GAS CHROMATOGRAPHY MASS SPECTROMETERY STUDIES OF CREOSOTE OIL FRACTION

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ABSTRACT: Creosote oil fractions were obtained through fractional distillation. The fraction 184-188°C (38 %) was analyzed by GC-MS. Sixteen components were separated and twelve were identified. The identified components reflect 96.9 % of the total components. The twelve identified components were comprised as hydrocarbon 5.4 %, aromatic hydrocarbon 29.1 % and phenols 67.8 %. The major components were found m-cresol (37.7 %) followed by o-cresol (28.8 %),1-methyl-1-phenyl ethylene (8.1 %), mesitylene (6.4 %), 1,3,7 octatriene-5-yne (5.4 %), β-methyl naphthalene, naphthalene (1.9 %), p-cresol (1.3 %), α-methyl naphthalene (1.3 %), m-xylene (1.2 %) and biphenyl(0.5%) respectively.

Key words: *Creosote oil, Fractional distillation, Gas chromatography, Mass spectrometry.*

INTRODUCTION

Creosote oil is a complex mixture of hydrocarbon compounds obtained from high temperature distillation of coal tar (Roger and Clair, 1988). Nearly eighty percent of the mixture is polycyclic aromatic hydrocarbons PAHs are nonionic, similar structured organic compounds characterized by low water solubilities and high partition coefficients with organic matter (Swartz et al., 1995 and Vilholth, 1999). Its chemical composition varies depending on the source of the coal tar and the distillation conditions and fraction removed. The World Health Organization (WHO, 2004) concluded that there might be 1,000 compounds present in a typical coal tar creosote mixture, though most of them are present in minute quantities. Creosote compounds can be distributed among several chemical classes, including polycyclic aromatic hydrocarbons (PAHs), alkyl-PAHs, tar acids/phenolics, tar bases/N-heterocyclics (quinolines and carbazoles), S-heterocyclics (thiophenes), oxygenated-hetrocyclics/ furans (dibenzofuran), and aromatic amines such as aniline (WHO, 2004 and Eisler, 2000). Composition of the creosote depends on the source and it has typically 85 % PAHs, 10% phenolic compounds, and 5 % hetrocycles (Xiao et al., 2002). However out of the 10 creosote compositions the greatest total of phenolic compounds (sum of phenol, 2,4- dimethylphenol, and cresols) were 3.5% (WHO, 2004).

Creosote is the most commonly used wood preservative worldwide, and comprises nearly 15% of the total volume of wood treatment preservatives used in the United States (Crawford et al., 2000). It is used as a fungicide, insecticide, miticide, and sporicide to protect wood and is applied by pressure methods to wood products, primarily utility poles and railroad ties. This treated wood is intended for exterior or outdoor uses only. Its commercial uses include railroad ties 70%, utility poles 15-20%, and other miscellaneous commercial uses 10-15% (Dillon, 2006).

Several studies have included summaries of creosote compositions, (Ingram et al., 1982, Cooper, 1991, and WHO, 2004). WHO, 2004 includes creosote compositional analyses from eight separate studies, including creosote s from the United States, Britain, Germany, and the former Soviet Union.

Rao and Kuppusamy (1992) conducted field leaching test s of tropical wood species treated with a creosote formulation and method that differ from those currently recommended for use in the United States. Whiticar et al., (1994) subjected untreated and creosote-treated poles and timbers to natural and simulated rainfall. The treated wood was treated to retentions of 166 kg/m3 or 198 kg/m3. PAHs are the most comprehensively studied group of chemicals found in creosote, due largely to the potency of some as carcinogens, and to their widespread, and apparently increasing, Occurrence in the environment (Vanmetre et al., 2000). The aim of this study was to determine the chemical constituents of creosote oil found in the Pakistan.

MATERIALS AND METHODS

Creosote oil was purchased from the local market and its fractions were obtained through fractional distillation. Fractions ranges from 180-184 °C, 185-188°C, 189-199°C, 200-202°C, 203-210°C, 211-240°C, and 241-270°C respectively. Gas

Chromatography of all these fractions was performed and it was observed that fraction 184-188°C gave maximum number peaks so it was selected for further studies.

GC and GC-MS Analysis: Gas chromatographic analysis for the creosote oil was conducted on a Shimadzu GC-14.The gas chromatograph was equipped with flame ionization detector having 25mx 0.22mmWCOT SE-30 fused column. Carrier gas used was helium with a flow velocity of 3ml/min and split ratio 1:100 and the sample size was 2µl. The column temperature was maintained at 70°C for four minutes with 4°C rise per minutes to 220°C respectively. Percentage composition of individual components was calculated on the basis of peak area using Shimadzu C-R4A chromatopac electronic integrator. Various compounds were identified by their retention time and peak enhancement with standard samples.

