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Effect of Zeolite Catalysts on Pyrolysis Liquid Oil

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Abstract

The aim of this study was to determine the quality and applications of liquid oil produced by catalytic pyrolysis of polystyrene (PS) plastic waste in comparison to thermal pyrolysis, using a small pilot scale pyrolysis reactor. Thermal pyrolysis produced maximum liquid oil (80.8%) with gases (13%) and char (6.2%), while catalytic pyrolysis using synthetic and natural zeolite decreased the liquid oil yield (52%) with an increase in gases (17.7%) and char (30.1%) production. The lower yield but improved quality of liquid oil through catalytic pyrolysis are due to catalytic features such as microporous structure and high BET surface area. The liquid oils, both from thermal and catalytic pyrolysis consist of around 99% aromatic hydrocarbons, as further confirmed by GC-MS results. FT-IR analysis showed chemical bonding and functional groups of mostly aromatic hydrocarbons, which is consistent with GC-MS results. The produced liquid oils are suitable for energy generation and heating purposes after the removal of acid, solid residues and contaminants. Further upgrading of liquid oil or blending with diesel is required for its use as a transport fuel.

Keywords: Energy; Natural zeolites; Pyrolysis oil; Polystyrene (PS); Thermal pyrolysis; Catalytic pyrolysis

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LIST OF ACRONYMS AND ABBREVIATIONS

AD: Anaerobic digestion

BET: Brunauere-Emmete-Teller

Btu: British thermal units

EDS: Energy dispersive spectrometer

FT-IR: Fourier transform infrared spectroscopy

GC-MS: Gas chromatography-mass spectrophotometry

GHG: Greenhouse gases

HDPE: High density polyethylene

HHV: Higher heating values

HR-TEM: Higher resolution transmission electron microscopy

ICP: Inductively coupled plasma

KSA: Kingdom of Saudi Arabia

LCA: life cycle assessments

LDPE: Low density polyethylene

MSW: Municipal solid waste

O₂: Oxygen

PE: Polyethylene

PP: Polypropylene

PS: Polystyrene

PTF: Plastic-to-fuel

RDF: Refuse derived fuel

SAED: Selected area electron diffraction

SCAPE: School of Chemical and Process Engineering

SEM: Scanning electron microscopy

WTE: Waste-to-energy

XRF: X-ray fluorescence

1. Introduction

The recent volatility in crude oil prices, shortages and unsustainable future supply, along with environmental pollution generated especially by greenhouse gas emissions (GHG), all support the development of alternatives to petroleum (Gardy et al., 2014; Demirbas et al., 2016). Treaties like the Kyoto Protocol and Agenda 21 are also forcing fossil fuel-based economies towards renewable energy-based economies (Ouda et al., 2016). Renewable energy sources like wind, solar, geothermal, waste-to-energy (WTE), and biomass are attracting significant attention to bridge the ever-increasing energy demand and supply gap (Lam et al., 2016). Technological advancements, and cost effective techniques along with governmental incentives are further increasing the growth of renewable energy sector (Nizami et al., 2016a, b; Rathore et al., 2016).

The pyrolysis of plastic waste has emerged as an effective WTE technology (Table 1) as a solution for plastic waste management and to generate energy (liquid oil) and value-added

79 products (char and gases) (Sharma et al., 2014). The pyrolysis process involves thermal and
80 catalytic cracking of complex organic molecules into smaller molecules or short chain
81 hydrocarbons (Demirbas et al., 2015a; Kartal et al., 2011). The overall process mechanism is
82 complicated but mainly involves four steps: initiation, transfer, decomposition and termination
83 (Faravelli et al., 2001). Computer simulation studies consider hundreds of possible reactions
84 happening during the thermal cracking of substrate (Zhang et al., 2015). The process depends
85 on a series of factors including temperature, residence time, heating rates, feedstock
86 composition, presence of moisture or toxic elements and the use and types of catalysts
87 (Miskolczi et al., 2009, Miandad et al., 2016a, d, e). Similarly, a wide range of reactors are
88 employed e.g. fixed bed reactor, tube reactor, rotary kiln reactor and batch, semi-batch and
89 pyrex batch pyrolysis reactors (Syamsiro et al., 2014).

90

91 In catalytic pyrolysis, the plastic waste is depolymerized into an improved liquid oil at lower
92 temperature (~400 °C) in comparison to thermal pyrolysis, which is carried out in absence of
93 catalyst at higher temperature (~500 °C) (Miandad et al., 2016b). The liquid oil of thermal
94 pyrolysis is often unstable, low-grade, acid-corrosive, tarry and discoloured (Al-Salem et al.,
95 2009; Hernandez et al., 2007). While the catalytic pyrolysis although decreases the liquid oil
96 yield, but increases its quality (Table 2). The selection of catalyst in catalytic pyrolysis depends
97 on the desired products such as liquid oil, char and gases and their quality (Walendziewski et
98 al., 2001).

99

100 Polystyrene (PS), polyethylene (PE) and polypropylene (PP) are the most used plastic types in
101 pyrolysis studies (Miandad et al., 2016a, b). Zeaiteer (2014) obtained liquid oil from catalytic
102 pyrolysis of high density polyethylene (HDPE) waste using modified zeolites. The liquid oil
103 can be used in modified diesel engine vehicles after upgrading its gasoline range hydrocarbons
104 (C₄ - C₁₂) through refining and blending with conventional fuels. Furthermore, the liquid oil
105 can be used in heat generation and electricity production after removing the acid, solid residues,
106 and contaminants present in the oil (Demirbas et al., 2015a). The value-added products such as
107 styrene, benzene, toluene and other condensed aromatic hydrocarbons either cyclic or arenes
108 can also be obtained by distillation and refining process of liquid oil (Demirbas 2004;
109 Mohammed et al., 2015; Kobayashi et al., 2016).

110

111 In the Kingdom of Saudi Arabia (KSA) and in Gulf region, there exists no WTE facility to
112 convert the plastic waste into energy and value-added products. Similarly, the plastic waste and
113 natural zeolite have not been characterized for their potential role as an energy source and
114 catalyst in pyrolysis technology. This study aims to determine the quality of liquid oils
115 produced from thermal and catalytic pyrolysis using PS plastic waste in a small pilot scale
116 pyrolysis reactor. The effect of synthetic and natural zeolite catalysts were studied on the
117 fractions of liquid oils, gases and char in comparison to thermal pyrolysis. The quality of
118 produced liquid oil is evaluated based on its physico-chemical properties and energy contents.

