

Full-Scale Hydrotreatment of Polychlorinated Biphenyls in the Presence of Used Lubricating Oils

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Approximately 850 000 L of used oil contaminated with polychlorinated biphenyls was processed through a full-scale re-refinery using a vacuum distillation/hydrotreatment technology. The catalytic reaction with hydrogen not only destroyed the PCBs but also generated useful petroleum products, including lubricating oil. Testing of the used oil feed as well as all intermediates, byproducts, and products allowed for the monitoring of the fate of the PCBs and demonstrated their destruction.

Introduction

Polychlorinated biphenyls (PCBs) were first developed in the 1920s and were manufactured and marketed worldwide under trade names such as Aroclor, Askarel, and Therminol. PCBs were extensively used as transformer oil, heat transfer fluid, hydraulic fluid, and even in paints due to being nonflammable and electrically nonconductive.

Production was halted in 1977 due to concerns over environmental persistence and alleged health effects, such as chloracne, swelling of eyelids, and gastrointestinal disturbances. The EPA now lists this class of compounds as carcinogenic (1), even though the evidence of extreme toxicity is not all that clear (2). This discrepancy is probably due to the degree of toxicity varying greatly among the various congeners and to most toxic species not being significant constituents in the predominant commercial mixtures (3).

In the United States, PCBs are a listed Toxic Substance Control Act (TSCA) waste and require special permits for storage, treatment, and disposal. In Canada, they are regulated under both Federal and provincial laws.

The commercial alternatives for waste streams found to have excessive PCBs (>50 ppm) are somewhat limited. Incineration or pyrolysis are the common techniques, with thermal requirements of 1200 °C and 2-5-s residence times usually specified (4). Recently, advances have been made in biological degradation techniques (5).

In Canada, the disposal options are extremely limited, and in some areas completely nonexistent. In these cases, the only option for handling PCBs is long-term storage. However, there is a readily available alternative destruction technology. The chemical structure of PCBs makes them very susceptible to dechlorination via catalytic hydrogenation because all the chlorine atoms are exocyclic (extending outside of the benzene rings).

An important advantage of the hydrogenation reaction chemistry is that the final products from PCB dechlorination are hydrocarbons (6). Since the hydrodechlorination is run in a hydrogen atmosphere, there is no opportunity for the formation of more hazardous products, such as polychlorinated dibenzofurans or dioxins. The chemistry involved in the catalytic destruction of PCBs has been well-documented (6-12). For the most part, these studies have been limited to bench- or pilot-scale experiments. The information provided in this paper describes the success of this technology in a full-scale trial. The data presented demonstrate PCB distribution and destruction over the course of the project.

Technology

Most of the used oil re-refining technology installed within recent years has included a catalytic hydrogenation finishing step. This involves the mixing of gaseous hydrogen at relatively high pressures with the liquid to be treated. The mixture is heated and passed down a vertical column of

