

CATALYTIC PYROLYSIS OF METAL FREE PCBs WITH ZSM-5 AND Ca(OH)₂

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Presence of heavier molecules and toxic brominated compounds in pyrolysis products of printed circuit boards (PCB) make their use difficult. In the present work to overcome this problem PCBs were pyrolyzed in presence of catalysts such as ZSM-5 and Ca(OH)₂ to study their effect on pyrolysis products. The comparison of non-catalytic pyrolysis of PCB was done with oil and gas compositions produced by both techniques. Pyrolysis experiments were done at a lab scale set-up. However, the increased concentrations of ZSM-5 were found to increase char and gases were found to be rich in CH₄ and O₂. The composition of oils was mainly composed of phenols, phenol derivatives and aromatic compounds, which increased with pyrolysis with ZSM-5 and Ca(OH)₂. Ca(OH)₂ was found effective in removing brominated compounds from oil and no halogens were observed in oil. Char produced during pyrolysis was mesoporous in nature and composed of some fractions of metals and glass fibers.

Keywords: catalytic pyrolysis, PCBs, ZSM-5, Ca(OH)₂, fuels

1. INTRODUCTION

The use of electrical and electronic equipment is increasing worldwide day by day. Aggressive research and competition in market is reducing cost and increasing availability of such equipment every day. Average life of such equipment is decreasing which is creating a large amount of waste of electrical and electronic equipment (WEEE) at a very high rate. WEEE accounted for 5% of municipal solid waste in 1997 and it rose to 10% in 2020 (de Marco et al., 2008). It showed annual growth of 7% from 2007 to 2012 (Hense et al., 2015). India is the second largest country in the world in terms of population and industrial growth. Hence, India has witnessed rapid growth in the use of electrical equipment and ultimately in rapid generation of WEEE in the last few years. WEEE recycling is one of the major concerns in India. About 95 % of WEEE recycling operations in India are managed by informal and unorganized institutes and people (Awasthi et al., 2016).

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Printed circuit boards (PCBs) are backbone of computers and telecommunication equipment. PCBs constitute a very complex combination of metals, plastics, and glass fibers. Such properties of PCBs make them very difficult to recycle (Hall and Williams, 2007). Some PCBs contain halogenated compounds as fire retardants, which may release toxic brominated compounds when combusted (Duan et al., 2012; Hao et al., 2014; Moltó et al., 2011; [23]Ortuño et al., 2014). Like other WEEEs, PCBs are conventionally recycled for metal recovery and the remaining part is either combusted or landfilled. Such practice poses hazard of seriously polluting air, soil and ground water (Kim et al., 2017; Moltó et al., 2011). PCBs are composed of about 30 to 40 % of hydrocarbon rich plastic and recycling to separate energy and metals is quite difficult using conventional methods. It can be pyrolyzed to produce fuel oils and gases from its plastic part (Barontini et al., 2005; Kim et al., 2015). However, the presence of toxic brominated compounds and compounds with high molecular weight in pyrolysis oils and gases makes their direct use as fuels highly challenging.

In previous studies efforts have been made to remove halogenated compounds from pyrolysis products of PCBs. Different catalysts such as tri-iron tetroxide sorbent (Li et al., 2014), activated Al_2O_3 (Wang et al., 2015) natural clays (Park et al., 2019), CaCO_3 (Gao et al., 2018; Qin et al., 2020; Sun et al., 2011b) were utilized. Some researchers worked on pyrolysis of brominated acrylonitrile butadiene styrene using calcium based additives such as CaO , $\text{Ca}(\text{OH})_2$ and oyster shells (Jung et al., 2012). Calcium based additives are easily available, cheap and have proven to be very efficient in removing halogens from pyrolysis oils and gases. Some researchers have used catalysts like ZSM-5, HY and biochar and e-waste char for reforming oils and gases from PCB pyrolysis (Areeprasert and Khaobang, 2018; Kim et al., 2017; Ng et al., 2014).

In this work, pyrolysis of PCBs with and without the use of catalysts such as ZSM-5 and $\text{Ca}(\text{OH})_2$ has been studied. ZSM-5 was used for its crystal structure, physicochemical properties and chemical composition with unique characteristics which promote selective bond cleavage and hydrocracking reactions (Kim et al., 2017; Ng et al., 2014). Ca-based catalysts are proven to be very effective at binding and removing halides generated during thermal treatments of waste (Jung et al., 2012). The products of pyrolysis such as oil, gas and char were characterized by GC-MS, GC, EDX and BET to identify the effect of catalyst on composition of oil, gas and char with non-catalytic pyrolysis products.

