



Formulation and Characterization of Pyrolytic Oil from Waste Tyre and Waste Plastic: A Comparative Study

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ABSTRACT

Elimination of solid waste generated by the engineering sector is the need of the present world. In this study, a comparative analysis has been made to formulate a petro-diesel like fuel from the waste tyre (WTPO) and waste plastic (WPPO), which is derived from unusable tyre and plastic waste materials, by the thermal pyrolytic reaction. A pyrolysis reactor is designed and fabricated to transform the solid waste into the pyrolytic oil through thermal cracking. The characterization of WTPO and WPPO is carried out using the gas chromatography, mass spectrometry, Fourier transform infra-red and elemental analysis. The GC-MS analysis of both WTPO and WPPO indicated the presence of naphtha and limonene compounds at higher concentration levels. The content of sulphur in WTPO is at higher level. The physico-chemical properties are also determined based on IS:1448 and it is found to be comparable with the commercial petro-diesel.

INTRODUCTION

Solid waste management continues to be a great challenge in the present engineering world. Plastics are one of the favourite material used in engineering industries as they are weightless, rust resistance, highly reusable and durable. With the increased usage of vehicles in the transportation sector, rubber based tyre finds a prominent place leading to a large waste creation every year. Hydrocarbon based plastics and tyres are the major sources of waste material that are non-biodegradable and difficult to recycle (Walendziewski & Steininger 2001, Kumar et al. 2013, Martinez et al. 2014, Murugan et al. 2008 and Yaxin et al. 2013).

Waste plastic and tyre together contribute about 80-85% of solid waste, which are disposed and a part of it was transformed into value added products. It was estimated that 22 million tonnes of waste tyre and 30 million tonnes of waste plastic are generated worldwide which made the researchers to identify promising ways for their reuse and transformation into value added products. As plastics and tyres are mainly composed of hydrocarbons besides minimal quantity of stabilizers, antioxidants, colorants and fillers, energy recovery by a combination of thermal, mechanical and chemical processes to produce diesel like fuel through gasification, combustion and pyrolysis techniques yielded better results. Reuse of waste plastic and rubber tyre consumes

huge amount of energy involving thermal, chemical and mechanical pre-treatment processes (Rada et al. 2012, Mani and Nagarajan 2009, Passamonti et al. 2012).

Usage of suitable catalysts like FCC, zeolite and other reforming catalysts enhanced the degradation of waste HDPE and LDPE plastic material thermally thereby leading to increased yield of value added products. Acid treated kaolin was used as a catalyst in the production of waste plastic oil through pyrolysis in a reactor furnace system. The reaction temperature was maintained at 450°C with an increment of 20°C/min followed by the condensation process. Elemental analysis and FTIR analysis involving CHNS analyser and Perkin Elmer Fourier transform infrared spectrometer were carried out to understand its suitability as a fuel (Kumar et al. 2013).

Thermogravimetric elemental analysis on waste tyre pyrolysis oil produced through thermal decomposition revealed the composition in it, which consists of tyre pyrolysis oil (40%), gas (20%) and solid char (40%). It was also reported that tyre pyrolysis oil had comparable calorific value with respect to commercial petro-diesel which increased the possibilities for energy valorisation (Rada et al. 2012). Transformation of waste LDPE into high octane fuel was studied by dissolving them with various proportions of vacuum gas at high operating temperatures ranging from

500°C to 550°C. As a result, coke, gasoline like fuel and dry gas were formed at various quantities due to catalytic cracking (Passamonti et al. 2012). Distilled tyre pyrolysis oil was produced through pyrolysis method followed by desulphurisation process. Multiple concentrations of TPO with commercial diesel was experimentally investigated in 4S single cylinder diesel engine to analyse the effect of it on emission, performance and combustion parameters (Murugan et al. 2008).

In the present study, formulation of pyrolytic oil from waste tyre and waste plastic in a customized designed pyrolysis reactor is discussed in detail. The extracted pyrolytic oil is subjected to various characterization techniques like GC/MS, FTIR and elemental analysis to understand its capability to be used as a fuel for commercial vehicle in the transportation sector. The physico-chemical properties of waste tyre and waste plastic is also studied and compared with the commercial petro-diesel.

