New Technique to Remove Asphalt from Microfossil-rich Matrix from Rancho La Brea

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ABSTRACT. Asphalt-preserved fossils present specific cleaning and preparation challenges not encountered with permineralized fossils. Asphalt is a complex mixture of mainly large hydrocarbon molecules that are totally insoluble in water and only sparingly soluble in many organic solvents. This study attempts to develop a faster and better procedure for dissolving asphalt, ideally making use of cheaper and greener solvents. One of the more promising of these is biodiesel. Pure biodiesel, or B100, is a liquid consisting of methyl esters of fatty acids produced by refining vegetable oil triglycerides and having similar properties to (petroleum-derived) diesel fuel. While biodiesel is not an effective asphalt solvent at room temperature, it becomes very effective when heated to temperatures greater than 70°C. We here provide a detailed guide and recommendations on the use of hot biodiesel as a solvent to process asphalt-impregnated fossiliferous matrix.

INTRODUCTION

The asphalt seeps at Rancho La Brea, located in Hancock Park, Los Angeles, California, are one of the world's richest terrestrial late Pleistocene fossil localities (e.g., Akersten et al., 1983; Shaw and Quinn, 1986; Stock, 1992) and present a unique window on the world at the end of the last ice age. Intensive collection at intervals during the past century has resulted in the recovery of hundreds of thousands of exceptionally well preserved mammalian bones ranging from saber-toothed cats to squirrels, plus large quantities of other vertebrates, invertebrates, and plant remains (Stock, 1992). Typical Rancho La Brea fossils are composed of unaltered organic material—bone, plant remains, shells, and insect exoskeletons. Extraordinary preservation of Rancho La Brea fossils is due principally to asphalt impregnation that helps protect the material from diagenetic changes. Vertebrate fossils from Rancho La Brea rarely display permineralization.

Early excavations between 1905 and 1915 concentrated on the recovery of larger and more spectacular fossil plants and animals; smaller organisms and important information pertaining to geology and taphonomy were rarely collected or documented. Pit 91 was reopened in 1969 by the Los Angeles County Museum of Natural History to rectify these collecting biases. New excavation techniques were developed in accordance with established paleontological and archaeological methods to sample intensely and carefully record biological and geological data (Shaw, 1982). A main goal of the excavation was the recovery of microvertebrate fossils, which have been shown to provide a wealth of information about past environments and ecosystems. The process of isolating large numbers of tiny and potentially fragile asphalt-preserved fossils presents specific cleaning and preparation challenges that are not encountered with permineralized fossils.

Asphalt comprises a complex mixture of hydrocarbon molecules of varying size and chemical makeup. Although asphalt composition can vary substantially between sources and even over time, in general it is composed of relatively large (>400 Da), nonpolar, highly condensed aromatic molecules that are totally insoluble in cold water (polarity index of 10) and only slightly soluble in nonpolar solvents like pentane (0.0). Historically, the asphalt-impregnated matrix was treated in a vapor degreaser unit at 73.3°C using 1,1,1-trichloroethane (methyl chloroform) as solvent (Shaw, 1982). Trichloroethane is highly effective in liberating the smaller fossils from the asphalt but has several significant drawbacks: It is hazardous to human health and the environment, difficult to dispose of, and potentially harmful to the earth's ozone layer. Trichloroethane

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Science Series, Number 42, pp. 169–174
Natural History Museum of Los Angeles County, 2015

production has been phased out in most of the world under the terms of the Montreal Protocol, an international treaty designed to protect the ozone layer by phasing out the production of numerous substances believed to be responsible for ozone depletion. To maintain the present processing methods, it was necessary to find a less hazardous alternative solvent that would be suitable to replace trichloroethane. Ideal solvents for asphalt should be slightly polar, such as dichloromethane (polarity index of 3.1), diethyl ether (2.8), or toluene (2.4), but all of these also have significant environmental and/or health and safety issues. Biodiesel is a liquid fuel generated by the hydrolysis and methylation of common vegetable oils, resulting in a series of fatty acid methyl esters of chain length C_{12}–C_{20}. With its long *n*-alkyl chains and single ester group, B100 has an overall polarity index of ca. 4. Thus asphalt should be moderately soluble in biodiesel.