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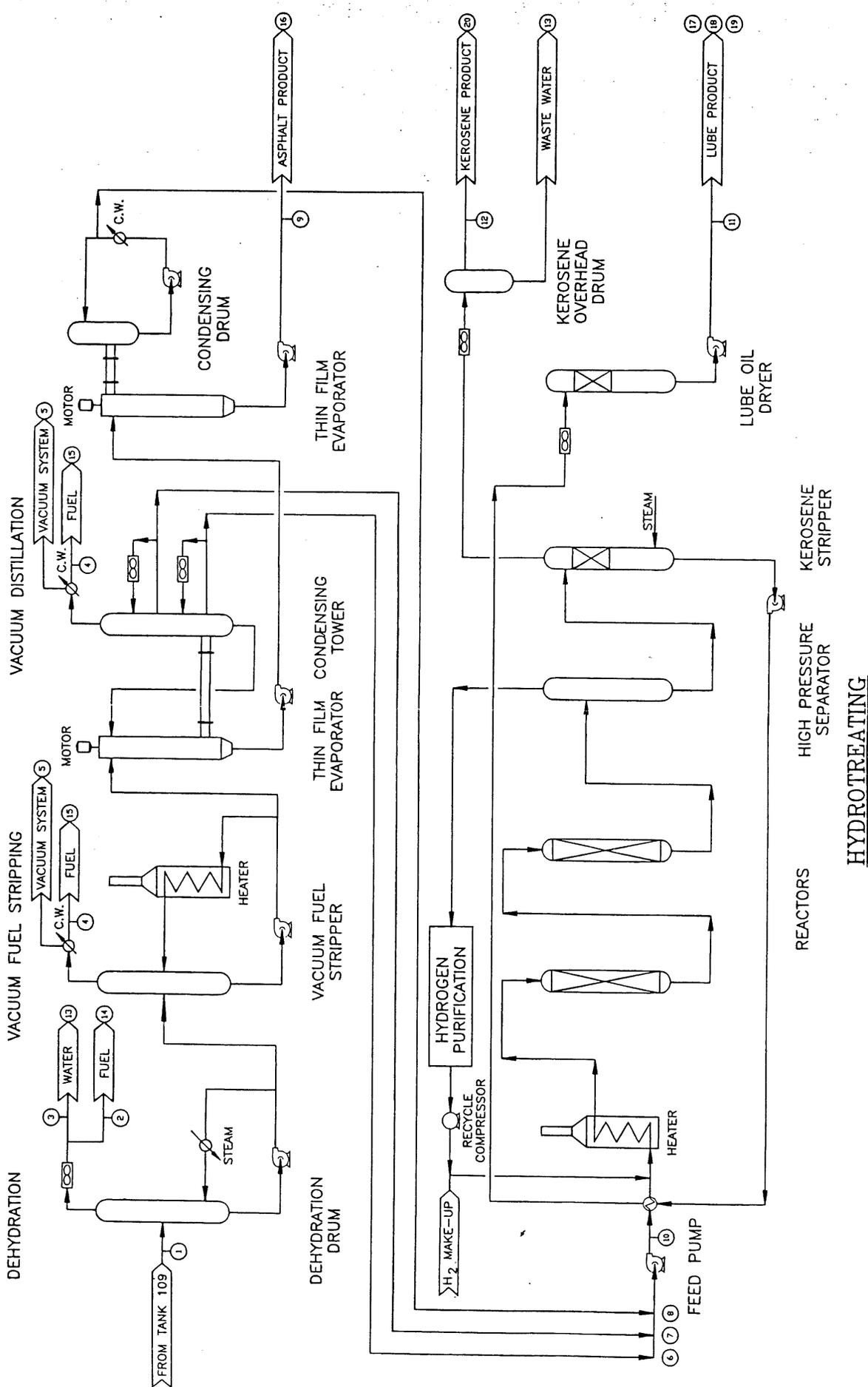


FIGURE 1. Process flow sheet with sampling points: 1, used oil feed; 2, dehydration overhead fuel; 3, dehydration overhead water; 4, vacuum fuel stripper fuel; 5, vent condenser fuel; 6, light distillate oil; 7, medium distillate oil; 8, heavy distillate oil; 9, asphalt rundown; 10, hydrotreater finished lube; 11, hydrotreater feed; 12, hydrotreated kerosene; 13, wastewater day tank; 14, dehydration fuel day tank; 15, vacuum fuel stripper fuel day tank; 16, asphalt storage tank; 17, hydrotreated light lube tank; 18, hydrotreated medium lube tank; 19, hydrotreated heavy lube tank; 20, kerosene tank.

