J. Mar. Sci. Eng. **2015**, *3*, 1244-1259; doi:10.3390/jmse3041244

OPEN ACCESS

Journal of
Marine Science and Engineering
ISSN 2077-1312
www.mdpi.com/journal/jmse

Article

Bitumen on Water: Charred Hay as a PFD (Petroleum Flotation Device)

Nusrat Jahan [1], Jason Fawcett [1], Thomas L. King [2], Alexander M. McPherson [1], Katherine N. Robertson [1], Ulrike Werner-Zwanziger [3] and Jason A. C. Clyburne [1,*]

[1] Atlantic Centre for Green Chemistry, Departments of Chemistry and Environmental Science, Saint Mary's University, Halifax, NS B3H 3C3, Canada; E-Mails: drnusrat2001@hotmail.com (N.J.); jafawcett@gmail.com (J.F.); mcpherson.alexm@gmail.com (A.M.M.); Katherine.Robertson@smu.ca (K.N.R.)

[2] Centre for Offshore Oil, Gas and Energy Research, Bedford Institute of Oceanography, Dartmouth, NS B2Y 4A2, Canada; E-Mail: Tom.King@dfo-mpo.gc.ca

[3] Department of Chemistry and Institute for Research in Materials, Dalhousie University, Halifax, NS B3H 4J3, Canada; E-Mail: ulrike.wernerzwanziger@gmail.com

* Author to whom correspondence should be addressed; E-Mail: Jason.Clyburne@smu.ca; Tel.: +1-902-420-5827.

Academic Editors: Merv Fingas and Tony Clare

Received: 6 August 2015 / Accepted: 12 October 2015 / Published: 20 October 2015

Abstract: Global demand for petroleum keeps increasing while traditional supplies decline. One alternative to the use of conventional crude oils is the utilization of Canadian bitumen. Raw bitumen is a dense, viscous, semi-liquid that is diluted with lighter crude oil to permit its transport through pipelines to terminals where it can then be shipped to global markets. When spilled, it naturally weathers to its original form and becomes dense enough to sink in aquatic systems. This severely limits oil spill recovery and remediation options. Here we report on the application of charred hay as a method for modifying the surface behavior of bitumen in aquatic environments. Waste or surplus hay is abundant in North America. Its surface can easily be modified through charring and/or chemical treatment. We have characterized the modified and charred hay using solid-state NMR, contact angle measurements and infrared spectroscopy. Tests of these materials to treat spilled bitumen in model aquatic systems have been undertaken. Our results indicate that bitumen spills on water will retain their buoyancy for longer periods after treatment with charred hay, or charred hay coated with calcium oxide, improving recovery options.

Keywords: petroleum; bitumen; dilbit; crude oil; asphaltene; remediation; spill; recovery; hay; flotation

1. Introduction

The development of the Canadian oil sands in northern Alberta has become a significant contributor to the Canadian economy. It could also become a significant contributor of oil to the world economy. Bituminous sands in Canada have been assessed to hold approximately 43% of the total global bitumen deposits, which represents approximately 26.9 billion m^3 or about 169.3 billion barrels of crude bitumen [1]. The locations of these Canadian bitumen deposits are far from both ocean and refinery access. Using current techniques crude bitumen can be refined to approximately 20% by weight of petroleum coke. This is of little value while landlocked but it could be valuable, even though high in sulfur, in "leading edge" environmental applications such as a source of activated carbon to reduce the toxins content in oil sands tailings [2]. In order to produce and transport bitumen profitably, ocean access for shipment is essential. Possible transportation routes might include: (1) railway to refinery or ocean port; (2) pipeline to railway or refinery or ocean port; or (3) truck to railway or refinery or ocean port.

The nature of these transportation methods, and the frequency and volume of product being transported, increases the risk of accidental spills or pipeline leaks. A review of the scientific literature indicates that there are limited options available to treat diluted bitumen (dilbit) spills. An article published by the Royal Society of Canada in 2010 assessed the environmental and health impacts of Canada's oil sands industry. This report outlines and summarizes a number of areas of concern regarding the environmental impacts of the oil sands industry, and suggests some of the necessary reclamation and monitoring practices necessary to mitigate these impacts [3]. A later 2012 publication in the journal, Environmental Science and Technology, discussed a number of shortcomings and oversights in the 2010 assessment [4]. However, both reports neglect to mention the need for new oil spill treatment technologies, given that bitumen and dilbit, under the correct circumstances, will sink. Conventional technologies, such as dispersants, will be rendered less effective in the event of a major dilbit spill either on site (e.g., land based) or during transport (e.g., entering aquatic systems).

The physical properties and composition of crude bitumen make it a very challenging material to manipulate. Bitumen is a heavy, viscous, semi-solid form of petroleum and is composed of a complex mixture of materials. At 15 °C, the complex viscosity of Athabasca bitumen has been reported to be 1.75×10^7 mPa·s [5]. The dynamic viscosity is reported to range from 1.9×10^4 to greater than 7.0×10^5 mPa·s at the same temperature [6], compared to conventional heavy crude, such as heavy fuel oil, HFO 6303, which has a reported viscosity of 2.28×10^4 mPa·s under the same conditions [6]. The same reference [6] reports the density of Athabasca bitumen as being 1.006 to 1.016 g cm^{-1}. A 2011 report in the Journal of Chemical and Engineering Data [5] details "Saturates, Aromatics, Resins and Asphaltenes" (SARA) analyses and Mass Fraction results which have been used to characterize the composition of Athabasca bitumen. These findings are outlined in Table 1 and notably include an asphaltene component of 18.6% ± 1.86% by weight in the bitumen studied.