119

120 *1.1. Energy demands and plastic waste management in KSA*

121

122 KSA is one of the world's largest energy consuming countries due to its rapid population
123 growth (around 3.4% per year), urbanization (around 1.5% per year) and a rise in living
124 standards resulting from high economic growth. In 2013, the total energy consumption in KSA
125 surpassed 9 quadrillion British thermal units (Btu) making the country one of the 12 largest
126 primary energy consumers in the world (Nizami et al., 2015a, b). Currently, around 55% of
127 KSA energy demands are satisfied by petroleum and the remaining 45% by natural gas. The
128 KSA government wants to generate about half of the country's energy (about 72 GW) from
129 renewable sources like nuclear (17.6 GW), solar (41 GW), wind (9 GW), geothermal (1 GW)
130 and WTE (3 GW) by 2032 (Nizami et al 2016b; Demirbas et al., 2015b). In the KSA, 15.3
131 million tons of municipal solid waste (MSW) was produced during 2014 (average 1.4
132 kg/capita/day) and it is estimated that figure will almost double to 30 million tons per year by
133 2033. Every year, around 6 million metric tons of plastic products are produced in KSA, and
134 thus it is the second largest waste stream of MSW (up to 17%) with total annual waste
135 generation of 2.7 million tons. All of the plastic waste, along with other MSW fractions, are
136 disposed in landfills or dumpsites. The plastic waste has detrimental environmental and
137 operational effects at landfill sites due to slow degradation rates and the presence of toxic dyes
138 and additives. Plastic waste is managed through different approaches, including reducing,
139 reusing, recycling and WTE. Conventional mechanical recycling techniques such as sorting,
140 grinding, washing and extrusion can recycle only 15-20% of all plastic waste. Beyond this
141 level, the plastics become contaminated with materials like soil, dirt, aluminium foil, food
142 waste and paper labels. Air and waterborne pollutants are emitted from uncontrolled plastic
143 combustion. In recent years, WTE technologies including gasification, pyrolysis, and refuse

144 derived fuel (RDF) and chemical recycling methods such as hydrolysis, methanolysis, and
145 glycolysis have been gaining significant attention.

146

147 **2. Material and methods**

148

149 ***2.1. Experimental setup***

150 A small pilot scale pyrolysis reactor has been designed and used for thermal cracking of plastic
151 waste into liquid oil, gases and char (Figure 1). The reactor is a closed system to operate in the
152 absence of O₂ and has a capacity to achieve up to 600 °C using desired heating rates. The
153 reactor is made of stainless steel and has a height of 360 mm with 310 mm diameter and a
154 capacity of 20 L (Table 3). There is also a pressure gauge connected with pyrolysis reactor to
155 monitor the pressure to switch off in case of excess pressure build-up. The system can work
156 both as a thermal or catalytic pyrolysis process. During the catalytic pyrolysis, the powder
157 catalyst was mixed with the feedstock in the pyrolysis reactor to study its effect on the final
158 products yield and quality. The sample was heated and melted in the reactor, producing organic
159 vapours. These vapours moved to a condenser unit and were converted into liquid oil by using
160 a chiller system attached to the condenser unit. ACDelco classic coolant was used in the chiller
161 to achieve maximum condensation of organic vapours for optimized liquid oil yields. The
162 condensed organic vapours (liquid oil) were collected from the oil collector assembly at the
163 bottom of the system. While the uncondensed products (gases) coming out from the same liquid
164 oil pipe were exhausted outside. The collected liquid oil was further analysed for its yield,
165 quality and potential applications.

166

167 ***2.2. Sample preparation and experimental scheme***

168 PS disposable plates were used as plastic waste and treated in the pyrolysis process to produce
169 liquid oil, gases and char. 1 kg of PS sample was used for each experiment, including thermal
170 pyrolysis, catalytic pyrolysis with natural zeolite and synthetic zeolite catalysts. 100 g of both
171 natural and synthetic zeolite catalysts were used, which gives the catalyst to feedstock ratio of
172 1:10. This ratio was fixed based on the recently published research (Ateş et al., 2005; Lopez et
173 al., 2011). The synthetic zeolite catalyst (ZEOLYST™ CBV 780 CY (1.6) Zeolite SDUSY
174 Extrudate) was purchased from Zeolyst International (Zeolyst, 2015) and used as received
175 without any further treatment. The chemical name of this synthetic zeolite catalyst is Zeolite
176 type SDUSY, hydrogen form, aluminium oxide and it has a specific gravity of greater than 1

177 with negligible solubility in water. The natural zeolite was extracted from the Harrat Ash-
178 Shamah area located in the northwest of KSA (Nizami et al., 2016a). The samples were
179 collected for research purpose without requiring any specific permission from Government or
180 any other agencies. It also confirm that the field studies did not involve endangered or protected
181 species. This catalyst was simply milled to micron sized particles and used without any other
182 pre-treatment or surface modification.

183

184 The raw material (PS plastic waste) was prepared by cutting the disposable plates into small
185 pieces to achieve sample homogeneity. Each sample was heated from room temperature to 450
186 °C using heating rate of 10 °C/min and the reaction time was fixed to 75 min. The fractions of
187 liquid oil, gases and char were estimated on their weight basis. The produced liquid oil was
188 further characterized to study the effect of thermal and catalytic pyrolysis under presence of
189 synthetic and natural zeolite catalysts. The optimum conditions of 450 °C and 75 min for non-
190 catalytic pyrolysis process was first determined by TGA (Mettler Toledo TGA/SDTA851)
191 analysis of the PS plastic sample under controlled conditions. The analysis was carried out by
192 heating 10 µg of PS sample at the rate of 10 °C per min from 25-900 °C under nitrogen flow
193 at a constant rate of 50 ml/min. The detailed experiments on effect of temperature and reaction
194 time on pyrolysis products and choosing optimum conditions as well as TGA results and
195 analysis have been published earlier by the authors (Miandad et al., 2016d).

