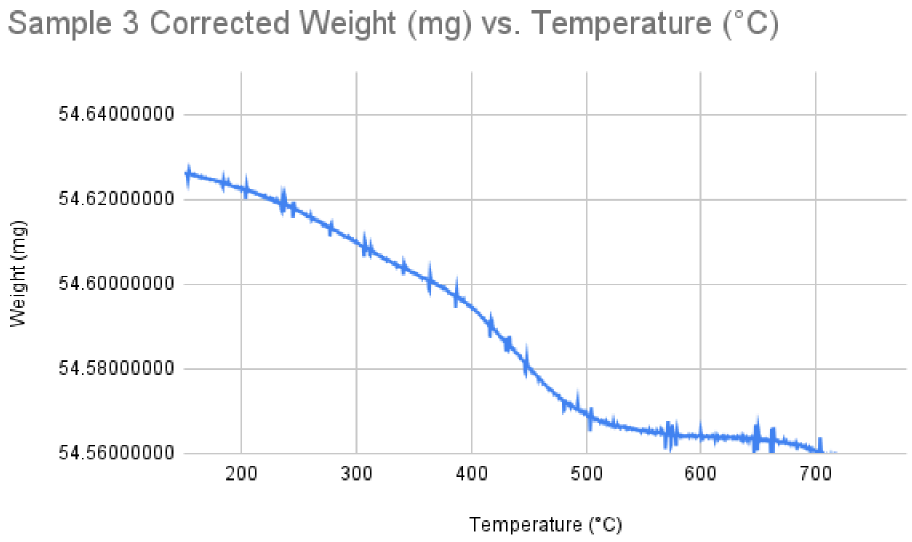

Fig. A7: Corrected weight percentage from 180°C to 800°C of Sample 3

As seen in Fig. A7, the weight percentage now continuously decreases as temperature increases. These results are much more sensible. The weight loss percentage can then be calculated with Eq. A2:

$$\frac{Weight\ at\ 180\,°C - Weight\ at\ 800°C}{Weight\ at\ 180\,°C} * 100 \tag{A2}$$

The resulting weight loss for Sample 3 then comes out to 0.109%. The weight loss for other samples is tabulated in Table A2. The Samples are numbered as shown in Fig. A2.

Table A2: Table of Weight Loss Percentage for Each Sample

Sample Number	Weight Loss Percentage
1	0.154
2	0.129
3	0.109
4	0.104
5	0.096

Beyond Sample Number 5, there was no weight loss that could be detected. These results qualitatively confirm that the majority of the asphaltene deposition occurs at the beginning of the tube. The results are also plotted and shown in Fig. A8.

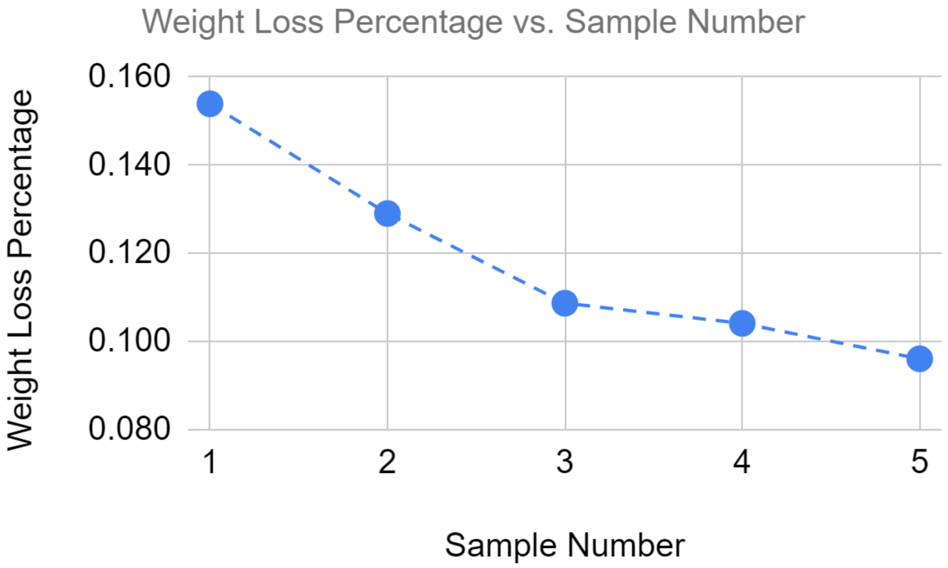

Fig. A8: Graph of Weight Loss Percentage for Each Sample

Due to the lack of uniformity in asphaltene deposition in these results, it was decided that flow measurements were not a suitable technique.