Table 1. Composition analyses of Athabasca bitumen (adapted from Bazyleva *et al.* [5], with permission from © 2011 American Chemical Society).

Elemental Composition	**Weight %**
Carbon	83.2 ± 0.9
Hydrogen	9.7 ± 0.4
Nitrogen	0.4 ± 0.2
Sulphur	5.3 ± 0.2
Oxygen	1.7 ± 0.3
SARA Analysis	**Weight %**
Saturates	16.1 ± 2.1
Aromatics	48.5 ± 2.3
Resins	16.8 ± 1.2
Asphaltene (C_5)	18.6 ± 1.8

A series of publications spanning the years 2010 to 2012 by Murray R. Gray *et al.*, have tackled the arduous challenge of characterizing the structures of various bitumen fractions [7–9]. The most significant component of bitumen, the one that differentiates it from conventional crude oil, is the abundant asphaltene fraction. Asphaltenes are the heaviest fraction of crude bitumen, and consist mostly of polycyclic-aromatic rings complexed with metals including nickel and vanadium.

Asphaltenes are problematic for bitumen processing for a number of reasons, arising mainly by their tendency towards aggregation. Aggregation occurs because of various acid-base interactions, hydrogen bonding and the formation of metal-containing coordination complexes. This aggregation results in the drastically higher viscosity observed for crude bitumen as compared to crude oil. This, in turn, gives rise to the observed difficulties in pumping and processing bitumen. In the case of an ocean or fresh water-based bitumen spill aggregation will more than likely result in the clumping and sinking of the spilled materials. Understanding the aggregation behavior of asphaltenes in bituminous oils is essential to developing methods and materials for spill treatment/recovery.

A recent report from the Federal Government of Canada assesses the spill behavior and fate of two diluted bitumen (dilbit) samples under different weathering conditions. The dilbit products selected were those most frequently transported in Canada. Preliminary laboratory investigations showed that the dilbit products remained buoyant under natural ocean-simulated weathering conditions (0–15 °C) except when mixed with fine to moderately sized sediments [10]. One gap in this investigation was that only two samples of dilbit (e.g., Cold Lake Blend and Access Western Blend) were tested, and they were not compared to a base sample of crude bitumen. Furthermore, the products were studied only in sea water conditions. It must be remembered that there is also significant risk of spills occurring in fresh or brackish waters.

To extend the initial results to such waters, King *et al.*, (2014) have investigated dilbit weathering, through meso-scale (e.g., wave tank) studies, under natural conditions. One of the same dilbit products (e.g., Access Western Blend) was shown to weather enough, without interaction with sediments, such that its density exceeded that of fresh and brackish waters [11,12]. The authors concluded that this product would initially float on aquatic systems, but that after 6 days of natural attenuation, the product would sink in aquatic systems. A very recent paper by Stevens *et al.*, offers proof that oil weathering can result in its sinking [13]. The authors have developed an evaporation/sinking (EVAPOSINK) model that can be used to predict such behavior.

The potential for diluted bitumen products to sink when spilled is problematic from both environmental and industrial perspectives. Sunken oil is more difficult to find and track, and there are no known spill countermeasures to treat submerged dilbit. Preliminary findings have shown dispersants to be ineffective in the treatment of a diluted bitumen spill [10]. Submerged oil could potentially cause significant and persistent loss of potable water, ecosystems (e.g., rivers and lakes, marine systems, *etc.*) and aquatic life. Further investigation into the spill behavior of crude bitumen in aquatic systems is essential for the development of a cheap and effective countermeasure for spill impact mitigation and recovery. There is a definite need to identify a material capable of reducing the bulk density of the bitumen to keep it floating on the aquatic surface for as long as possible. This would prolong the window of opportunity available during the flotation phase to treat the spill by either mechanical means, such as booming or skimming the surface, or through *in situ* combustion.

Our preliminary investigations led us to hay, a cheap and abundant material with a large surface area. We felt that it might be a suitable material to adsorb bitumen and act as a flotation device. Attempts were made to modify the surface of the green hay so that it would also act as a natural dispersant. The hay was first immersed and coated with the organic-based surfactant, “Zep”, a limonene-based household degreasing product. This surface modification was unsuccessful; the surfactant did not result in a modification of the surface properties of the hay. When this preliminary treatment failed, charring the hay and/or coating it with calcium oxide were investigated as means of surface modification. It was anticipated that charring the hay surface would render it more hydrophobic by removing surface OH groups and exposing the carbon backbone, while addition of CaO could possibly generate an *in situ* surfactant, improving the dispersant properties of the system. The results of the investigation are reported herein.

2. Experimental Section

2.1. Chemicals, Oils and Oil Spill Treating Agents

Athabasca bitumen was provided by the Centre for Oil Sands Innovation, Edmonton, Alberta and was used as received. Timothy hay (*Phleum pretense*) was purchased at Walmart, as supplied by Pestell Pet Products of Ontario, Canada. The composition of the hay is listed as follows: crude protein (min. 7.5%), crude fat (min. 2.0%), crude fibre (max. 35%), moisture (max. 12.0%), and calcium (min. 0.25%–max. 0.60%). “Instant Ocean” Sea Salt is distributed by United Pet Group Inc. of Cincinnati, OH, USA. It was prepared as directed on the packaging. “Zep” Heavy Duty Citrus Degreaser, with the active ingredients, d-limonene and monoethanolamine, was obtained from the Home Depot (Zep Superior Solutions, Atlanta, GA, USA). Reagent grade nitric acid, ACS reagent grade dichloromethane ≥99.5%, PCR reagent grade chloroform ≥99% and reagent grade calcium oxide and potassium bromide were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada) and used as obtained.

