

GC/MS study of the oil recovered by the oxidative thermal degradation of the mixture of HDPE, LDPE and different natural fibers of Indian origin

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Abstract

According to the GC/MS analysis of the oil samples, recovered by the oxidative thermal degradation of the mixture of HDPE, LDPE and natural fibers of Indian origin, it was reported that on varying the natural fibers into the reaction mixture the resultant oxidative products were also varies. It was found that when the mixture of HDPE and LDPE degraded in the oxidative environment the recovered oxidative products were 1 ring chain saturated hydrocarbons, 1 saturated long chain hydrocarbon, 5 unsaturated long chain hydrocarbons and 1 methyl ester. When the mixture of Jute, HDPE and LDPE thermally degraded the recovered oxidative products were 1 phytol, 2 saturated fatty acids, 2 unsaturated fatty acids and 2 silica containing derivatives, similarly when Flax fiber was used instead of Jute fiber the recovered oxidative products were 8 unsaturated long chain hydrocarbons and 3 methyl esters.

Keywords -GC/MS, oxidative thermal degradation, hdpe, ldpe, natural fibers, oxidative products

List of Abbreviations

GC/MS:	Gas Chromatography Mass Spectrometry
HDPE:	High Density Polyethylene
LDPE:	Low Density Polyethylene
Oil _{WPB} :	Oil recovered by Waste Plastic Blend
Oil _{JFWPB} :	Oil recovered by Jute Fiber Waste Plastic Blend
Oil _{FFWPB} :	Oil recovered by Flax Fiber Waste Plastic Blend
min.:	Minute
μL:	Micro Liter
°C:	Degree Centigrade
NIST:	National Institute of Standards and Technology
GC/MS _{WPB} :	Gas Chromatography Mass Spectrometry of Oil _{WPB}
GC/MS _{JFWPB} :	Gas Chromatography Mass Spectrometry of Oil _{JFWPB}
GC/MS _{FFWPB} :	Gas Chromatography Mass Spectrometry of Oil _{FFWPB}
m/z:	Mass to charge ratio

I. INTRODUCTION

Discarded polyethylene waste (including HDPE & LDPE) could be used as raw material for the recovery of oil like substance having the good calorific value. Pyrolysis of plastic into petroleum grade fuel is a promising method which involves the thermal break down of polymeric material at elevated temperature and in the absence of oxygen. Catalytic pyrolysis of a variety of plastic into fuel by using commercial catalysts such as mesoporous silica [1], amorphous silica-alumina [2,3], HY zeolite [4,5], zeolite based HZSM-5 [6,7], zeolite beta [8], zeolite [9] has been reported. The co-pyrolysis of different plastic materials by mixing biomass, like karanja&niger seeds [10], red oak [11], rice husk [12], almond shell [13], oil shell [14], pine cone [15], wood biomass [16], forestry biomass wastes [17], lignocellulosic materials [18] has been also reported. The object of this research work is to comparative GC/MS study of the oil samples recovered by the thermal degradation of the mixture of shredded HDPE and LDPE in the oxidative environment conditions, by varying the natural fibers into the reaction mixture.

II. EXPERIMENTAL

A. Materials

The oil samples for the GC/MS study were recovered by the oxidative thermal degradation of the mixture of waste HDPE, LDPE and natural fibers of Indian origin such as Jute and flax [19].

B. Methods

1) Nomenclature of the Recovered Oil

The oil recovered by the oxidative thermal degradation of the mixture of shredded HDPE and LDPE defined as Oil_{WPB}, by the mixture of HDPE, LDPE and Jute fiber defined as Oil_{JFWPB} and by the mixture of HDPE, LDPE and Flax fiber defined as Oil_{FFWPB}.

2) **GC/MS analysis**

GC/MS study of recovered oil samples were done by using JEOL GCMATE II GC-MS. The instrument set up program was; run time: 44.50 min, sampling rate: 1.5625 pts/s. pre-injection solvent washes:2, post-injection solvent washes(A):6, injection volume:0.5 μ L. detector parameters; initial set point: 280°C, Oven program cryogenics: Off, initial temp: 40°C, initial hold: 1 min, ramp 1:10.0 0/min to 325°C, hold for 15 min, maximum temp: 330°C, equilibrium time: 0.5 min. Compound identification used NIST library and fuel compound probability match with NIST library.

