

# Co-Pyrolysis of PCB with Cotton Stalk: Product Characterisation

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## Research Article

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# Abstract

With advancing technology, PCB (Printed circuit board), one of the most important components of e-waste, has become a source of pollution due to an ineffective waste management system. This problem can be solved by converting PCB waste into a valuable product which will emerge to maximize the renewable energy supplies. In this aspect, co-pyrolysis is advantageous in both simple and successful in producing high-quality pyrolysis oil. In this paper, cotton stalk (CS) as biomass was used for co-pyrolysis with PCB. Slow pyrolysis of PCB, CS, and co-pyrolysis of PCB:CS (1:1) have been carried out for temperatures up to 500 °C in a fixed-bed reactor. The products of pyrolysis: oil was analysed by GC-MS and FTIR and gas had been analysed by GC. The results indicate that there is an increase in oil yield from 19.6% to 27.5 % by weight and phenol and phenolic compounds in oil of co-pyrolysis from 60.94–76.82% than literature available. As per authors knowledge co-pyrolysis of PCB:CS has been attempted first time and the products characterisation were found completely different than any other biomass co-pyrolysis with PCB.

## 1. Introduction

Pyrolysis, one of the thermal decomposition techniques, is carried out in the absence of oxygen. The technique is well known to produce fuel oil from biomass. Additionally, the char and gas produced as a by-product can be used in a variety of ways (Madhu et al., 2018). Furthermore, other wastes can also be pyrolysed such as e-waste plastic which is present 50–60 % in printed circuit boards (PCB). However due to presence of a significant proportion of ash, it has a lower heating value and low thermolysis efficiency. In this context, adding biomass with PCB could be an alternative strategy that improves these two criteria. The term "co-pyrolysis" refers to a process that uses a mixture of two or more materials as a feedstock. Many research has demonstrated that co-pyrolysis improved the properties of oil generated, as well as increased oil yield. Secondly, biomass has a higher H/C molar ratio than PCBs, thus this high hydrogen content can act as a hydrogen donor to PCBs during co-pyrolysis (Panchasara & Ashwath, 2021). Further, water is one of the most significant components in biomass, and it can function as a reactive agent, stimulating further cracking of PCB tar and raising pyrolysis oil yields. Most importantly, the use of biomass as an additive is the approach for dehalogenation and prevention of highly toxic PBDD/F (Poly-Bromodibenzodioxins/furans) and PCDD/F (Poly-Chlorodibenzodioxins/furans), due to a high amount of hydrogen (W. J. Liu et al., 2013; Abnisa et al., 2014). After consideration of these factors, cotton stalk was chosen as biomass which was added in PCB during pyrolysis due to its readily availability with local farmers. The leftover cotton stalk after removing cotton is of no use and is burnt in open area which has an adverse effect on the environment. Additionally, it contains a large amount of volatile matter and lower O/C (Madhu et al., 2018); Kim et al., 2013) which gives an expectation of high bio-oil yield with improved quality (W. J. Liu et al., 2013; Madhu et al., 2018). Therefore, there were two wastes which were combined to produce energy in the form of fuel oil and gas.

The prime objective of this study is to perform pyrolysis of PCB, cotton stalk (as biomass), and co-pyrolysis of PCB:CS (1:1) to generate oil and to apply qualitative and quantitative analysis. The liquid phase obtained from the co-pyrolysis is highly dependent on the reactor conditions like temperature, heating rate, pressure, and composition (Abnisa et al., 2014; Xu et al., 2011; El-Sayed & Mostafa, 2014). Moreover, fuel oil generated and gas were analysed in GC-MS and GC, respectively to know the composition of oil and gas.

## 2. Materials And Methods

### 2.1 Sample Preparation

The cotton stalk waste samples used in this work was collected from the local farm Chandisana district, Gandhinagar, Gujarat located in India. The cotton stalk waste samples were crushed and air-dried to a residue. The PCB waste samples, on the other hand, were obtained from Shiwalik solid waste management in Punjab, where metals from PCB were removed by physical separation after crushing in hammer mill. Both samples were grounded and sieved to obtain an average particle size 100–200  $\mu\text{m}$  to assure homogeneity of the sample.

## 2.2 TGA Analysis

Mettler Toledo equipment is used to perform Thermogravimetric Analysis (TGA) and Derivative Thermogravimetric Analysis (DTG). To avoid combustion, the system was purged with nitrogen gas with 50  $\text{ml}/\text{min}$  of volumetric flow rate. The degradation of all three samples were performed at three different heating rates: 5, 10, and 15  $^{\circ}\text{C}/\text{min}$  with approximately 10 mg. The sample was kept in a ceramic crucible inside the furnace and heated from ambient temperature to 700  $^{\circ}\text{C}$  with the mentioned heating rates.

## 2.3 Pyrolysis experiments

The pyrolysis experiments were performed in a fixed-bed reactor under nitrogen as an inert gas, mainly including a pyrolysis furnace, an electrical controller, a cooling system, a liquid collector, and a gas collection system. The cylindrical reactor is made of SS 316 (I.D 100 mm, height 320 mm, and 7 mm thickness) and heated by three parallel electrical heaters each of 2 kW, and was well insulated with glass wool. The top of the reactor is openable from where feed was entered and sealed during experiment. After the experiment the same top was opened to remove char. The bottom of the reactor was fitted with a silica frit through which nitrogen was passed and acted as a support to the reactor. The reactor was initially charged with 200 gm of the material and purged for 20 min with nitrogen removing any oxygen. After that the temperature of the reactor was raised as per the heating rate required up to 500  $^{\circ}\text{C}$ . As the temperature rose, the vapors of the feed evolved and collected in a glass condenser attached with a chiller which maintained running water at  $2 \pm 1$   $^{\circ}\text{C}$ . Non-condensable gases were collected in a PTFE balloon for further composition analysis through GC.