2.2. Experimental Design

Simulated bitumen slicks were prepared in 250 mL glass beakers. A measured volume of 100 mL of either deionized water or Instant Ocean solution was added to each beaker. Bitumen slicks were generated by applying a known mass (1.8 g) of crude bitumen to the surface for both fresh water and Instant Ocean (artificially created salt water) samples. Samples were left at room temperature (23 °C) and were stirred for 2–3 min every 12 h. Samples were also periodically photographed to record bitumen aggregation and subsequent sinking of the product over time. At the end of the observation period, samples of the experimental solutions were collected. These were analyzed for trace metals, total petroleum hydrocarbon content and density.

Hay samples were cut into lengths of approximately 1.0 cm, sufficiently short to fit into the experimental beakers. The cut hay (all from a single source) was mixed to randomize its distribution before use, but no other attempts were made to homogenize the hay in the samples and replicate measurements were not performed for the charring process itself. The surface properties of the straw were then altered as follows: (1) the hay was charred to remove hydrogen and oxygen from its surface; and/or (2) the hay was coated with calcium oxide for, potentially, *in situ* surfactant formation. Addition of bitumen to the CaO-treated hay could possibly result in the deprotonation of the carboxylic acids, which would generate an *in situ* surfactant.

(1) The charred hay was prepared by placing the clippings in a sealed Schlenk flask and then placing the flask under vacuum. A propane torch was carefully applied to the bottom of the flask as it was mixed to endure uniform heating. Heating was performed at 10 min intervals, and the flask allowed to cool between heating cycles. Depending on the experiment, heating was continued for approximately 30 or 60 min total. During the hay charring process, a clean solvent trap was inserted into the Schlenk line and liquid nitrogen was used to condense the evolved gases. The condensate was washed from the trap using acetone, which was subsequently removed by evaporation. Preliminary experiments have been carried out to analyze the condensate for its principle components using gas chromatography coupled with mass spectrometry (GC/MS).

(2) Calcium oxide coated hay samples were prepared using the following procedure. A supersaturated solution of calcium carbonate (5 g) was prepared by adding just enough deionized water to make a paste. Then 2.5 g of uncharred hay clippings were mixed and coated with the paste and the mixture was left for 24 h at room temperature. A portion of the original mixture (the CaO-coated, uncharred hay sample) was then transferred to a Schlenk flask and charred under vacuum (see above) to produce the CaO-coated, charred hay samples. Heating was continued until the surface of the hay turned dark brown-black.

Buoyancy and bitumen adsorption of the charred hay samples (30 or 60 min) were evaluated by preparing sample slicks, containing approximately 2.0–2.3 g of bitumen in 100 mL of solution, as outlined above. The slicks were treated by adding 1.0 g of charred hay. Samples were shaken daily, and observed and photographed as outlined in the procedure above. A final set of buoyancy experiments examined the effectiveness of charred straw relative to CaO-coated charred straw. Instant Ocean solution (350 mL) was added to 125 × 65 mm^2 glass dishes to which were also added 3 g of bitumen and either 2 g of charred hay or 5 g of CaO-coated charred hay. The bitumen and straw were well mixed and then the dishes were placed on an orbital shaker operating at 65 rpm at room temperature. Once again, samples were observed and photographed periodically as outlined above.

2.3. Sample Analyses

2.3.1. Density

The densities of the deionized water and the Instant Ocean solution were measured by accurately determining the mass and volume of a specified quantity of each solution at room temperature. The density of Athabasca bitumen has been reported to be 1.006 to 1.016 g cm^{-1} [6].

2.3.2. Contact Angle Measurements

The differences in the *potential* strength of adsorption to the altered hay surfaces were evaluated via contact angle measurements of water droplets on flat surfaces of both the charred and the uncharred hay. Contact angle measurements were performed using a First Ten Angstroms (FTA) 135 Drop Shape Analyzer and FTA-32 Video software (Portsmouth, VA, USA).

2.3.3. Infrared Spectroscopy

Infrared spectra were recorded on a Bruker Vertex 70 Infrared Spectrometer (Bruker Optics Ltd., Milton, ON, Canada), with samples prepared as KBr pellets. Data processing was completed using OPUS 6.0 software (Bruker Optics Ltd., Milton, ON, Canada).

2.3.4. Nuclear Magnetic Resonance (NMR) Spectroscopy

The solid state ^{13}C cross polarization (CP)/magic angle spinning (MAS) NMR spectrum of raw hay was compared to those of two different samples of charred hay, one charred for 30 min and the other charred for 60 min. These NMR experiments were carried out in the NMR-3 Facility of Dalhousie University on a Bruker Avance DSX NMR spectrometer with a 9.4 Tesla magnet (400.24 MHz ^{1}H and 100.64 MHz ^{13}C Larmor frequencies) using a probe head for rotors of 4 mm diameter (Billerica, MA, USA). The parameters for the ^{13}C CP/MAS experiments with TPPM proton decoupling were optimized on glycine, whose carbonyl resonance also served as an external, secondary chemical shift standard at 176.06 ppm. For the final ^{13}C CP/MAS NMR spectra 1200 scans were acquired with 13.5 kHz sample spinning, 2.6 ms cross-polarization times and 3 s repetition times, as determined from the ^{1}H spin lattice relaxation times, T_1. Additional spectra, taken at 5.0 kHz sample spinning and also with a ^{13}C CP/MAS sequence followed by TOSS (TOtal Sideband Suppression), showed that there is no significant overlap between spinning sidebands and center bands.

