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Effectiveness of Hydrotreatment in Reducing the Toxicity of a Coal Liquefaction Product to Juvenile Channel Catfish

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H-Coal is a process for the direct liquefaction of coal under high temperatures and pressures to produce synthetic petroleum-substitute fuels. Because it can convert high-sulfur coal to low-sulfur fuel oil or transportation fuels, commercialization of the H-Coal process could supplement the existing supply of petroleum-based oil and gasoline. However, because coal-derived oils contain many organic compounds, such as phenols and anilines, that are readily soluble in water and also toxic to aquatic biota, coal oil spills are expected to be more damaging to the environment than petroleum oil spills (Giddings 1982). For example, numerous studies with a variety of aquatic organisms have demonstrated that H-Coal oils commonly have acute toxicities one to two orders of magnitude greater than those of analogous petroleum-based materials (Cada 1982, Cowser 1982).

One of the ways in which the environmental effects of coal liquids may be ameliorated is through an upgrading process known as hydrotreatment. Hydrotreatment consists of reacting the synthetic crude oil with hydrogen in the presence of a catalyst and has a number of process benefits including the desulfurization of liquid fuels, removal of substances (e.g., nitrogen compounds) that deactivate catalysts used in subsequent treatment, and, as commonly employed in petroleum refineries, general upgrading of crude oils to facilitate further refining (Glasstone 1982). By reducing the concentrations of nitrogen-, oxygen-, and sulfur-containing compounds (e.g., phenols and anilines), hydrotreatment has the additional potential for reducing the hazards of coal liquids to aquatic organisms.

The purpose of our study was to evaluate the effectiveness of hydrotreatment in reducing the acute toxicity of a representative coal liquefaction product. Acute bioassays with juvenile channel catfish (Ictalurus punctatus) were used to compare the toxicities of raw (nonupgraded) H-Coal oil, four samples of the same H-Coal oil subjected to different degrees of upgrading by hydrotreatment, and a petroleum crude oil. Channel catfish were chosen because they have considerable commercial and sport fisheries value and are likely to be abundant in large rivers where commercial coal liquefaction facilities will be located. The sensitivity of fish early life history stages to a variety of environmental stresses, coupled with their relatively low ability to avoid stresses, makes juvenile fish useful subjects for evaluating the direct effects of toxicants on higher trophic levels in aquatic ecosystems.

MATERIALS AND METHODS

The coal liquids tested in this study were produced from Illinois No. 6 coal at the H-Coal Pilot Plant at Catlettsburg, Kentucky, on September 25, 1981. Samples of both "light oil" and "heavy oil" products were sent to Chevron Research Company, Richmond, California, where they were blended in a 1:1.5 (w/w) light:heavy distillate ratio prior to hydrotreatment.

Five H-Coal oils were bioassayed. The raw H-Coal blend which constituted the feedstock for subsequent hydrotreatment was sampled. The raw oil was hydrotreated to three different levels: low severity (with a target of 50% nitrogen reduction or 2650 ppm), medium severity (with a final nitrogen content of 535 ppm), and high severity (with a final nitrogen content of 0.1 ppm, suitable as heating fuel). It was found during the medium-severity hydrotreatment process that high chlorine content of the raw H-Coal feedstock caused ammonium chloride plugging of the process lines. To avoid this, the subsequent low- and high-severity hydrotreatment runs used feedstock that had been washed two times with an equal weight of distilled water. A sample of the water-washed, nonhydrotreated oil was also obtained for testing. Liquefaction and hydrotreatment conditions under which these samples were prepared, as well as chemical and physical characteristics of the oils, are summarized in Griest et al. (1983). Because these oils were obtained from a pilot plant, they are not necessarily identical to future commercial products. However, they do represent some of the best materials available to examine the environmental effects of this developing synfuels technology.

A sixth oil, Wilmington crude, was also bioassayed. Wilmington crude is a petroleum, rather than a coal-derived, crude oil. Because more is known about the impacts of petroleum spills, comparisons of acute toxicities of reference petroleum crude oils with those of raw and upgraded coal liquids give some indication of the relative environmental hazards of transporting new synfuels products.