DESIGN AND FABRICATION OF THE PYROLYSIS REACTOR

The pyrolysis reactor is designed and modelled using catia software with an overall measurement of $410 \times 200 \times 456$ cm. The pyrolysis reactor consists of an inner and outer cylinder which is made up of SS316L grade stainless steel and filled with glass wool in between which acts as an insulation. A conical convergent lid attached with an exhaust chute acts as a cover which directs the pyro gas into the condensation chamber. The conical shaped lid is also provided an opening through which a temperature sensor is placed into the reactor and it is connected with the cut-out relay. Three koyos electric heating coil with a heating range of 250°C to 750°C is used to elevate the temperature of the feed stock inside the reactor. Safety cut-off relays are used to disconnect the electric power supply during adverse conditions (Hariram & Ismail 2015).

The pyrolysis reaction takes place between 275°C and 550°C for both waste plastic and waste tyre. Pyro gas, which is produced during this process, is collected in the condensation chamber filled with water. Condensed pyro gas in the liquid form emerges at the top layer which is then separated carefully through an outlet in the condensation chamber. The detailed sketch and pictorial view of the pyrolysis reactor is shown in Fig. 1.

Fuel characterization: The capability of the oil which is to be used as a fuel and its quality has been analysed using the instruments and techniques listed below.

GC/MS: JEOL GC Mate 2 data system employed with a higher resolution was used. It is a double focussing type instrument having a maximum resolution of 6000 with a

calibrated mass (max) of 1500 Daltons and electron ionization impact.

FTIR: FTIR analysis is performed using the Perkin Elmer spectrum instrument which consists of mercury and global vapour lamps as the source. It is used to obtain the interference pattern on Fourier transform resulting in mass spectrum. The interferometer chamber has beam splitter (KBr and mylar) along with detector and sample chamber. This instrument has a scan range of MIR 450-4000 cm^{-1} with a resolution of 1.0 cm^{-1} .

Elemental analyser: 2400 CHN elemental analyser was used to perform elemental analysis. Two to three mg of waste tyre and waste plastic pyrolysis oil is inoculated separately in a tin capsule with additional oxygen. Mineralization takes place at 950°C in the presence of tungsten trioxide catalyst and the presence of various organic and inorganic compounds are identified.

RESULTS AND DISCUSSION

Physico-chemical properties: Table 1 compares the physico-chemical properties of waste tyre pyrolysis oil (WTPO) and waste plastic pyrolysis oil (WPPO) with commercial diesel. It can be seen that the kinematic viscosity at 40°C of WPPO lies close to commercial diesel. But, WTPO shows a drastic increase in the value (3.4 cSt). The gross calorific value of commercial diesel is higher than both WPPO and WTPO. The flash and fire points of WPPO and WTPO are lower than the commercial diesel. It can be noticed that the density at 15°C for WTPO is 936 kg/m^3 and WPPO is 837.5 kg/m^3 whereas, for commercial diesel it is 832 kg/m^3 . The calculated Cetane index of WPPO is found to be higher at 68 whereas, for WTPO it is 55 which is 20 to 25% higher than the commercial diesel. WTPO showed a higher content of sulphur at 0.99%, whereas, WPPO and commercial diesel exhibited almost the same as 0.034% and 0.047% respectively. It can also be seen that the carbon residue in WPPO is found to be 72.79% while WTPO and commercial diesel, the values are 2.21% and 0.37% respectively. The ash content in WPPO is also very less and it correlates with the findings of Mitsuhara et al. (2001).

Gas chromatography mass spectrometry analysis: JEOL GC mate 2 GC MS data system was used to categorize the different compounds present in WPPO and WTPO. With a residence time of 6 seconds, 3 mL of WPPO and WTPO is inoculated into the spectrometer separately. GC/MS fragmentation pattern and mass spectrum revealed the presence of 16 different compounds in WPPO and 12 different compounds in WTPO across diversified retention period. NIST 2 library is used to identify the presence of different compounds on comparison with the fragmentation pattern. The