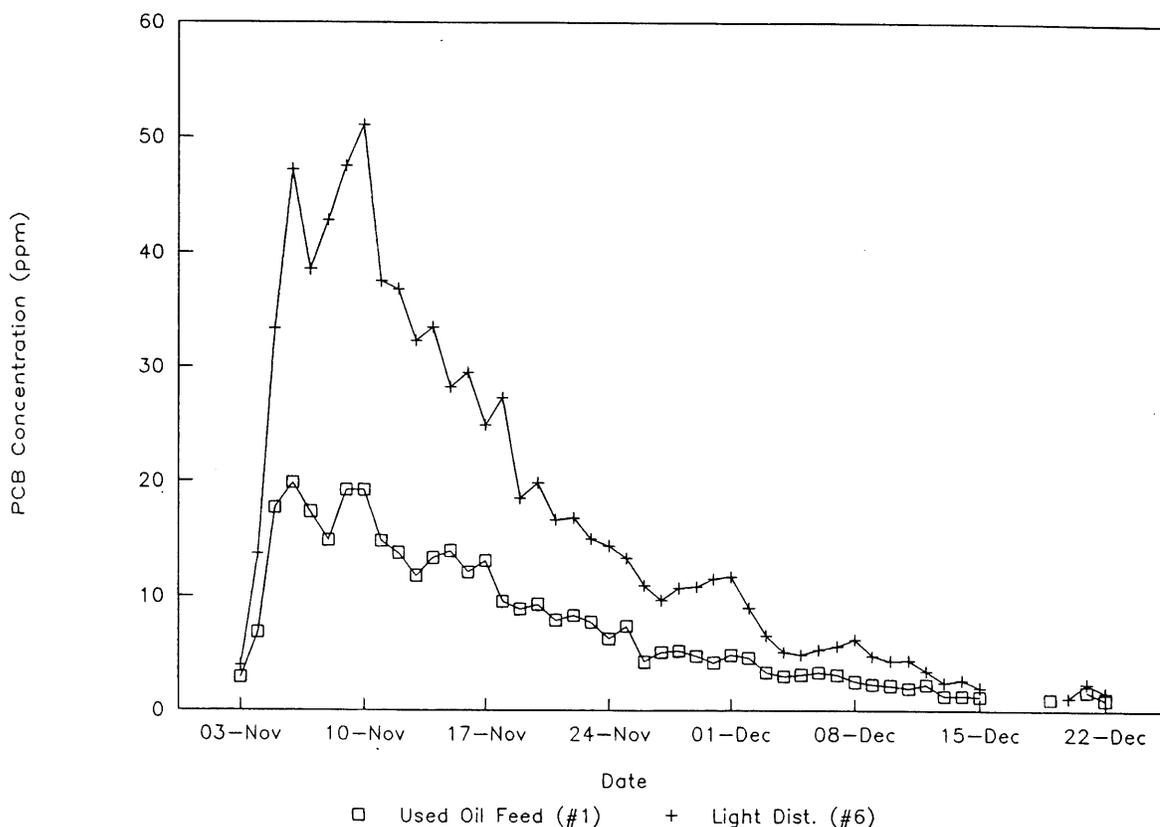


FIGURE 2. Feed and distillate concentrations.

solid catalyst, usually made of alumina beads impregnated with cobalt, nickel, and/or molybdenum. The high pressure and temperature and the catalyst dramatically speed up reactions that would occur very slowly under ambient conditions.

This technology is essentially identical to that used by the virgin lube oil manufacturers (13, 14). Indeed, some of the petroleum companies have been involved in re-refining process design. Phillips Petroleum Company made the most progress, actually commercializing their Phillips Re-refined Oil Process (PROP) in three locations. In one paper describing their process, they state "... the PROP process effectively destroys any PCBs in the feedstock ..." (15). The PROP process only involves two stages. Since the initial diammonium phosphate chemical treatment step only removes organometallics and sludge, it would not affect the PCBs. Thus, all of the destruction must occur in the hydrotreatment step of this two-stage process.

Other well-known process companies have addressed the same issue. UOP, Inc., which develops and markets process units to industry, reported decreases in PCB concentrations of >99.9% using a relatively similar operation (16).

In some cases, other halogenated species are also monitored. A Canadian study examined the removal of pesticides as well as PCBs. Under proper conditions, all were essentially removed (17). Even when the starting material contained over 70% PCBs, "all detectable PCBs had been removed" (18) as part of a patented process developed by Ciba-Geigy. Other patents make similar claims (19).

Experimental Design

Used Oil Feed. Approximately 850 m³ (225 000 gal) of used oil contaminated with PCBs was processed. This material

TABLE 1
Gas Chromatography Parameters

column	30 m x 0.32 mm i.d. x 0.25 μm film thickness 5% phenyl methyl silicone
oven temperature profile	
initial value	125 °C
initial time	3 min
level 1	
program rate	12 °C/min
final value	270 °C
final time	2 min
carrier gas	hydrogen
head pressure	depend on DCB RT (~15 psi)
column flow	3.1 mL/min (approximately at 270 °C)
makeup gas	nitrogen
makeup gas rate	approximately 65 mL/min
splitless mode	
purge off	0 min
purge on	1.0 min
pure rate	50 mL/min
sample injection	2.0 μL
injector inlet system	250 °C
detector	315 °C

was introduced systematically into a large feedtank (total capacity = 5455 m³; 1.5 million gal) such that the input concentration would be limited initially to about 40 ppm. Concentrations were subsequently adjusted so that process streams would be kept below 50 ppm.