2. EXPERIMENTAL

2.1. Materials and experimental set-up

Samples of metal free PCBs were obtained from Shiwalik Solid waste management (Chandigarh, India) after physically separation of metals. The PCBs were crushed by grinding in a hammer mill up to a size of 100-300 microns and metals were separated based on density on a vibrating table. This metal free, shredded PCB were used for all experiments. Laboratory grade ZSM-5 and $\text{Ca}(\text{OH})_2$ were received from Merck and were of analytical quality. A cylindrical shell equipped with other peripheral equipment such as electrical heater, nitrogen system, series of condensers, brine chiller and systems for oils and gases collections were used for all pyrolysis experiments as shown in Figure 1.

2.2. Experimental run and product analysis

In a typical experiment run, a mixture of feed and catalyst was kept inside pyrolyser and sealed. Nitrogen was purged for 15 minutes to completely remove oxygen from the system. After inertising the system, temperature was raised up to desired level for different experiments at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ and maintained there for desired time for different reactions. Vapors coming out of pyrolyser were condensed

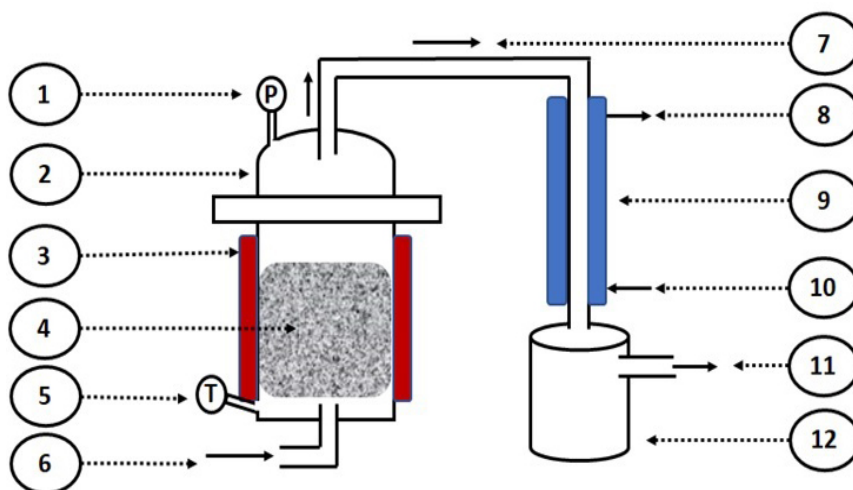


Fig. 1. Pyrolysis set-up: 1) pressure gauge, 2) pyrolyser, 3) electrical heater, 4) feed bed, 5) temperature sensor, 6) nitrogen entry, 7) vapours leaving pyrolyser, 8) chilled water outlet, 9) condenser, 10) chilled water inlet, 11) gases collection, 12) oil collection

in a condenser with running chilled brine of 3 to 4 °C and collected as oil products. Non-condensable gases were collected as gas product. Solids remaining in pyrolyser were collected as char at the end of each experiment. Three sets of catalyst i) ZSM-5, ii) $\text{Ca}(\text{OH})_2$ and iii) mixture of ZSM-5 and $\text{Ca}(\text{OH})_2$ in equal proportion were used for catalytic experiments. Catalytic experiments were conducted by maintaining pyrolysis temperature of 500 °C, reaction time of 1 hour and by varying catalyst concentrations as 1%, 5% and 10% of feed on weight basis. Experiments on PCB pyrolysis without catalyst were conducted with varying time.

Oil samples were analysed using Thermo Scientific TSQ 8000 Gas Chromatograph – Mass Spectrometer. Gas samples were analysed using Shimadzu GC-2014. Char samples were analysed using Brunauer–Emmet–Teller (BET), Field Emission Scanning Electron Microscope (FESEM) and X-ray energy dispersive system spectroscopy (EDS) techniques.

3. RESULTS AND DISCUSSION

3.1. DTG curves of non-catalytic and catalytic pyrolysis

In the first part of experiments, thermogravimetric study was conducted to understand degradation mechanism of PCBs in presence and absence of different catalysts. DTG curves for catalytic and non-catalytic experiments are shown in Figure 2. As observed in DTG curves, degradation reaction started at temperature of around 240 °C with first maximum degradation peaks at 300 °C. Similar observations are also available in the literature (Alenezi and Al-Fadhli, 2018; Evangelopoulos et al., 2015; Gao et al., 2020; Hao et al., 2014; Kim et al., 2013; Rajagopal et al., 2017; Sun et al., 2012; Xiong et al., 2020). It can be seen from Fig. 2 that maximum degradation peak did not shift for any catalyst, indicating initiation of the reaction is independent of the catalyst. Intensity of maximum degradation peak was lower for catalytic experiments when compared with non-catalytic pyrolysis of PCB. Another difference can be noted that non-catalytic pyrolysis showed only one peak beyond 350 °C while multiple peaks were observed for catalytic experiments. However, as temperature progressed degradation became non-significant beyond 600 °C (Liu et al., 2019). Thus, maximum temperature of 600 °C was considered for pyrolysis experiments.