196

197 ***2.3. Analytical characterization***

198 The characterization of natural zeolite was carried out at the School of Chemical and Process
199 Engineering (SCAPE), University of Leeds, UK and detailed results have been published
200 earlier by the authors (Nizami et al., 2016a). The Brunauere-Emmete-Teller (BET) surface
201 area, pore size and volume of natural zeolite catalyst were analysed by using Micromeritics
202 TriStar 3000 (UK) surface analyser and the experimental details are provided in earlier study
203 (Nizami et al., 2016a). The particle size and morphology distribution of natural zeolites was
204 examined by Hitachi scanning electron microscopy (SEM). The elemental analysis of natural
205 zeolite was carried out by energy dispersive spectrometer (EDS) attached with SEM. A
206 homogeneous suspension of sample was prepared by mixing zeolite powder in acetone using
207 ultrasonic bath. Few drops of this homogenous diluted sample was then added on SEM stubs
208 and the stubs were dried and transferred to a cleaning zone. UV-Ozone radiation unit was used
209 at pressure 1 Pa for 10 min to remove any possible contamination. The cleaned samples were

210 finally installed in SEM and images at different magnifications and EDS were collected for
211 detailed analysis. The produced liquid oils from thermal and catalytic pyrolysis with natural
212 and synthetic zeolite catalysts were further characterized by a number of analytical techniques.
213 The chemical structure and the functional groups present in PS plastic raw material and
214 produced liquid oil samples were studied by Fourier transform infrared spectroscopy (FT-IR),
215 Perkin Elmer's, UK. A minimum of 32 scans were performed at average signal of IR with a
216 resolution 4 cm^{-1} in the ranges of $500\text{-}4000\text{ cm}^{-1}$.

217

218 Gas chromatography coupled with mass spectrophotometry (GC-MS) of Hewlett-Packard HP
219 7890 was used to analyse the chemical composition of produced liquid oils by both thermal
220 and catalytic pyrolysis. The produced liquid oils were mixed with polar solvent
221 dichloromethane and injected to GC-MS for analysis. The GC-MS system used a 30 m long
222 with 0.25 mm diameter capillary column coated with 0.25 μm thick film of 5% phenyl-
223 methylpolysiloxane and worked with a 5975 quadrupole detector. The initial temperature of the
224 oven was kept at $50\text{ }^{\circ}\text{C}$ for 2 min and then increased to $290\text{ }^{\circ}\text{C}$ at the rate of $5\text{ }^{\circ}\text{C}$ per min at
225 holding rate of 10 min. The ion source and transfer line temperatures were kept at $230\text{ }^{\circ}\text{C}$ and
226 $300\text{ }^{\circ}\text{C}$ respectively. The GC-MS was operated in full scan mode between m/z 33-533 using
227 splitless injection function at $290\text{ }^{\circ}\text{C}$ and solvent interval of 3 min. The obtained peaks based
228 on their retention times were matched with standard compound peaks in NIST08s mass spectral
229 data library. The percentage fractions of different hydrocarbon and other compounds present
230 in the liquid oil samples were determined by total ion chromatogram peak areas using the
231 software. The energy contents, in terms of higher heating values (HHV) of the PS plastic raw
232 material and produced liquid oil, were analysed by bomb calorimeter (Parr 6200 Calorimeter,
233 US) based on the ASTM D 240 method.

234

235 The characteristics of pyrolysis liquid oils were determined by relevant techniques based on
236 standard ASTM methods. The viscosities of the liquid oil were measured by a Discovery
237 Hybrid Rheometer (HRI from TA instruments) with a 40 mm parallel plates geometry. A small
238 amount of the liquid oil sample was placed on the bottom horizontal plate. The upper 40 mm
239 plate was lowered at a controlled rate so that the sample was sandwiched between the two
240 plates. The temperature was set to $40\text{ }^{\circ}\text{C}$ and the shear rate range was set between 1-500 1/s.
241 The rheometer was first calibrated using viscosity standard liquid followed by actual liquid
242 viscosity measurements. Flash point of produced liquid oil was determined by Automatic

243 Pensky-Martens Closed Tester (Koehler, US) based on the ASTM D 93 method. For pour point,
244 AWD-12 Pour Point Tester was used with temperature of -10 °C for one tank (left tank) and
245 the temperature of -56 °C for other tank (right tank). The sample was poured in the sample tube
246 up to the mark. The sample was first put in the left tank till the temperature reduces to 0 °C and
247 then transferred to the tank on the right side. The sample tube was taken out periodically from
248 the tank after every 2 °C decrease in temperature to observe the flow by holding the tube
249 horizontally for 4 seconds. This process was continued until the pour point was reached. For
250 density measurement, a portable density meter (DMA 35 from Anton Paar) was used, which
251 was first calibrated with distilled water and then rinsed with acetone and allowed to dry
252 between each sample, before taking the next measurements.

253

254 **3. Results and discussion**

255

256 **3.1. Characteristics of KSA's natural zeolite**

257 The SEM images revealed that mostly spherical shaped particles were between 50-200 nm size-
258 range (Figure 2). However, some larger grains with irregular morphology were also observed
259 in 0.5-1 nm size range. The BET surface area, pore size and volume of natural zeolite were
260 found to be 4.3 m²/g, 18.7 Å and 0.02 cc/g respectively (Nizami et al., 2016a). The microporous
261 nature of zeolite plays a vital role in thermal cracking reactions by adsorbing selective larger
262 hydrocarbon chain molecules and other impurities to produce improved liquid oil. The surface
263 area and pore volume of the catalyst can be increased significantly by chemical treatment such
264 as acid leaching or thermal activation that will further enhance its catalytic functions
265 (Sriningsih et al., 2014). Similarly, the impurities present in natural zeolite catalyst can also be
266 removed by chemical or thermal treatment (Syamsiro et al., 2014). To study the in-depth
267 microporous structural features of natural zeolites, samples must be milled to below 100 nm
268 size range. Higher resolution transmission electron microscopy (HR-TEM) analysis can be
269 used to obtain detailed structural features including particle size, clear morphology,
270 crystallographic phases from HR-TEM images, atomic fringes, selected area electron
271 diffraction (SAED) and EDS analysis (Rehan et al., 2011, 2015). This would be the subject of
272 our future studies.

