Oil Spills Abatement: Factors Affecting Oil Uptake by Cellulosic Fibers

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ABSTRACT: Wood-derived cellulosic fibers prepared in different ways were successfully employed to absorb simulated crude oil, demonstrating their possible use as absorbents in the case of oil spills. When dry fibers were used, the highest sorption capacity (six parts of oil per unit mass of fiber) was shown by bleached softwood kraft fibers, compared to hardwood bleached kraft and softwood chemithermomechanical pulp (CTMP) fibers. Increased refining of CTMP fibers decreased their oil uptake capacity. When the fibers were soaked in water before exposure to the oil, the ability of the unmodified kraft fibers to sorb oil was markedly reduced, whereas the wet CTMP fibers were generally more effective than the wet kraft fibers. Predeposition of lignin onto the surfaces of the bleached kraft fibers improved their ability to take up oil when wet. Superior ability to sorb oil in the wet state was achieved by pretreating the kraft fibers with a hydrophobic sizing agent, alkylsuccinic anhydride (ASA). Contact angle tests on a model cellulose surface showed that some of the sorption results onto wetted fibers could be attributed to the more hydrophobic nature of the fibers after treatment with either lignin or ASA.

1.0. INTRODUCTION

The unplanned release of crude or refined petroleum products has the potential to cause significant harm to aquatic environments.1−3 Effects on aquatic life, as well as birds, have been well documented.4−5 Strategies for collection or removal of spilled oil have included mechanical collection (i.e., “skimming”), incineration, treatment with dispersants or enzymes, membrane filtration, and the use of absorbent materials.6−9 Many of these approaches tend to be expensive, and their efficiency can be inadequate.10

When addressing environmental problems, one should seek solutions that, by their implementation, do not place significant additional burdens on the environment. For example, the use of dispersants in the treatment of oil spills may influence the toxicity of the oil, spread it out, or cause it to sink, making it difficult to collect.11,12 Likewise, some widely used absorbent materials, such as those used in floating booms for the containment and collection of spilled oil, have been synthesized from nonrenewable, petroleum-based resources.13,14

The effectiveness of candidate sorbent materials can be expressed as the mass of oil (or other contaminant) taken up per unit mass of the solid. Promising results have been obtained with fine polypropylene fibers, for which uptake levels in the range of 4−13 g/g have been reported.13,14 Natural materials also can be used to remove spilled oil from aqueous systems.15−23 Studies have documented capacities in the range of 2−50 g/g, even with unmodified natural cellulosic products.15,19,21

A question to be addressed in the present work is what factors affect how much oil uptake can be achieved with a widely available, relatively inexpensive, and renewable re-source—cellulosic fibers of the type used in papermaking. Large supplies of such materials are potentially available from wastepaper collection programs. Some wastepaper is sorted according to fiber type, potentially making it feasible to employ low-cost fibers from, for instance, old newspaper (ONP), old corrugated container (OCC), or mixed office waste (MOW) pulp. In principle, ONP pulp might be considered especially promising for oil absorption due to the presence of the aromatic lignin component, which is abundant on the fiber surfaces.24 Alternatively, kraft fibers in either OCC or MOW might be promising in such applications due to their greater porosity, surface area, and more extensive degree of fibrillation.25

When attempting to determine whether the wettability of different types of cellulosic fibers makes a difference in terms of oil uptake, fiber morphology can be a challenge. A typical mechanically processed fiber has a markedly different shape from that of a kraft fiber. Mechanical pulping does extensive physical damage as the fibers are separated from each other.26 By contrast, chemical pulping, such as the kraft process, yields fibers with little mechanical damage and removes most of the lignin. The chemical fibers are typically more conformable and are present in paper products in the form of flattened ribbons, which bond effectively with each other.27 Previous work has shown that treatments to make cellulosic materials more hydrophobic can increase their sorption capacity for oleophilic...
2.2. Oil Sorption by Cellulosic Fibers. In a typical experiment, two 5 g samples of fiber were weighed. One sample was prewetted by submerging it in 300 mL of deionized water for 10 min. It was then drained with a Buchner funnel using house vacuum (ca. 60 kPa) for 15 s. Each 5 g sample was then separately submerged in oil for one hour. The oil comprised a 50−50 mixture by volume of Bitumen heavy crude oil (API gravity of 10°, from the Province of Alberta, Canada) and kerosene (Sigma-Aldrich) in order to simulate a light crude oil. After diluting the crude oil with kerosene, the resultant API gravity was 31°. Hereafter, this oil will be referred simply as "oil". After soaking, the excess oil was drained by a Buchner funnel with house vacuum applied until the filter paper was no longer covered by a thin layer of the excess oil (about 2 min).