3) **Nomenclature of the GC/MS Chromatogram of Recovered Oil Samples**

GC/MS chromatogram of Oil_{WPB} defined as GC/MS_{WPB}, Oil_{JFWPB} defined as GC/MS_{JFWPB} and Oil_{FFWPB} defined as GC/MS_{FFWPB} respectively.

III. RESULTS AND DISCUSSION

As per the GC/MS analysis of the different samples of recovered oil it was clear observed that in the same oxidative condition inside the reactor the synthesis of oxidative products varies by changing the natural fiber into the reaction mixture. As the polyethylene consisted of the long chain of ethylene monomers so according to the GC/MS_{WPB}(Fig. 1), 1 ring chain saturated hydrocarbons identified as Cyclohexane,1,1-dimethyl-2-propyl- (Fig.1-B) and 1 saturated long chain hydrocarbon identified as Heptadecane, 2,6,10,15-tetramethyl- (Fig. 1-G), 5

unsaturated long chain hydrocarbons identified as 2,4-Dimethyl-1-heptene (Fig. 1-A), 1-Octadecene (Fig. 1-C), Z-8-Hexadecene (Fig. 1-D), 1-Heptadecene (Fig. 1-E), 1-Octadecene (Fig. 1-F), and 1 methyl ester identified as 2,4-Hexadien-1-one,1,3,5-triphenyl (Fig. 1-H). As per GC/MS_{JFWPB}(Fig 2) analysis, 1 phytol identified as 3,7,11,15- Tetramethyl -2-hexadecen-1-ol (Fig. 2-A), 2 saturated fatty acids identified as Methyl tetradecanoate and Pentadecanoic acid,14-methyl-methyl ester (Fig. 2-B & 2-D) and 2 unsaturated fatty acids identified as 7-Hexadecenoic acid, methyl ester, (Z) and 9-Octadecenoic acid (Z)-, methyl ester (Fig. 2-C & 2-E). Along with this 2 silica containing derivatives (Fig. 2-F & 2-G) were also identified which supposed to be recovered due to the degradation of secondary cell wall of jute fiber as the silica is the chief constituent of cell wall.As per GC/MS_{FFWPB}(Fig. 3) analysis 8 unsaturated long chain hydrocarbons identified as 5-Tetradecene, [Z]- (Fig. 3-A), 8-Heptadecene, 8-methyl-, [E]- (Fig. 3-B), 2-Methyl-E-7-hexadecene (Fig. 3-C), 1,21-Docosadiene (Fig. 3-E), 9-Nonadecene (Fig. 3-F), 1-Eicosene (Fig. 3-G), 5-Methyl-Z-5-docosene (Fig. 3-I), Z-12-Pentacosene (Fig. 3-J) and 3 methyl esters identified as 2,5-Octadecadienoic acid, methyl ester (Fig. 3-D), 9, 12-Octadecadienoic acid [Z,Z]-, methyl ester (Fig. 3-H) and 1-Phenanthrenecarboxylic acid, tetradecahydro-7-[2-methoxy-2-oxoethylidene]-1, 4a,8-trimethyl-9-oxo-,methyl ester (Fig. 3-K).The synthesis of alcohol and methyl esters, inside the reactor takes place by the hydration of unsaturated hydrocarbon fragments and by the oxidation of unsaturated hydrocarbons respectively [19].