## 2.4 Sample analysis

The produced liquid was collected and analyzed using Thermo Scientific TSQ 8000 Gas Chromatograph - Mass Spectrometer. The MS element of the system consists of a Triple Quadrupole paired with a TRACE 1300 GC and an auto-sampler for automated sample processing. Helium was used as the carrier gas at a constant flow rate of 1.5  $\text{ml}/\text{min}$  through a 15 m long, 0.25 mm i.d., and 0.25 mm thick film (SQC). Peaks were scanned in the  $m/z$  range from 40 to 650 with an ionizing voltage of 70 eV and an emission current of 350 A of electron ionization (EI). Furthermore, probable functional groups of the co-pyrolyzed oil were determined by FTIR (Fourier Transform Infrared Spectroscopy) analysis on Perkin Elmer - Spectrum RX-IFTIR with a resolution set at  $1\text{ cm}^{-1}$  and the spectral region at  $600\text{--}4000\text{ cm}^{-1}$ . Additionally, gas samples were analysed in gas chromatography on model Shimadzu GC- 2014.

# 3. Results And Discussion

## 3.1 TGA results

Figure 1 shows the Thermogravimetric (TGA) and Derivative Thermogravimetric (DTG) curves for all three samples at three different heating rates of 5, 10, and 15 $^{\circ}\text{C}/\text{min}$ . A very slow and initial weight loss of up to 180 $^{\circ}\text{C}$  temperatures in PCB was observed because of the release of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{HBr}$  (Lin & Chiang, 2014) and in the CS

sample it was a result of moisture loss associated with depolymerization and vitrification transition (Leroy et al., 2010; Ranzi et al., 2008). The main pyrolysis process begins at around 180–200 °C temperature range and nearly at 577 °C temperature the devolatilization ceases to act for all three samples, which indicates the char generation and carbonization stage (Quan et al., 2013; Aboulkas & Harfi, 2008; Leroy et al., 2010; Chen et al., 2018). As can be seen in Table 1, CS has higher volatile material and lower ash content that favours the production of a large amount of pyrolysis oil upon condensation as it has an advantage of high reactivity which results in lesser yields of char and more condensable gases as oil. Moreover, CS tends to have high moisture content than PCB, the mixture will contribute to the reduction of water content in the pyrolysis oil, which consecutively helps to increase HHV.

It is also worth to be noted that the residue of PCB which is collected as char at the end of the process is relatively very high (50–60 %) while using PCB:CS (1:1) composition char was decreased to 16–27 %. Moreover, when compared to the degradation patterns of PCB and CS; the degradation profiles of mixed samples initiated at a lower temperature.

Table 1  
Proximate and ultimate analysis of samples.

Sample	HCV Cal/gm	LOD (%)	Proximate Analysis			Ultimate Analysis			
			Ash (%)	Volatile Material (%)	Fixed C (%)	C (%)	H (%)	N (%)	S (%)
PCB	1415	14.05	43.95	41.87	0.13	26.73	2.39	1.93	0.19
CS	2319	23.93	5.49	70.51	0.07	32.52	4.12	2.15	0.16
PCB:CS (1:1)	2279	12	23.73	64.2	0.07	29.76	5.45	2.86	0.148

The appearance of the shoulder in the DTG curve may be due to the degradation of the hemicellulose and lignin in the CS sample and attributed to the decomposition of tetra-bromo-bisphenol-A in the PCB sample (Quan et al., 2012; Kim et al., 2013; Chen et al., 2018). Whereas, a continuous slow degradation in CS and mixture may correspond to the slow decomposition of lignin (Mailto et al., 2018; Dhaundiyal et al., 2018; Mankhand et al., 2012).

For the PCB sample, this slow degradation is due to the rupture of ether bonds in brominated resin into bisphenol A, propyl alcohol, tetra-bromo-bisphenol-A, and small phenolic molecules (Islam et al., 2018). The total weight loss at the end of 700 °C were 42–50, 94–95, 73–84 (wt %) for PCB, CS and PCB:CS (1:1), respectively. The total weight loss in CS was higher due to higher volatile matter and lower ash content, as shown in Table 1. From the same table, one can also observe that there is a higher H/C ratio for PCB:CS (0.183) in comparison to PCB (0.089) and CS (0.126). This could be the reason for the higher calorific value.

### 3.2 FTIR result discussion

The analysis of oil was done to see resultant functional groups in produced co-pyrolysis oil. A typical spectral output for co-pyrolyzed oil is shown in Fig. 3. The large absorbance peak of O–H stretching vibration of 3315 cm<sup>-1</sup> characterizes the alcohols and phenols in the pyrolysis liquid. It could also be related to H<sub>2</sub>O release. The asymmetric C–H stretching vibrations of aliphatic bonding to the aromatic ring are attributed to the absorption

band at  $2965\text{ cm}^{-1}$  (Pütün et al., 2005). The presence of ketones and aldehydes is indicated by the presence of C=O absorbance peaks in the frequency range  $1601\text{--}1700\text{ cm}^{-1}$ . The stretching of carbon-carbon bonds in benzene rings created two wave bands at  $1601$  and  $1506\text{ cm}^{-1}$  (Quan et al., 2012). The medium narrow absorbance peaks of C-C vibrations of  $1449$  and  $1374\text{ cm}^{-1}$ , respectively, indicate the methyl and dimethyl groups (Ali et al., 2015). Alcohols, carboxylic acids, ethers, and esters were represented by the potential absorbance peak of C-O of wave number  $1112\text{--}1374\text{ cm}^{-1}$ . An absorbance peak with a wavenumber of  $749\text{--}878\text{ cm}^{-1}$  are indication for the presence of aromatic chemicals. Furthermore, the peak at  $2731$  and  $2865$  could be the reason of presence of HBr indicated that the cleavages of the C(phenyl)-Br is taken place (Quan et al., 2012).