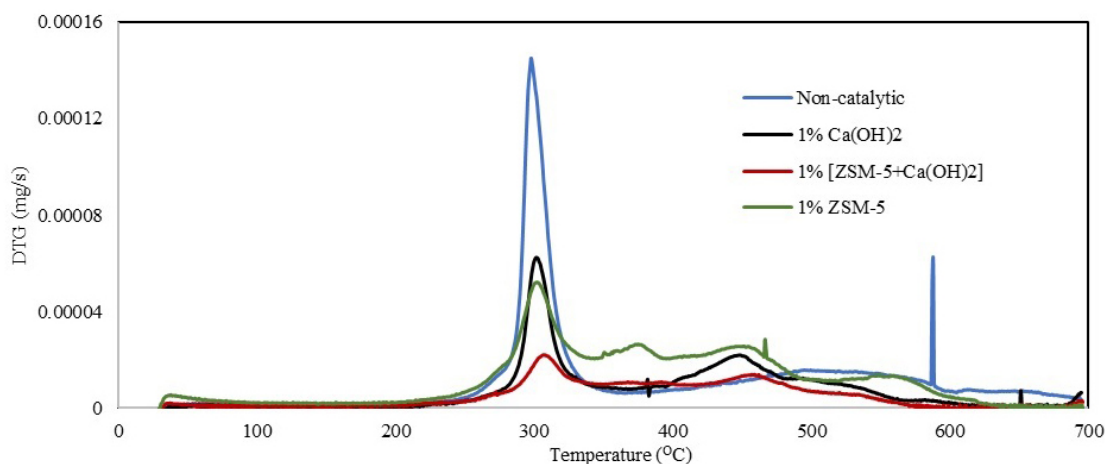


Fig. 2. DTG curves for catalytic and non-catalytic reactions

3.2. Non-catalytic and catalytic pyrolysis experiment results

Yields of different pyrolysis products for varying reaction time for non-catalytic experiments of PCB are shown in Figure 3(a). At constant temperature of 400 °C, as the time of reaction increased, the recovery of oil increased up to 4 hrs and decreased if time of reaction was further increased. It suggests that maximum degradation occurred in 4 hr and beyond that PCB hydrocarbons were not cracking into smaller molecules and there may also be the possibility that some of the evolved gases got condensed in the reactor at the later stage and did not come out as gas or oil products. It can also be confirmed from the DTG curve that 500 °C is an optimum temperature for completing PCB pyrolysis, Figure 2. Maximum combined yield of oil and gas was 40%. These observations are in concurrence with a previous work (Jie et al., 2008).

