

OXIDATIVE THERMAL DEGRADATION OF THE MIXTURE OF HDPE, LDPE AND JUTE FIBER INTO FUEL- A TECHNOLOGY FOR GREEN ENVIRONMENT

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Abstract

Thermal degradation of the HDPE and LDPE by mixing Jute fiber in the oxidative environment causes the effective degradation of the polyethylene waste at early temperature and the reported improvement in the yield of fuel like liquid was 56%. The comparative FTIR study of recovered fuel samples clearly evident that, on thermal degradation of the shredded HDPE and LDPE by mixing Jute fiber, the unsaturated, hydrocarbon fragments transformed into the respective oxidative products and according to the GC/MS analysis, these oxidative products were identified as phytol, free fatty acids and silica derivatives.

Keywords: Oxidative thermal degradation, polyethylene waste, jute fiber, technology for green environment

Introduction

Waste to energy (WTE) technology is a promising way to transform the municipal solid waste (MSW) into the energy resource. According to Plastic Europe Market Research Group, the reported global production of plastic is 322 million tons in the year 2015 [1] in which only United States individually contributes 250 million tons of municipal solid waste (MSW) [2] which generates numerous environmental problems. Pyrolysis is a thermal degradation process of organic materials which operated at very high temperature in the absence of oxygen. On pyrolysis of plastic by mixing biomass causes the improvement in liquid product yield than the plastics pyrolyzed individually [8]. Co-pyrolysis of plastic waste with different biomass such as karanja & niger seeds [3], red oak [4], rice husk [5], almond shell [6], oil shell [7], pine cone [8], wood biomass [9], forestry biomass wastes [10], lignocellulosic materials [11] has been studied widely. Jute (*Corchorus olitorius*) is golden brown vegetable fibers which produced from plant classified in the genus *Corchorus*, family Sparrmanniaceae. Jute fibers are extracted from the bark of the jute plant. About 95% of world jute is grown in India and Bangladesh. Annual output in the last decade ranges from 2.5 to 3.2 million tons. India and Bangladesh account for about 60% and 30% respectively, of the world's production [12].

In this research work the mixture of Jute fiber, HDPE and LDPE in the ratio of 1:3:1 by weight % and the mixture of HDPE and LDPE in the ratio of 3:1 by weight % were

thermally degraded in the oxidative environment in a self-designed, laboratory scale, stainless steel reactor from room temperature to 180°C with a heating rate of 1°C/min. This research work explains the mechanism of degradation of polymeric chains of polyethylene at early temperature by mixing Jute fiber into the mixture of HDPE and LDPE and the synthesis of their respective oxidative products from the unsaturated hydrocarbon fragments inside the reactor and also explains the improvement in liquid product yield from JFWPB than WPB.

Experimental

Material

Waste, broken buckets made up of HDPE (High density polyethylene) and shopping carry bags made up of LDPE (Low density polyethylene) were collected from neighboring domestic sources. These collected samples of waste polyethylene were characterized by Central Institute of Plastics Engineering and Technology (CIPET) Bhopal India. These samples were prepared for the thermal degradation experiments by washing with tap water, cleaning by cloth, drying under the sunlight and shredded into the pieces of 3X3 inches. The natural fibers of Indian origin like Jute, Hemp, Sisal and Flax were purchased from the local area market and prepared for experiment by washing with distilled water, dried

under the sunlight for a week and then chopped and sieved by using, BSS-14 (British Sieve Size No. 14).

Methods

Experimental setup

For the oxidative thermal degradation experiments, a laboratory scale reactor was self-designed. This reactor consisted of a vertical, air tight chamber made up of stainless steel, with the height of 500 mm and inner diameter of 200 mm (Fig. 1-A), below the chamber, a heating source of 2 Kilo Watt was placed (Fig.1-B), a ‘J’ type thermocouple was used to sense the temperature inside the chamber (Fig.1-D), this heating source and ‘J’ type thermocouple were combined with the digital temperature controller (Fig.1-C) to raise the temperature with the heating rate of 1°C/min. To collect only liquid product, a collector (Fig.1-G) was specially designed, this collector connected to the exhaust pipes (Fig.1-E) of the reactor by using rubber tubes (Fig.1-F). The real picture of self-designed reactor presented in Figure 1. The liquid, solid and gaseous product % yields were determined by using equation 1 to 3 [13].