### 3.3 Pyrolysis experimental results

As per TGA analysis, the optimum temperature for producing maximum oil was in the range of  $300\text{--}500^\circ\text{C}$ . Above  $500^\circ\text{C}$  the operation reduces liquid and char production and provides an increased amount of gas, several studies have explored the same effect (Madhu et al., 2018; Mankhand et al., 2012). This reduced liquid and char at higher temperatures and could be the reason of the secondary reaction for the liquid fraction of the volatiles and further decomposition of the char particles. However, lowering the temperature below  $300^\circ\text{C}$  may cause incomplete decomposition of the biomass (Quan et al., 2012).

As the pyrolysis reaction progresses while increasing temperature, vapours generated were cooled with chilled water in a condenser and collected as oil. Non-condensable gases were collected as gas product and the residue remaining after the completion of pyrolysis reactions were received as char. The yield of these three products were calculated based on feed by weight. The density of oil from three different samples were found to be  $1.2$ ,  $0.98$  and  $1.02\text{ gm/ml}$  for PCB, CS and PCB:CS (1:1), respectively. The yield of different components with reference to the % fraction of generated oil, gas, and char is shown in Fig. 2 (b). As demonstrated, the amount of oil was increased significantly with co-pyrolysis of PCB:CS (1:1) to  $27.5\text{ wt \%}$  while  $19.6\text{ wt \%}$  was obtained for PCB.

PCB generated oil is dark brown in colour compared to CS alone. As shown in Fig. 2 (a), light colour of CS could be the reason of higher water content, which leads to low energy density, corrosivity, and chemical instability, also high oxygen content makes it difficult to blend with fossil fuels. Whereas, blending it with PCB helps lower water content. A number of studies evidenced that a sufficient amount of water can have a positive effect to use it as fuel, like reduced viscosity, reduced pollutant emissions, which contributes to a micro explosion of droplets in combustion and increased oxidation (Lu et al., 2009; Zhang et al., 2007). Furthermore, solid particles in CS oil makes phase separation difficult due to the presence of lignin which makes solids adsorbed with it and generates gummy tars whereas, during the co-pyrolysis event, radical interaction can enhance the development of a stable pyrolysis oil that avoids phase separation (Lu et al., 2009; Oasmaa & Czernik, 1999; Oasmaa et al., 2005; Brebu & Spiridon, 2012).

### 3.4 Liquid analysis

The collected oil was analysed in GC - MS and the chromatograms for all three samples are presented in Fig. 4. Various hydrocarbons present in the oil of three samples are shown on peaks of the spectrum. In the first 20 minutes of GC/MS spectra acquisition, more than 25 distinct aromatic compounds were discovered in each sample. The components were identified with an increase in retention time. The compounds that had an area % of more than 0.1 are discussed here. The area % of the peak for a compound was correlated with the percentage of that compound in the oil. The liquid analysis performed in a GC-MS showed that the main products of the pyrolysis

of PCB were fragments of polycarbonate epoxy resin. Table 2 shows all the detected compounds in PCB, CS, and PCB:CS (1:1) listed from higher to the lower area %.

A large difference in product distribution can be observed for PCB, CS and PCB:CS (1:1) samples for phenol and phenolic compounds like, phenol, 2-methyl,phenol, 4-methyl,Phenol, phenol,3,4-dimethyl-, phenol,3-(1-methylethyl), Phenol, 2-ethyl, Phenol, 3,4,5-trimethyl-, Phenol, m-tert-butyl-, phenol, 3-ethyl and P-isopropenylphenol.

Phenol present in PCB by area % was 38.47 which is in accordance with literature. A number of studies have examined PCB oil components and different results found for phenol which varies from 10–40% due to compositional and pyrolysis parameter difference (Hall & Williams, 2007b)(Ng et al., 2014), whereas (Quan et al., 2010) has pyrolyzed PCB up to 600 °C and found phenol as a most dominant compound (58.58%).

Figure 5 (a) reveals that there is an increase in phenol from 38.47 % to 54.83 % when co-pyrolysis was done with PCB. Other phenolic compounds were present in PCB, CS and PCB: CS (1:1) as 22.47, 4.09 and 21.99 % area, respectively, so total of 60.94, 25.94, 76.82 % area Phenol and phenolic compounds are present in PCB, CS and PCB:CS (1:1) which also shows highest in co-pyrolysis mixture. This result is true in accordance that the addition of polycarbonate in the pyrolysis of biomass can increase the phenol compounds in the oil where bisphenol A present in PCB is a poly carbonate which has enhanced the amount of phenol during co-pyrolysis with CS (Brebú & Spiridon, 2012). It's also worth noting that the high amount of phenolic compounds in CS, may be originated from the decomposition of lignin, and can help to enhance phenolic concentration in PCB:CS (1:1).

Furthermore, Naphthalene and other polycyclic aromatic hydrocarbons (PAHs) has the highest concentration in PCB, like Naphthalene, 2-methyl, anthracene, naphthalene, 2-ethenyl, acenaphthylene, fluorene, fluoranthene, Pyrene, 4H-Cyclopenta[def]phenanthrene with others listed in Table 2, having total 13.92 % area covered, with carbon ranges from C10-C18. In contrast, CS sample contains aliphatic hydrocarbons only, ranging from C3-C8.