Catfish were exposed to WSFs* of the test oils, which were prepared by floating the oil on distilled water in a closed glass vessel at a 1:8 oil:water ratio (v/v). The mixture was stirred slowly, without vortex, for 48 h. The aqueous layer containing the WSF was filtered through Whatman's #41 filter paper to remove oil droplets and refrigerated for no more than

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*water soluble fractions

48 h before use. Preparation of WSFs, as well as the bioassays themselves, were conducted under gold fluorescent lights to minimize photochemical changes in the test materials.

Juvenile channel catfish were received from the Cohutta National Fish Hatchery, Cohutta, Georgia. They were maintained in fiberglass, continuous-flow-through stock tanks for at least 10 d before testing. Fish in the stock tanks were fed commercial trout chow once daily. Fish were not fed during the tests to minimize adsorption of the toxicant to food or fecal material. Mean total length of the catfish was 1.9 cm (range: 1.8 to 2.1 cm) and mean wet weight was 0.05 g.

Well water or chemically similar spring water was used for all testing. Temperature of the stock and test tanks were maintained at a constant 21°C. Alkalinity, total hardness, and calcium hardness of the WSF dilution water were 150, 160, and 105 mg/L, respectively. Conductivity was 300 µS/cm and mean pH was 6.9.

Five or six test concentrations and one control were used for each of the WSFs tested. Three replicates for each concentration and control were used. A replicate consisted of a glass aquarium containing 3.5 L of toxicant solution, or dilution water for controls, into which 20 catfish had been added. A static renewal technique was employed for the 96-h bioassay, i.e., at 48 h the toxicant solution (or dilution water in the case of controls) was replaced. Because the test tanks were stocked with catfish well below the recommended maximum loading capacity of 1 g/L (Organisation for Economic Co-operation and Development 1981), the tanks were not aerated in order to minimize loss of volatile components of the WSF solution. No oxygen stress was observed among the fish.

Mortalities were observed at least daily for 96 h. Dead fish were removed at each observation period.

All test mortalities were corrected for control mortalities using Abbott's formula (Daniels et al. 1982). The relationship between WSF concentration and mortality response was linearized using a logarithmic transformation of the concentration and a probability function transformation (Probit) of the proportion of animals responding, corrected for controls (Finney 1978). A weighted least-squares analysis (SAS Institute, Inc. 1979) using the transformed variables was used to derive a 96-h LC_{50} as well as a linear concentration-response relationship for each WSF.

Differences among the slopes of the concentration-response regression lines for the different WSFs were tested by analysis of variance with a covariable (log of the concentration). The F-statistic, based on full and reduced models, was used to detect significant differences in slopes. Details of the procedure are provided in Daniels et al. (Daniels et al. 1982).

RESULTS AND DISCUSSION

The 96-h LC_{50}s for the WSFs tested are presented in Table 1. Raw H-Coal oil WSF was the most toxic material studied, killing 50 percent of the catfish at an estimated concentration of 0.17 percent. On the other hand, an analogous material, petroleum crude oil, was relatively nontoxic; full-strength WSF of petroleum crude oil killed 26 percent of the channel catfish in 96 h. Water-washing and/or low- or medium-severity hydrotreatment significantly reduced the toxicity of H-Coal oil WSFs by a factor of approximately 4 (Table 1). In practical terms, however, these slightly or moderately upgraded coal liquids were still relatively toxic, producing an estimated LC_{50} at less than 1 percent concentration of the WSF. Only the high-severity hydrotreatment yielded a coal liquefaction product whose toxicity was comparable to that of petroleum crude oil. The full strength WSF of high severity hydrotreated H-Coal oil killed only 5 percent of the catfish in 96 h.

Figure 1 shows the concentration-response curves for four of the WSFs (petroleum crude oil and high severity hydrotreated oil could not be plotted because of their low toxicity). Three of the four WSFs had similar dose-response curves, i.e., the slopes were not significantly different. However, the slope of the regression line for water-washed H-Coal oil WSF was significantly greater ($\alpha = 0.05$) than those of the other WSFs. Consequently, although the LC_{50} of water-washed oil WSF was similar to other WSFs (Table 1), at high concentrations it was relatively more toxic and at low concentrations relatively less toxic than the WSFs of low- and medium-severity hydrotreated oils. The reason for this anomalous response is unknown; as with the other oils, the test aquaria and catfish had been randomly assigned and the bioassay for this WSF included a good range of replicated test concentrations, both above and below the estimated LC_{50} (Figure 1). It is possible that the water-washing procedure used to remove chlorine from the feedstock oil had some effect on the subsequent concentration-response relationship, although this would also have been expected in the regression for water-washed, low-severity hydrotreated oil WSF.