Figure 1: The actual picture of the experimental setup.

$$\% \text{ yield of liquid} = \frac{\text{Weight of recovered liquid}}{\text{Total weight of mixture}} * 100 \quad (1)$$

$$\% \text{ yield of solid residue} = \frac{\text{Weight of solid residue}}{\text{Total weight of mixture}} * 100 \quad (2)$$

$$\% \text{ yield of gaseous products} = 100 - [\% \text{ yield of liquid} + \% \text{ yield of solid residue}] \quad (3)$$

Thermo gravimetric analysis

In a NETZSCH TG 209 F1 thermo gravimetric analyzer, approximately 10 mg sample of the Jute fiber, HDPE and LDPE was heated from room temperature to 700°C with a heating rate of 5°C/ min., in the inert atmosphere of nitrogen by flowing with the rate of 100 ml/min.

Thermal degradation experiments

The thermal degradation experiments were accomplished in the self-designed reactor in the presence of Oxygen (oxidative environment) with different types of natural fibers of Indian origin like Jute, Sisal, Hemp and Flax. The mixture of polyethylene was prepared by mixing shredded HDPE and LDPE in the ratio of 3:1 by wt% and 1 ratio of different natural fiber by wt% was added to the mixture of shredded polyethylene waste and the final amount of each reaction mixture was 500 g.

Nomenclature of the samples and products

The mixture of shredded waste HDPE and LDPE in the ration of 3:1 was nominated as WPB and the mixture of shredded Jute, HDPE and LDPE in the ratio of 1:3:1 was nominated as JFWPB. The recovered liquid products by WPB and JFWPB were nominated as OilWPB and OilJFWPB respectively.

Fourier transform infrared spectroscopy

The Shimadzu IR Affinity-1 was used for the FTIR analysis of recovered liquid products. A NaCl cell of thickness 0.025 mm was used for sample holding. The samples were scanned between 4000 to 400 cm⁻¹, with total scan of 64 and the resolution of 4 cm⁻¹. The FTIR spectrum was recorded in percent transmittance (%T). The obtained FTIR of WPB and JFWPB were nominated as FTIRWPB and FTIRJFWPB respectively.

Gas Chromatography Mass Spectrometry

The JEOL GCMATE II GC-MS was used for the GC/MS analysis of OilJFWPB to identify the existing chemical compounds with in the OilJFWPB. The GC/MS 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.

Results and discussion

The chemical composition of employed natural fibers summarized in Table 1 and the distribution of the product % yield was presented in Figure 2. The highest liquid % yield was reported with Jute fiber.

Table 1: The chemical composition of employed natural fibers

Name of the fiber	Chemical composition of the employed natural fibers (%)				
	Cellulose	Hemicellulose	Lignin	Fat & wax	Water soluble
Jute	~65.2	~22.2	~10.8	~0.3	~1.5
Flax	~92	~2	~4	--	--
Hemp	~77.77	~18	~6	~0.5	~1.73
Sisal	~71.5	~18	~6	~0.5	~1.7

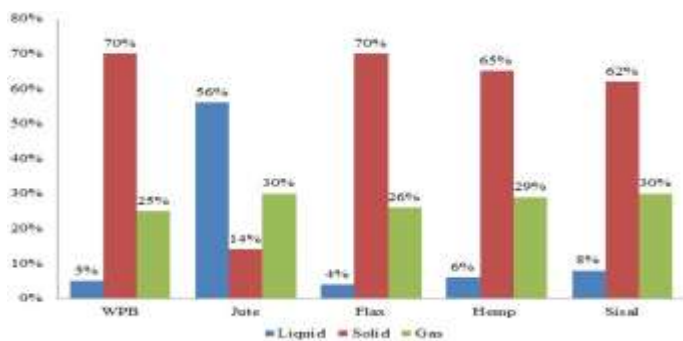


Figure 2: Distribution of the product % yield with employed natural fibers of Indian origin

According to the TG and DTG profile shown in Figure 3, it was clearly observed that Jute fiber effectively degraded between 85 to 110°C with the reported mass loss of 55.66% and the maximum mass loss was reported at ~100°C. Similarly the HDPE and LDPE effectively degraded between 400 to 460°C and the reported mass loss of approximately 70 and 50% respectively and the maximum mass loss reported ~450°C.