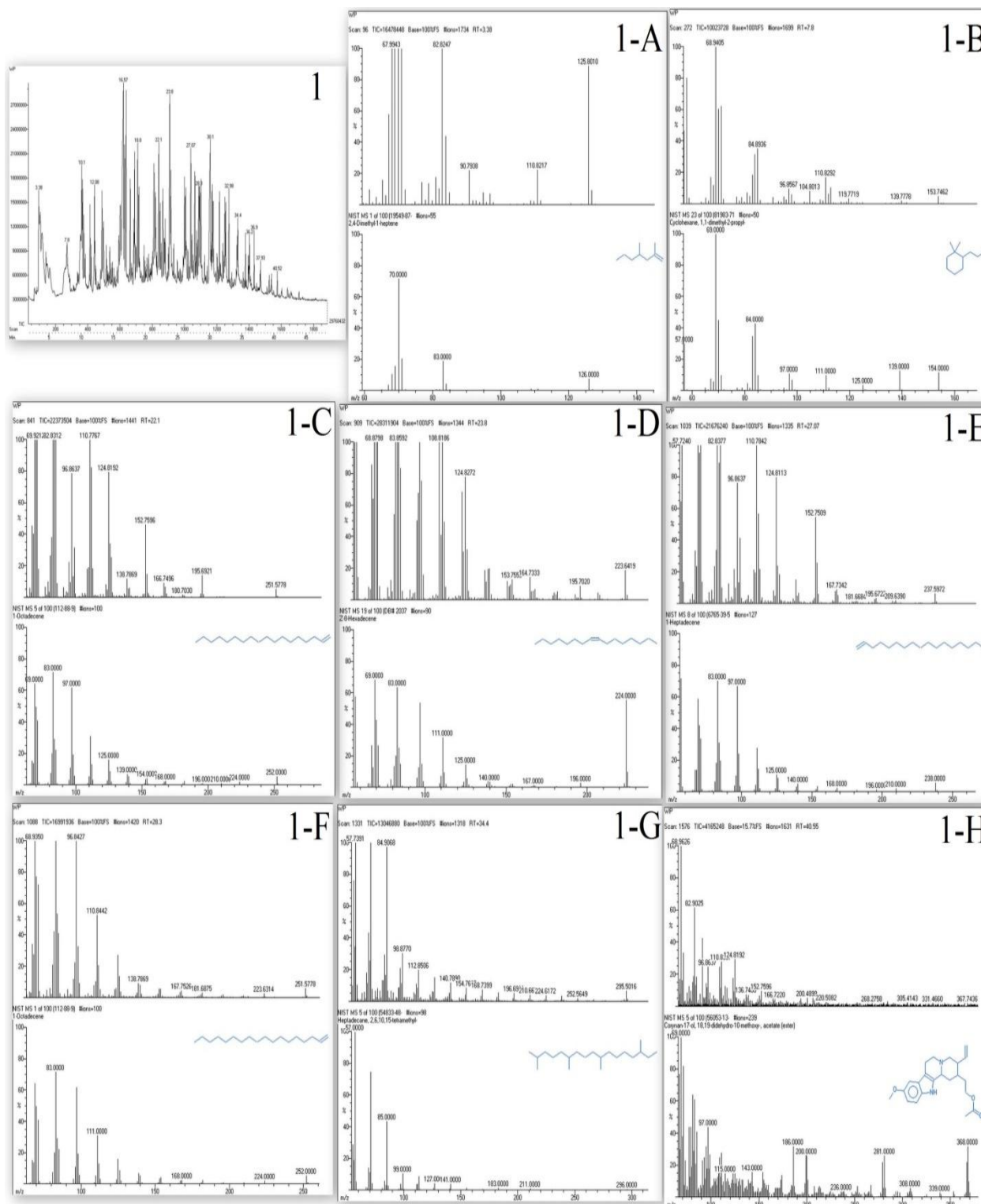


Figure 1: Total ion Chromatogram of Oil_{WPB}, Ring Chain Saturated Hydrocarbons (1-B), Saturated Long Chain Hydrocarbon (1-G), Unsaturated long Chain Hydrocarbons (1-A, 1-C, 1-D, 1-E, 1-F) and Methyl Ester (1-H).