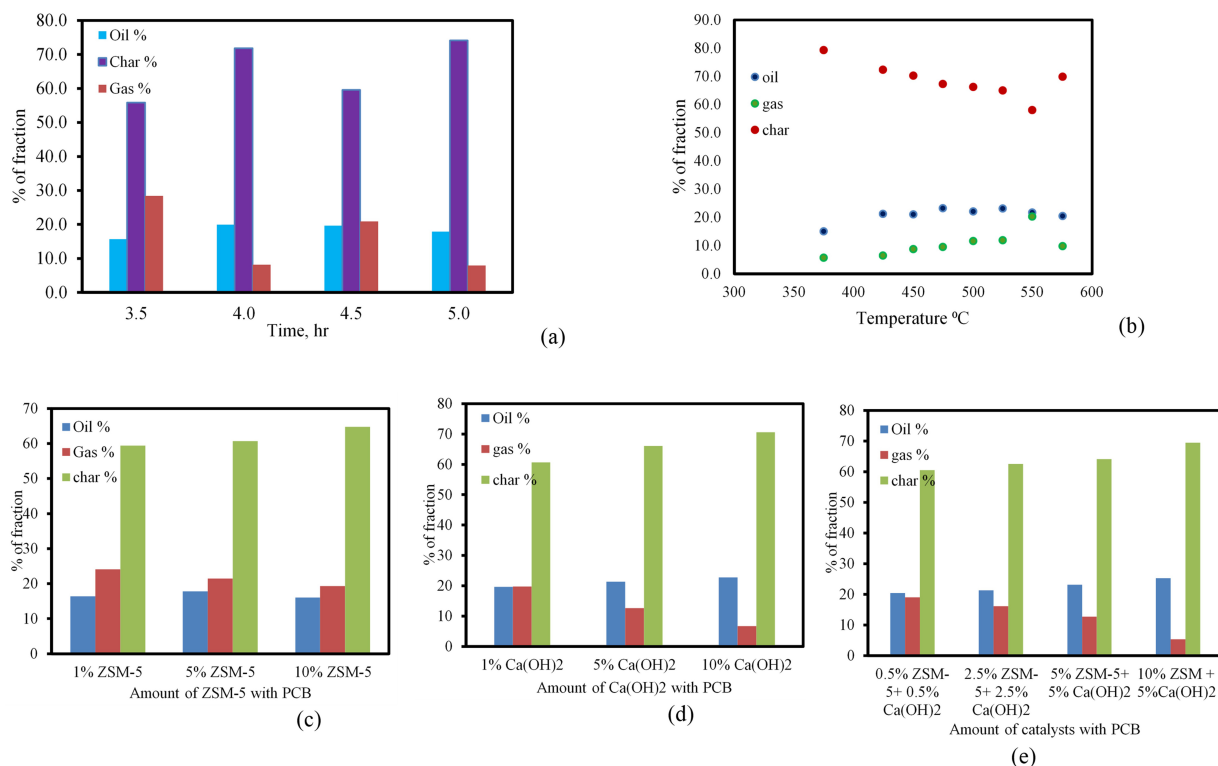


Fig. 3. Experimental results of catalytic and non-catalytic pyrolysis to produce oil, gas and char: (a) pyrolysis of PCB at varying time, (b) pyrolysis of PCB with 10% $\text{Ca}(\text{OH})_2$ with varying temperature, (c) pyrolysis of PCB with different fraction of ZSM-5, (d) pyrolysis of PCB with different fractions of $\text{Ca}(\text{OH})_2$, (e) pyrolysis of PCB with different compositions of ZSM-5 and $\text{Ca}(\text{OH})_2$

Further experiments were conducted with different compositions of catalysts. Yield of different pyrolysis products of PCB at varying temperature with 10% Ca(OH)₂ are shown in Figure 3(b). The pyrolysis reactions at varying temperature with Ca(OH)₂ were conducted to confirm the behavior of pyrolysis with catalyst and it was observed that the temperature range was similar as of non-catalytic pyrolysis of PCB. However, the oil and gas were yielded more than the non-catalytic pyrolysis. During pyrolysis experiments, the first vapours observed between 200 to 220 °C which were hazy white and non-condensable.

These vapours were supposed to be low volatiles such as methane and water. In the feed some oxygen may be present which after heating at this temperature breaks down and evolves as oxygen (Evangelopoulos et al., 2015). As the temperature rose to 300–310 °C, vapour colour changed to brown. These vapours were condensable and were collected as oil. It can also be seen in DTG curve that mass loss starts after 300 °C and the same behaviour is also followed in experiments (Rajagopal et al., 2017; Xiong et al., 2020). This observation was confirmed for both catalytic and non-catalytic pyrolysis which indicates that PCB sample starts to degrade at this temperature. The plastic in PCB sample is thermosetting which has tendency to sublime as it gets thermal energy and hence catalysts placed in solid-solid contact with feed do not affect initiation of reaction (Kim et al., 2017). After reaching the temperature of 420 to 440 °C, brown fumes begin to diminish and finally disappear. As the temperature is increased further again white hazy fumes begin to appear which are non condensable and more volatile at secondary or tertiary reactions where char begins to appear for final degradation of feed. Beyond 480 °C, all vapours stop and no further fumes are observed. This shows the completion of pyrolysis reaction for the experiments.

Figure 3(c) shows the yield of various products for pyrolysis with ZSM-5. Combined oil and gas yield of non-catalytic pyrolysis justifies the fact that plastic content in metal free PCBs is around 40% (Ortuño et al., 2014; Williams, 2010; Zhao et al., 2017). Char yield for lower concentrations of catalysts was similar to that of non-catalytic experiment. As concentrations of ZSM-5 were increased, char yield also increased. In case of experiment with ZSM-5, even though overall degradation was reduced with concentration, ratio of gas to oil yield was higher than that of non-catalyst experiment. It indicates that actual gas yield was increased and it is attributed to secondary degradation reactions which takes place inside catalyst pores to promote isomerization and produce light molecular weight and gaseous products (Kim et al., 2017).

In contrast, increased char yield suggests incomplete degradation which is the consequence of inefficient heat transfer inside the feed bed. The presence of catalysts increases surface diffusion resistance which leads to limitations in heat transfer (Sun et al., 2011a; Zhao et al., 2017). Figure 3(d) shows the yield of pyrolysis products of PCB with varying concentrations of Ca(OH)₂, ratio of gas to oil yield was significantly lower than that of non-catalytic pyrolysis. It is a combined effect of heat transfer limitations due to the presence of Ca(OH)₂ and suppression of secondary degradation reaction due to absence of catalytic pores and acidic sites. Figure 3(e) shows the pyrolysis products of PCB with a mixture of both catalyst at varying concentrations. It is revealed in Figure 3(e) that char, oil and gas yields were intermediate to that of both catalysts individual yield.