2.3.5. Gas Chromatography with Flame Ionization Detection

Residual oil in the samples was analyzed using the method outlined by Cole *et al.* [12]. Briefly, the method is a modified version of EPA 3500C, where the sample container is used as the extraction vessel. Dichloromethane (DCM) was added to the sample bottle containing dispersed oil in solution. The sample was placed on a Wheaton R_2P roller (VWR International Ltd., Mississauga, ON, Canada) for 18 h. The roller had been modified to accommodate 3 inch diameter PVC pipe into each roller slot, so that sample containers of different sizes could be used. Once extraction was complete, the samples were removed and the DCM recovered. The recovered DCM was placed in a pre-weighed 15 mL centrifuge tube and the solvent volume reduced under a nitrogen evaporator to 1.0 mL. The extracts were analysed by gas chromatography using flame ionization detection. The original bitumen product was used to prepare calibration standards that were then used to generate a calibration curve from which oil concentrations in the extracts could be calculated. A mean percent recovery of 90.8 ± 4.6% was calculated from all oils spiked into water. The method detection limit was <0.5 mg/L. The method of extraction and analyses has been validated against the US EPA 3510C and provides better extraction efficiency for oils. The GC-FID method (EPA 8015B) is a standard US EPA method for analysing oils. The method has been published as supplementary material in an article in Environmental Engineering Science in 2015 [14].

2.3.6. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

All samples for ICP-MS analysis were freshly prepared. The required components for each sample, bitumen, green straw, charred straw, CaO-coated green straw, or CaO-coated charred straw, were placed into either deionized water or Instant Ocean solution. All straw-containing samples included 100 mL of solution (deionized water or Instant Ocean), 1 g of bitumen, and 0.5 g of straw (green or charred, with or without a CaO coating). The non-straw samples contained 100 mL of solution, 2 g of bitumen and in half of the samples added CaO (0.5 g). They were all left in the refrigerator for 48 h. The sample solutions were filtered through a 0.45 μm pore size (GHPP, Pall Gelman Acrodisc, purchased from Sigma-Aldrich Canada, Oakville, ON, Canada) syringe filter and acidified using 10% nitric acid to a pH of less than 2, prior to ICP-MS analyses for dissolved metals. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was performed at the Saint Mary's University Center for Environmental Analysis and Remediation (CEAR) on a VG PQ ExCell instrument (Thermo Elemental, Winsford, UK) by Patricia Granados.

3. Results and Discussion

3.1. Density

The densities of deionized water and the Instant Ocean solution were measured at 23 °C and determined to be 0.980 and 1.004 g/mL, respectively. Both are lower than a literature value reported for bitumen of 1.006 to 1.016 g/cm^3 [6].

3.2. Characterization of Charred versus Uncharred Hay

Preliminary experiments have been carried out on the condensate collected during the hay charring process. GC/MS analysis of the hay condensate showed that it contained many compounds, with three significant contributors being vanillin lactoside, 2,6-dimethoxyphenol (syringol) and 5-hydroxymethyl-2-furaldehyde. All of these are known components of combustion extracts [15].

3.2.1. Contact Angle Measurements

Contact angle measurements were made to characterize the impact of modification of the hay surface through the charring process on the bulk properties of the material. The expectation was that charring the hay would liberate hydrogen and oxygen from its surface, increasing C=C bond formation, and result in an overall increase in the hydrophobicity. Contact angle measurements for deionized water on charred and raw hay surfaces showed a significant increase in the contact angle after charring (e.g., from approximately 64°, Figure 1 (left) to approximately 126°, Figure 1 (right) and therefore, a definite change in the hydrophobic properties of the surfaces.

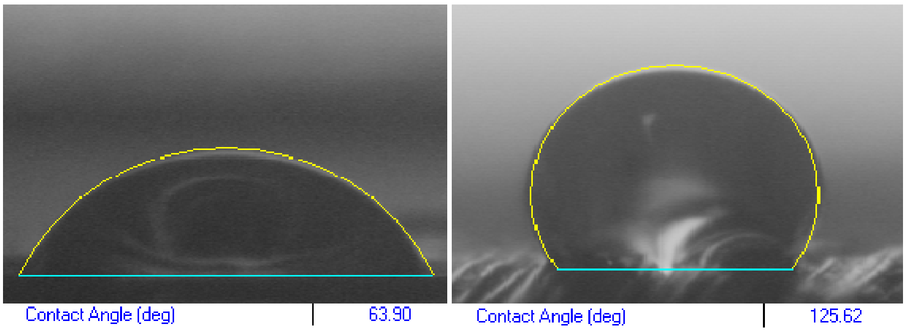

Figure 1. Contact angle measurements, before (**left**) and after (**right**) charring of the hay surface.

If the contact angle of water is less than 30°, a surface is designated as hydrophilic; wetting of the surface is favourable, and the water will spread over a large area. On a hydrophobic surface, water forms into distinct droplets. As the hydrophobicity increases, the contact angle of the droplets with the surface increases. Surfaces with contact angles greater than 90° are designated as hydrophobic [16]. The measured change in contact angle for our samples supports the conclusion that chemical modifications resulting from charring have produced a more hydrophobic surface. Variations in the observed contact angles were noted after subsequent measurements, however, samples consistently revealed larger contact angles, and thus increased hydrophobicity, after charring.