273

274 Natural zeolites are alumina-silicates complex structured minerals containing a number of earth
275 metals such as Na, Ca, K, Mg, and Fe (Nizami et al., 2016a). The energy dispersive spectra

276 (EDS) were taken from different regions of the SEM image, which showed some differences
277 in the weight percentage composition, and spectrum 4 is presented in figure 3. The weight
278 percentage of major components were found to be O (57.2%), Si (26.7%) and Al (7.0%). The
279 minor components included Na (2.2%), Mg (0.6%), S (0.4), K (2.7%), Ca (0.5%), Ti (0.2%)
280 and Fe (2.5%) (Figure 3). The elemental analysis of compounds like zeolites are generally
281 performed by SEM-EDS with enough degree of accuracy, however the results obtained do vary
282 from sample to sample. This is because the spectrum is taken from one single point that may
283 not always be a true representative of the whole sample. However, the most accurate
284 quantitative elemental analysis including all major and minor components including impurities
285 can be achieved by inductively coupled plasma (ICP) and X-ray fluorescence (XRF).

286

287 **3.2. Analysis of pyrolysis products yield**

288 Figure 4 and table 4 show the results for amounts of liquid oil, gases and char produced from
289 thermal and catalytic experiments. Thermal pyrolysis produced maximum liquid oil (80.8%)
290 with gases (13%) and char (6.2%), while catalytic pyrolysis decreased the liquid oil yields to
291 54% and 50% from natural zeolite and synthetic zeolite respectively. Natural zeolite having
292 BET surface area of 4.3 m²/g produced 54% liquid oil yield, while synthetic zeolite with surface
293 area of 780 m²/g produced 50% liquid oil yield. The char produced from catalytic pyrolysis,
294 32.8% with natural zeolite and 27.4% with synthetic zeolite, was higher than 6.2% from
295 thermal pyrolysis. Similarly, gases production was at a maximum with synthetic zeolite 22.6%
296 and 12.8% with natural zeolite as compared to 13% from thermal pyrolysis (Figure 4). Lopez
297 et al. (2012) and Syamsiro et al. (2014) also reported similar products yield trends that use of
298 the catalyst decreased overall liquid oil yield with an increase in char and gases production.

299

300 The lowest liquid oil yield and highest gas production in catalytic pyrolysis with synthetic
301 zeolite can be due to its microporous structure and high BET surface area (Figure 5). Seo et al.
302 (2003) also reported that use of microporous catalyst with high BET surface area will lead to
303 an increase in gas and decrease in liquid oil yields. The natural zeolite has lower BET surface
304 area and microporous structure as compared to synthetic zeolite, thus increasing the char
305 production. Lopez et al. (2011) reported the similar results by using ZSM-5 and red mud
306 catalysts having BET surface area of 412 m²/g and 27.1 m²/g respectively. Moreover, catalysts
307 with higher acidity increase the cracking process that also increases the gases production and
308 decreases liquid oil yield (Sriningsih et al., 2014). The synthetic catalyst used in the present

309 study was more acidic than natural zeolite, thus it increased the gases production with a
310 decrease in liquid oil (Figure 4 & 5).

311

312 **3.3. Analysis of pyrolysis liquid oil quality**

313 The chemical composition of PS plastic raw material and pyrolysis liquid oils were studied by
314 using FT-IR spectra and are drawn on the same graph (Figure 6). This technique identifies the
315 chemical bonds in a molecule by producing an infrared absorption spectrum, leading to
316 identification of functional groups. Many clear peaks were generated, ranging from 697-3070
317 cm^{-1} . The FT-IR spectra for all three pyrolytic liquid oils are very similar for peak positions
318 except for minor differences in some peak intensities possibly due to the variations in
319 percentage compositions of different aromatic hydrocarbons found in these liquid oils (Figure
320 6). The FT-IR peaks were characterized and matched with the standard characteristic IR
321 absorption peaks given in Orgchem (2015). The two strongest sharp peaks found at 697 and
322 775 cm^{-1} , attributed to the =C-H out of plane bending vibrations for mono-substituted benzene
323 rings. Another medium peak found at 1490 cm^{-1} falls within the 1500-1400 range
324 corresponding to C=C stretch for substituted aromatic hydrocarbons. One weak peak at 1450
325 cm^{-1} can be assigned to C-H bend in alkanes. Two sharp peaks appeared at 905 and 989 cm^{-1}
326 are corresponding to =C-H bend in alkenes. Many weak absorption peaks found at the higher
327 frequency range from $2800\text{-}3100 \text{ cm}^{-1}$ and were at 2850, 2920, 2940 cm^{-1} and 3020, 3030, 3070
328 cm^{-1} fall within standard ranges of $3100\text{-}3000$ for sp^3 C-H stretch in alkanes and $3100\text{-}3000$
329 cm^{-1} for sp^2 C-H stretch in aromatics, respectively (Figure 6). These FT-IR results presented
330 strong evidence that aromatic hydrocarbons were the major components found in the liquid oils
331 produced from both thermal and catalytic pyrolysis.

332

333 The FT-IR analysis of the PS plastic raw material was also carried out and its spectrum is
334 shown in figure 6. Most of the peaks found for raw material matched closely with the FT-IR
335 peaks of pyrolytic liquid oils. The minor differences in the peak frequencies and intensities in
336 raw material to liquid oil samples were possibly due to different phases and degree of
337 crystallinity of styrene, some impurities or additives present in the plastic feedstock. The other
338 strong peak at 533 cm^{-1} might be attributed to the =C-H OOP of mono-substituted benzene
339 ring. This absorption band also observed for the native styrene (raw material), but it has not
340 been previously reported in the literature (Pavia et al., 2008). These results (Figure 6) are also
341 consistent with other related studies, where it is reported that the liquid oil obtained from PS

342 plastic feedstock mainly produce aromatic hydrocarbons with paraffins (alkanes), olefins
343 (alkenes) and naphthenes (cycloalkanes) in minor quantities (Siddiqui et al., 2009; Lee et al.,
344 2002; Ramli et al., 2011; Kim et al., 2002).