Whereas, Co-pyrolysis includes Naphthalene as well naphthalene,2-ethenyl, acenaphthylene, fluorene, anthracene and fluoranthene as major PAHs having 3.64 % area of total. As overall PCB compounds include hydrocarbons ranging from C6 to C12, Whereas CS and the mixture includes components with C6-C18 and C6-C25, respectively, with the highest molecular weight 453. 5 of 3-Bromobenzoic acid, octadecyl ester ( $C_{25}H_{41}BrO_2$ ) in the mixture, but with a very small amount. Heat deterioration is the consequence of a number of competing breakdown events which shows complex behaviour of the reaction mechanism.

Additionally, Tetrabromobisphenol-A (TBBA) is the most widely used fire retardants in PCB, and degradation of this compound in presence of oxygen release brominated dibenzodioxines and furans, but as evidenced by the GC/MS results listed in Table 2, pyrolysis of PCB products do not contain PBDD/Fs because the de-hydrogen or de-hydroxyl radicals is difficult to happen in this reductive environment (W. Liu et al., 2013) also, at higher temperatures, brominated materials undergo debromination and additional deterioration, inhibiting the production of PBDD/Fs.

Furthermore, at the retention time of 22.53, triphenyl phosphate was observed which is a phosphorous based fire retardant. The phosphate based flame retardants are mostly found in thermoplastics, hence their presence in PCB pyrolysis oil is most likely attributable to the pyrolysis of plastic components attached to the printed circuit boards (Hall & Williams, 2007a). Some authors presented TBBA degradation mechanism and release of brominated compounds in their research (Grause et al., 2008; W. J. Liu et al., 2013; Kim et al., 2013). Moreover, Furans are highly toxic components and they are present in PCB oil in the form of Benzofuran, 2-isopropenyl-3-methyl-, Dibenzofuran, and 2(5H)-furanone, 3-hydroxy-4,5-dimethyl- (total of 1.44 % area) but their quantity decreased to

0.78 % area with co-pyrolysis, see Table 2. This is also evidenced by some researchers (W. J. Liu et al., 2013; W. Liu et al., 2013; Lu et al., 2009) that lower temperatures of pyrolysis, say up to 500 °C, the amount of furans decreases. In actual with co-pyrolysis, amount of Benzofuran in oil sample is relatively decreased but could not be diminished totally. Overall, 98.25 % area of the PCB pyrolysis oil, 99.47 % area of the CS pyrolysis oil, and 96.17 % area of the PCB:CS (1:1) pyrolysis oil in total were identified.

### **3.5 Gas Analysis**

From GC analysis of collected gas, it was observed that there were two peaks indicating a significant amount of O<sub>2</sub> and CH<sub>4</sub> gas in all three samples, and a small amount of CO and CO<sub>2</sub> were also observed at the initial stages of pyrolysis. From Fig. 5 (b), it can be seen that the PCB gas sample had a higher amount of O<sub>2</sub> and a lower amount of CH<sub>4</sub> in comparison to CS and the mixture. However, a lower amount of methane and oxygen similar to CS sample were obtained.

Table 2  
Compounds detected by GC-MS for PCB, CS and PCB:CS (1:1) samples

PCB		CS		PCB: CS (1:1)	
Area %	Compounds	Area %	Compounds	Area %	Compounds
38.47	Phenol	27.72	Guanidine, N,N-dimethyl	54.83	Phenol
7.95	Styrene	21.85	Phenol	6.17	phenol, 3-(1-methylethyl)
5.66	4-methyl, Phenol	12.82	N-cyano-2-methylpyrrolidine	5.04	2-methyl, phenol
5.07	2-methyl, phenol	8.71	2-cyclopenten-1-one, 3,5,5-trimethyl	4.46	1,6:2,3-Dianhydro-4-O-acetyl-beta-d-gulopyranose
4.6	1h-pyrrolo[2,3-b]pyridine,1-methyl-	5.44	2-pentanone, 4-hydroxy-4-methyl	3.77	4-methyl, Phenol
4.31	phenol, 3-(1-methylethyl)	3.73	2-methyl, phenol	2.47	Thiourea, ethyl
4.01	Naphthalene	2.25	2-acetyl-2-methyl-succinonitrile	2.36	phenol, 2,3-dimethyl
3.83	P-Xylene	2.19	2-cyclopenten-1-one, 3-methyl	1.89	Naphthalene
2.94	P-isopropenylphenol	1.62	1-Methoxy-1,3-cyclohexadiene	1.88	Cyclohexanol, 3,3-dimethyl-
2.54	phenol, 3,4-dimethyl-	1.54	Acetic formic anhydride	1.62	phenol, 3,4-dimethyl-
1.59	1,2-Benzenedicarbonitrile	1.32	Pyridine, 2,3-dimethyl-	1.31	P-isopropenylphenol
1.4	phenol, 3-ethyl	1.32	9-Undecenal, 2,10-dimethyl-	0.98	5',6',7',8'-Tetrahydro-2'-acetonephthone
1.32	Benzene,1-ethynyl-4-methyl	1.27	3,4-Dihydro-1-methylpyrrolo[1,2-a]pyrazine	0.89	5-Methyloxazolidine
1.06	Naphthalene, 2-methyl-	1.16	7-Hydroxy-6-methyloct-3-enoic acid	0.88	Phenol, m-tert-butyl-
1	Anthracene	1.14	Cyclohexanol, 3-(acetyloxymethyl)-2,2,4-trimethyl-	0.81	1-Heptanol, 6-methyl-
0.99	3-Hydroxybiphenyl	1.07	Pentadecanoic acid, 14-methyl-, methyl ester	0.54	Phenol, 3,4,5-trimethyl-
0.86	1-Naphthalenol, 5,8-dihydro-	1.02	2-Octanol, 2-methyl-6-methylene-	0.51	Heptanoic acid, 6-oxo-
0.86	naphthalene, 2-ethenyl	0.71	8-Methyl-6-nonenamide	0.42	Benzofuran, 2-isopropenyl-3-methyl-

