

## CHAPTER 35

# OIL SORPTION BY LIGNOCELLULOSIC FIBERS

Beom-Goo Lee, James S. Han, and Roger M. Rowell

### ABSTRACT

The oil sorption capacities of cotton fiber, kenaf bast fiber, kenaf core fiber, and moss fiber were compared after refining, extraction, and reduction in particle sizes. The tests were conducted on diesel oil in a pure form. Cotton fiber showed the highest capacity, followed by kenaf core and bast fibers. Wetting, extraction, and reduction in particle size all contributed to the changes in sorption capacity. The most significant change was due to the reduction in particle sizes of cotton and kenaf bast fibers; however, the kenaf core was not affected. Usually, lignocellulosic fibers are hydrophilic and the oil sorption capacity is very low. These hydrophilic fibers must be converted to hydrophobic fibers to improve the oil sorption capacity.

### INTRODUCTION

Transportation of petroleum from oil fields to consumers may require 10 to 15 transfers. Petroleum is transported by tankers, pipelines, trains, and tank trucks and stored temporarily in a number of facilities. Accidents may occur during each of these transportation and storage steps (Fingas et al. 1979). Offshore and shoreline waters can be polluted by runoff from offshore oil exploration and production and spills from ship transport of oil. Inland water can be polluted by runoff from oil fields and refinery areas and, in some cases, process effluent from petroleum and petrochemical plants (Johnson et al. 1973).

Under favorable conditions, oil in a clean water body may continue to spread over the water surface and form a monomolecular layer. The oil film on the surface of water impairs the exchange of energy, heat, moisture, and gases between the water reservoir and the atmosphere (Pushkarev et al. 1983).

Crude oil consists of different hydrocarbons that range from a light gas

(methane) to heavy solids. The most important and prevalent elements in petroleum are hydrogen and carbon, which comprise up to 98% of some crude oils and 100% of many refinery products. Other constituents of petroleum are hydrocarbon derivatives containing oxygen, sulfur and nitrogen, as well as vanadium, nickel, and mineral salts (Fingas et al. 1979). When oil is spilled on water or on land, the physical and chemical properties of oil change progressively. This process is referred to as "weathering". The volatile components evaporate quickly. Some of the medium-sized polycyclic aromatic hydrocarbons are slightly soluble. Some of the products, which are degraded by sun and microorganisms, are highly soluble. Weathering rates are not constant but are usually highest in the first few hours. Major processes of weathering of oil spilled on water include evaporation, dissolution, oxidation, emulsification, and microbial degradation. The less volatile components form a residue which has a higher specific gravity and viscosity than the original oil. If the residual oil is adsorbed to other material of high specific gravity such as silt or clay suspended in the water, the specific gravity of the residual may exceed 1.0 and sink. If not, the residue continues to spread from an area of dense saline water to less dense freshwater and may then sink. In the case of crude oil, evaporation plays an extremely important role in its volumetric loss after a spill; 25% of the total volume of spilled crude may be evaporated within one day. No. 2, No. 4, and No. 6 fuel oils typically lose 13.1%, 2.5% and 2.0%, respectively, after 40 h at 23°C. Gasoline loses about 50% of its original volume within 7 to 8 min at 20°C (Fingas et al. 1979, Gait et al. 1991).

The spilled oil contributes an undesirable taste and odor to drinking water and causes severe environmental damage (Blumer 1969). Contaminated water cannot be used for municipal water supply, for industry, nor for irrigation (Blumer 1969, Morita et al. 1987). Public concern for sustaining a healthy environment has resulted in stronger environmental regulations regarding water quality and use of hazardous chemicals and substances. This concern has resulted in the need for improved techniques and methods for the use and reuse of hazardous chemicals and for remedial measures where contact with the environment does occur. Improved techniques for control and removal of oil slicks is one area of research under active development.