The amount of oil remaining attached to the fiber was determined by Soxhlet extraction, using a 50−50 mixture by volume of heptane and toluene. The extractions were run until all of the oil was removed, as demonstrated by clear solvent running through the sample. Extract was tested with a UV spectrometer to obtain the absorbance at 280 nm. The method used is an internal standard in FIRP lab (Merida, Venezuela). A full wavelength scan with a solution of 50 mg/L was used to verify the UV maximum, and the corresponding absorbance measured for each test was compared to a calibration curve based on the absorbance of solutions of known concentrations of oil in the solvent. Linear regression coefficients greater than 0.99 were determined for the concentration ranges 0−10 mg/L and 0−100 mg/L. After accounting for dilution, the amount of oil in the solution was calculated. The weight of the dried fiber + tared thimble, after extraction, was used to determine the amount of oil sorbed per gram of fiber.

2.3. Contact Angle Determination. Contact angles of droplets (20−40 μL) of either deionized water or the oil (Section 2.2) on the cellulose film (Section 2.1) were obtained with an NRL Contact Angle Goniometer (model 100−00 115 from Ramé-Hart, Inc., Mountain Lakes, NJ). Angles were measured 10 s after application of the droplets. A parallel set of tests, which was evaluated after 60 s of contact, gave essentially the same trends with respect to the effects of surface treatments. Though wettability of a flat film is inherently different from that of a pad of fibers, studies have shown that the two phenomena can be physically related, as shown by applications of the Lucas-Washburn equation.

3.0. RESULTS AND DISCUSSION

3.1. Oil Sorption by Cellulosic Fibers. Results of sorption tests carried out with different kinds of cellulosic fibers are summarized in Figure 1, which shows 90% confidence intervals for uptake of oil by dry (unfilled bars) and by prewetted (hatched bars) cellulosic fibers. The highest uptake ratio, even exceeding a mass ratio of 6:1 of oil on the substrate, was achieved with the bleached softwood Kraft fibers. Nearly as promising results were achieved with dry hardwood Kraft fibers and with dry mechanical pulp (CTMP) fiber.

In the case the CTMP, the data suggest that the less refined fibers (400 mL CSF) may have been more effective for oil sorption than the fiber with a higher level of refining (120 mL CSF). Because the corresponding data cover ranges that overlap with each other (see open bars in lower half of Figure 1), such a difference was not significant at the 90% level of confidence. However, these results suggest that oil uptake capability is not dominated by the effective surface area of the fibers, a factor that tends to be correlated with the degree of refining or freeness. Rather, a possible explanation may involve the bulky nature of the packed CTMP fibers, depending...
show 90% confidence intervals of the data.

As a first step in interpreting the results shown in Figures 1 and 2 it was assumed that the ability of fibers to take up either water or oil would be correlated to the ability of those liquids to spread onto the solid surfaces. To simplify, one can envision a sorbent material as having uniform, cylindrical pores. Based on such a model it would be predicted that the ability of the liquid to be taken up by the porous material would be critically dependent on the value of contact angle. According to the Lucas-Washburn equation, \[ \frac{dL}{dt} = \frac{\gamma R \cos \theta}{(4\eta L)} \] or after solving for \( L \), \[ L = \left(\frac{\gamma R \cos \theta}{(2\eta)}\right)^{0.5} \]