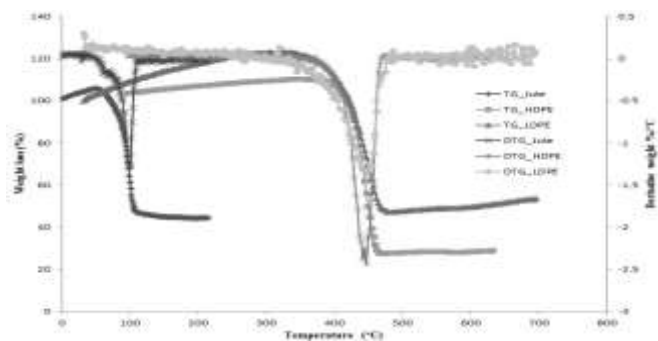


Figure 3: TG and DTG profile of Jute fiber, HDPE and LDPE respectively.

According to the FTIR_{WPB} shown in Figure 4, the characteristic transmittance bands appear at 3072.60 cm^{-1} , 1649.14 cm^{-1} , 1375.25 cm^{-1} , 1359.82 cm^{-1} , 1328.95 cm^{-1} , 972.12 cm^{-1} and 887.26 cm^{-1} , corresponds to =CH₂ stretch, -C=C- stretch, CH₂ bend, -CH=CH₂ (in plane), CH₃ bend, -CH=CH₂ (out of plane) respectively. The appearance of these characteristic transmittance bands strongly evident that Oil_{WPB} consisted of various unsaturated hydrocarbon fragments which were formed by the thermal decomposition of polymeric chains of polyethylene (HDPE and LDPE). In the FTIR_{JFWPB} shown in Figure 4, the appearance of a transmittance band at 3612.67 cm^{-1} indicates the presence of a primary alcohol (R-OH), the band at 3348.42 cm^{-1} indicates the presence of either amide or N-H containing amine functional group. The sharp, small band at 2185.35 cm^{-1} indicates the presence of nitrile (-C≡N) functional group. The band at 1730.15 cm^{-1} indicates the presence of carbonyl group (C=O), which could be an aldehyde or ketone or carboxylic acid or ester or amide or anhydride or acyl halide. The two close bands at 908.47 cm^{-1} and 887.26 cm^{-1} corresponds to the presence of mono substituted aromatic compounds. The presence of some common transmittance bands with reduced intensities was also reported. In FTIR_{WPB} the band at 3072.60 cm^{-1} with intensity 43.86 corresponds to =CH₂ bond, in FTIR_{JFWPB} the position of this band was slightly shifted at 3074.53 cm^{-1} with reduced band intensity of 14.39. Similarly the band at 1649.14 cm^{-1} with intensity 42.69 corresponds to C=C, shifted to 1643.35 cm^{-1} and the band intensity reduced to 14.58, The bands at 1375.25 cm^{-1} , 1359.82 cm^{-1} , 1328.95 cm^{-1} with the band intensities 18.91, 36.12, 53.91 corresponds to CH₂, -CH=CH₂

(in plane), CH_3 respectively were shifted at 1444.68 cm^{-1} , 1435.04 cm^{-1} , 1415.75 cm^{-1} with the reduced intensities of 11.55, 12.62, 16.21. The persistence of these characteristic bands with the reduced intensity and appearance of some new characteristic bands clearly indicates that these bands were transformed from one functional group (unsaturated hydrocarbons) to other functional groups (alcohols, carbonyls, amines, nitriles, and aromatic compounds) in the oxidative environment of the reactor.