345
346 The GC-MS results also showed the presence of aromatic hydrocarbons as being dominant
347 compounds in liquid oils from both thermal and catalytic pyrolysis (Figure 7). In thermal
348 pyrolysis, styrene was the main compound (48.3%) with ethylbenzene (21.2%), toluene
349 (25.6%) and benzo(b)triphenylene (1.6%). In catalytic pyrolysis with natural zeolite, styrene
350 was also the major compound (60.8%) with methylstyrene (10.7%), azulene (4.8%), 1H-indane
351 (2.5%) and ethylbenzene (1.3%) (Figure 7). In catalytic pyrolysis with synthetic zeolite, the
352 following compounds were found in descending concentrations: alpha-methylstyrene (38.4%),
353 benzene (16.3%), styrene (15.8%), ethylbenzene (9.9%), isopropylbenzene (8.1%),
354 propenylbenzene (4.2%) and propyl benzene (3.5%) (Figure 7). These findings are in
355 agreement with other studies that observed the chemical composition of liquid oil produced
356 from MPW mainly consists of aromatic hydrocarbons with some paraffins (alkanes: C_nH_{2n+2}),
357 olefins (alkenes: C_nH_{2n}), and naphthenes (cycloalkanes) (Shah and Jan, 2014; Ukei et al.,
358 2000). Moreover, the chemical composition of liquid oil depends on plastic types and various
359 process conditions, including temperature reaction time, and type and amount of catalyst used.
360 For example, benzene, styrene, ethylbenzene, toluene, α -methylstyrene and indane derivate are
361 the major compounds reported by many researchers (Shah and Jan, 2014; Ukei et al., 2000;
362 Lee et al., 2002). Lee et al. (2002) reported that liquid oil produced from catalytic degradation
363 of PS consists more than 99% of aromatic compounds with minor quantities of n-paraffin
364 (0.02%), iso-paraffin (0.1%), olefins (0.03%) and naphthenes (0.1%), which is in agreement
365 with our findings (Figure 7). Similarly, the liquid oil produced by Ramli et al. (2011) from
366 thermal and catalytic pyrolysis contained 80% and 85-90% of aromatic hydrocarbons
367 respectively. The high ratio of aromatic compounds found in the pyrolytic liquid oil from
368 thermal and catalytic degradation of PS is due to the high stability of these compounds, which
369 inhibit the further cracking or hydrogenation into paraffin and olefins (Saptoadi et al., 2015).
370 The GC-MS results revealed that pyrolysis liquid oils mainly consist of aromatic hydrocarbons,
371 which is in agreement with FT-IR results (Figure 6).

372
373 In both thermal and catalytic pyrolysis of PS, styrene was the main compound found in
374 produced liquid oils with some other aromatic compounds such as ethylbenzene, toluene and

375 methylstyrene. Styrene production in thermal pyrolysis oil was 48.3%, while in catalytic
376 pyrolysis oil there was an increase in the production of styrene (60.8%) using natural zeolite.
377 The styrene with synthetic zeolite however decreased down to 15.8% with an increase in its
378 derivatives alpha-methylstyrene (38.4%). Many researchers reported similar results that
379 styrene, ethylbenzene, toluene and methylstyrene were the major compounds from the
380 degradation of PS (Aguado et al., 2003; Artetxe et al., 2015; Bartoli et al., 2015). According to
381 Onwaduili et al. (2009), there is no direct production of toluene and ethylbenzene from the
382 plastic waste raw material and they may be produced by the reaction of styrene itself.
383 Moreover, production of styrene initially increases with an increase of temperature but further
384 increase in temperature to above 500 °C showed a declining trend in the styrene production.
385 Beyond 500 °C, it is reported that styrene production decreases with the increase in the
386 production of toluene and ethylbenzene, which shows further decomposition of styrene at high
387 temperature (Demirbas, 2004; Onwudili et al., 2009).

388

389 It has been reported by many researchers that increase in pyrolysis temperature and reaction
390 time decreases the production of styrene with the increase of toluene and ethylbenzene. (Aguado
391 et al., 2003; Artetxe et al., 2015; Bartoli et al., 2015). This increase in the production of
392 ethylbenzene, toluene and methylstyrene is attributed to the hydrogenation of styrene at high
393 temperature due to secondary reactions (Ukei et al., 2000). In addition increase in reactor
394 pressure also decreases the production of styrene with the increase in toluene and ethylbenzene
395 which is due to the hydrogenation of styrene into its derivate (Shah and Jan, 2014). Overall
396 decrease in styrene production with the increase in ethylbenzene, toluene, methylstyrene or
397 production of high molecular weight hydrocarbon (benzene, 3-butynyl) either may be due to
398 further cracking of styrene via hydrogenation (Lee et al., 2002) or recombination of styrene to
399 higher molecular weight via H-abstraction followed by cyclization (Hu and Li, 2007). Overall
400 secondary reactions are responsible for the decrease in the production of styrene (Karaduman,
401 2002).

402

403 Styrene production is also effected by the selection of catalyst. Styrene production is higher in
404 catalytic pyrolysis as compared to thermal pyrolysis when solid base catalyst was used (Shah
405 and Jan, 2014). Ukei et al. (2000) used solid base catalyst (BaO) for the degradation of PS and
406 achieved maximum styrene recovery. Adnan et al. (2014) used Cu base catalyst and achieved
407 up to 60% of styrene recovery. However use of solid acid catalyst decreases the production of

408 styrene and increase the production of ethylbenzene, toluene and methylstyrene. Audisio et al.
409 (1990) reported the very low production of styrene (below 5% weight) by using silica alumina,
410 REY or HY zeolite at 350 °C. Lee et al. (2003) reported that use of solid acid catalyst decreases
411 the production of styrene as compare to thermal pyrolysis. Thermal pyrolysis achieved 52.2%
412 of styrene recovery however it decreases with the use of solid acid catalyst such as NZ (50.8%),
413 HNZ (48.1%), HSCLZ (47.7%) and SA (36.1%). The decrease in styrene production is may be
414 due to high acidity of catalyst which increases the rate of secondary reactions. This is possibly
415 the reason for a decrease in styrene production in liquid oil from synthetic zeolite catalytic
416 pyrolysis in this study (Figure 6). Since the structure of the synthetic zeolite would be more
417 pure and highly crystalline than natural zeolite, it is therefore probably more acidic in nature
418 as well. This observation is in line with the work of Nizami et al. (2016a) and Miandad et al.
419 (2016a, b).