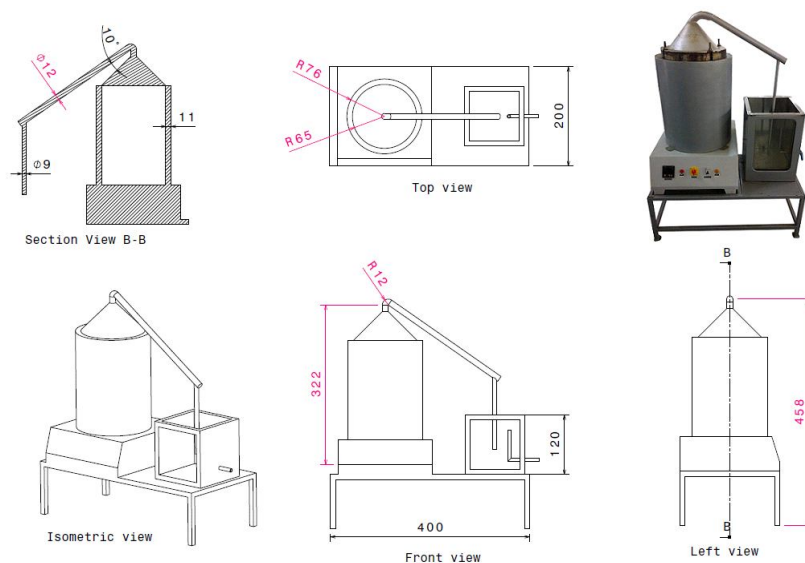


Fig. 1: Pyrolysis reactor.

retention time of WPPO is noticed between 2.97 min and 21.65 min. But, WTPO showed a retention time (RT) between 5.55 min and 19.15 min. The major composition of WPPO is found to be 2-hexadecanoic acid, 2,3-dimethyl naphthalene at RT 18.92 as shown in Fig. 2.

The secondary compound is found to be a phenolic substrate named methanone (3-methyl phenyl) phenyl at RT 14.35. Few other compounds were also identified. They are Spiro [2.4] heptane, 1-ethenyl-5-(1-propenylidene) at RT 2.97, 1,6-heptadien-3-yne, 5-methyl at RT 3.27, 2-nitro-1-phenyl-ethanol at RT 4.07, methyl styrene at RT 4.95, 1,5,5-trimethyl-6-methylene-cyclohexene at RT 9.15, 5-caranol, (1S,3R,5S,6R)-(-) at RT 9.57, 1-propene-1-amine, N-benzylidene-2-methyl at RT 10.28, 1h-inden-1-one 2,3-dihydro-3-phenyl at RT 14.62, 2h-1-benzopyran,3,4-dihydro-2-phenyl at RT 15.48, pentadecanoic acid 13-methyl- methyl ester at RT 17.13, heptadecanoic acid 14-methyl-methyl ester at RT 19.12 and methanone, (4-(2-hydroxy-5-methyl benzylidene) phenyl at RT 21.65.

The GS/MS mass fragmentation pattern of WTPO revealed the presence of limonene compound at RT 18.95 in major proportions. Cyclohexane 3 methyl-6-(1-methylethenyl) (3R-Trans) at RT 5.55 and Bicyclo [3.1.0] hexan-2-one, 6, 6-dicyano-5-(1) at RT 14.65 are also found in prominent quantities. Minimal proportions of few other chemical compounds including 1-ethyltricyclo [5.2.1.1 (2,6)] undue-8-en-11-ol at RT 10.27, naphthalene, 1,2,3,4-tetrahydro-2,5,8-trimethyl at RT 10.75, 1,1,4a-trimethyl-5,6-dimethylene decahydronaphthalene at RT 11.35,

naphthalene, 1,2,4a,5,8, 8a-hexahydro,4,7-dimethyl-1-(1-methylethyl) at RT 11.78, tricyclo [5.3.1.1(2,6)] dodecan-11-ol,11-methyl-12-methylene at RT 12.48, cycloheptene, 4-methoxy-phenyl at RT 12.83, 1-azatricyclo [7.3.0.0 (2,7)] dodecan-11-ol-12-one, 8-methyl at RT 16.95, bicyclo [2.2.1] heptan-2-one, 3-(4-methoxybenzylidene)-1,7,7-trimethyl- at RT 17.17 and 1-phenyl-3-ethylprop-1-ene(1-3)sultine at RT 19.15 were also found which reiterates the findings of Marcilla et al. (2008) and Ali et al. (2005).

In general, the GC/MS analysis exposed the presence of aromatic and aliphatic compounds in WTPO and WPPO with a magnitude of 47% to 53%. The detailed list of compounds present in the WTPO and WPPO is given in Table 2.