where \( L \) is the liquid penetration distance after an elapsed time \( t \), \( \gamma \) is the interfacial tension of the liquid, \( R \) is the capillary radius (or an equivalent radius, when applying the model to noncylindrical pores), and \( \theta \) is the contact angle (drawn through the liquid at the three-phase contact line). A key prediction of this simplified analysis is that no imbibition of liquid will occur if the contact angle exceeds 90 degrees. In fact, as has been noted by others, deviations from ideal smooth cylindrical pores tend to further inhibit passage of liquids through porous materials, even in cases where the contact angle on a corresponding smooth surface is less than 90 degrees.

Results of contact angle tests on cellulose films are given in Figure 3. As shown by the plotted circles, increasing levels of ASA treatment increased the hydrophobic nature of the cellulose. The effect was very noticeable as the ASA treatment level was raised from zero to about 0.1% by mass; the contact

on the manner of their preparation, which would affect the space available around the fibers for the uptake of oil.

Prewetting the fibers with water profoundly affected oil uptake by the bleached softwood kraft fibers. Highly variable results were obtained for prewetted hardwood kraft fibers, and intermediate results were obtained for prewetted CTMP fibers. Hardwood kraft fibers, in addition to being much smaller on average than softwood fibers, also have more carboxylic acid groups, which contribute to higher water-wettability. Also, levels of extractives present in different classes of pulp can be expected to affect water wetting and absorption. Such results are important because many unplanned spills of crude or refined petroleum occur in water reservoirs, and thus any absorbent material used for collection is likely to become wetted by water.

Bleached softwood kraft fibers were used to further investigate the effect of treatments with the hydrophobic sizing agent (alkenylsuccinic anhydride, ASA) and with lignin. As shown in Figure 2, pretreatment of the fibers with lignin, ASA, or ASA followed by lignin resulted in modest changes in the amount of oil taken up by the dry fibers. The results from untreated bleached kraft fibers are included in Figure 2 as a reference. Deposition of lignin onto the fibers resulted in the highest sorption values for dry fibers obtained in this study. It is hypothesized that the more aromatic nature of the lignin, compared to cellulose, may have contributed to its effectiveness of increasing oil uptake. Specifically, an affinity is expected between the aromatic groups of lignin and those in the oil due to \( \pi-\pi \) interactions. The increase in oil uptake due to lignin was about 10% relative to the untreated bleached softwood kraft fibers. Interestingly, treatment of the same fibers with the hydrophobic agent ASA reduced oil uptake. Treatment of the fibers with ASA, followed by lignin deposition led to results that were clearly less promising than those of the untreated fibers and lignin-treated fibers in terms of oil uptake in the dry condition.

The hatched bars in Figure 2 show, also in this case, that prewetting of the fibers with water generally decreased their ability to take up the oil. However, the treatment of the fibers with either lignin or ASA generally (except for certain samples) increased the amount of oil sorbed by the prewetted samples. The reason for the wide scatter in some of the results is not known. The most promising results were achieved at the higher treatment level of ASA, for which the results were comparable with those obtained with the corresponding dry fibers. The combination of ASA treatment followed by lignin deposition yielded results that were not as favorable as those achieved with ASA treatment alone. ASA treatment is widely applied to printing papers, so it is already expected to be present on many of the fibers in mixed office wastepaper, as collected in recycling programs. Likewise, substantial amounts of lignin are already present in and on fibers within typical batches of old newspaper or old magazine pulps.

3.2. Contact Angles and Wettability. As a first step in interpreting the results shown in Figures 1 and 2 it was assumed that the ability of fibers to take up either water or oil would be correlated to the ability of those liquids to spread onto the solid surfaces. To simplify, one can envision a sorbent material as having uniform, cylindrical pores. Based on such a model it would be predicted that the ability of the liquid to be taken up by the porous material would be critically dependent on the value of contact angle. According to the Lucas-Washburn equation, \[ \frac{dL}{dt} = \frac{\gamma R \cos \theta}{(4\eta L)} \] or after solving for \( L \), \[ L = \left(\frac{\gamma R \cos \theta}{(2\eta)}\right)^{0.5} \]

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angles did not change as much with further increase to about 0.6%. However, yet higher treatment levels of ASA resulted in a reversal of the hydrophobizing effect. The amount of scatter in the results is typical for experiments carried out on film surfaces, since the spreading droplets are not necessarily at equilibrium.33 Rather, it is to be expected that local mechanical and chemical heterogeneities will cause hysteresis, that is, differences related to advancing and receding contact angles.