3.3. Oil composition analysis with GC-MS

Chromatograms from GC-MS analysis are presented in Figure 4. Components were identified by comparing mass spectrum of the component with that of standard mass spectrums from library. As reported in previous work, during thermal degradation, epoxy resins in PCBs rupture into bisphenol A and tetrabromobisphenol A. The bisphenol A's further undergoes degradation to form phenols, phenols derivatives and other small molecules (Rajagopal et al., 2017; Shin et al., 2019; Xiong et al., 2020). In the present oil samples phenolic and aromatic compounds were found to possess a major fraction of oil. Table 1 shows detailed compounds of the oils from PCB and PCB with different catalysts. It can be observed that oil produced from catalytic experiment had higher phenol content than non-catalytic experiment (Kim et al.,

2013; Long et al., 2010; Quan et al., 2010). Pores of ZSM-5 effectively trap larger molecules during pyrolysis reaction and it has higher selectivity towards aromatics where smaller molecules break down higher molecular weight compounds into lower molecular weight compounds (Kim et al., 2017). This explains increased phenol content in oil. However, catalytic pyrolysis with $\text{Ca}(\text{OH})_2$ produced a similar composition as non-catalytic pyrolysis but it increased other aromatic compounds than phenolic compounds. Halogen content in pyrolysis oil was much lower than what is reported in literature. Halogens tend to escape in the environment from PCBs during mechanical processing as weak bonds of halogens break down due to localized heating.