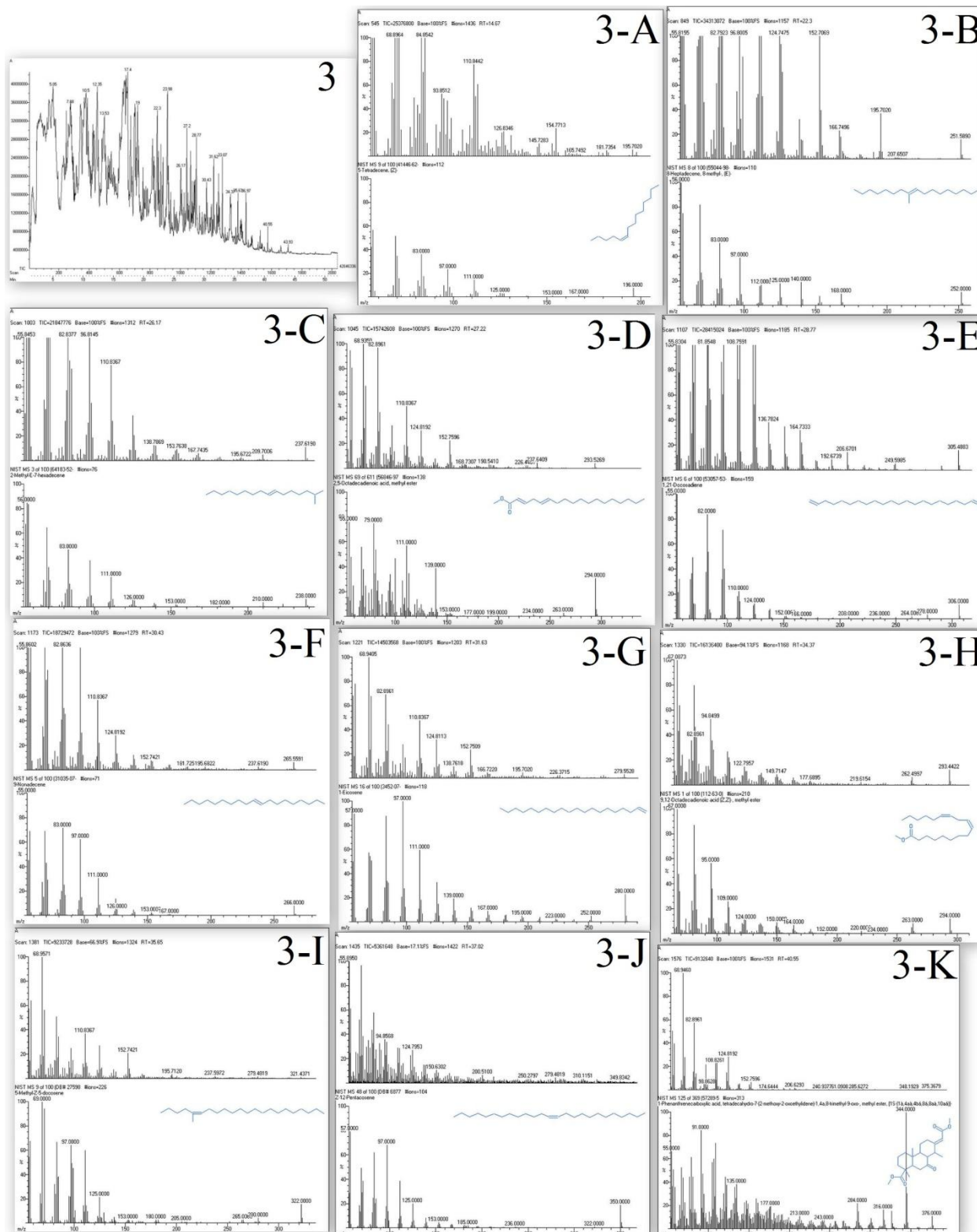


Figure 3: Total ion Chromatogram of Oil_FFWPB, Unsaturated Long Chain Hydrocarbons (Fig. 3-A, 3-B, 3-C, 3-E, 3-F, 3-G, 3-I, 3-J), Methyl Esters (Fig. 3-D, 3-H, 3-K).

Table 1: The GC/MS Analysis of Oil_{WPP}

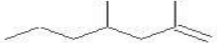
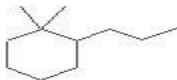




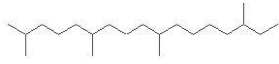
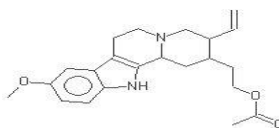

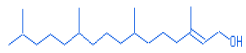

Retention time	Compound name	Fragmentation (m/z)	Molecular formula	Molecular structure
3.38	2,4-Dimethyl-1-heptene	125,110,90,82,67	C ₉ H ₁₈	
7.8	Cyclohexane, 1,1-dimethyl-2-propyl	153,139,119,110,104,96,84,68	C ₁₁ H ₂₂	
22.1	1-Octadecene	251,195,180,166,152,138,124,110,96,69	C ₁₈ H ₃₆	
23.8	Z-8-Hexadecene	223,195,164,153,124,108,83,68	C ₁₆ H ₃₂	
27.07	1-Heptadecene	237,209,195,181,167,152,124,110,96,82,57	C ₁₇ H ₃₄	
28.3	1-Octadecene	251,223,181,167,138,110,96,68	C ₁₈ H ₃₆	
34.4	Heptadecane, 2,6,10,15-tetramethyl-	295,252,224,210,196,168,154,140,112,98,84,57	C ₂₁ H ₄₄	
40.55	Corynan-17-ol, 18,19-didehydro-10-methoxy-, acetate	367,331,305,268,220,200,166,152,136,124,110,96,82	C ₂₃ H ₃₂ O ₃ N ₂	