Retention of oil over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent are important properties of sorbents (Schatzberg 1971, Halligan et al. 1976, Melvold et al. 1988). Sorbent materials applied to an oil slick changes liquid oil to a semi-colloid. The oil can then be removed in an efficient and easy manner (Halligan et al. 1976). Inorganic mineral products, i.e., organic synthetic products and organic vegetable products, can be used as oil sorbent materials (Schatzberg 1971). Mineral products include perlite, vermiculite, sorbent clay, and diatomite (Schatzberg 1971, Melvold et al. 1988). However, these materials do not have adequate buoyancy and their oil sorption capacity is generally low (Schatzberg 1971). Synthetic products, such as polypropylene, polyethylene, polypropylene booms and polyurethane foam, have highly oleophilic and hydrophobic properties and are the most widely used

sorbents in the remediation of oil spills (Schatzberg and Jackson 1972, Herrick et al. 1982, Schrader 1991). However, these materials degrade very slowly relative to mineral or vegetable products. In the case of floating polypropylene booms, it is difficult to recover all the absorbent material, The residual, nonbiodegradable material contaminates the environment similar to the parent material (Schrader 1991).

The limitations of the above-mentioned methods have led to the study of alternative methods for oil removal using biodegradable materials such as lignocellulosic fibers (Anthony 1994). Agricultural products and residues are inexpensive and readily available. Moreover, cellulosic products exist in fibrous form and can be easily formed into mats, pads, and nonwoven sheets (Fanta et al. 1986).

Organic vegetable products such as straw, corn cob, and wood fiber show poor buoyancy characteristics, relatively low oil sorption capacity, and low hydrophobicity (Schatzberg 1971). However, unscoured, unbleached natural fibers such as milkweed, kapok, and cotton have greater potential as sorbents in remediation of oil spills compared with commercially available synthetic materials. These natural fibers sorb oil 1.5 to 3.0 times greater than commercial polypropylene fibers or mats (Johnson et al. 1973, Choi and Choi 1992, Choi et al. 1993). Kapok, kenaf, and milkweed have native hydrophobic properties due to the large amount of wax on the fiber surfaces. Kapok and milkweed have larger and noncollapsing lumen which give greater pore volume for absorbed chemicals (Choi and Choi 1992). Therefore, the fibers which have a large amount of wax on the fiber surface and the noncollapsing lumen are preferred in oil sorption. These fibers could be used as a substitute for non-biodegradable synthetic materials in remediation of oil spills, thereby reducing or potentially eliminating the need for synthetic sorbents.

The mechanism for oil sorption by cotton fiber is controlled by adsorption on the fiber surface and capillary action through its lumen. On the contrary, oil sorption of polypropylene is through capillary bridges between fibers (Choi and Choi 1992).

Fibers float and have high sorption capacity. Thus, they may be structured into continuous belts, sheets, booms, or pads which would simplify sorbent deployment, retrieval, and disposal of oil-laden sorbent. Fibers are reusable and easier to control in either open or confined spaces, and facilitate collection (Johnson et al. 1973, Brewers 1982, Choi and Choi 1992). The production of nonwoven fiber sheets or pads is of particular interest because of the availability of raw material, steady supply, and low cost. Kenaf bast has high fiber strength and kenaf core has hydrophobic properties due to the presence of surface wax. The capacity of kenaf to sorb oil, however, has not received extensive study. This study will examine the feasibility of using kenaf bast and kenaf core and cotton for sorption of oil in a water bath and in a pure form.

## MATERIALS AND METHODS

### Scope of Experiment

Sorbents are generally not effective for cleanup of oils (Bunker C type) having high viscosity and high specific gravity. These oils tend to sink partially or completely after contact with water (Choi et al. 1993). Furthermore, light-weight hydrocarbon oils evaporate readily during the early stages of exposure; thus, it is not possible to initiate remedial measures (Galt et al. 1991). Therefore, to simplify the variables in this study, only light crude oil (diesel) was used in the experiments.

Direct comparison of oil sorption capacity of different types of fibers would be difficult due to the fact that most of the fibers have different physical and chemical properties. Physically, when the fibers undergo a similar refining process, the aggregates of fiber will be reduced to individual fibers. To measure the difference in sorption capacity, fibers can be ground to the same particle size, i.e., a size that is far larger than the width of their respective fibers. Also, using a similar process of solvent extraction, it may be possible to differentiate the chemical composition of each of the fibers studied. Thus, experiments were conducted on the fibers using three separate treatments.