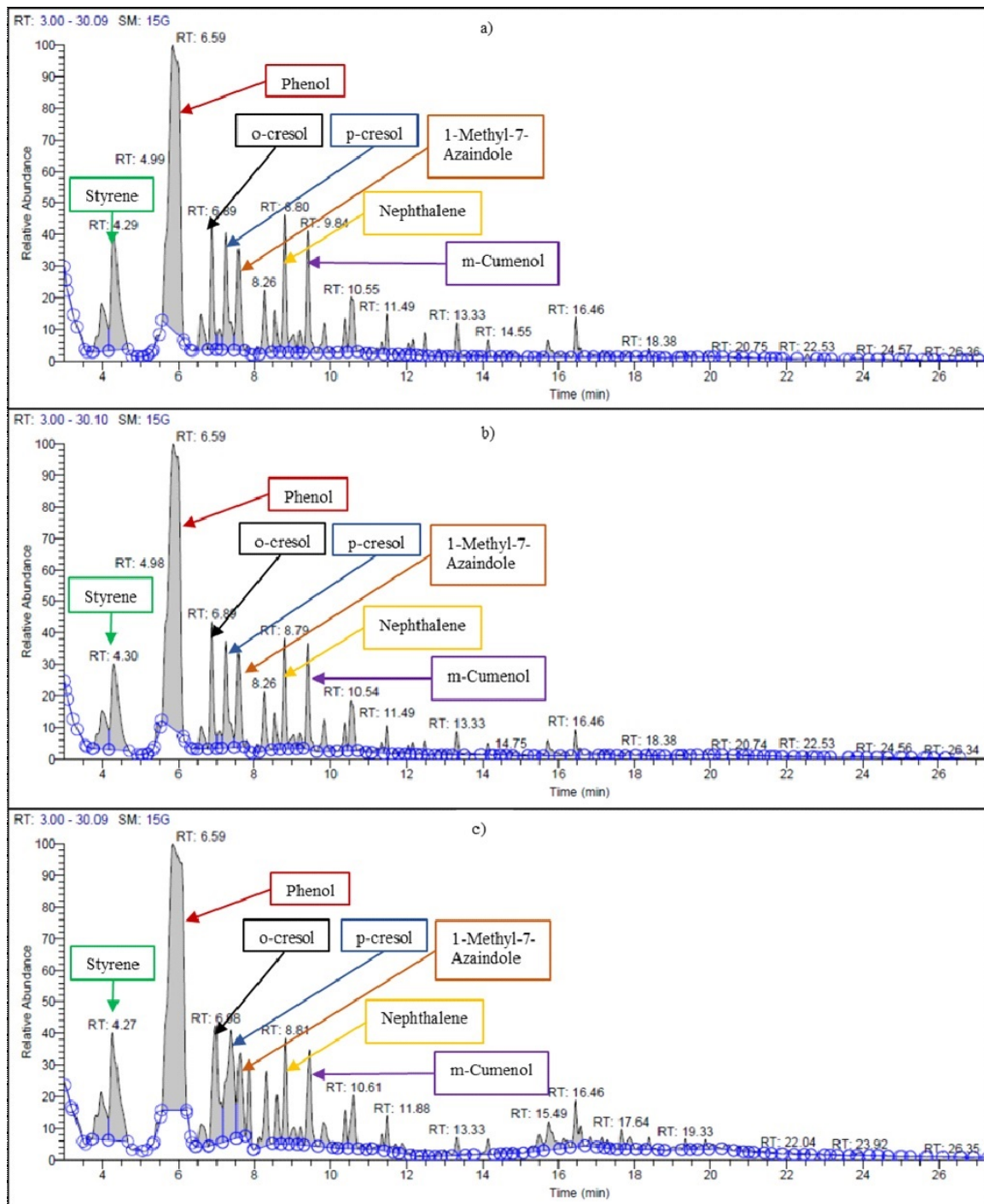


Fig. 4. GCMS chromatogram for oil from a) Non-catalytic pyrolysis of PCB, b) PCB with 10% ZSM-5 and c) PCB with 10% $\text{Ca}(\text{OH})_2$ pyrolysis experiment (Sun et al., 2011b). As these PCBs were mechanically processed, such release of halogens can explain lower halogen content in oils. $\text{Ca}(\text{OH})_2$ was effective in removing halogenated compounds from pyrolysis oil

Table 1. Composition of oil with and without catalyst analysed by GC-MS

RT	Compound name	Molecular formula	Mol. weight (g/mol)	Peak intensity (% area)		
				Non-catalytic	ZSM-5	Ca(OH) ₂
5.87	Phenol	C ₆ H ₆ O	94.11	33.96	38.47	33.53
4.3	Styrene	C ₈ H ₈	104.15	9.91	7.95	7.67
7.25	p-cresol	C ₇ H ₈ O	108.14	5.55	5.66	7.82
8.79	Naphthalene	C ₁₀ H ₈	128.17	4.75	4.01	3
6.89	o-cresol	C ₇ H ₈ O	108.14	4.6	5.07	6.58
9.41	m-Cumenol	C ₉ H ₁₂ O	136.19	4.57	4.31	3.76
7.58	1-Methyl-7-Azaindole	C ₈ H ₈ N ₂	132.16	4.49	4.6	3.63
3.98	p-Xylene	C ₈ H ₁₀	106.17	4	3.83	3.5
10.54	4-isopropenylphenol	C ₉ H ₁₀ O	134.18	2.94	2.94	2.16
8.26	phenol, 3,4-dimethyl-	C ₈ H ₁₀ O	122.16	2.49	2.54	2.77
6.59	4-Ethynyltoluene	C ₉ H ₈	116.16	1.89	1.32	1.32
8.54	3-ethylphenol	C ₈ H ₁₀ O	122.16	1.45	1.4	1.37
16.46	Anthracene	C ₁₄ H ₁₀	178.23	1.34	1	1.75
9.83	Phthalonitrile	C ₈ H ₄ N ₂	128.13	1.32	1.59	1.29
11.49	2-vinylnaphthalene	C ₁₂ H ₁₀	154.21	1.11	0.86	0.95
13.33	Dibenzofuran	C ₁₂ H ₈ O	168.19	1.08	0.83	0.57
10.38	β-Methylnaphthalene	C ₁₁ H ₁₀	142.20	1.07	1.06	1.09
15.71	p-Xenol	C ₁₂ H ₁₀ O	170.21	1.04	0.99	1.72
9.03	5,8-Dihydro-1-naphthol	C ₁₀ H ₁₀ O	146.19	1	0.86	0.79
7.08	N-(1-Cyanovinyl) benzamide	C ₁₀ H ₆ CINO ₂	207.61	0.86	0.8	nd*
9.18	2-Propenal, 2-methyl-3-phenyl-	C ₁₀ H ₁₀ O	146.19	0.85	0.63	0.5
12.48	Acenaphthylene	C ₁₂ H ₈	152.19	0.62	0.42	0.17
11.34	6-Acetyl tetralin	C ₁₂ H ₁₄ O	174.24	0.55	0.56	0.52
14.14	Fluorene	C ₁₃ H ₁₀	166.22	0.55	0.42	0.52
12.18	Benzofuran, 2-isopropenyl-3-methyl-	C ₁₂ H ₁₂ O	172.22	0.48	0.39	0.17
12.05	Naphthalene, 2,3-dimethyl-	C ₁₂ H ₁₂	156.22	0.35	0.29	nd*
17.14	1H-Indene, 1-(phenylmethylene)-	C ₁₆ H ₁₂	204.27	0.32	0.19	0.34

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Table 1 [cont.]