Table 2: The GC/MS Analysis of Oil_{JFWPB}

Retention time	Compound name	Fragmentation (m/z)	Molecular formula	Molecular structure
15.25 tetradecanoate	Methyl 199,143,101,	242(parent peak), 74 (base peak)	C ₁₅ H ₃₀ O ₂	
16.78	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	296 (parent peak),278, 249,193,179,138, 123 (base peak), 96,8,56	C ₂₀ H ₄₀ O	
17.17	7-Hexadecenoic acid, methyl ester, (Z)	278 (parent peak), 236, 194,152,123,110,95, 82 (base peak), 74	C ₁₇ H ₃₂ O ₂	

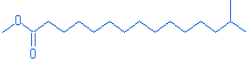

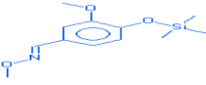
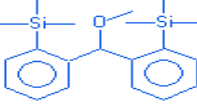

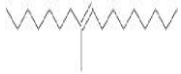
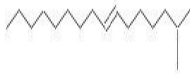




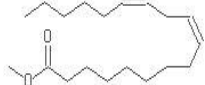
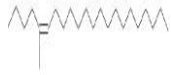

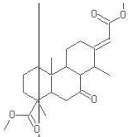
17.43 methyl ester	Pentadecanoic acid, 14-methyl-, 86 (base peak)	270 (parent peak), 227, 213,185,171,143,101,	$C_{17}H_{34}O_2$	
19.2	9-Octadecenoic acid (Z)-, methyl ester	296 (parent peak), 264, 235,222,194,180,152, 137, 110, 96, 83, 69 (base peak)	$C_{19}H_{36}O_2$	
5.9	Benzaldehyde, 3-methoxy-4- [(trimethylsilyl)-, O-methyloxime	281 (parent peak), 253 (base peak), 223,207, 191, 176,149,119,104,73	$C_{12}H_{25}O_3NSi$	
8.65 methyl ether	2,2'- Bis-trimethylsilyl benzhydryl 73	355 (parent peak),327,281, 223,207,133,89 (base peak),	$C_{20}H_{42}OSi_2$	

Table 3: The GC/MS Analysis of Oil_{FFWPB}

Retention time	Compound name	Fragmentation (m/z)	Molecular formula	Molecular structure
14.67	5-Tetradecene, [Z]-	195,181,165,154,145, 126,110,93,84,68	$C_{14}H_{28}$	
22.3	8-Heptadecene, 8-methyl-, [E]-	251,207,195,166,152, 124,96,82,55	$C_{18}H_{36}$	
26.17	2-Methyl-E-7- hexadecane	237,209,195, 167,153, 138,110,96,82,55	$C_{17}H_{34}$	
27.22	2,5-Octadecadienoic acid, methyl ester	293,237,226,190,168, 152,124,110,82,68	$C_{19}H_{34}O_2$	
28.77	1,21-Docosadiene	305,249,206,192,164, 136,108,81,55	$C_{22}H_{42}$	
30.43	9-Nonadecene	265,237,195,181,152,	$C_{19}H_{38}$	

31.63	1-Eicosene	124,110,82,55 279,226,195,166,152, 138,124,110,82,68	$C_{20}H_{40}$	
34.37	9, 12-Octadecadienoic acid [Z,Z]-, methyl ester	293,262,219,177,149, 122,94,82,67	$C_{19}H_{34}O_2$	
35.65	5-Methyl-Z-5-Docosene	321,279,237,195,152, 110,68	$C_{23}H_{46}$	
37.02	Z-12-Pentacosene	349,310,279,250,200, 150,124,94,55	$C_{25}H_{50}$	
40.55	1-Phenanthrene carboxylic acid, tetradecahydro-7-[2-methoxy-2-oxoethylidene]-1, 4a,8-trimethyl-9-oxo-,methyl ester	375,348,285,240,206, 174,152,124,108,98,82, 68		

IV. CONCLUSION

- When the mixture of HDPE and LDPE was degraded the major oxidative products in the recovered oil were a ring chain saturated hydrocarbons, a saturated long chain hydrocarbon, 5 unsaturated long chain hydrocarbons and 1 methyl ester.
- When the mixture of HDPE, LDPE and Jute fiber was degraded the major oxidative products in the recovered oil were a phytol, 2 saturated fatty acids, 2 unsaturated fatty acids and 2 silica derivatives.
- When the mixture of HDPE, LDPE and Flax fiber was degraded the major oxidative products in the recovered oil were 8 unsaturated long chain hydrocarbons and 3 methyl esters.

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