### Source of the Fibers and Equipment

Kenaf bast and core fibers of cultivar Cubano 108 (C-108) were taken from the 1993 crop grown by the Forest Products Laboratory, USDA, Madison, WI. The kenaf whole stalks were air-dried, and the bast and core fibers hand separated to 99% purity. Cotton was purchased from Absorbent Cotton Company, Division of Sterile Products Corporation (Valley Park, MO) (Note: It was difficult to refine the cotton fiber and natural cotton was used in place of refined cotton.) Sphagnum moss was supplied by AgResearch International, Incorporated (Madison, WI).

The apparatuses included a distillation apparatus (technique described in ASTM D95-70), an orbital shaker (Model G 10 Gyrotory Shaker, New Brunswick Scientific Co., Inc., New Brunswick, NJ), a refiner (Sprout-Bauer Inc., A Subsidiary of Combustion's Engineering Inc., Muncy, PA, Model No. 12 1 CP), a soxhlet extractor, a test sieve shaker (Humboldt MFG. Company, Norridge, IL), and a Wiley Mill (Arthur H. Thomas Company, Scientific Apparatus, Philadelphia, PA).

The reagents were diesel oil, pure Wesson canola oil, toluene, and xylene.

## Sample Preparation

The particle size distribution was controlled using a Wiley Mill. Test samples were ground to pass through 600-, 425-, 300-, 250-, 212-, and 180- $\mu\text{m}$  (30-, 40-, 50-, 60-, 70- and 80-mesh) screens. The ground fibers were placed in a test sieve shaker with sieves stacked in order of increasing mesh sizes (decreasing particle sizes) to ensure the uniformity of the particle sizes when shaken over time. Kenaf core and kenaf bast fibers were ground to pass a 212/180- $\mu\text{m}$  (70/80-mesh) screen and cotton samples to pass a 850- $\mu\text{m}$  (20-mesh) screen. Moss samples were ground to pass 600-, 425-, 250-, 212-, and 180- $\mu\text{m}$  (30-, 40-, 60,70 -and 80-mesh) screens.

The purpose for fiber refining was to maintain the integrity of the fibers. Refining was conducted by first pre-steaming the fiber for 10 min at 207 kPa (30 psi) and then running them through the Sprout-Bauer refiner for a period between 2 to 5 min. The type of refining plate used was C2976 and the plate gap was set at 0.25 to 0.50 mm (0.01 to 0.02 in.).

Fibers were placed in a Soxhlet extractor with diethyl ether and extracted for 6 h. Due to the presence of fatty acids and alcohols, some of the fibers were oleophilic. Other extractives were present, and it was noted that the extraction process altered chemical properties.

## Procedure

The sorption capacity of each modified fiber was measured as described by Choi and Choi (1992) but with some modification. Twenty g of diesel oil was added to a 500-mL beaker containing 250 mL of water. To this mixture 0.5 g of sorbent material was added, the beaker placed on an orbital shaker, and then shaken for 10 min at 100 cycles per min. The wetted sorbent was then removed from the beaker, oil and water were filtered for one min using a wire strainer, and then weighed. The water content of the sorbent was measured using the distillation technique described in ASTM D9570. Canola oil was used with the sphagnum moss. The wetted sorbent to the oil/water was refluxed with a mixture of toluene and xylene (20/80, v/v). Organic solvents and water were continuously condensed into a trap. The water settled in the graduated section of the trap and the solvent was returned to the still. Oil content was determined by subtracting the water content and the initial sorbent weight from the total weight of the wetted sorbent. (Note: The percent extractive content of a given fiber was analyzed and the weight adjusted.) The weight of oil sorbed was recorded as g per g of sorbent. Three replications were made for each sample. One hundred mL of diesel oil was placed in a 200-mL beaker and the sorbent immersed in the bath. After orbital shaking and straining as described above, the amount of oil sorbed by the sorbent was determined by subtracting the initial sorbent weight from the total weight of the wetted sorbent. Three replications were made for each sample in this procedure as well.

## RESULTS AND DISCUSSION

### Refined Sorbents

Figure 35.1 shows the oil sorption characteristics of kenaf bast, kenaf core, and cotton in water baths containing 20 g of oil. Among the sorbent materials examined in this research, cotton (30.62 g/g) showed the highest oil sorption capacity followed by kenaf core (7.16 g/g), and kenaf bast (7.06 g/g) (Table 35.1).