3.2.2. Infrared Spectroscopy

Infrared spectra were recorded for samples of both raw and charred hay. Transmittance in the 1600–1700 cm^{-1} (wavenumber) region was observed to be reduced after the hay was charred (boxed region in Figure 2). This has been attributed to the removal of absorbed water on charring, with a concomitant decrease in the observed OH bending signal. Charring should also expose the carbon backbone and thereby alter the hydrophobic properties of the hay surface. In this regard it is important to note the changes in the $O–CH_3$ methyl stretching region [17] at 2850–2815 cm^{-1} (* in Figure 2), and in the small peak at 809 cm^{-1} (C–C–O and C–O–C deformations) which disappears completely on charring. Other peaks also change in relative intensity, and all of this suggests that actual chemical modification has occurred. There is also a small possibility that these differences could have arisen from differences in the original hay samples themselves since the experiment was not performed on replicate samples. Although the spectra may appear only slightly different overall, the effect on the surface properties supports the evidence from the contact angle measurements that chemical modification of the surface has been achieved.

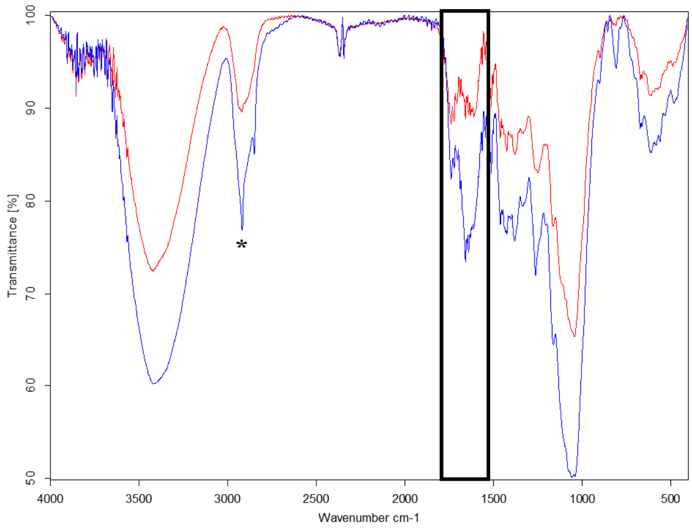

Figure 2. Overlay of infrared spectra comparing a raw hay sample (blue/bottom) to a charred hay sample (red/top). The boxed and starred areas show regions where the two spectra are distinctly different (see text).

3.2.3. ^{13}C CP/MAS Nuclear Magnetic Resonance Spectroscopy

All of the ^{13}C CP/MAS NMR spectra shown in Figure 2 exhibit typical cellulose signatures, with the alcoholic carbons between 50 and 90 ppm and the acetyl groups around 105 ppm. In addition, they show resonances for aliphatic groups between about 50 and 0 ppm. On the high chemical shift side, signals of carboxyl groups (around 173 ppm) and of unsaturated carbon groups, between about 110 and 155 ppm, of aromatic and possibly aliphatic origins are detected. In particular, the region between 140 and 155 ppm, corresponds to aromatic carbons bridging to other carbons or hetero-nuclei, such as oxygen. Comparison between the three samples shows that, relative to the largest peak, the intensities of the unsaturated (aromatic) region, the carboxyl groups and some aliphatic groups increase with increased charring time (indicated by *) (see Figure 3).

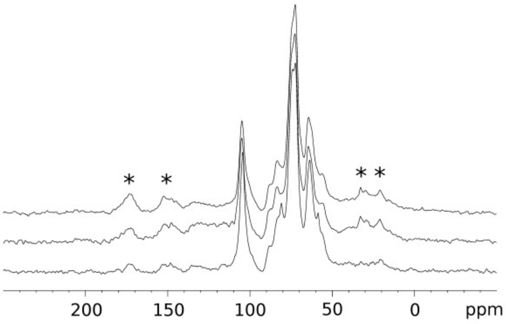

Figure 3. ^{13}C CP/MAS NMR spectra of raw hay (bottom) and charred hay samples (30 min middle, 60 min top) showing the relative intensity increases in the carboxyl, aryl and alkyl regions (isotropic center bands indicated by *) with charring time.

3.3. Application of Treated Hay to Bitumen Samples in Aqueous Environments

3.3.1. Flotation Analysis

A sample of bitumen in tap water with no additives was found to aggregate in the beaker and subsequently sink after a period of 4 days (96 h) at room temperature (23 °C). In the initial stages of the experiment, there was an even distribution of the bitumen on the surface of both the water solution and the Instant Ocean solution (Figure 4A,B, respectively). At 4 days, the bitumen sample in deionized water was observed to aggregate into a ball and sink to the bottom of the beaker on stirring (Figure 5A). As expected, the sample of bitumen in Instant Ocean solution remained afloat longer than the water sample because of the greater density of the Instant Ocean solution. As time passed the Instant Ocean solution became gradually more yellow in color and the bitumen slick increased in diameter (Figure 5B). It showed a tendency to aggregate and sink on stirring but it would remain suspended in the solution (never sinking to the bottom of the beaker) before rising again and dispersing across the surface of the solution. When the experiment was terminated after 121 h, the bitumen was still floating on the Instant Ocean solution.

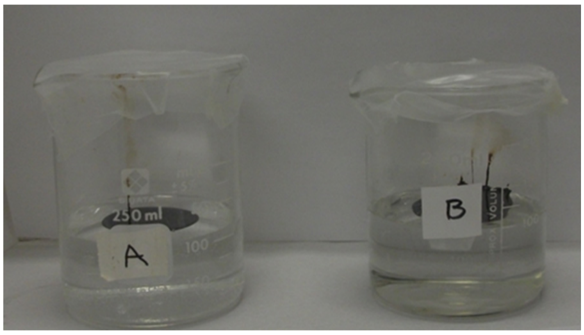

Figure 4. Bitumen samples in deionized water (**A**) and Instant Ocean solution (**B**) at room temperature (23 °C) and time = 0 h.