PCB		CS		PCB: CS (1:1)	
0.83	Dibenzofuran	0.43	Bis(tridecyl) phthalate	0.42	9,10-Ethanoanthracene, 9,10-dihydro-11,12-diacetyl-
0.8	N-(1-Cyanovinyl)benzamide	0.41	Eicosane, 9-cyclohexyl-	0.4	Fluorene
0.63	2-Propenal, 2-methyl-3-phenyl-	0.36	phenol, 3,4-dimethyl-	0.36	Dibenzofuran
0.56	5',6',7',8'-Tetrahydro-2'-acetone	0.32	2-Azidomethyl-1,3,3-trimethyl-cyclohexene	0.32	1,4-Bis(1'-hydroxycyclopentyl)-1,3-butadiyne
0.45	Cyclotetrasiloxane, octamethyl-	0.3	5,8-Decadien-2-one, 5,9-dimethyl-, (E)-	0.31	naphthalene, 2-ethenyl
0.42	Acenaphthylene	0.28	Pyrazine, 2,5-dimethyl-3-(1-propenyl)-, (E)-	0.3	Phenol, 2-ethyl
0.42	Fluorene	0.27	Z-8-methyl-9-tetradecenoic acid	0.28	Carbonic acid, heptyl phenyl ester
0.39	Benzofuran, 2-isopropenyl-3-methyl-	0.22	1,4-Dioxanyl hydroperoxide	0.28	10,12-Octadecadiynoic acid
0.29	Naphthalene, 2,3-dimethyl-			0.28	Pentadecanoic acid, 14-methyl-, methyl ester
0.29	4H-Cyclopenta[def]phenanthrene			0.25	4,5-di-epi-aristolochene
0.28	Phenol, 2-ethyl			0.23	Anthracene
0.28	9H-Xanthene			0.23	Pentadecanenitrile
0.27	Methanone, (2-methylphenyl)phenyl-			0.22	Ethanone, 1-(2,3-dihydro-1H-inden-5-yl)-
0.27	4-Cyclohepta-2,4,6-trienyl-phenol			0.2	6-Hydroxyhexan-2-one
0.25	Cyclopentasiloxane, decamethyl			0.2	Triphenyl phosphate
0.24	Fluoranthene			0.18	Cyclotetrasiloxane, octamethyl-
0.23	Benzoic acid, 2(cyanomethyl), methyl ester			0.17	Carbamic acid, phenyl ester
0.23	Naphthalene, 2-phenyl-			0.16	Methanone, (2-methylphenyl)phenyl-
0.22	2(5H)-furanone, 3-hydroxy-4,5-dimethyl-			0.13	Fluoranthene
0.21	9H-Fluoren-9-ol			0.12	Acenaphthylene
0.19	1,1'-Biphenyl, 4-methyl-			0.12	3-Bromobenzoic acid, octadecyl ester

PCB	CS	PCB: CS (1:1)	
0.19	1H-Indene, 1-(phenylmethylene)-	0.1	cyclopentasiloxane, decamethyl
0.19	Triphenyl phosphate	0.08	Ethanone, 2-(benzoyloxy)-1-[1,1'-biphenyl]-4-yl-
0.18	Phenanthrene, 4-methyl-		
0.17	Pyrene		

## 4. Implications Of The Products Obtained Through Pyrolysis

The uses of bio-oils are well known and can be found in the literature (Mohan et al., 2006; Xu et al., 2011; Hasan et al., 2017) and contribute to a high-quality fuel oil production or can be used to extract high value chemical compounds. As discussed with composition of oil by GC-MS a major concentration of PCB and CS sample oil was of phenol and phenolic compounds, and the concentration increased with co-pyrolysis. Therefore, it may be a good source for phenol and phenolic compounds. Phenol can also be used as a raw material to produce binder through crosslinking reactions.

Furthermore, to use this oil as a fuel in industrial burners, furnaces, and boilers, its fuel characteristics, like thermal stability, calorific value, viscosity, and acidity need to be monitored. Hydrodeoxygenation (HDO) reaction can also be used to increase the fuel property by removing oxygen (Panchasara & Ashwath, 2021; Xu et al., 2011). Although, some attempts have been made to address this issue, it is still very expensive since external hydrogen is needed in the engine and a metal oxide catalyst is added in the process. Moreover, pyrolyzed oils should be checked for water content, viscosity, and coking tendency, as this property makes them difficult to atomize, resulting in incomplete combustion and higher emissions (Sánchez-Borrego et al., 2021). Several new strategies are proposed like the addition of methanol or ethanol as polar solvents to improve some of the oil's problematic features, such as calorific value and volatility which reduces viscosity and acidity of the resulting fuel (Raje, 2020). However, in this work, fuel characteristics and improvement methods are not discussed as the main purpose was to find the product distribution of all three samples.

## 5. Conclusion

It can be concluded from the results that the TGA degradation profiles of PCB:CS samples were initiated at a lower temperature when compared with PCB and CS degradation profiles. The synergistic effect of mass loss can be seen in mixture of PCB:CS (1:1).