RT	Compound name	Molecular formula	Mol. weight (g/mol)	Peak intensity (% area)		
				Non-catalytic	ZSM-5	Ca(OH) ₂
17.87	Methylenephenanthrene	C ₁₅ H ₁₀	190.24	0.32	0.29	0.57
16.12	Methanone, (2-methylphenyl)phenyl-	C ₁₄ H ₁₂ O	196.24	0.27	0.27	0.49
18.38	β-Phenylnaphthalene	C ₁₆ H ₁₂	204.27	0.26	0.23	0.37
14.75	9H-Fluoren-9-ol	C ₁₃ H ₁₀ O	182.22	0.23	0.21	0.18
19.32	Fluoranthene	C ₁₆ H ₁₀	202.25	0.23	0.24	0.35
8.07	2-ethylphenol	C ₈ H ₁₀ O	122.16	0.22	0.28	nd*
17.64	Phenanthrene, 4-methyl-	C ₁₅ H ₁₂	192.25	0.21	0.18	0.57
13.62	Methyl 2-(cyanomethyl) benzoate	C ₁₀ H ₉ NO ₂	175.18	0.2	0.23	0.08
15.49	9H-Fluorene, 4-methyl-	C ₁₄ H ₁₂	180.24	0.19	0.16	0.74
10.86	5-bromo-2-fluorobenzonitrile	C ₇ H ₃ BrFN	200.01	0.18	0.16	nd*
11.88	Naphthalene, 1,7-dimethyl	C ₁₂ H ₁₂	156.22	0.17	0.1	0.48
14.55	2-Hydroxyfluorene	C ₁₃ H ₁₀ O	182.22	0.17	0.14	0.14
19.85	Pyrene	C ₁₆ H ₁₀	202.25	0.17	0.17	0.41
16.83	4-Cyclohepta-2,4,6-trienyl-phenol	C ₁₃ H ₁₂ O	184.23	0.16	0.27	0.36
7.8	N(Trifluoroacetyl) N,O,O',O''tetrakis (trimethylsilyl) norepinephrine	C ₂₂ H ₄₂ F ₃ NO ₄ Si ₄	553.90	0.13	0.25	nd*

nd* = not detected

3.4. Gas composition

Gas samples were collected from experimental setup during temperature range of 330 to 400 °C for all experiments. During analysis, standards of CH₄, CO₂, CO and O₂ were used. In Figure 5 it is visible that samples had only methane and oxygen. CO₂ and CO were not present in gas samples. It is contrary to previous work, where CO and CO₂ were also part of gas composition (Hall and Williams, 2007; Long et al., 2010). However, in some studies oxygen was detected in pyrolysis gases (Jie et al., 2008). The possible reason for this observation is the temperature range in which gas samples were collected. In the temperature range of 300 to 400 °C, epoxy resins rupture into bisphenol A and tetrabispheol A. These bisphenols further degrade to form phenols and phenol derivatives and the non-condensable gases like methane and oxygen which was released during cracking reactions were found in the gas samples (Rajagopal et al.,

2017; Shin et al., 2019; Xiong et al., 2020). Some other unidentified compounds were also present in gases in a very low quantity. The gas samples were collected at the same time.

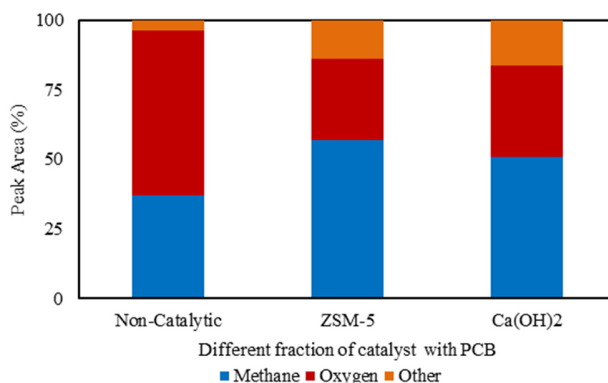


Fig. 5. Effect of catalyst on PCB pyrolysis in generation of non-condensable gas composition

It was observed that methane composition increased while oxygen composition decreased for both catalytic pyrolysis. In the case of experiment with ZSM-5, it was understood from the experimental results that ZSM-5 promoted hydrocracking reactions. This characteristic of ZSM-5 has helped in increasing methane concentration in gas and phenol concentration in oil. As phenol yield increased, some oxygen molecules were transferred to oil which in turn reduced the number of oxygen molecules that were released in gas. This explains reduction of oxygen yield in gas. In the case of pyrolysis of PCB with $\text{Ca}(\text{OH})_2$, oxygen was also utilized by aromatic compounds which are higher in this pyrolysis as suggested by oil analysis by GC-MS. Halides were not detected in gas sample; this could be due to the limitations of analytical method or release of volatile halides during mechanical processing of PCBs while removing metals.