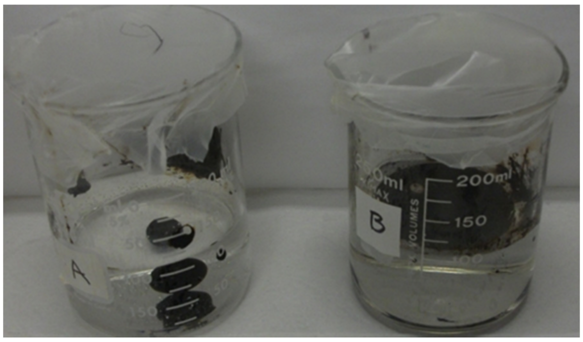

Figure 5. Bitumen samples in deionized water (**A**) and Instant Ocean solution (**B**) at room temperature (23 °C) and time = 96 h.

In solution, bitumen did not interact to any great extent with green, uncharred hay. Instead, the hay just became waterlogged and sank while the bitumen floated on the surface of the solution. However, samples of bitumen treated with charred hay as a flotation additive were buoyant on the water surface for up to 186 h. The application of hay charred for 60 min to the bitumen slicks is shown in Figure 6 (at time = 0 h) and in Figure 7 (at time = 186 h, where both samples have sunk). Samples containing the hay charred for 60 min remained buoyant for equally long (Instant Ocean) or longer (water) than the samples containing hay charred for only 30 min. In fact, the bitumen and charred hay sample (30 min) sank in water after only 72 h. Comparing Figure 7 to Figure 6, dramatic color changes can be seen in the solutions (both water and Instant Ocean). These changes can be attributed to surface interactions between the charred hay and the hydrophobic fractions of the bitumen resulting in dissociation of some of the more polar fractions of the bitumen sample into the solutions over time. For the same reason, all of these samples are more highly colored than the samples of bitumen alone (Figure 5).

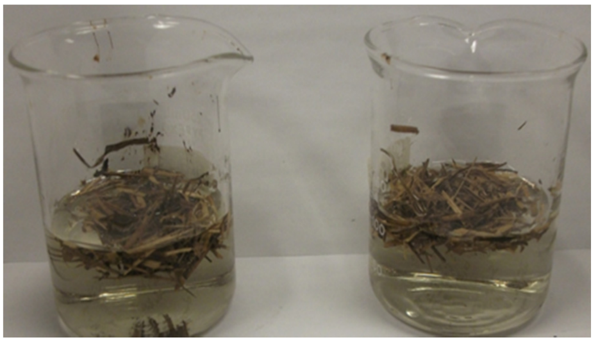

Figure 6. Bitumen samples with charred hay (60 min) added in deionized water (**left**) and Instant Ocean solution (**right**) at room temperature (23 °C) and time = 0 h.

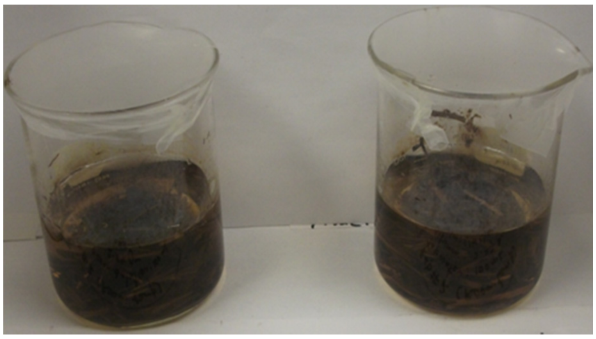

Figure 7. Bitumen samples with charred hay (60 min) added in deionized water (**right**) and Instant Ocean solution (**left**) at room temperature (23 °C) and time = 186 h.

Samples of bitumen treated with charred hay (Figure 8) or CaO-coated charred hay (Figure 9), a flotation *and* dispersant additive, were buoyant for more than 408 h (17 days) at which point the experiment was terminated. In both samples, it is clear that the bitumen adsorbed to the surface of the hay undergoes dispersion. However, this dispersion appears to be greater when the charred straw has been treated with calcium oxide. It was also noted that the Instant Ocean solution did not yellow as much over time when CaO-coated hay was used as the dispersant. This may be the result of the increased dispersion or it may indicate a reduction in the fractional dissolution of the polar compounds with time for the coated sample. The latter idea is supported by the leached hydrocarbon analyses presented in the following section.

Figure 8. A bitumen sample in Instant Ocean treated with charred hay at room temperature (23 °C) and time = 288 h.

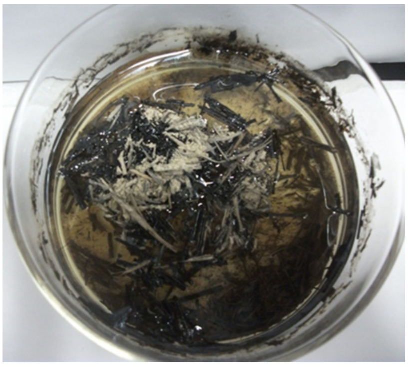

Figure 9. A bitumen sample in Instant ocean treated with CaO-coated charred hay sample at room temperature (23 °C) and time = 336 h.