By experiment on lab-scale pyrolysis equipment, it was observed that PCB individually produced less amount of oil compared to CS and the mixture of PCB:CS. Whereas, the addition of CS had improved the yield of oil which was the main objective of the work. On the other hand, after characterization of oil by GC/MS, it was found that there were more oxygenated compounds like phenols and other aromatics in the oil produced for PCB:CS mixture compared to PCB and CS alone. It is due to high amount of phenolic compounds originated from decomposition of lignin in CS facilitated increasing phenolic compounds in the mixture. Moreover, the analysis of gas by GC indicating a significant amount of O<sub>2</sub> and CH<sub>4</sub> gas in all three samples. The co-pyrolysis of PCB:CS has been done

as per authors knowledge in literature first time and the products received were completely different than any other co-pyrolysis of PCB with other biomass.

## Declarations

Ethical Approval

Not applicableConsent to Participate

Not applicableConsent to Publish

Authors give their consent for publication.Authors Contributions

Sonalben B Prajapati has contributed in analyzing, interpreting and investigating the experimental data, also writing- original draft. Shina Gautam and Alok Gautam was funding acquisition and a major contributor in writing- review and editing the manuscript. All authors read and approved the final version of the manuscript.Funding

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The authors declare that they have no competing interests.

Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

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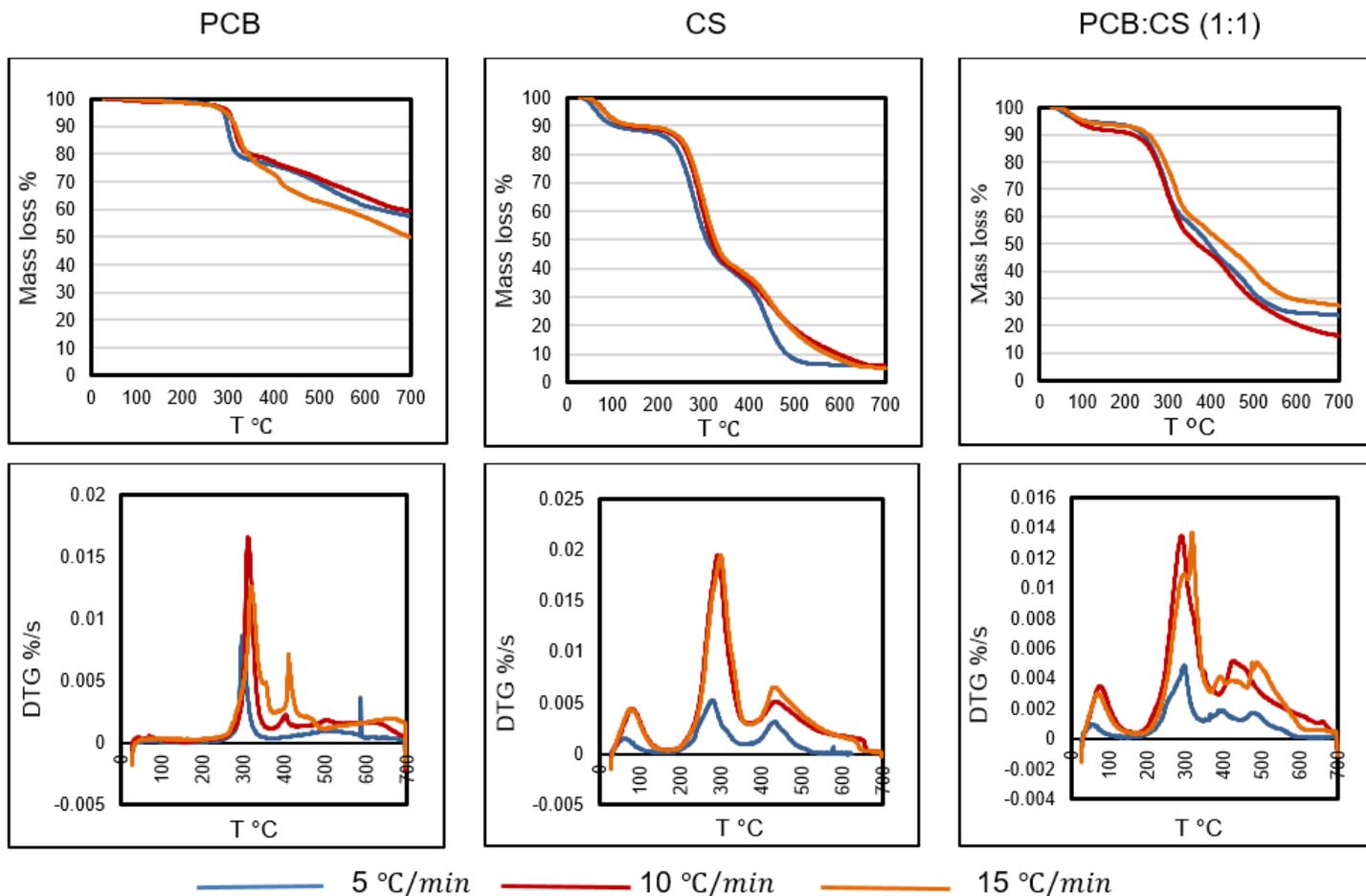
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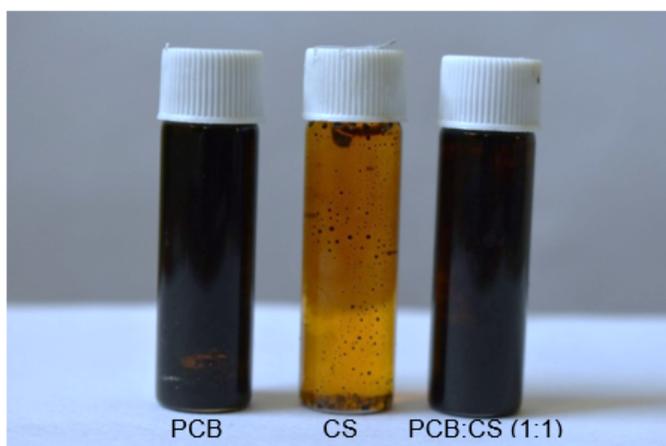
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## Figures