The term "biodiesel" arises because of the similarity in physical properties and combustibility to diesel fuel, making it a direct replacement in diesel engines. However, unlike petroleum-derived diesel fuel, biodiesel is entirely renewable, nontoxic, nonvolatile, and rapidly degraded in the environment. It is flammable but, with a flash point greater than 130°C, it is quite difficult to ignite. Its low volatility also minimizes emissions that are problematic for air quality and for those using it. These characteristics make it a very environmentally friendly liquid, though it is not typically used as a solvent. As a commodity fuel, biodiesel is also cheaper than most industrial solvents. Unfortunately, the dissolution kinetics of asphalt are also problematical, as the relatively high molecular weight and aromatic character of asphaltene molecules cause them to dissolve very slowly. Dissolution rate favors solvents of smaller molecular size; accordingly, asphalt dissolves more rapidly in dichloromethane and trichloroethane than in toluene or most other hydrocarbon solvents. With its relatively large molecular size, biodiesel will dissolve asphalt exceedingly slowly at room temperature. However, dissolution rate is an exponential function of temperature, and—in our tests of asphalt dissolution—roughly doubled about every 10°C. Thus by heating the biodiesel to greater than 70°C, we were able to achieve sufficiently rapid dissolution to make this a practical choice.

MATERIALS AND METHODS

The fossiliferous asphaltic-impregnated sediment used in this study comes from Project 23. Project 23 is an ongoing excavation of 16 asphaltic fossiliferous deposits recovered from the western edge of Hancock Park in 2006 (Harris et al., 2011). The deposits were exposed, crated into 23 wooden boxes, and transported to a nearby, enclosed compound for future excavation of the fossils. Typical fossil deposits consist of dense bone accumulations surrounded by asphalt-saturated fine to coarse sand and coarse sand lenses with subangular to rounded pebbles and cobbles. Because matrix composition affects processing time and ease, we separate matrix by sediment type—focusing on asphaltic fossiliferous matrix rather than sterile sediment.

The technique for the biodiesel de-asphalting operation is based on our own observations and experiments. The methods and results presented here should be viewed as a case study rather than a definitive process.

While biodiesel itself is relatively nontoxic, the fumes emitted after the introduction of asphaltic matrix and heat may be hazardous. There are no guidelines for exposure to a mixture of heated biodiesel and asphalt, but existing literature on exposure to bitumen fumes and, separately, cooking oil fumes suggests respiratory protection is warranted (Binet et al., 2002; DHHS/NIOSH, 2003; Pan et al., 2008). Our process also involves a second solvent, *n*-propyl bromide (1-bromopropane), a known neurotoxin and possible carcinogen (DHHS/NIOSH, 2013). Accordingly we advocate the use of a half-face respirator with organic vapor cartridges, gloves (we use 11-mm nitrile gloves), a chemical-resistant apron, safety glasses or goggles, and a well-ventilated space in which to perform the operation. Biodiesel heated to around 80°C (175°F) is hot but is well below temperatures used in deep frying (175°C–200°C/350°F–375°F). At our advocated working temperatures, a gloved hand can be immersed briefly without burns; nevertheless, hot biodiesel and drum heaters should be treated with caution.

To set up the biodiesel de-asphalting station, place 8-gallon (30-L) metal drums in a plastic chemical spill tray large enough to contain the amount of biodiesel in the drums. The chemical spill tray should be set to a comfortable working height, for example, on top of a wood pallet or cinder blocks. Additionally, placing the heated biodiesel wash drum on paving bricks will insulate the hot drum from the plastic spill tray. Position the drum heater on the lower half of the metal drum and adjust so it sits snuggly against the outside of the drum (Fig. 1). Magnetic clips can be used on the outside of the drums to hold matrix information tags and are easily moved through steps of the processing. We found that partially filling the metal drums with 5 gallons (19 L) of biodiesel B100 works best.

Because biodiesel is quite involatile, it does not air-dry, and so cleaned matrix will remain solvent-wet for a very long time. To remove this oily residue, we currently use a rinse with room temperature *n*-propyl bromide that also removes any remaining asphalt. Ethanol also works well for removing biodiesel but is both more volatile

Figure 1 Eight-gallon metal drum with drum heater attached in chemical spill tray.

and more flammable. A solvent rinse station is set up adjacent to the biodiesel processing station rinse station and consists of a plastic chemical spill tray with up to five 8-gallon metal drums each containing 2 gallons of *n*-propyl bromide (see "Processing Methodology" below).

We provide a list of recommended materials in Table 1 and a materials resource list in the Appendix. Some of these items may be purchased, but others will have to be fabricated (e.g. 5-gallon (19-L) metal buckets with screened bottoms).

PROCESSING METHODOLOGY

Here we present a detailed guide to processing asphalt-impregnated sediment with biodiesel, but see Table 2 for an abridged version. Our multi-step process involves soaking and agitating asphaltic matrix in hot biodiesel followed by rinsing in room temperature *n*-propyl bromide.