Becker and Crass (1982) reported that under static conditions, bacterial decomposition of phenols in synfuels WSFs can lower dissolved oxygen concentrations in the test tanks to unacceptable levels. Although dissolved oxygen concentrations were not monitored during our bioassays, we do not believe that low dissolved-oxygen stress was a problem in comparing the relative toxicities of these WSFs for the following reasons: (1) dissolved-oxygen concentrations did not decline seriously in the Becker and Crass study (1982) before 48 h; we replaced the test solutions with fresh, aerated toxicant solutions at 48 h, (2) on the average, 41 percent of the mortality we observed occurred in the first 24 h of the tests, well before low dissolved-oxygen concentrations would have been a problem, and (3) no signs of oxygen stress (e.g., gulping at the water

Table 1. Acute toxicities of WSFs of test oils to juvenile channel catfish. Values with asterisk are not significantly different at the $\alpha = 0.05$ level

Oil	LC_{50} [a]	95% Fiducial Limits
Raw H-Coal oil	0.17	0.07-0.89
Water-washed H-Coal oil	0.80*	0.59-1.16
Low-severity hydrotreated H-Coal oil	0.61*	0.03-1.45
Medium-severity hydrotreated H-Coal oil	0.68*	0.18-1.05
High-severity hydrotreated H-Coal oil	>100[b]	---
Petroleum crude oil	>100[c]	---

[a] 96-h LC_{50}, i.e., the estimated percent concentration of the WSF that kills 50% of the test organisms in 96 h.
[b] Mortality at 100% concentration of the WSF was 5%.
[c] Mortality at 100% concentration of the WSF was 26%.

surface) were observed throughout the tests. As Becker and Crass (1982) noted, in the natural environment bacterial decomposition of phenols can also lead to low dissolved-oxygen levels. Consequently, laboratory flow-through tests which maintain dissolved-oxygen levels at saturation may not be better at evaluating the impacts of synfuels spills in natural systems than static-renewal tests in which decomposition-related dissolved-oxygen declines are not an overriding constraint.

Data on the acute toxicity of raw H-Coal oil to juvenile channel catfish were similar to those reported for other aquatic organisms by previous investigators. For example, the 48-h LC_{50} of the WSF of the raw H-Coal oil blend used in this study to Daphnia magna was 0.13 percent (Griest et al. 1983). The 48-h LC_{50}s of light and heavy oils produced at the H-Coal pilot plant on other 1981 dates ranged from 0.75 to 3.73 (percent concentration of the WSF) for the midge, Chironomus tentans, and 1.0 to 1.5 for the fathead minnow, Pimephales promelas (Cowser 1982). Chronic bioassays using fish embryos and larvae were performed on samples from the H-Coal Process Development Unit (PDU), an earlier stage in the evolution of the H-Coal liquefaction process (Cada 1982). The percent concentration of the raw PDU H-Coal oil WSF which caused 50 percent accumulative embryo-larval mortality was 0.14, 0.41, and 0.06 for channel catfish, bluegill sunfish (Lepomis macrochirus), and rainbow trout (Salmo gairdneri), respectively (Birge and Black 1981). Thus, juvenile channel catfish acute bioassays of H-Coal oils yielded results similar not only to acute bioassays using other aquatic organisms, but also to longer-term, chronic bioassays using sensitive fish early life history stages.