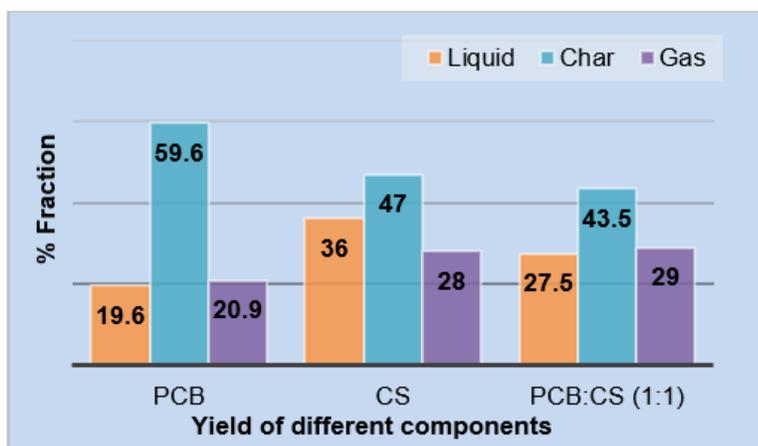


**Figure 1**

DTG as a function of temperature plots for the sample PCB, CS and PCB:CS (1:1) at heating rates of 5, 10 and 15 °C/min.