Fill an 8-gallon steel wash drum with 5 gallons of biodiesel B100 and heat to between 80°C and 90°C. Biodiesel will begin to emit visible fumes around 100°C. Drum heaters with adjustable heat and thermostat settings are used to heat biodiesel and maintain a relatively constant temperature. Use of a thermostat is essential to prevent accidental overheating of the biodiesel, which would then present a significant fire risk. A thermometer or thermocouple is also used to monitor the biodiesel temperature as it heats. Drum heater settings for desired temperature will

Table 1 List of materials for setting up a biodiesel processing station.

Item	Purpose
Biodiesel B100	Solvent
n-propyl bromide	Solvent
5-Gallon metal buckets with stainless steel 20-mesh screened bottoms	Screened washing containers
8-Gallon metal drums with lids	Washing tanks
Containment tray	Chemical spill containment
Drum heater with adjustable temperature and thermostat to fit around washing drum	Heat biodiesel
Drying rack to hold 5-gallon buckets	Drying processed condensate
Immersible thermometer	Measure biodiesel temperature, calibrate drum heaters
Hanging scale	Weigh matrix and condensate (optional but handy for quantifying reduction)
Magnetic clips	Attach matrix identification labels/tags to wash drums
55-Gallon drums with open tops and lids	Store liquid and solid biodiesel and *n*-propyl bromide solvent waste

vary depending on wattage of the band heater, amount of biodiesel to be heated and ambient temperature.

Matrix is processed in batches of 8–10 pounds (3.6–4.5 kg). We have found that this is a manageable amount of matrix to handle physically and ensures a greater solvent to matrix ratio with faster dissolution of the asphalt. The weighed matrix is placed in a screened bucket. These can be constructed by removing the bottom of a 5-gallon metal bucket and attaching stainless steel No. 20 mesh screen (850-μm openings) with machine screws and a large-diameter hose clamp (Fig. 2). Gently lower the screened bucket with matrix into the heated biodiesel wash drum. We recommend agitating slowly by rotating the bucket back and forth to saturate the matrix thoroughly and start dissolution. Agitate once or twice more depending on rate of breakdown until most of the matrix is disaggregated and sand and larger clasts and fossils are visible on the bottom of the bucket when lifted out of the biodiesel. When the majority of asphalt has dissolved and fine sediment (<No. 20 mesh) has been screened out, pull the bucket out of the solvent and angle it within the opening of the wash drum so that the bucket is stable, and allow it to drain completely.

Matrix composition affects the speed and ease of processing. We have observed that highly asphaltic sand matrix will dissolve and disaggregate rapidly in as little as 10–15 minutes. When the mineral matrix contains appreciable silt and/or clay, processing time slows considerably, requiring more agitation and, when necessary, manual break down of sediment clumps. Stubborn fine-grained matrix benefits from overnight soaking in solvent. Other factors that influence processing time are the degree of asphalt oxidation (weathering), ratio of matrix to solvent, and loading of solvent with dissolved asphalt.

Following soaking in biodiesel, the concentrate goes through five sequential rinses of *n*-propyl bromide, each in a separate drum. The number of *n*-propyl bromide wash drums isn't fixed. Fewer would work, too, but would require more frequent replacement of the biodiesel and asphalt-saturated *n*-propyl bromide. After the concentrate has been rinsed, the 5-gallon screened bucket is hung on a rack to dry. When concentrate has dried it is bagged and weighed, gravel-size clasts are removed, and it is stored in 1-gallon (4-L) cans. Depending on the nature of the matrix, a bucket of 4–5 gallons (15–19 L) of asphaltic matrix will reduce to a gallon or less

Table 2 Guide to processing asphalt-impregnated fossiliferous matrix in biodiesel.

Processing guide
1. Fill wash drums with 5 gallons of biodiesel.
2. Heat biodiesel to 80°C.
3. Weigh out 8–10 pounds of asphaltic matrix in 5-gallon screened bucket.
4. Slowly immerse bucket and matrix in heated biodiesel and agitate by gently rotating back and forth.
5. Soak matrix. Check after 15–30 minutes for dissolution. Agitate again if necessary.
6. Pull bucket out to drain when asphalt has dissolved and matrix has disaggregated. Drain completely.
7. Move bucket with concentrate through series of *n*-propyl bromide rinse drums. Agitate, and allow to soak in each drum.
8. Remove bucket with concentrate from final *n*-propyl rinse and hang to dry.

Figure 2 Five-gallon metal-screened bucket is constructed by removing the bottom of the bucket and attaching stainless steel 20-mesh screen with machine screws and a large-diameter hose clamp.

of concentrate (10%–35% of starting weight). A batch of 5 gallons of biodiesel can be used to de-asphalt about 10 gallons (38 L) or 80–100 pounds (36–45 kg) of asphaltic matrix before becoming too saturated and viscous.

