review of the toxicity of catalytically cracked clarified oil

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ABSTRACT

The toxicology of catalytically cracked clarified oil (CCCO) is reviewed and safe handling procedures are described.

There is evidence that CCCO may present a serious health hazard. It may cause liver damage, is a potent dermal carcinogen, is a mutagen and may be a reproductive toxin.

Exposure to CCCO should be minimized by issuing appropriate warnings and instituting safe working practices.

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1. INTRODUCTION

Catalytic cracking is used in petroleum refineries to break down higher boiling feedstocks into lower boiling components which are fractionated into various distillate streams. The bottoms fraction which is known as slurry oil, is passed through a slurry settler to remove catalyst. The resulting brownish-black liquid is known as catalytically cracked clarified oil (CCCO), or alternatively, clarified (or catalytic) slurry oil, decant oil or heavy clarified oil. According to the American Petroleum Institute (API), CCCO (CAS No. 64741-62-4) contains "hydrocarbons having carbon numbers predominantly greater than C_{20} and boiling above approximately 350°C (622°F)" (1). The primary uses of CCCO are as feedstocks to coker units and as a component in heavy fuels (i.e. Bunker C and No. 6 fuel oil). It may also be used in cut-back and emulsified bitumens; feedstocks for petroleum cokes, petroleum pitch and carbon black; dust suppressant road oils; enhanced oil field recovery oil; and rubber extender oils; process oils and ink oils. Some of these uses have declined or have been discontinued in recent years (2). It is estimated that CCCO production in Europe (OECD countries) is approximately 8.3 million tons per annum. The principal route of exposure to CCCO is dermal.

The petroleum industry has long recognized the hazardous nature of CCCO and has instituted stringent industrial hygiene practices in its plants. Therefore CCCO tends to be processed in closed systems. Workers wear protective clothing and are instructed on safe handling procedures. Customers are provided with hazard communications, i.e. Material Safety Data Sheets (MSDS) and/or notification letters, which warn of the dangers and provide advice on safe working practice with CCCO. The number of people potentially exposed and the extent of their exposure to CCCO are believed to be small (2).

2. CHEMICAL AND PHYSICAL CHARACTERISTICS OF CCCO

Table 1 summarizes the chemical and physical characteristics of CCCO provided to API by fifteen companies. Of particular note are the high concentrations of aromatic (75%) and low concentrations of saturated (10%) hydrocarbons. Although the chemical composition of CCCO has not been fully characterized, it is known that a significant fraction of the aromatic hydrocarbons are 4- to 6-condensed ring aromatic hydrocarbons (PAHs). It has been indicated that CCCO is likely to contain "5% wt or more" of these PAHs (1) and as much as 30% wt 4- to 5-ring PAHs (3). Concentrations of specific PAH-species have also been determined. For example, benzo(a)pyrene (BaP) was first reported as a component of CCCO in 1951 (4); subsequently, concentrations of BaP have been shown to range from less than 500 ppm (5) to 2500 ppm (2). CCCO may also contain significant amounts of benzocarbazoles and dibenzothiophenes, depending upon the nitrogen and sulphur contents of the catalytic cracker feedstock (2). One analysis indicated that CCCO contained 8-10% wt carbazole derivatives (3). The nitrogen content of 8 samples of CCCO varied between 1300-5400 ppm.

3. SUMMARY OF TOXICITY

3.1 ACUTE TOXICITY

API sponsored a series of acute toxicity tests on CCCO (6). The findings are summarized in Table 2. The acute (oral and dermal) toxicity of CCCO is low and it is virtually non-irritant to skin and eyes on single exposure. However, data from Mobil Research and Development Corporation indicates that CCCO is hepatotoxic; it was lethal to rabbits following a single oral exposure of 1.0 - 2.0 g/kg (private communication).

3.2 CUTANEOUS SENSITIZATION

When API tested for skin sensitization potential with a closed patch technique, CCCO gave negative results, while positive results were obtained by SOHIO using the Guinea Pig Maximization Test (7). SOHIO indicated that these results were not clear cut and required clarification by further testing.

3.3 SUBCHRONIC TOXICITY

Four subchronic dermal toxicity studies have been conducted on a single sample of CCCO. The protocols for these studies are summarized in Table 3. Animals were killed by the higher dosage levels and systemic effects as well as changes to the skin followed repeated applications of CCCO. Hepatotoxicity was indicated by increases in liver weight, elevated serum levels of hepatic enzymes, hepatocellular hypertrophy and degeneration, fibrosis, hepatitis, necrosis and cholangiolitis. In addition, thymic atrophy or hypoplasia, anaemia and erythroid hypoplasia were observed in one or more of these studies. CCCO also induced chronic dermal irritation, as shown by erythema, cracking, flaking, ulceration, hyperplasia and hyperkeratosis. Systemic toxicity was, however, not observed in long-term skin painting studies conducted on C3H mice using CCCO concentrations of approximately 10-170 mg/kg (Exxon, unpublished data). Mobil Research and Development Corporation also conducted dermal penetration studies (both in-vivo and in-vitro) with CCCO (3). The results suggested that carbazoles were more readily absorbed than the other classes of compounds present in CCCO (diaromatics, 3- to 5-ring PAHs, paraffins). The Mobil data were submitted to the US EPA as an 8(e) notification (8) under the Toxic Substances Control Act (TSCA).

3.4 REPRODUCTIVE TOXICITY

A TSCA 8(e) notification (9) was also made by Mobil on the reproductive toxicity of CCCO (10). CCCO was applied topically to female rats on days 0-19 of gestation at doses ranging from 0-150 mg/kg/day. Signs of toxicity were consistent with those found in subchronic dermal toxicity studies. CCCO did not appear to affect implantation but a dose-dependent increase in resorptions occurred. There were no surviving foetuses in the high dose group. At lower dosage levels, surviving foetuses were shorter and lighter than controls, and some soft tissue anomalies were observed. However, the data were insufficient to determine whether CCCO exerted these effects directly (indicating CCCO is a teratogen) or indirectly by injury to the mothers.