Fourier transform infra-red analysis: Table 3 gives the comparison of FTIR analysis on WTPO and WPPO by describing the presence of various functional groups. It can be seen that WTPO mainly constitutes both aromatic and aliphatic hydrocarbon compounds between the wavelength frequencies of 1620 cm^{-1} to 2620 cm^{-1} . Stretching and bending spectrum is also seen between 710 cm^{-1} to 1320 cm^{-1} and it is mainly composed of alkenes and amines. Phenyl ring substitute is also observed between 1905 cm^{-1} to 2102 cm^{-1} . Alternate stretching and bending vibrations which is noticed between 2720 cm^{-1} to 3015 cm^{-1} is due to hydrocarbon bonding. Similarly, WPPO represented C-S stretching from 845 cm^{-1} to 1615 cm^{-1} which comprises of amines and alkenes. C-H bend and C=C stretch, an aromatic compound is also observed between 1812 cm^{-1} to 2246 cm^{-1} . Phenyl ring substitute is also noticed between wavelengths of 2346

Table 1: Physio-chemical properties of diesel, WTPO and WPPO.

Properties	Units	Commercial Diesel	WTPO	WPPO	TestingMethods
Gross calorific value	MJ/kg	43.9	42.7	39.45	IS:1448 P:6
Kinematic viscosity, @ 40°C	cSt	2.1	3.4	2.2	IS:1448 P:25
Flash point	°C	52	46	44	IS:1448 P:20
Fire point	°C	57	53	47	IS:1448 P:20
Density @ 15°C	kg/m ³	832	936	837.5	IS:1448 P:16
Cetane index	-	46.4	55	68	IS:1448 P:9
Carbon residue	%	0.37	2.21	72.79	IS:1448 P:122
Sulphur content	%	0.047	0.99	0.034	IS:1448 P:33
Ash content	%	0.01	0.33	0.00027	IS:1448 P:126

Table 2: Gas chromatography mass spectrometry analysis.

RT (min)	Name of Compounds	Molecular Formula
GC/MS of Waste Tyre pyrolysis oil (WTPO)		
5.55	Cyclohexane 3 methyl-6-(1-methylethenyl) (3R-Trans)	C ₆ H ₁₂
10.27	1-Ethyltricyclo[5.2.1.1(2,6)]undec-8-en-11-ol	C ₂₃ H ₃₃ N ₃ O
10.75	Naphthalene, 1,2,3,4-Tetrahydro-2,5,8-Trimethyl	C ₁₀ H ₈ , C ₁₃ H ₁₈
11.35	1,1,4a-Trimethyl-5,6-dimethylenedecahydronaphthalene	(CH ₃) ₃ PO ₄ , C ₁₁ H ₂₀
11.78	Naphthalene, 1,2,4a,5,8,8a-hexahydro,4,7-dimethyl-1-(1-ethylethyl)	C ₁₅ H ₂₄
12.48	Tricyclo[5.3.1.1(2,6)]dodecan-11-ol,11-methyl-12-methylene	C ₁₀ H ₁₆
12.83	Cycloheptene, 4-methoxy-phenyl	C ₁₄ H ₁₈ O
14.65	Bicyclo[3.1.0]hexan-2-one,6,6-dicyano-5-(1)	C ₆ H ₁₀
16.95	1-Azatriicyclo[7.3.0.0(2,7)]dodecan-11-ol-12-one, 8-methyl	C ₁₄ H ₂₁ N
17.17	Bicyclo[2.2.1]heptan-2-one,3-(4-methoxybenzylidene)-1,7,7-trimethyl	C ₁₆ H ₂₀ N ₃
18.95	Limonene	C ₁₀ H ₁₆ N ₂
19.15	1-Phenyl-3-ethylprop-1-ene(1-3)sultine	C ₁₉ H ₃₈ NH ₂
GC/MS of Waste plastic pyrolysis oil (WPPO)		
2.97	Spiro[2.4]heptane,1-ethenyl-5-(1-propenylidene)	C ₁₂ H ₁₆
3.27	1,6-heptadien-3-yne,5-methyl	C ₁₂ H ₁₇
4.07	2-nitro-1-phenyl-ethanol	C ₈ H ₉ NO ₃
4.95	Methyl styrene	C ₉ H ₁₀
9.15	1,5,5-trimethyl-6-methylene-cyclohexene	C ₁₀ H ₁₆
9.57	5-Caranol, (1S,3R,5S,6R)-(-)-	C ₁₀ H ₁₈ O
10.28	1-propene-1-amine,N-benzylidene-2-methyl	C ₁₁ H ₁₃ N
14.35	Methanone, (3-methylphenyl)phenyl-	C ₁₄ H ₁₂ O
14.62	1h-inden-1-one 2 3-dihydro-3-phenyl	C ₁₈ H ₁₄ O
15.48	2h-1-benzopyran,3,4-dihydro-2-phenyl	C ₁₅ H ₁₄ O
17.13	Pentadecanoic acid 13-methyl- methyl ester	C ₁₇ H ₃₄ O ₂
18.92	2-hexadecanoic acid ,2,3-dimethyl naphthalene	C ₁₉ H ₃₆ O ₂
19.12	Heptadecanoic acid 14-methyl- methyl ester	C ₁₉ H ₃₈ O ₂
21.65	Methanone,(4-(2-hydroxy-5-methyl benzylidene) phenyl) (phenyl)	C ₁₅ H ₁₄ O ₅