Maintenance of the processing operation entails removing the fine sediment waste that builds up on the bottom of wash drums and replacing the asphalt-saturated solvents when they are no longer effective. Fine sediment buildup (fine sand, silt, and clay) will need to be removed after processing 5–10 gallons of asphaltic matrix. This sediment can be scooped from the bottom of wash drums when the biodiesel is cool using metal coffee cans with holes poked in the sides to allow liquid to drain. When biodiesel and *n*-propyl bromide become saturated with asphalt, wash drums need to be cleaned out and refilled with fresh solvent. Waste solvent and any solids should be placed in labeled 55-gallon (208-L) drums and disposed of as hazardous waste.

CONCLUSIONS

Hot biodiesel is an effective and efficient solvent for separation of microvertebrates in asphalt-impregnated sediments from Rancho La Brea. While biodiesel is not an effective solvent at room temperature, it becomes very effective when heated to temperatures between 70°C and 80°C, which is still well below its flash point of 130°C. Residual biodiesel can subsequently be removed from the treated fossil materials by rinsing in *n*-propyl bromide or ethanol. Our current excavation, Project 23, has yielded large quantities of microfossil-rich asphaltic sand. We have found heated biodiesel to be a safe, effective, and efficient solvent for processing these asphaltic sediments.

ACKNOWLEDGMENTS

Karin Rice thanks John Harris for his curiosity in investigating alternative solvents for removal of asphalt from fossiliferous matrix and for the invitation to publish on our technique. We thank Eric Lauzon and José Rios of GeoGreen Biofuels Inc. for discussions and their donations of biodiesel. A preliminary study was partially funded by a California Institute of Technology's Summer Undergraduate Research Fellowship to Katherine Lai.

LITERATURE CITED

Akersten, W.A., C.A. Shaw, and G.T. Jefferson. 1983. Rancho La Brea: Status and future. *Paleobiology* 9:211–217.

Binet, S., A. Pfohl-Leszkowicz, H. Brandt, M. Lafontaine, and M. Castegnaro. 2002. Bitumen fumes: Review of work on the potential risk to workers and the present knowledge on its origin. *The Science of the Total Environment* 300:37–49.

Department of Health and Human Services Centers for Disease Control and Prevention National Institute for Occupational Safety and Health (DHHS/NIOSH). August 2003. *Reducing roofers' exposure to asphalt fumes*. DHHS/NIOSH Publication 2003-107, Atlanta, (accessed February 12, 2014).

DHHS/NIOSH. July 2013. OSHA/NIOSH hazard alert: 1-Bromopropane. DHHS/NIOSH Publication 2013-150, Atlanta, https://www.osha.gov/dts/hazardalerts/1bromopropane_hazard_alert.html (accessed February 12. 2014).

Harris, J.M., A. Farrell, C. Howard, K. Scott, and C.A. Shaw. 2011. Contribution from project 23 to our understanding of the Rancho La Brea biota. *Journal of Vertebrate Paleontology* 31(Suppl. 3): 122A.

Pan, C.-H., C.-C. Chan, and K.-Y. Wu. 2008. Effects on Chinese restaurant workers of exposure to cooking oil fumes: A cautionary note on urinary 8-hydroxy-2-deoxyguanosine. *Cancer Epidemiology Biomarkers & Prevention* 17:3351–3357.

Shaw, C.A. 1982. Techniques used in excavation, preparation, and curation of fossils from Rancho La Brea. *Curator* 25(1):63–76.

Shaw, C.A., and J.P. Quinn. 1986. Rancho La Brea: A look at coastal southern California's past. *California Geology* 39:123–133.

Stock, C. 1992. *Rancho La Brea: A record of Pleistocene life in California*, revised J.M. Harris. Natural History Museum of Los Angeles County, Science Series no. 37, 113 pp.

Received 17 January 2014; accepted 20 March 2014.

Appendix

MATERIALS RESOURCE LIST

Drum heater: Wrap-It Heat drum heater model TRX-16L15 low heat range 1500W, http://www.thermalinc.com

Respirator and cartridges: North Model 7700 Silicone half-mask respirator with organic cartridges 75SCP 100L or 7581P100L, http://www.northernsafety.com

Gloves: Ansell Sol-Vex 11-mm chemical-resistant nitrile gloves, model 37-145, http://www.ansellpro.com

Spill trays and 8-gallon drums: Eagle spill containment basin model 1631; Skolnik 8-gallon carbon steel drum model HM0802, http://www.grainger.com