Jeol model JMS-AX505H mass spectrometer combined with Hewlett Packard 5890 gas chromatograph was used for analysis of essential oil. The essential Oil sample was injected on a 25 m x 0.22 mm WCOT BP5 (5 % phenyl methyl siloxane) fused silica column, using Helium as a career gas with split ratio 1:100, EI (electron impact) mode ionization current 100A, programmed column temperature at 70 °C for 4 minutes with 4 °C per minutes rise to 220 °C. Data acquisition and processing were performed by Jeol JMA-DA 5000 system. The comparison of the fragmentation pattern of the individual component of the oil using Nist library search helped in the identification and confirmation of the components.

RESULTS AND DISCUSSION

The creosote oil was distilled and fractions from 180-184 °C, 185-188°C, 189-199°C, 200-202 °C, 203-210 °C, 211 240 °C, and 241-270°C were analyzed by gas chromatograph following the method of Wright et al., 2005 and Rishbeth, 2008. Gas chromatographic results revealed that maximum components were found in fraction 184-188 °C. This fraction was 38 % of the creosote oil sample.

The gas chromatography coupled with mass spectroscopic analysis revealed the presence of sixteen components of the oil, out of which twelve components could be identified as hydrocarbons,

Table 1: Analysis of creosote oil by GC-MS

Peak No.	Compound	% Age	m / z ratio with relative percentages
2.	m-Xylene	1.2	106(79.21), 91(100), 77(12.57), 65(6.63), 51(9.11)
3.	1,3,7 Octatrien-5-yne	5.4	104(90), 91(37.62), 77(100), 63(33.66), 51(85)
5.	Mesitylene	6.4	119(100), 105(90), 94(88.12), 77(76.73), 65(41.09), 51(38.61)
7.	1-Methyl-1-phenyl ethylene	8.1	117(100), 105(89), 91(60.40), 77(37.62), 65(22.57), 51(28.71)
9.	1,2-Hydrindene	1.3	117(100), 103(4.36), 91(14.85), 77(3.46), 63(7.92), 51(6.93)
10.	o-Cresol	28.8	116(90), 107(100), 90(85), 63(88.12), 51(61.39)
11.	p-Cresol	1.3	108(100), 90(9.80), 77(21.98), 63(5.44), 51(12.08)
12.	m-Cresol	37.7	124(18.81), 107(100), 89(65.35), 79(90), 63(51.48), 51(85)
13.	Naphthalene	1.9	128(100), 102(54.26), 87(11.39), 77(32.08), 64(59.80), 51(83.17)
14.	β-Methyl naphthalene	3.2	142(100), 126(1.98), 115(34.65), 89(6.93), 71(8.42), 51(5.94)
15.	α-Methyl naphthalene	1.3	142(100), 115(24.75), 89(4.95), 70(2.97), 51(3.96)
16.	Bi-phenyl	0.5	154(100), 115(6.04), 91(3.96), 77(12.38), 64(12.38), 51(10.89)

aromatic hydrocarbons and phenols Table-1. m-Cresole was found as major component (37.7 %) followed by o-cresol (28.8 %),1-methyl-1-phenyl ethylene (8.1 %), mesitylene (6.2 %), 1,3,7 octatriene-5-yne (5.4 %), β-methyl naphthalene (3.2 %), Naphthalene (1.9%), p-cresol (1.3%), α-methyl naphthalene (1.3%), m-xylene (1.2%) and biphenyl (0.5%).Twelve components identified represent the 96.9% of the sample while remaining peaks represent 3.1% of the sample. These components have also been reported in the creosote oil by various authors.

The phenolic contents in the creosote oil (m-cresol 37.7 %, o-cresol 28.8 %) were quite high and p-cresol 1.3 % was low as compared to the USA creosote oil, which contain m-cresol 8.3%, p- cresol 7.9 % and 0-cresol 4.6 % (Kwang et al., 2005). Naphthalene (1.9 %) contents were high in our sample as compared to the Sung et al., 2005 they reported 0.53 % along with other twelve poly aromatic hydrocarbons in the Korean creosote oil. Poly aromatic hydrocarbon percentage 85 and 80 were reported in Sweden (Xiao et al., 2002 and WHO, 2004). These PAHs percentages are quite high as compared to our findings while low percentage of poly-aromatic hydrocarbon has been reported in the USA (Ozretich et al., 2000). Xiao et al., 2002 and WHO, 2004 reported low phenol contents 10 % and 3.5 % respectively in Sweden creosote as compared to the phenols in our finding which 67.8% was. Eight poly aromatic hydrocarbons were present in our creosote oil. Bestari et al., 1998 and Sung et al., 2005, studied fifteen and sixteen components of poly aromatic hydrocarbon in Canadian and Korean creosote oil. PAHs were also reported in high concentration (Ingram et al., 1982 and 1984 and Dillon, 2006) in the USA creosote oil.

It has been concluded that this fraction of creosote contains maximum components. After resolving through GC MS, it has found that it contain o-cresol and m-cresol in maximum concentration. So creosote oil fraction 184-188 °C can be used as a source of cresols. As cresols possess more powerful disinfectant action than phenol therefore this fraction can be used in place of phenol.

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