3.3.2. Residual Oil Concentration

The solutions remaining in the beakers (both Instant Ocean and deionized water) at the end of the floatation experiments were analyzed for leached hydrocarbons. The liquid phase was separated from the hay and bitumen residues prior to measurement. As can be seen in Table 2, all samples containing bitumen showed leaching of hydrocarbons into solution, and this leaching was generally greater in Instant Ocean than in fresh water (deionized). Bitumen samples treated with raw hay in both Instant Ocean solution and deionized water showed slightly more leaching of petroleum hydrocarbons than any of the other treatments. However, this relative amount is statistically insignificant with p-values > 0.05 (2-factor ANOVA). Bitumen samples treated with only CaO showed the smallest quantity of leached petroleum hydrocarbons in both Instant Ocean solution and deionized water. We speculate that the strong base, CaO, either saponifies or deprotonates acidic species in the bitumen thus generating an *in situ* surfactant that better bonds the hydrocarbons to the charred straw.

Samples of bitumen treated with hay did show ppm levels of hydrocarbons (e.g., aliphatic, and parental and alkylated polycyclic aromatic hydrocarbons), entering the water phase at a slow rate over several days due to dispersion. The aromatics that enter the water column would contribute to toxicity in organisms exposed to the contaminated water. However, in an open marine environment, where there are no boundaries, these chemicals would spread over a greater spatial area and be exposed to natural dilution depending on sea states and environmental conditions. The natural dilution of these hydrocarbons would reduce their environmental impacts.

Table 2. Total Petroleum Hydrocarbons (TPH) in water samples collected from water column after treatment.

Sample	TPH (mg/L)	
	Instant Ocean Solution	**Deionized Water**
Standard (water)	<1.0	<1.0
Bitumen	47	28
Bitumen + raw hay	60	52
Bitumen + charred hay	54	21
Bitumen + CaO	18	18
Bitumen + CaO-coated raw hay	19	21
Bitumen + CaO-coated charred hay	52	29

3.3.3. Inductively Coupled Plasma—Mass Spectroscopy

ICP-MS experiments were performed under a variety of conditions in order to assess, if possible, any observable trends resulting from metal ion interaction (leached from the bitumen) with the biomaterial (hay). Reliable results were obtained from the fresh water samples only. Results of experiments performed in the Instant Ocean solutions were complicated due to interference from its high concentration of salts with the metal ions being studied. All samples were tested for V, Cr, Mn, Co, and Cu.

Analysis of the deionized water used in sample preparation showed no (or only trace levels of) V, Mn and Co. Levels of Cr measured 20 ppb and Cu 90 ppb. Analysis of the Instant Ocean solution showed that the product itself contained no Co or Cr, though Cr was present in the solution at the same level found in the water used to prepare it. Instant Ocean was also found to contain V 60 ppb, Mn 30 ppb and Cu 230 ppb (partially from the water).

Addition of bitumen to deionized water resulted in no change to the levels of V, Cr or Co measured. Mn was found to leach into the water, the concentration increasing from a trace (2 ppb) to 20 ppb. The opposite effect was observed for the levels of Cu in solution. Bitumen appears to absorb copper from the solution as the levels decreased from 90 to 30 ppb for Cu. The results when bitumen was added to Instant Ocean were similar. No change in the concentration was observed for V, Cr, Mn or Co. In the case of Mn there already was a concentration of 30 ppb in the solution which may have prevented more from leaching in from the bitumen. The bitumen in Instant Ocean also appeared to absorb some of the copper from solution.

The addition of straw (no CaO) to solutions of bitumen in deionized water had little observable effect on metal ion concentrations. V, Cr and Co levels were totally unaffected. The addition of green straw slightly increased the levels of Mn and Cu in the water, while charred straw had no effect. This may be because the hay itself contains both Cu and Mn which may leach more easily from the green straw. The addition of straw (no CaO) to bitumen in Instant Ocean did not affect the measured concentrations of Cr, Co or Cu. The level of V increased, while the level of Mn increased appreciably upon the addition of the straw, and in both cases the impact of the charred hay was greater than that of green hay.

The effect of a CaO-coating on the straw samples was assessed by comparing the green and charred straw numbers to the corresponding CaO-coated green and charred straw results. For the deionized water solutions the results, whether green or charred straw was used, were very consistent. The V, Cr and Co levels remained relatively constant while the Mn concentrations increased and the Cu concentrations decreased upon using straws coated with CaO. For the Instant Ocean solutions the results were a bit more scattered. However, overall the Cr, Co and Cu concentrations remained relatively constant while the V levels increased and the Mn levels decreased with the introduction of the CaO coating on the straws.

4. Conclusions

This work has shown that charred hay (and in particular CaO-coated charred hay) is an effective substrate for adsorption and flotation of bitumen. With further testing and fine-tuning it could become a valuable tool in the treatment of bitumen and dilbit spills (dilbit tests are ongoing) in aqueous environments. We have shown that its use should prolong the window of opportunity for skimming or *in situ* combustion of spilled oil by increasing the time the bitumen remains afloat. One clear advantage of charred hay is the strong interactions that form between its modified surface and the bitumen, limiting any washing out effect that might occur via wave action or weathering. Hay is also cheap, biodegradable and easily produced in bulk quantities. Additionally, charred hay demonstrates potential for prophylactic treatment on shorelines to prevent bitumen/dilbit from adhering to and contaminating shoreline materials such as sand, rocks and sensitive habitat.