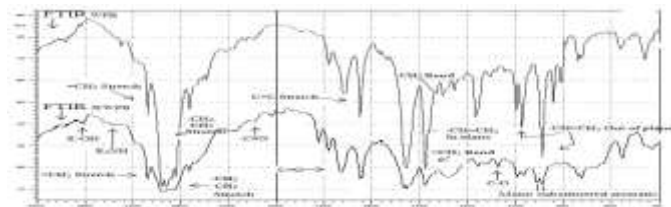


Figure 4: Comparative FTIR of Oil_{WPB} and Oil_{JFWPB}

As per the structure the polyethylene was a high molecular weight polymeric material which consisted of several repeated monomer units of ethylene ($-\text{H}_2\text{C}=\text{CH}_2-$) and by the thermal treatment, the low molecular weight hydrocarbon fragments such as $=\text{C}-\text{H}$, $\text{C}=\text{C}$, $=\text{CH}_2$, were produced randomly and recovered as the mixture of hydrocarbon as oily substance. When WPB heated up to 180°C inside the oxidative atmosphere of reactor there were negligible degradation takes place because polyethylene effectively degraded between $400-500^\circ\text{C}$ [3-11] and scissoring of polymeric chains not initiated [14], which results into the negligible degradation of polyethylene and the reported liquid yield was also negligible i.e. $< 5\%$. After that, when JFWPB was thermally degraded, the Jute in the reaction mixture was degraded at 100°C (Fig. 3). In the oxidative atmosphere of the reactor the chief components of Jute like water molecules (H_2O), cellulose ($[\text{C}_6\text{H}_{10}\text{O}_5]_n$), hemicellulose (a complex molecule), lignin ($[\text{C}_9\text{H}_{10}\text{O}_2, \text{C}_{10}\text{H}_{12}\text{O}_3, \text{C}_{11}\text{H}_{14}\text{O}_4]$), amino acids ($\text{R}-\text{CH}(\text{NH}_2)-\text{COOH}$) etc. were decomposed randomly which consequences into the generation of free radicals (A^\bullet), intermediate species ($[\text{A}^+\text{B}^-]$), electrophiles ($\text{A}^{\delta+}$), nucleophiles ($\text{A}^{\delta-}$) and the reactor get fulfilled with these highly energetic reactive species and these reactive species randomly attacks on the polymeric chains of HDPE and LDPE into the mixture and causes the random scissoring of these polymeric chains effectively which results, the early decomposition of polyethylene and generation of unsaturated hydrocarbon fragments at a comparatively low temperature (180°C). To achieve the saturation and stability, these generated reactive chemical species from biomass and polyethylene starts reacting randomly with each other's and unsaturated hydrocarbon fragments (Alkenes) quickly converted into the alcohols ($\text{R}-\text{OH}$), primary amines ($\text{R}-\text{NH}_2$), carbonyls (RCOOR), and

nitriles (RCN) etc., and these instant synthesized chemical compounds were collected as an improved liquid product yield (Fig. 5).