cm⁻¹ to 2679 cm⁻¹. Presence of aldehydes, alkenes and alkanes with C-H bend is also seen between 2697 cm⁻¹ to 3287 cm⁻¹. The FTIR analysis on WTPO and WPPO provides a favourable scenario for both to be used as a substitute fuel for commercial petro-diesel. This finding validates the earlier results of Walendziewski (2002) and Kumar et al. (2011).

Elemental analysis: The elemental analysis of WTPO and WPPO is given in Table 4. CHN elemental analyser is employed to identify the various organic and inorganic compounds present in the WTPO and WPPO. The carbon

content present in WTPO is found to be 81.44% whereas, WPPO exhibited 83.58%. The content of hydrogen showed significant variations from 6.57% in WTPO to 10.31% in WPPO. Nitrogen and ash content is found to be higher in WTPO than WPPO. WTPO exhibited 1.59% of sulphur along with a higher quantity of oxygen by up to 7.29%.

CONCLUSION

Based on the present comparative study involving characterization techniques, the following conclusions are drawn:

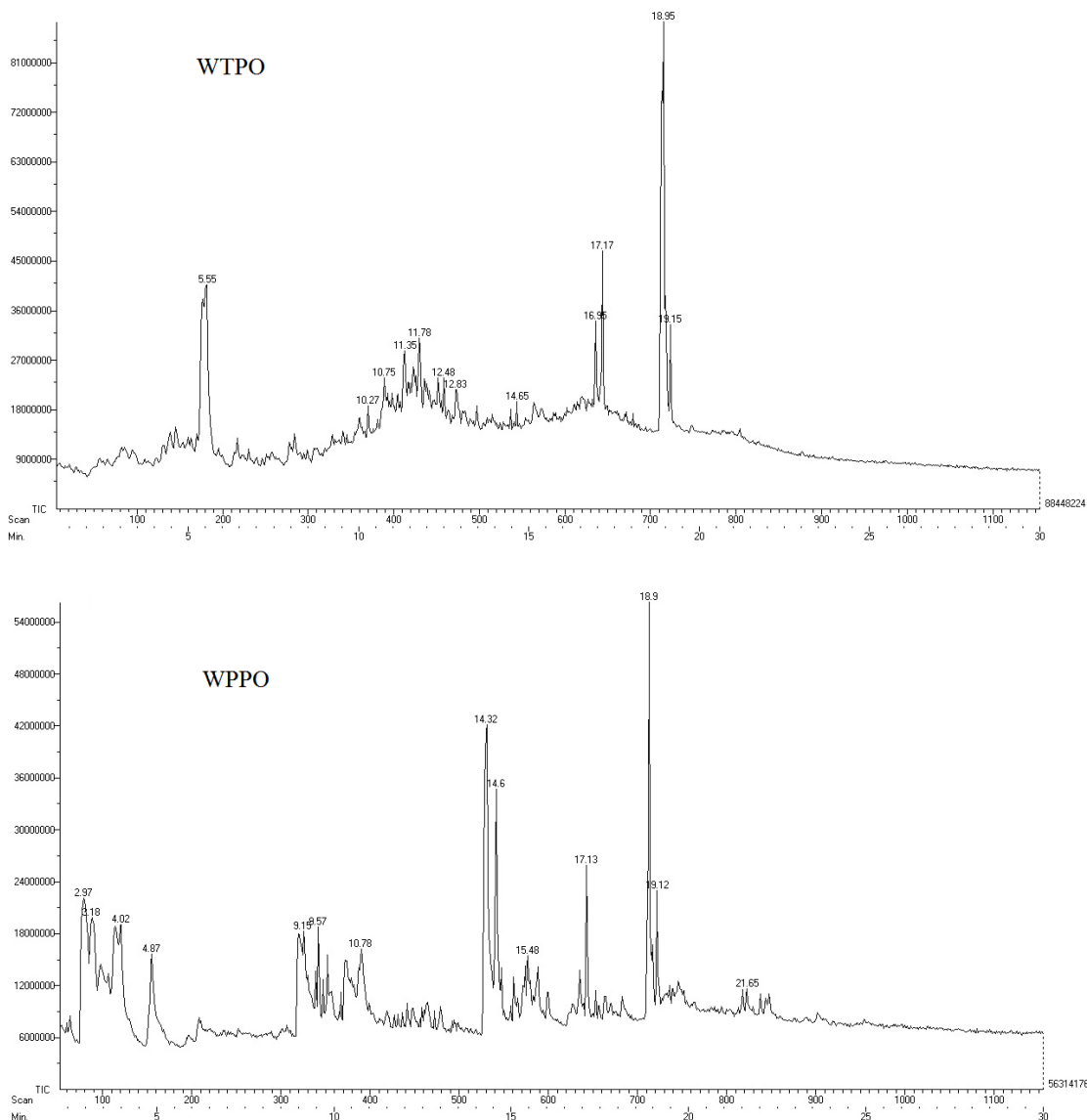


Fig. 2: GC/MS mass spectrum of WTPO and WPPO.

- A pyrolysis reactor with a feed capacity of 13 kgs is designed and fabricated to process both waste plastic and waste tyre with a heating range up to 750°C.
- GC-MS analysis of WPTO and WPPO revealed the presence of naphtha and limonene compounds in greater concentration respectively.
- Fourier transform infra-red spectrometry analysis also supported the GC-MS data by identifying the aromatic and aliphatic hydrocarbons in wavelengths of 1620 cm⁻¹ to 2620 cm⁻¹ for WTPO. In WPPO, phenyl ring substitute is observed between 2346 cm⁻¹ and 2676 cm⁻¹ along with a minimal quantities of aldehydes, alkenes and alkanes.