Supplementary Materials

Figures S1 and S2—Contact Angle Measurements
Tables S1 and S2—Statistical Analysis of the Residual Oil Concentrations
Tables S3–S8—ICP-MS Data Summary Tables

Acknowledgments

We thank the Natural Sciences and Engineering Research Council of Canada (through the Discovery Grants Program to JACC). JACC acknowledges generous support from the Canada Research Chairs Program, the Canadian Foundation for Innovation and the Nova Scotia Research and Innovation Trust Fund. We are grateful to NMR-3 (Dalhousie University) for NMR data acquisition and Patricia Granados (CEAR) for helpful discussions of the ICP-MS results. We would also like to acknowledge the Dalhousie University research group of J. Dahn for their assistance with contact angle measurements.

Author Contributions

Nusrat Jahan: Lab Experimentation;
Jason Fawcett: Lab Experimentation;
Thomas King: Residual Oil Analysis, Report Writing/Editing;
Alex McPherson: Experiment Design, Lab Experimentation, Report Writing/Editing;
Katherine N. Robertson: Data Analysis and Manuscript Preparation;

Ulrike Werner-Zwanziger: NMR Data Acquisition, NMR Analysis and NMR Writing/Editing;
Jason Clyburne: Funding, Intellectual Property, Experiment Design and Report Writing/Editing.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. *ST98-2011: Alberta's Energy Reserves 2010 and Supply/Demand Outlook 2011–2020*; Energy Resources Conservation Board: Calgary, AB, Canada, 2011.
2. Zubot, W.; MacKinnon, M.D.; Chelme-Ayala, P.; Smith, D.W.; El-Din, G.M. Petroleum coke adsorption as a water management option for oil sands process-affected water. *Sci. Total Environ.* **2012**, *427–428*, 364–372.
3. Gosselin, P.; Hrudey, S.E.; Naeth, M.A.; Plourde, A.; Therrien, R.; van Der Kraak, G.; Xu, Z. *The Royal Society of Canada Expert Panel: Environmental and Health Impacts of Canada's Oil Sands Industry*; The Royal Society of Canada: Ottawa, ON, Canada, 2011.
4. Timoney, K. Environmental and health impacts of Canada's bitumen industry: In search of answers. *Environ. Sci. Technol.* **2012**, *46*, 2496–2497.
5. Bazyleva, A.; Fulem, M.; Becerra, M.; Zhao, B.; Shaw, J.M. Phase behavior of Athabasca bitumen. *J. Chem. Eng. Data* **2011**, *56*, 3242–3253.
6. Environmental Science and Technology Division. Environment Canada Oil Spill Properties Database. Available online: http://www.etc-cte.ec.gc.ca/databases/OilProperties/ (accessed on 22 May 2014).
7. Borton, D., II; Pinkston, D.S.; Hurt, M.R.; Tan, X.; Azyat, K.; Scherer, A.; Tykwinski, R.; Gray, M.; Qian, K.; Kenttämaa, H.I. Molecular structures of asphaltenes based on the dissociation reactions of their ions in mass spectrometry. *Energy Fuels* **2010**, *24*, 5548–5559.
8. Gray, M.R.; Tykwinski, R.R.; Stryker, J.M.; Tan, X. Supramolecular assembly model for aggregation of petroleum asphaltenes. *Energy Fuels* **2011**, *25*, 3125–3134.
9. Rueda-Velásquez, R.I.; Freund, H.; Qian, K.; Olmstead, W.N.; Gray, M.R. Characterization of asphaltene building blocks by cracking under favorable hydrogenation conditions. *Energy Fuels* **2013**, *27*, 1817–1829.
10. *2013 Federal Government Technical Report: Properties, Composition and Marine Spill Behaviour, Fate and Transport of Two Diluted Bitumen Products from the Canadian Oil Sands*; Cat. No.: En84-96/2013E-PDF; Government of Canada: Ottawa, ON, Canada, 2013; pp. 1–85.
11. King, T.L.; Robinson, B.; Boufadel, M.; Lee, K. Flume tank studies to elucidate the fate and behavior of diluted bitumen spilled at sea. *Mar. Pollut. Bull.* **2014**, *83*, 32–37.
12. Cole, M.G.; King, T.L.; Lee, K. *Analytical Technique for Extracting Hydrocarbons from Water Using Sample Container as Extraction Vessel in Combination with Roller Apparatus*; Canadian Technical Report of Fisheries and Aquatic Sciences #2733; Fisheries and Oceans Canada: Québec, QC, Canada, 2007; pp. 1–12.

13. Stevens, C.C.; Thibodeaux, L.J.; Overton, E.B.; Valsaraj, K.T.; Nandakumar, K.; Rao, A.; Walker, N.D. Sea surface oil slick light component vaporization and heavy residue sinking: binary mixture theory and experimental proof of concept. *Environ. Eng. Sci.* **2015**, *32*, 694–702.
14. King, T.; Robinson, B.; McIntyre, C.; Toole, P.; Ryan, S.; Saleh, F.; Boufadel, M.; Lee, K. Fate of surface spills of Cold Lake blend diluted bitumen treated with dispersant and mineral fines in a wave tank. *Environ. Eng. Sci.* **2015**, *32*, 250–261.
15. Baldwin, I.T.; Staszak-Kozinski, L.; Davidson, R. Up in smoke: I. Smoke-derived germination cues for postfire annual, Nicotiana attenuata Torr. Ex. Watson. *J. Chem. Ecol.* **1994**, *20*, 2345–2371.
16. Arkles, B. Hydrophobicity, hydrophilicity and silanes. *Paint Coat. Ind. Mag.* **2006**, *22*, 114–123.
17. Coates, J. *Interpretation of Infrared Spectra: A Practical Approach. Encyclopedia of Analytical Chemistry*; Meyers, R.A., Ed.; John Wiley & Sons Ltd.: Chichester, UK, 2000; pp. 10815–10837.