420

421 The energy content is one of the most important characteristics of any fuel in its applications
422 and it can be characterised by its HHV. The higher the HHV value of a fuel, the higher the
423 energy content of the fuel, meaning the required performance can be achieved with less fuel
424 quantity (Saptoadi et al., 2015). In this study, the average HHV of PS plastic raw material,
425 liquid oils produced from thermal and catalytic pyrolysis with natural and synthetic zeolite
426 catalysts were found to be 39.3, 41.6, 41.7 and 40.6 MJ/kg respectively (Table 5). The slightly
427 lower HHV of raw material to liquid oils can be due to its solid phase form. Similarly, the
428 minute difference in HHV of oil from synthetic zeolite catalyst to other oils may be due to the
429 presence of ash or catalyst particulates in final product. These results are in agreement with
430 many other studies such as Syamsiro et al. (2014) that reported the HHV of 36.3 MJ/kg for
431 liquid oil produced from pyrolysis of PS plastic raw material at 450 °C. Lopez et al. (2011)
432 reported a HHV of 41.5 MJ/kg for liquid oil produced from pyrolysis of packaging plastic
433 waste at 440 °C. Moreover, the HHV of pyrolytic liquid oils are very close to HHV (43.1
434 MJ/kg) of conventional diesel (Table 5), which further affirms its suitability to be used for
435 energy production. Some studies have also suggested that pyrolytic oil, having slightly lower
436 HHV than diesel, can be suitably utilized as it is as a fuel or after mixing it with kerosene oil
437 (Saptoadi et al., 2015).

438

439 The thermal pyrolysis oil was further characterized for various parameters such as dynamic
440 viscosity, kinematic viscosity, density, pour point and flash point and compared with reported

441 conventional diesel values (Table 6). The dynamic and kinematic viscosity was found to be 1.8
442 mPa.s and 1.9 cSt, which are comparable to 1-4.1 mPa.s and 2.0-5.0 cSt ranges of conventional
443 diesel respectively. The density was found to be 0.9 g/m³ which is also close to reported density
444 range of 0.8-0.9 g/m³ for conventional diesel. The flash point was found to be 30.2 °C, which
445 is below the conventional diesel range of 55-60 °C. One of the possible reason for this lower
446 flash point could be that pyrolysis liquid oil mainly consist of aromatic hydrocarbons.

447

448 ***3.4. Potential applications of pyrolysis technology in KSA and other developing countries***

449 There is a huge potential applications for pyrolysis technology in KSA and other developing
450 countries of Asia, Africa and Latin America. The liquid oil produced by pyrolysis process is
451 suitable to be used as a feedstock for value-added chemicals production, energy generation,
452 transport fuel and heating purposes (Islam et al., 2010; Ouda et al., 2016; Rehan et al., 2016).
453 The consumption and generation of plastic waste in these countries have increased to an
454 alarming rates (Ouda et al., 2016). For instance, in KSA, around 6 million metric tons of plastic
455 products are produced every year and therefore, it is the second largest waste category of MSW
456 with total generation of 2.7 million tons per year.

457

458 Rehan et al. (2016) have recently described a case study of Makkah on the amounts of liquid
459 oil that can be generated from all the plastic waste produced in Makkah city together with
460 details on achieving economic savings and other environmental benefits. Rehan et al. (2016)
461 estimated that around 87.91 MW of electricity can be produced along with global warming
462 potential savings of 199.7 thousand Mt.CO₂ eq. in Makkah city by utilizing all of the plastic
463 waste in the pyrolysis process. A total economic savings of 297.52 million SAR or 79.33
464 million USD will be achieved from carbon credits, landfill diversion and electricity production
465 from pyrolytic liquid oil. Moreover, the pyrolysis has an advantage over other WTE
466 technologies including incineration and plasma arc gasification due to less annual capital cost
467 (\$17-25/ton) and net operational cost (\$2-3/ton) (Table 1).

468

469 The quality of liquid oil produced needs to be improved further in terms of removing some of
470 the heavy hydrocarbons and impurities (Figure 8). Many studies have been recently published
471 on improving the pyrolytic liquid oil quality by various methods such as filtration, chemical
472 treatment, by blending it with conventional fuels and distillation and refining (Islam et al.,
473 2010; Moheballi and Ball, 2016; Chong and Hochgreb, 2015). Pyrolysis has also been reported

474 to be an effective way to recover the styrene from PS plastic. Several researchers have reported
475 the production of styrene, ethylene benzene and toluene with some other styrene monomers
476 from the thermal degradation of PS plastic (Jung et al., 2013; Artetxe et al., 2015). Recovered
477 styrene can be used as feedstock in various industries for PS polymerization (Achilias et al.,
478 2007). Biodegradable plastic i.e. polyhydroxyalkanoate can also be produced from pyrolytic
479 liquid oil produced from thermal degradation of PS plastic wastes (Nikodinovic-Runic et al.,
480 2011).

481

482 The oil produced in this study was found to have similar chemical composition and HHV values
483 as conventional diesel (Table 7). Thus produced liquid oil has the potential to be used as
484 alternative of conventional diesel. However produced liquid oil should be upgraded or blended
485 with conventional diesel as it contains high aromatic content. The high percentage of styrene
486 found in liquid oils from both thermal and catalytic pyrolysis could be used as valuable
487 chemicals for improving the octane number of petrol fuel produced from crude oil by blending
488 them in different proportions. The octane number of petrol fuel mainly depends on their
489 hydrocarbon composition such as n-paraffins and olefins are less desirable compared to iso-
490 alkanes, naphthenic and aromatic compounds. Furthermore, higher octane number is favoured
491 for prevention of early ignition which leads to cylinder knock (Andras et al., 2007; Corma
492 1996; Madon 1991).

493

494 Several studies have reported the mixing and blending of pyrolytic oil with conventional fuel
495 in different ratios to further improve its quality (Sharuddin et al., 2016; Li et al., 2016; Kumara
496 et al., 2013). For example, the produced liquid oil was blended with the diesel oil with different
497 ratios i.e. 5%, 10%, 20%, 30%, 40% and 45% (Frigo et al., 2014; Nileshkumar et al., 2015;
498 Lee et al., 2015). Wongkhorsub and Chindaprasert (2013) directly injected the pyrolytic liquid
499 oil produced from wastes tires and wastes plastic into diesel engine. All aforementioned studies
500 reported the successful use of pyrolytic liquid oil for energy generation. Engine performance
501 and exhaust emissions were also examined with the use of pyrolytic liquid oil. The results
502 concluded that among all the used ratios 20/80% (pyrolytic liquid oil/conventional diesel) ratio
503 showed similar performance as conventional diesel. Lee et al. (2015) reported 13% decrease in
504 engine performance at 2450 rpm while it reaches to 17% at 3500 rpm with 20/80% ratio.
505 Nileshkumar et al. (2015) also recommended the same ratio for the better performance of
506 engine. However fuel consumption increased with the increase in blending ratio due to slightly

507 lower calorific value of pyrolytic liquid oil (Cleetus et al., 2013). In addition exhaust emissions
508 also increased as blending ratios increased reaching to its maximum at 50/50% blending ratio.
509 Nileshkumar et al. (2015) reported that at 20/80% blending ratio, CO_x and NO_x emissions
510 were (0.5 and 0.7 g/km) and (0.3 and 0.4 g/km) for low and full load respectively. However for
511 conventional diesel the reported emissions were 0.5 and 0.7 g/km for CO_x while, 0.3 and 0.4
512 g/km for NO_x respectively. More comprehensive studies are required to fully understand the
513 transformation of pyrolytic liquid oil into pure clean transportation fuel and its effect on
514 internal combustion engine performance, stability and structural damage as well as the type
515 and impact of gases emissions.