The middle set of results in Figure 3 (diamonds) corresponds to contact angles of oil on dry cellulose film. ASA treatment, even at quite low levels, tended to increase the contact angle of the oil, resisting its tendency to spread. These results are consistent with the oil uptake effects shown in Figure 2 for dry softwood kraft fibers. Such effects also are consistent with the expected chemical interactions; a surface with higher free energy can be expected to yield relatively low values of contact angle with most liquids.33 Treatment of the surface so that it is covered by alkyl groups (as in the case of ASA treatment) will reduce polar and other interactions between water and the substrate. Also, the Hamaker constant associated with alkyl groups will be lower than that of the untreated cellulose,42 leading to weaker dispersion interaction with the aromatic groups in the oil. The predictable effects of such differences are consistent with the present results.

Prewetting the cellulose film with water (wet film) tended to make the surface more easily wettable by oil, not less. Notably, an intermediate level of treatment with ASA tended to inhibit spreading of oil onto the prewetted cellulose film to some extent. Again, the results are consistent with the general rule that lower-energy liquids will tend to spread readily on higher-energy surfaces.

A mechanism to account for the effects of ASA at different treatment levels is illustrated in Figure 4. In the absence of ASA treatment, the cellulose was hydrophilic, and the water drops spread with a low contact angle (Figure 1A). Though ASA is initially in the form of an anhydride, upon its reaction with cellulose (or hemicellulose) hydroxyl groups on the fiber or cellulose film surface, one can expect the formation of an ester bond, as shown at the right in Figure 4.42,43 Opening of the anhydride ring yields a carboxylic acid group, but it remains essentially covered up by the relatively long hydrophobic alkyl or alkenyl tails (typically a combined tails length within the range C16 to C22) of the ASA molecule. Under the intermediate conditions (see Figure 4B) much of the ASA reacts to form a monolayer, resulting in a predominantly hydrophobic surface.42–46 However, under conditions of an overdose, one can expect the formation of a bilayer, since the hydrophobic tails of subsequent molecules can associate with the first layer (see Figure 4C). Such a second layer of ASA will tend to present a pair of carboxylate groups outward from the substrate, increasing the hydrophilic character. A reversal of ASA sizing effects at very high treatment levels has been noted,47 but this is apparently the first time that the effects has been demonstrated with contact angles on a cellulose film substrate.

4.0. IMPLICATIONS OF THIS WORK

Cellulosic fibers were shown to sorb 3–7 times their mass of simulated crude petroleum in the absence of water. Results depended modestly on the type of pulping used to prepare the fibers. When the fibers had been soaked with water, the amounts of oil were decreased, but not to zero. The largest reduction in oil uptake was observed with bleached softwood Kraft fibers, a substrate known to be relatively hydrophilic. The ability of such fibers to take up oil, even when wet by water, could be increased by pretreating them to make them less hydrophilic. This was demonstrated with lignin and with alkenylsuccinic anhydride. The effectiveness of such treatments implies that various fibers already present in typical wastepaper batches have features that lend themselves well to this kind of application. Such features include substantial quantities of lignin (in recycled newspapers and magazines), hydrophobic sizing agents (in office waste fibers, food packaging, and container-board), and hydrophobic inks (in paper printed by xerography or offset lithography).

Though the present results indicate that cellulosic fibers have some potential to be used in oil sorption, even under wet conditions, some important questions are left open for further
investigation. In particular, there is uncertainty about the best way to process or dispose of oil-bearing cellulosic material.

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