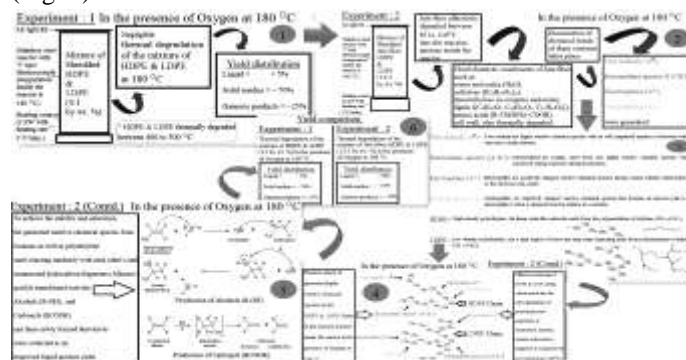


Figure 5: Mechanism of Oxidative thermal degradation

According to the GC/MS analysis, in the obtained total ion chromatogram of the Oil_{JFWPB} (Fig. 6-A), the Phytol identified as 3,7,11,15- Tetramethyl -2-hexadecen-1-ol (Fig. 6-B). Synthesis of this Phytol (Alcohol) could be understand by that, as the JFWPB was degrading inside the reactor the present water molecules in Jute fiber were start vaporizing, which causes the hydration[15] of available unsaturated hydrocarbon fragments ($\text{C}=\text{C}$) and results into the conversion of alkenes ($\text{R}=\text{R}$) into alcohols ($\text{R}-\text{OH}$). As per the mechanism of hydration reaction of Alkenes (Fig. 5), in the initial step the protonation of double bond causes the generation of carbocation, on which the water molecule (nucleophile) attacks and finally the alcohol (ROH) formed by the quick removal of protons. Similarly 2 saturated fatty acids, Methyl tetradecanoate and Pentadecanoic acid, 14-methyl- methyl ester (Fig. 6-C & 6-D) and 2 unsaturated fatty acids, 7-Hexadecenoic acid, methyl ester, (Z) and 9-Octadecenoic acid (Z)-, methyl ester (Fig. 6-E & 6-F) were synthesized by the oxidation of unsaturated hydrocarbons [16] inside the reactor as per the scheme shown in Figure 6. Two silica containing derivatives (Fig. 6-G & 6-H) 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 constituents of cell wall. The GC/MS analysis of Oil_{JFWPB} was summarized in Table 2.

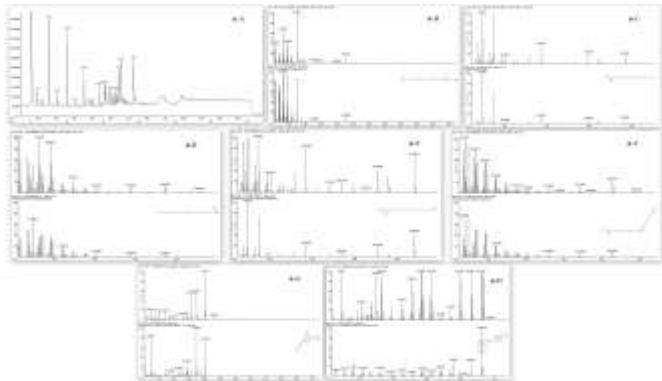



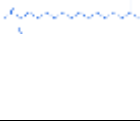

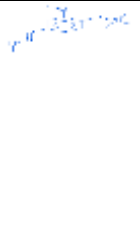



Figure 6: 6-A; Total ion chromatogram of Oil_{JFWPB}, 6-B; phytol, 6-C to 6-F; free fatty acids, 6-G to 6-H; silica derivatives respectively.

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

Retention time	Compound name	Fragmentation (m/z)	Molecular formula	Molecular structure
15.25	Methyl tetradecanoate	242,199,143,74	C ₁₅ H ₃₀ O ₂	
16.78	3,7,11,15-Tetramethyl-2-hexadecen-1-ol	296,278,249,193,179,138,123,96,81,56	C ₂₀ H ₄₀ O	
17.17	7-Hexadecenoic acid, methyl ester, (Z)	278,236,194,152,123,110,95,82,74	C ₁₇ H ₃₂ O ₂	
17.43	Pentadecanoic acid, 14-methyl-, methyl ester	270,227,213,185,171,143,101,86	C ₁₇ H ₃₄ O ₂	
19.2	9-Octadecenoic acid (Z)-, methyl ester	296,264,235,222,194,180,152,137,110,96,83,69	C ₁₉ H ₃₆ O ₂	
5.9	Benzaldehyde, 3-methoxy-4-[(trimethylsilyl)-O-methyl]oxime	281,253,223,207,191,149,119,104,73	C ₁₂ H ₂₅ O ₃ NSi	

8.65	2,2'-Bis-trimethylsilyl benzhydryl methyl ether	355,327,281,223,207,133,89,73	C ₂₀ H ₄₂ OSi ₂	
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Conclusion

Oxidative thermal degradation is a cost effective waste to energy technology by which the polyethylene waste effectively degraded at early temperature and the liquid yield improved up to 56%. The recovered fuel like liquid possesses good heating value, due to which this recovered liquid could be used as fuel to run vehicles and industrial motors. By transforming polyethylene garbage into the petroleum grade fuel effectively at commercial level, the oxidative thermal degradation could be a good technology for the green environment.

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