516

517 ***3.5. Future perspective***

518 There is much scope in the optimization of the pyrolysis process on a large scale by detailed
519 investigations of the effect of various process parameters, feedstock type, and type of catalyst
520 used. Most of the pyrolysis plants at pilot and commercial scale use synthetic catalysts
521 intensively in order to improve the yield and quality of liquid oil and to overall optimize the
522 pyrolysis process. Despite the recent advancements in pyrolysis technology, several issues and
523 scope for further process optimization still remain. For example, the use of synthetic catalysts
524 in pyrolysis technology is making the overall process more energy intensive and economically
525 expensive. In such scenario, a significant research is underway on exploring new and cheap
526 catalysts, reusing catalyst, using natural minerals as catalysts, and using of catalysts in less
527 quantities. Another area of further research would be to study the activation of produced char
528 with steam and other appropriate gases and to study its various potential applications such as
529 removal of heavy metals and other toxic contaminants from wastewater and soil (Aktaş and
530 Çeçen, 2007; Qin et al., 2013). Jindaporn and Lertsatitthanakorn et al. (2014) reported that the
531 char produced from pyrolysis of HDPE waste has a calorific value of 4,500 cal/g and its surface
532 area and volume increased by thermal activation at 900 °C for 3 hours.

533

534 Natural zeolite catalysts are used successfully in the pyrolysis process; however, there is scope
535 for further improvement in their catalytic performance by removing some of the impurities
536 present and by increasing their surface area and volume. This surface and structural
537 modifications can be carried out by acid leaching, and thermal treatment and wet impregnation
538 (Nizami et al., 2016a). Syamsiro et al. (2014) reported that the natural zeolite's catalytic
539 performance was improved by removing the volatile impurities through thermal treatment at

540 500 °C for 3 hours. Similarly, the catalytic performance of natural zeolites was improved by
541 removing impurities and increasing the overall catalyst acidity via HCl leaching process
542 (Sriningsih et al., 2014). Wet impregnation method is an important technique widely used to
543 modify and generate heterogeneous catalysts (Adnan et al., 2014). The life cycle assessments
544 (LCA) of feedstock, products and process are also recommended (Nizami, 2015; Shahzad et
545 al., 2015; Singh et al., 2010; Nizami and Ismail, 2013) that are very important to fully
546 understand the economic, technical and environmental aspects of pyrolysis technology before
547 its installation at a commercial scale.

548

549 **4. Conclusions**

550

551 The GC-MS results showed that around 99% aromatic hydrocarbons were found in liquid oils
552 produced by both thermal and catalytic pyrolysis. In thermal pyrolysis oil, the major
553 compounds were styrene (48.3%), ethylbenzene (21.2%), toluene (25.6%) and benzo (b)
554 triphenylene (1.6%). In catalytic pyrolysis with natural zeolite, the major compounds were
555 styrene (60.8%), methylstyrene (10.7%), azulene (4.8%), 1H-indane (2.5%) and ethylbenzene
556 (1.3%), while, in catalytic pyrolysis with synthetic zeolite, the major compounds were alpha-
557 methylstyrene (38.4%), styrene (15.8%), benzene (16.3%), ethylbenzene (9.9%), and
558 isopropylbenzene (8.1%). The FT-IR analysis also revealed chemical bonding and functional
559 groups of mostly aromatic hydrocarbons found in all samples, which is in agreement with GC-
560 MS results. The average HHV of PS plastic feedstock, liquid oil produced from thermal and
561 catalytic pyrolysis with natural zeolites and synthetic zeolites were found to be 39.3, 41.6, 41.7
562 and 40.6 MJ/kg respectively. The produced liquid oils are suitable for heating and energy
563 generation applications after post-treatment. However, the high percentage of aromatic
564 compounds (up to 99%) in liquid oil make it less suitable as a transportation fuel until it further
565 goes through refining stages including blending with diesel. This will upgrade the liquid oil to
566 gasoline range hydrocarbons (C₄ - C₁₂).