- Elemental analysis revealed the presence of carbon and hydrogen in major compositions. Sulphur content in WTPO is found to be on the higher side.
- Physico-chemical properties of WTPO and WPPO are comparable with the commercial diesel by having a higher Cetane index which makes them favourable as a substitute fuel.

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Table 3: Fourier transform infra-red analysis of WTPO and WPPO.

Wavelength frequency (cm ⁻¹)	Functional group
FTIR of WTPO	
710-815	C-H _{Bend} (Alkenes)
852-1045	C=C _{Stretch} (Alkenes)
1220-1320	C-S _{Stretch} (Amines)
1380-1590	C-H _{Bend} (Alkanes)
1620-1820	C=C _{Stretch} (Aromatic Compounds)
1905-2150	C-H (Phenyl ring substitute)
2250-2620	C-H _{Stretch} (Aldehydes)
2720-2940	C-H _{Stretch}
2985-3015	C-H _{Bend}
3080-3150	C=C _{Stretch} (Alkenes)
FTIR of WPPO	
845-974	C-S _{Stretch} (Amines)
992-1157	C=C _{Stretch} (Alkenes)
1341-1427	C-S _{Stretch} (Amines)
1493-1616	C=C _{Stretch} (Alkenes)
1687-1794	C-H _{Bend} (Alkanes)
1812-1941	C=C _{Stretch} (Alkenes)
1954-2246	C=C _{Stretch} (Aromatic Compounds)
2349-2679	C-H (Phenyl ring substitute)
2697-3021	C-H _{Stretch} (Aldehydes)
3087-3111	C-H _{Bend} (Alkenes)
3120-3287	C-H _{Bend} (Alkanes)
3299-3361	C-H _{Bend}

Table 4: Elemental composition of WTPO and WPPO.

Elements	WTPO (wt. %)	WPPO (wt. %)
Carbon	81.44	83.58
Hydrogen	6.57	10.31
Nitrogen	0.24	0.17
Sulphur	1.59	0.41
Oxygen	7.29	5.43
Ashes (Inorganic)	2.8	0.1

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