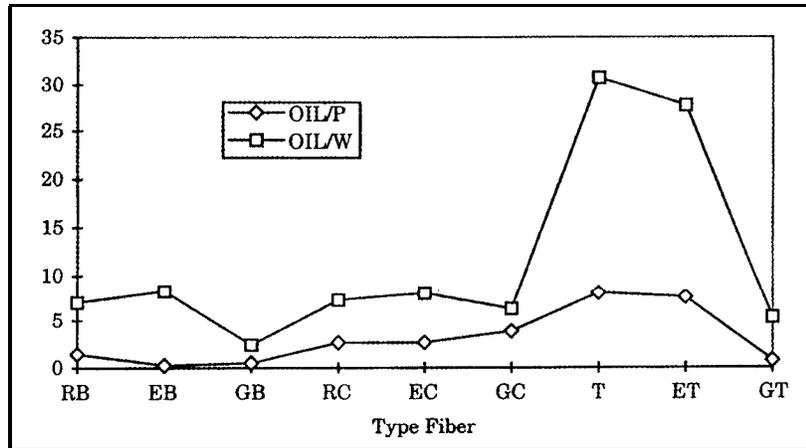


Figure 35.1. Oil sorption capacities of fibers in the 100% diesel oil(oil/p) and water bath with 20 g of floating diesel oil (oil/w).

RB : Refined kenaf bast  
 EB : Extracted kenaf bast  
 GB : Ground kenaf bast  
 RC : Refined kenaf core  
 EC : Extracted kenaf core  
 GC : Ground kenaf core  
 T : Cotton  
 ET : Extracted cotton  
 GT : Ground cotton

Table 35.1. Oil sorption of fibers in the water bath containing 20 g of diesel oil and in pure oil.

	Refined Kenaf Bast	Refined Kenaf Core	Cotton
Oil Type	g/g	g/g	g/g
oil/water	1.54	2.74	8.07
oil/pure	7.08	7.16	30.62

According to Gregg and Sing (1967), the sorptive capacity in a vast range of solids depends on the surface area and pores. Lignocellulosic have more surface area than nonporous materials; therefore, they are a good candidates for sorption material. At the initial stage, oil is sorbed by some interaction and van der Waals force between oil in the bath and wax in the natural sorbents on the fiber surface. This sorption is due to the fact that both oil and wax are hydrocarbons and there is physical trapping of oil on the fiber surface through its irregular surface morphology. Sorption of oil within the fiber occurs by defusion through internal capillary movement into sorbent lumens. Cellulose molecules of lignocellulosic fiber have a hydrophilic nature due to hydroxyl groups. Oil sorption into the pores in the secondary wall maybe negligible (Choi et al. 1993).

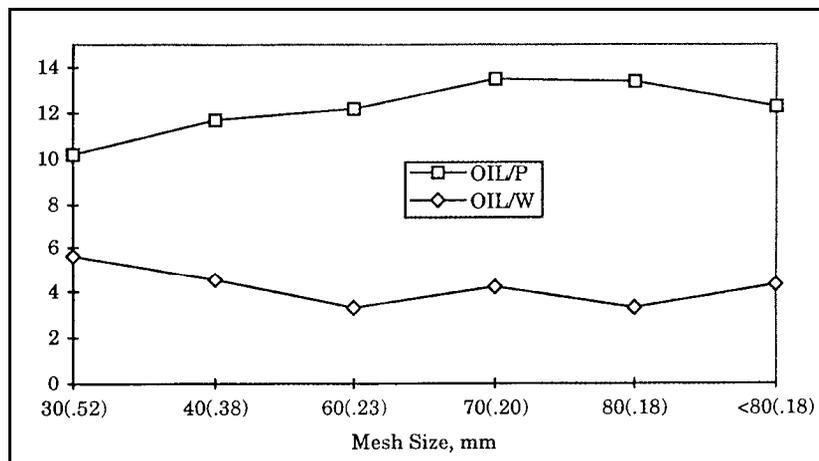
In experiments conducted using the pure oil bath, kenaf bast fiber exhibited approximately the same oil sorption capacity as kenaf core. However, sorption capacity decreased when using the water bath containing oil. Kenaf bast fiber has a higher specific gravity value than kenaf core. Kenaf bast fiber sank within seconds in the water bath, while kenaf core fiber floated throughout the experiment. Kenaf core has waxes on the surface; however, the oil sorption capacity is lower relative to cotton. Kenaf core has very low fiber strength and a lumen that collapses easily; therefore, oil may not be trapped inside the collapsed lumen. The high oil sorption capacity of cotton might be due to the presence of waxes on the surface, to a hollowed surface structure, and to its non-collapsed lumen.