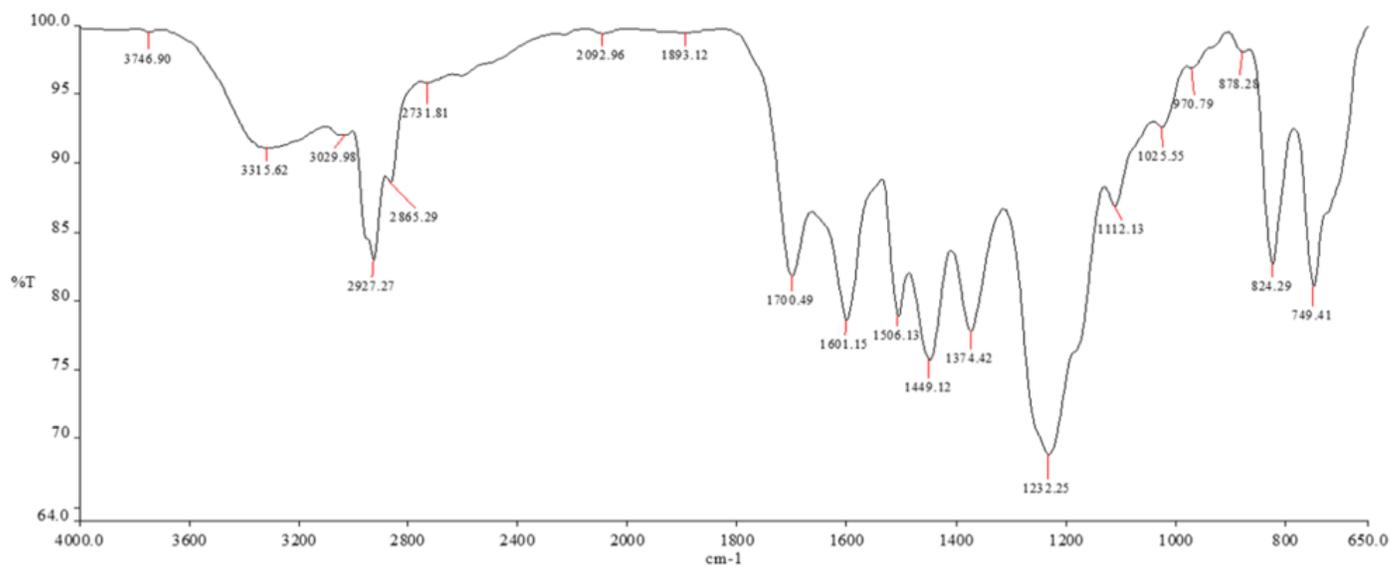
**(a)**



**(b)**

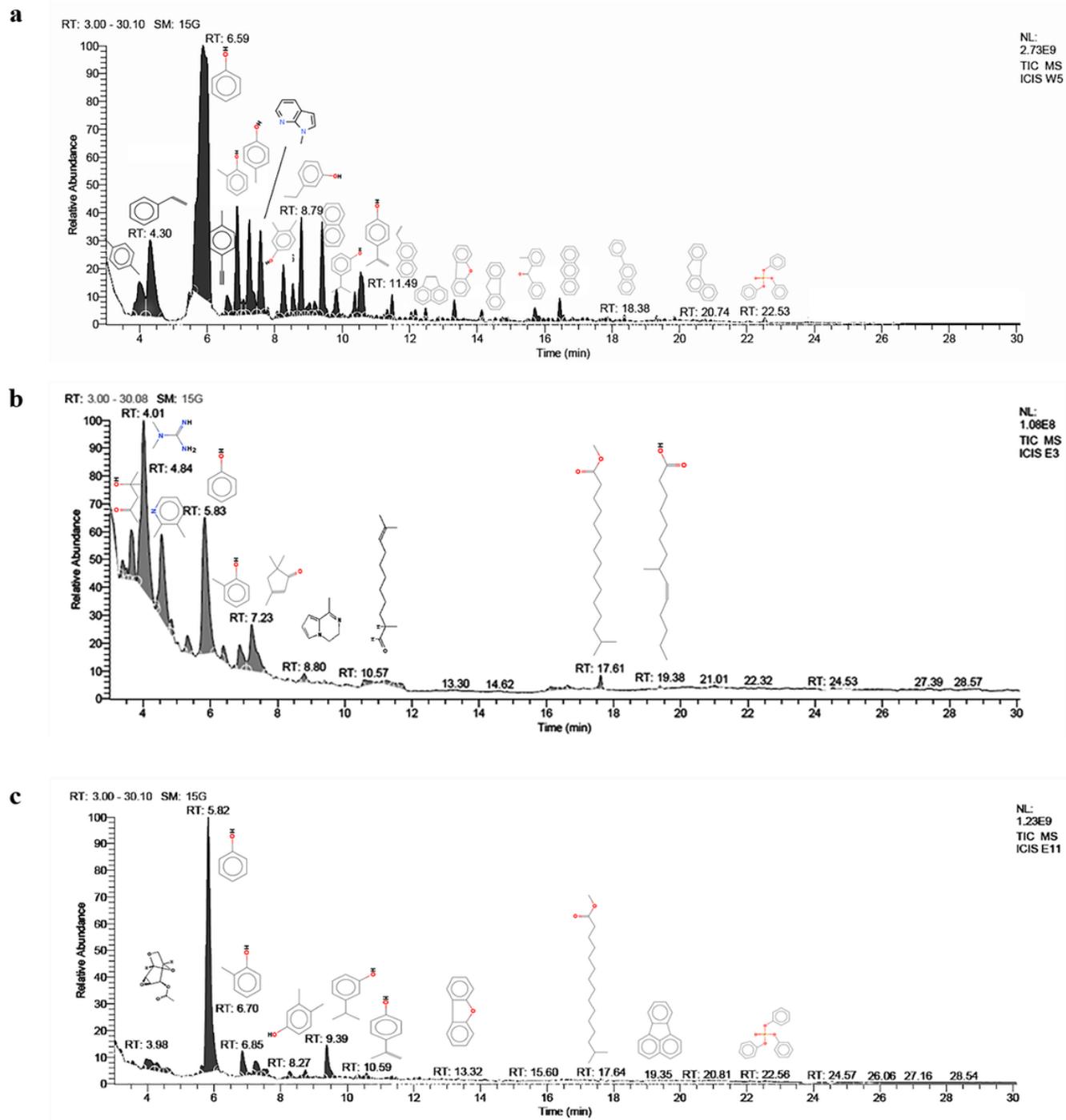
**Figure 2**

(a) Appearance of generated oil with different feedstock, (b) Different feedstock with generated amount of liquid oil, solid char and gas in percentage



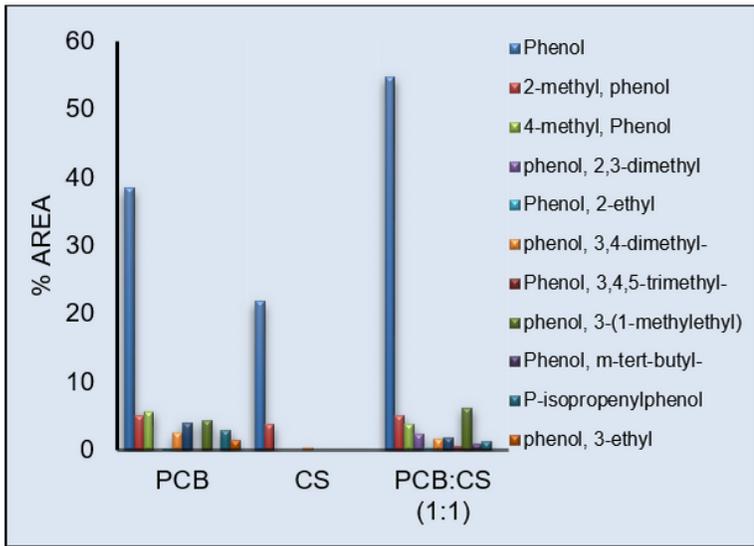
**Figure 3**

FTIR transmittance spectra of pyrolysis liquid PCB:CS (1:1)

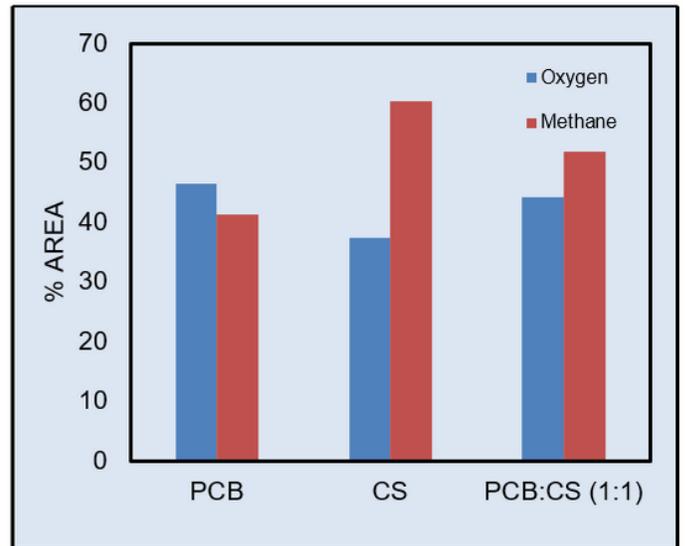


**Figure 4**

GC-MS chromatograms of oils collected during pyrolysis for the samples (a) PCB, (b) CS and (c) PCB:CS (1:1)



(a)



(b)

**Figure 5**

(a) Area % comparison of the major phenolic components presents in the PCB and PCB:CS (1:1) oils, (b) Quantitative comparison of generated gas.