Re-Refining Process. The process itself is described in detail elsewhere (20). A flow sheet is shown in Figure 1. The circled numbers represent sampling points for monitoring PCB levels. The sampling points are described in the caption of Figure 1. Sampling points 1-12 represent process samples, while points 13-20 are storage tank

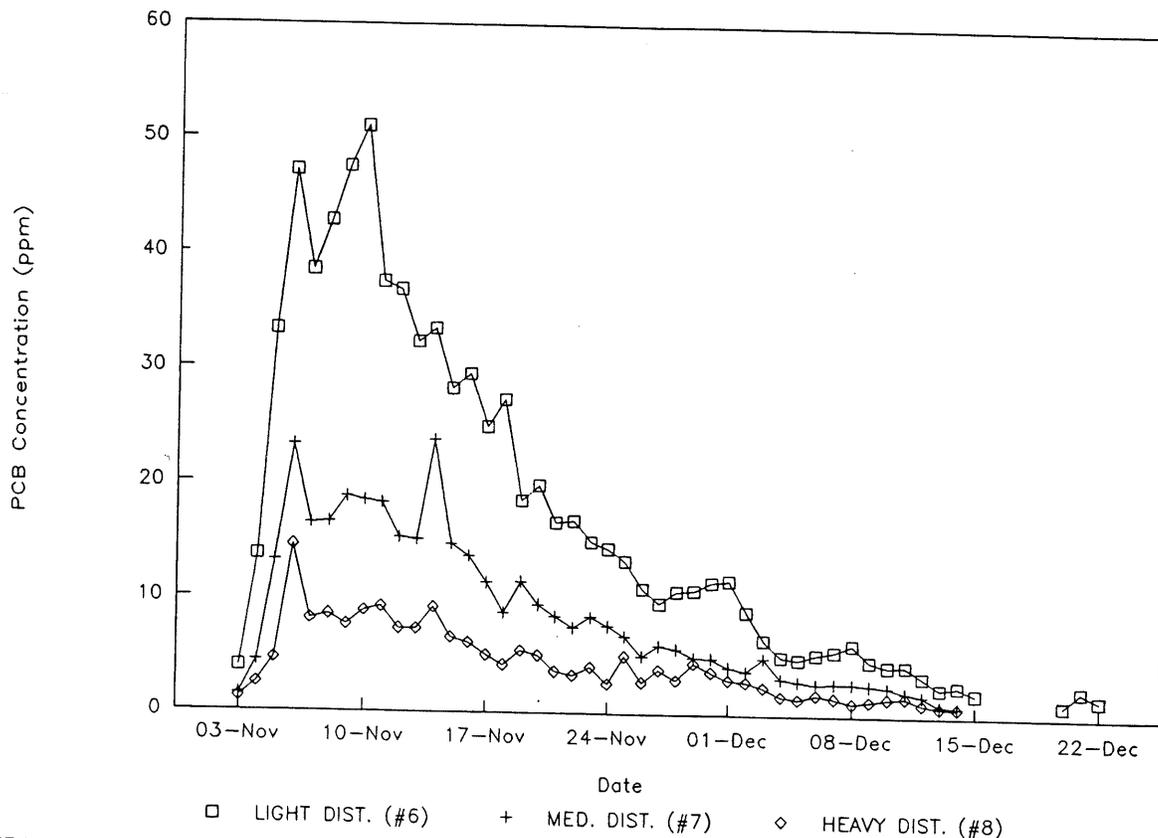


FIGURE 3. Vacuum distillates concentrations.

TABLE 2
Selected PCB Data: Daily Averages^a

sample point	total PCBs (ppm)											
	Nov 3	Nov 4	Nov 6	Nov 12	Nov 18	Nov 19	Nov 25	Dec 2	Dec 8	Dec 14	Dec 15	Dec 22
1, used oil feed	2.9	6.8	19.9	13.8	9.6	8.9	7.4	4.6	2.6	1.3	1.2	0.9
2, dehydration fuel*	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
3, dehydration water*	<1.2	<1.2	9.9	2.9	3.4	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2	<1.2
4, vacuum stripper fuel*	2.2	6.6	18.3	15.1	11.5	6.6	7.8	3.1	1.8	0.7	<1.2	<1.2
5, vent condenser fuel*	2.4	4.4	13.0	10.9	9.3	8.8	7.5	3.3	2.4	0.7	<1.2	0.3
6, light vacuum distillate	4.0	13.7	47.2	36.8	27.3	18.5	13.3	9.0	6.2	2.7	2.0	1.6
7, medium vacuum distillate	1.5	4.4	23.3	15.3	8.7	11.5	6.8	3.9	2.9	0.9	<1.2	<1.2
8, heavy vacuum distillate	1.3	2.5	14.6	7.3	4.2	5.4	5.1	2.9	1.2	0.8	<1.2	<1.2
9, asphalt	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
10, hydrotreated feed	0.2	1.0	1.6	35.5	24.7	23.4	6.9	8.1	2.2	4.3	1.6	1.2
11, hydrotreated product**	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
12, hydrotreated kerosene	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2