### Ground Sorbents

The oil sorption capacity of ground kenaf core in pure oil or mixed oil was higher than that of either ground kenaf bast fiber or cotton (Table 35.2). The fiber length of kenaf core fiber (0.8 mm) is much shorter than either kenaf bast fiber (2.7 mm) or cotton (18 mm). During fiber processing with the Wiley Mill, each of the fibers passed through the 850- $\mu\text{m}$  (20-mesh) screen. Kenaf core fiber had the least damage to the lumen; thus, the lumen was able to hold more oil and more water. It was observed that the oil sorption capacity is affected by grinding. Once the fibers were ground to less than their fiber length, the sorption capacity decreased. This conclusion is supported by another experiment using moss fiber having significantly less fiber length (0.16 mm) relative to the other fibers (Figure 35.2). The sorption capacity increased relative to the mesh size; however, at 180  $\mu\text{m}$  (80 mesh), the sorption capacity started to decrease.

**Table 35.2.** Oil sorption of ground fibers in the water bath containing 20 g of diesel oil and in pure oil.

	Ground Kenaf Bast	Ground Kenaf Core	Ground Cotton
Oil Type	g/g	g/g	g/g
oil/water	0.45	3.95	0.76
oil/pure	2.34	6.36	5.19



**Figure 35.2.** Oil sorption capacities of moss fiber at various mesh sizes in the 100% diesel oil (oil/p) and in a water bath with 20 g of floating diesel oil (oil/w).

### Extracted Sorbents

The Soxhlet extraction of sorbents with diethyl ether slightly changed their oil sorption capacities in the bath containing pure oil and in water bath containing 20 g of diesel (Table 35.3). As indicated in Figure 35.1, the extraction process could either increase or decrease the oil sorption capacity. The general assumption that the extraction process will remove the hydrophilic or hydrophobic substances depends on what kinds of extractives are predominant. Removal of fatty acids, etc., will reduce the sorption capacity. A plausible explanation for an increased capacity is that the fiber remains oleophilic due to residual organic solvents.

**Table 35.3.** Oil sorption of extracted fibers in the water bath containing 20 g of diesel oil and in pure oil.

Oil Type	Extracted Kenaf Bast	Extracted Kenaf Core	Extracted Cotton
	g/g	g/g	g/g
oil/water	0.31	2.69	7.49
oil/pure	8.15	7.94	27.73

## Presoaking Sorbents

As shown in Table 35.4, the presoaking of sorbent by water decreased oil sorption capacity in kenaf core. Kenaf bast and cotton sank during the presoaking process; thus, the oil sorption capacity could not be determined.

**Table 35.4.** Oil sorption of prewater-soaked kenaf core in a water bath containing 20 g of diesel oil.

Time	Oil (g/g)
0 min	2.69
10 min	1.26

## Oil Sorption Without Water Medium

The sorbents also can be used to remove oil in situations where water is not present. Since the sorption environment may be different, the capacity of sorbents may also be different. In addition, this method can be used to determine the maximum amount of oil sorbed by a particular sorbent. Figure 35.1 shows that oil sorption by the sorbent in the oil bath was much higher than the oil sorption in the water bath containing 20 g of oil. Cotton had considerably higher oil sorption capacity than either kenaf bast or core.

## CONCLUSIONS

Cotton exhibited the highest capacity for oil sorption among the fibers examined. This sorption is due to the large amount of wax on the fiber surface, the hollowed surface, and the larger, noncollapsing lumen of the fiber. Solvent extraction slightly reduced the oil sorption characteristics of the cotton. Presoaking in water and reduction in particle size slightly changed the oil sorption capacity of kenaf core. On the other hand, a reduction in particle size reduced the oil sorption capacity of kenaf bast and cotton. The surface area, pore size, oil content, shape, and strength of fibers are factors that affect oil sorption capacity. Typically, lignocellulosic fibers are hydrophilic, resulting in low capacity to sorb oil. In order to improve the affinity for oil, these hydrophilic fibers must be converted to hydrophobic fibers. Further research is warranted in the application of lignocellulosic fibers for sorption in order to define the factors contributing to sorption, and to investigate the potential for modification of the surface chemistry to increase sorption capacity.