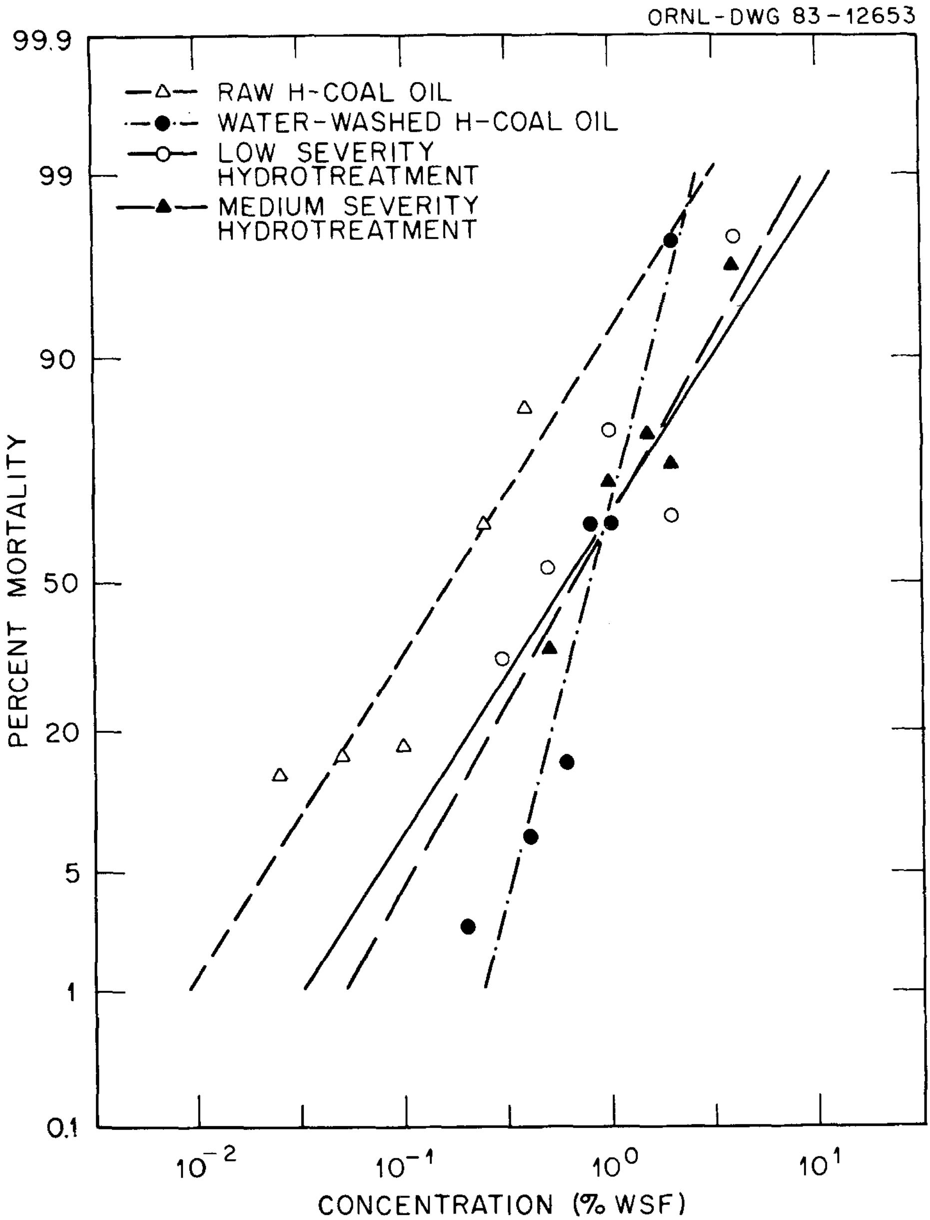

Figure 1. Mortality response of juvenile channel catfish to different concentrations of four H-Coal oil WSFs.

Griest et al. (1983) observed that increasing the severity of hydrotreatment caused coal liquids to become more volatile, less dense, and less viscous. The aromaticity and nitrogen, sulfur, and oxygen content of the oils all decreased as hydrogen was incorporated through hydrotreatment. These changes in the chemical and physical characteristics of hydrotreated oils were reflected in decreased toxicity of their WSFs to *Daphnia magna* and the green alga, *Selenastrum capricornutum* (Griest et al. 1983), as well as to the channel catfish in the present study.

Our results indicate that upgrading by means of hydrotreatment can be an effective mitigative measure for reducing at least the short-term environmental hazards of coal liquids. Although a relatively high severity of hydrotreatment was necessary, the acute toxicity of H-Coal oil was reduced to a level comparable to or below that of petroleum crude oil. Because the cost of hydrotreating coal liquids may be offset by the subsequent process engineering advantages it confers, as well as the reduced need for special storage, handling, and transportation facilities, hydrotreatment should prove to be a valuable tool in the environmentally sound development of coal liquefaction technologies.

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