^a (*) indicates material recycled to feed to reduce PCB level. (**) final lubricating oil product.

samples. PCB destruction occurs in the latter section designated hydrotreating. This involves a fixed-bed of Ni-Mo catalyst operated at specific temperatures and pressures that favor removal of chlorine as well as nitrogen, oxygen, and sulfur.

Sampling Plan. Samples were taken every 6 h during the first week of operation and every 12 h after that. Samples were placed in clean glass jars with screw lids and hand-carried to the on-site laboratory for testing.

PCB Analysis. A GC/ECD analysis using a capillary column was used to monitor hydrocarbon samples. The protocol is equivalent to EPA Method 8080. Instrument parameters are presented in Table 1. Since most of the PCBs were present as Aroclor 1254, the quantitation was performed based on an Aroclor 1254 calibration. Method detection limits were determined for each matrix type. Some

water analyses were conducted by an independent laboratory using a GC/MS procedure.

Results and Discussion

The distribution of PCBs within the system was theoretically modeled prior to processing. This modeling was later confirmed using bench-scale distillation apparatus.

Based on this preliminary evaluation, it was anticipated that most of the PCBs would be carried along with the light lubricating oil portion of the process stream because they share similar boiling ranges (sample point 4). Figure 2 illustrates light vacuum distillate PCB concentrations versus process feed concentrations (sample point 1) over the 7-week run (Note: unit was down in mid-December for routine maintenance). Concentrations in the light vacuum stream were found to be typically greater than twice the

feed concentrations. This stream made up about 15% (vol) of the original feed.

Lower values for PCBs were found in the remaining two vacuum distillates (medium and heavy). This was expected due to the natural overlap of all three vacuum oil boiling ranges (sample points 6–8) from 300 to 550 °C. Figure 3 demonstrates this distribution.

Table 2 provides selected data points for all sampling points. These were compiled from mean concentrations collected from daily sampling. These data demonstrate the total destruction of the PCBs from relatively high levels in the distillates (47 ppm) to less than detectable amounts (<0.5 ppm).

There were PCBs detected once during the run in the final product. A concentration of 0.6 ppm was observed on November 19 when the temperature in the reactor dropped due to the loss of a heater. As soon as the temperature was returned to normal, the PCBs disappeared. This confirmed both the sensitivity of the monitoring scheme and the effectiveness of the process conditions used.

As mentioned earlier, a routine maintenance shutdown occurred in mid-December. This accounts for the breaks in the line charts.

Note that small amounts of PCBs were found in two of the three fuel streams generated by the process (sampling points 2 and 4). These streams were either processed through the hydrotreater or were recycled back to the feedtank if they contained any PCBs, using intermediate tanks to store each stream until it had been cleared for sale. This exhaustive destruction, including a limit of 5 ppb for wastewater, confined the PCBs within the process equipment until they had been chemically converted. Wastewater was then further processed using dissolved air flotation prior to biological treatment. At no point during the run were any PCBs found in the discharge water.

Conclusions

On the basis of exhaustive testing, the efficient destruction of PCBs by catalytic hydrodechlorination within a commercial process has been verified. Complete conversion is attainable at relatively mild conditions.

The long residence time in the reactor and the carefully controlled hydrogen atmosphere actually make the chemistry more predictable than that found in an incinerator, where the presence of oxygen might lead to dioxin, furan, and other byproducts in a gaseous state.

Being liquids, all streams from the vacuum distillation/hydrotreating process can be isolated, analyzed to demonstrate conversion, and re-introduced to the hydrotreater if any PCBs remain. Thus, catalytic dechlorination would seem to be a preferred pathway for PCB destruction.

The fact that this project was performed on a large scale gives added value to this technology. This is especially true in Canada where commercial alternatives for waste streams found to have excessive PCBs (>50 ppm) are limited. This demonstration has proven that this process is a safe and commercially viable option for the destruction of PCBs in used oil.

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