## ACKNOWLEDGEMENTS AND DISCLAIMER

The Forest Products Laboratory is maintained in cooperation with the University of Wisconsin. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain and not subject to copyright. This research was partly supported by AgResearch International, Inc. of Madison, Wisconsin and Construction Fabrics & Materials Corp. of Cottage Grove, Wisconsin.

## REFERENCES

- Anthony, W.S. 1994. Absorption of oil with cotton products and kenaf. *Appl. Eng. Agric.* 10(3):357-361.
- Blumer, M. 1969. In: *Oil on the Sea*. D.P. Hoult (ed.), Plenum Press, New York, NY, p. 6
- Browsers, S.D. 1982. Understanding sorbents for cleaning up spills. *Plant Eng.* 3:219-221.
- Choi, H., and R.M. Choi. 1992. Natural sorbents in oil spill cleanup. *Environ. Sci. Technol.* 26:772-776.
- Choi, H., H. Kwon, and J.P. Moreau. 1993. Cotton nonwovens as oil spill cleanup sorbents. *Textile Res. J.* 63(4):211-218.
- Fanta, G.F., R.C. Burr, and W.M. William. 1986. Oil absorbency of graft copolymers from softwood pulp. *Polymer Sci. Technol.* 33:107-114.
- Fingas, M.F., W.S. Duvall, and G.B. Stevenson. 1979. *The basics of oil spill cleanup*. Environ. Emergency Branch, Environ. Protection Serv., Environ. Canada.
- Galt, J.A., W.J. Lehr, and D.L. Payton. 1991. Fate and transport of the Exxon Valdez oil spill. *Environ. Sci. Technol.* 25(2):202-209.
- Gregg, S.J., and K.S.W. Sing. 1967. *Adsorption, Surface Area and Porsity*, Academic Press Inc., New York, NY, p. 1, 4-5, 252-253.
- Halligan, J.E., A.A. Ball, and G.F. Meenaghan. 1976. U.S. Coast Guard Rep. No. CG-D-63-76. U.S. Coast Guard Headquarters, Washington, DC.
- Herrick, E.C., D. Carstea, and G. Goldgraben. 1982. Sorbent materials for

cleanup of hazardous spills. EPA-600/2-82-030. Environ. Protection Agency, Washington, DC.

Johnson, R.F., T.G. Manjrekar, and J.E. Halligan. 1973. Removal of oil from water surfaces by sorption on unstructured fibers. *Environ. Sci. Technol.*, 7(5):439-443.

Melvold, R.W., S.C. Gibson, and R. Scarberry. 1988. Sorbents for liquid hazardous substance cleanup and control, Noyes Data Corp., Park Ridge, NJ.

Morita, M., M. Higuchi, and I. Sakata. 1987. Binding of heavy metal ions by chemically modified woods. *J. Appl. Polymer Sci.* 34:1013-1023.

Pushkarev, V.V., A.G. Yuzhaninov, and S.K. Men. 1983. Treatment of Oil-Containing Wastewater, Allerton Press, Inc., New York, NY, p. 3-5.

Schatzberg, P. 1971. U.S. Coast Guard Rep. No. 724110.1/2/1. U.S. Coast Guard Headquarters, Washington, DC.

Schatzberg, P., and D.F. Jackson. 1972. U.S. Coast Guard Rep. No. 724209.9. U.S. Coast Guard Headquarters, Washington, DC.

Schrader, E.L. 1991. Remediation of floating, open water Oil spills: Comparative efficacy of commercially available polypropylene sorbent booms. *Environ. Geol. Water Sci.* 17(2):156-166.

In: Kenaf Properties, Processing and Products; Mississippi State University, Ag & Bio Engineering, 1999. pp. 423-433. ISBN 0-9670559-0-3. Chapter 35