3.5 MUTAGENICITY

API has conducted a number of mutagenesis assays with CCCO. The results, which are summarized in Table 4, indicate that the sample of CCCO tested had mutagenic activity. Similar results have been reported by other investigators (11).

3.6 CARCINOGENICITY

The petroleum industry has long recognized that CCCO is a potent dermal carcinogen. Since 1951, numerous experimental epidermal carcinogenicity studies have been reported (12-18).

4. SAFE HANDLING ADVICE

Contact between CCCO and the skin should be avoided at all times and high standards of personal hygiene should be adopted. If work clothes are contaminated with CCCO, they should be removed immediately and laundered before they are worn again. If contamination occurs, the skin should be thoroughly washed with soap and water immediately.

The following protective clothing/equipment should be worn when handling CCCO:

a) Normal operation

- chemical mono-goggles or full face shield
- neoprene or nitrile rubber apron
- neoprene or nitrile rubber gauntlet type gloves
- safety boots without lace holes or fitted with integral tongue.

Note: If safety boots become contaminated such that they cannot be cleaned sufficiently to avoid further skin contamination they should be discarded.

Respiratory protection is not normally required. In the event that a mist, fume or aerosol of CCCO is produced, a full face piece respirator filled with a combination particulate and organic vapour cartridge or canister (Normal Protection Factor 20) should be worn. Care should be taken to ensure that fresh canisters are used when necessary.

b) Spillage clean-up

- chemical mono-goggles or full face shield
- neoprene or nitrile rubber one-piece chemical suit
- neoprene or nitrile rubber gauntlet type gloves
- neoprene or nitrile rubber Wellington type safety boots
- if there is a risk of exposure to mist, fume or aerosol of CCCO a full face piece respirator fitted with a combination particulate and organic vapour cartridge or canister (Normal Protection Factor 20), or self-contained breathing apparatus, should be used.

5. CONCLUSIONS

CCCO is a complex material composed of a variety of aromatic, saturated and sulphur and nitrogen-containing hydrocarbons. The composition varies with type of catalytic cracker feedstock and there is at present some uncertainty as to whether such variations in composition might significantly effect the toxic properties of CCCO. There is, however, evidence that CCCO may present a serious health hazard. It can cause liver damage and it is rich in PAHs. It is a potent dermal carcinogen and has mutagenic activity. With prolonged dermal exposure, CCCO will produce dermatitis. Some evidence suggests that CCCO may be a reproductive toxin. Because different samples of CCCO may vary considerably in chemical composition, the potential to induce the above forms of toxicity may also vary. Nevertheless, it is clear that CCCO is an extremely hazardous material and it is imperative that exposure be minimized by issuing appropriate warnings and by instituting appropriate industrial hygiene practices.

6. REFERENCES

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Table 1: Range of physical and chemical properties of CCCO

Property	Range
Specific gravity, 60/60 °F	1.0687-1.1515
Gravity, API	0.9-8.6
Viscosity, SUS/210	55.3-139.6
Flash point, °F	170-370
Pour point, °F	30-55
Average molecular weight	280-320
Viscosity-gravity constant	1.06-1.15
Ash, % wt	<0.001-0.13
Carbon residue	9.86-14.3
Sulphur, % wt	1.43-5.898
Gross Composition % wt	
Asphaltenes	2.4-10.0
Saturated hydrocarbons	5.5-7.1
Polar aromatic hydrocarbons	6.3-16.9
Aromatic hydrocarbons	74.1-76.8

From reference (2)

Table 2: Summary of API acute toxicity tests on CCCO

STUDY	SPECIES	RESULTS
Acute Oral LD_{50}	rat	female LD_{50}-4.2 g/kg male LD_{50}-5.3 g/kg
Acute Dermal Toxicity	rabbit	no deaths at 2.0 g/kg
Primary Dermal	rabbit	primary irritation index - 0.2
Ocular irritation	rabbit	24 hours Draize score (washed and unwashed) - 2.0
Skin sensitization (Closed patch test)	guinea pig	non-sensitizer

From reference (6)

Table 3: Summary of subchronic dermal toxicity studies on CCCO

SPECIES	No. OF ANIMALS/DOSAGE LEVELS (mg/kg)		APPLICATION FREQUENCY AND DURATION	REFERENCE
Rabbit	5/sex/group	200 1000 2000	3x/week, 4 weeks	(6)
Rat	Not available	400 1000 2000 4000	1x/day, 12 days	(6)
Rat	10/sex/group	40 200 400	5x/week, 12 weeks	(6)
Rat	10/sex/group	8 30 125 500 2000	5x/week, 2-13 weeks	(3)

Table 4: Summary of API Mutagenesis studies with CCCO

ASSAY	RESULTS
Modified Ames +S9	++
Mouse Lymphoma -S9	+
+S9	++
Cytogenetics (rat bone marrow)	-
Sister Chromatid Exchange -S9	++
(Chinese Hamster Ovary) +S9	++
Sister Chromatid Exchange (in vivo, mice)	++
Unscheduled DNA Synthesis, rat hepatocytes (in vivo dosage)	++
Unscheduled DNA, Synthesis, rat hepatocytes (in vitro)	++
CHO/HGPRT Forward Mutation	-
Cell Transformation -S9	-
(BALB/3T3 mouse embryo cells) +S9	+/-

a. ++ : positive;
+ : weakly positive;
+/-: suspect;
- : negative

From reference (2)