3.5. Char analysis

Char is a product which has the highest yield in pyrolysis reactions from PCB yet very less explored for its composition and applications in literature. Char from non-catalytic experiment was analysed using techniques such as Brunauer–Emmet–Teller (BET) method, Field Emission Scanning Electron Microscope (FESEM) and X-ray Energy Dispersive Spectrometry (EDS). EDS Spectrum and FESEM image are shown in Figure 6. EDS spectrum suggests that char was composed of metals like Fe, Ca, Si, Al etc. As 30% weight fraction of PCBs is made up of metal, it is possible that some metals may still remain in PCBs

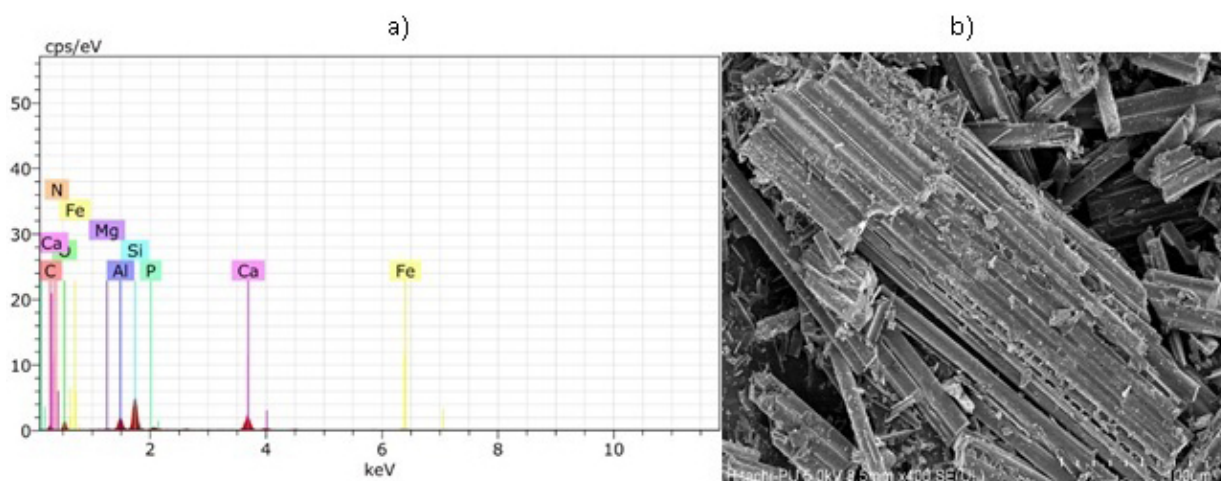


Fig. 6. a) EDS spectrum and b) FESEM image of char from non-catalytic pyrolysis of PCB

even after mechanical processing and these metals became part of char. This may be due to the presence of multi-layer PCB boards and it is sometimes difficult to remove metals in between layers. Glass fibre is another most abundant material in char which constitutes around 30% of PCBs. FESEM image in Figure 6(b) at 100 μm magnification shows the presence of glass fibres coated with coke in char. Coke generated during pyrolysis reactions gets deposited on glass fibres and becomes part of char. Some studies have focused on combustion of char from pyrolysis to remove coke and separate glass fibres for its reuse (Quan et al., 2010). From BET study average pore diameter, surface area and total pore volume was found to be 3.458 nm, 2.575 m^2/g and 0.005 cm^3/g respectively. Char was found to be meso-porous in nature.

4. CONCLUSIONS

The paper describes the difference of catalytic and non-catalytic pyrolysis of PCB. It was found that ZSM-5 and $\text{Ca}(\text{OH})_2$ were effective catalysts for pyrolysis of PCBs. With catalyst the fraction of oil was increased, and the composition of phenol and its derivatives were also found in higher quantity than in non-catalytic pyrolysis. The pyrolysis reactions were in agreement of temperature range with DTG curve of different fractions of PCB and catalysts. Gases were mainly composed of methane and oxygen. CO, CO_2 and halogenated compounds were not observed in pyrolysis gases. ZSM-5 was found to increase gas yield and reduce oil yield due to cracking of further hydrocarbons which could not happen in non-catalytic pyrolysis. $\text{Ca}(\text{OH})_2$ was observed to suppress secondary degradation reaction due to heat transfer limitations and absence of catalytic pores. It was effective in removing halogenated compounds from pyrolysis oil. Although char was found to contain some metals and glass fibres, it was meso-porous in nature.

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