567

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574

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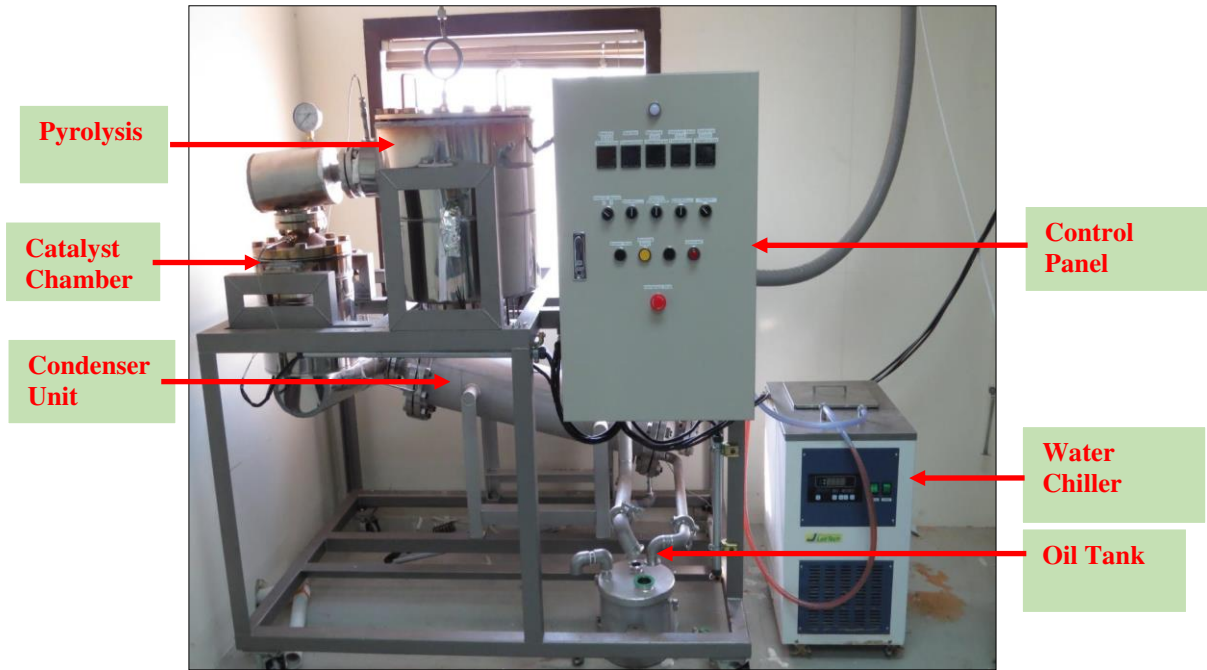
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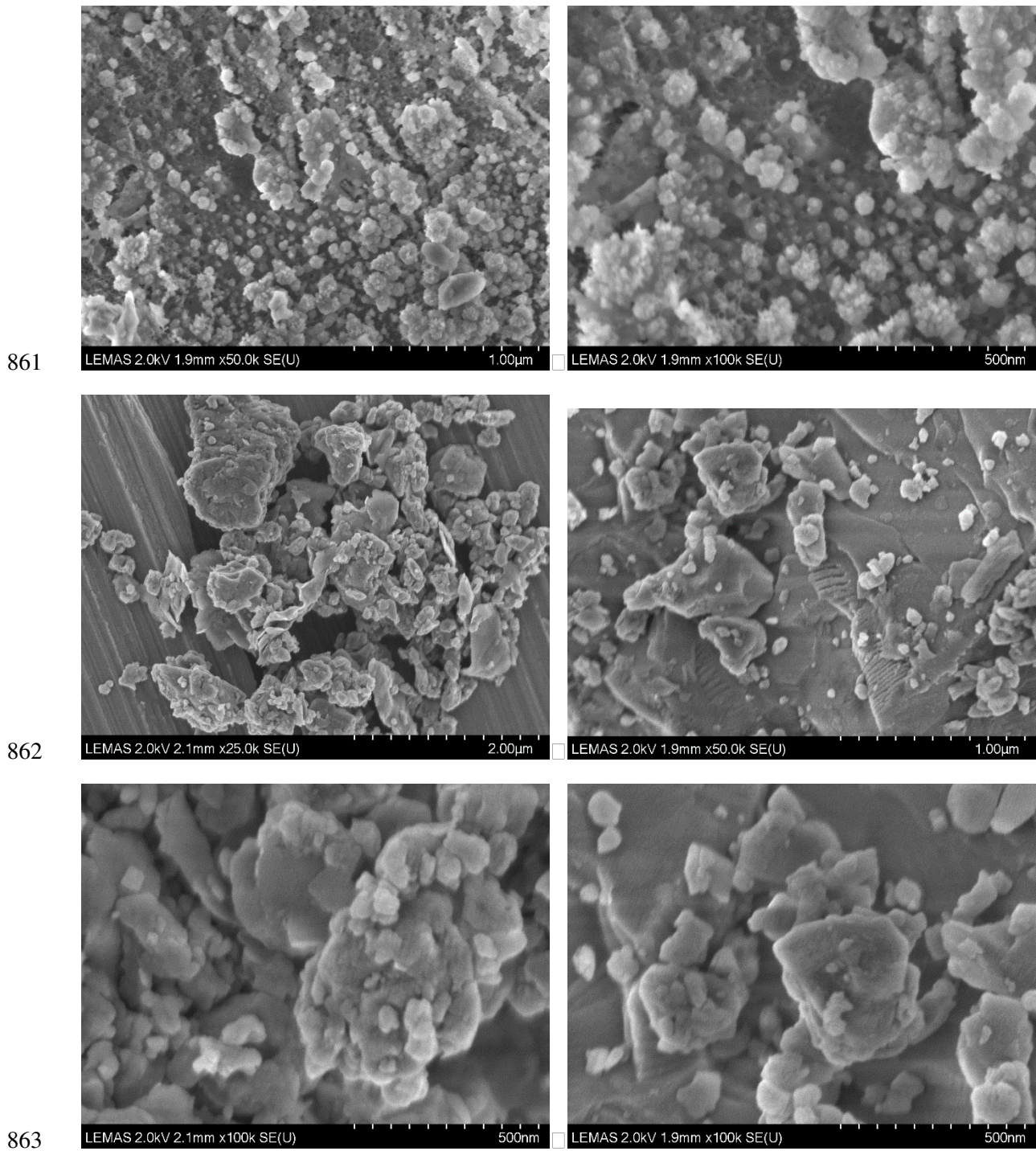
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Figure 1. Small pilot scale pyrolysis reactor (Miandad et al., 2016d).

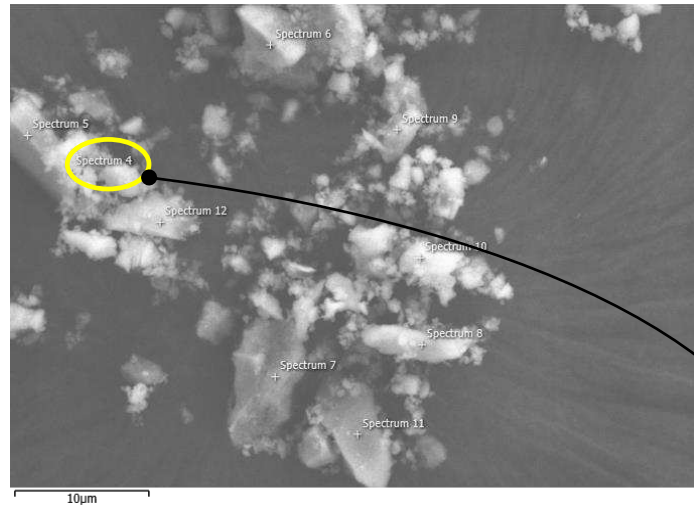
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864 Figure 2. SEM images of the Saudi Arabian natural zeolites.

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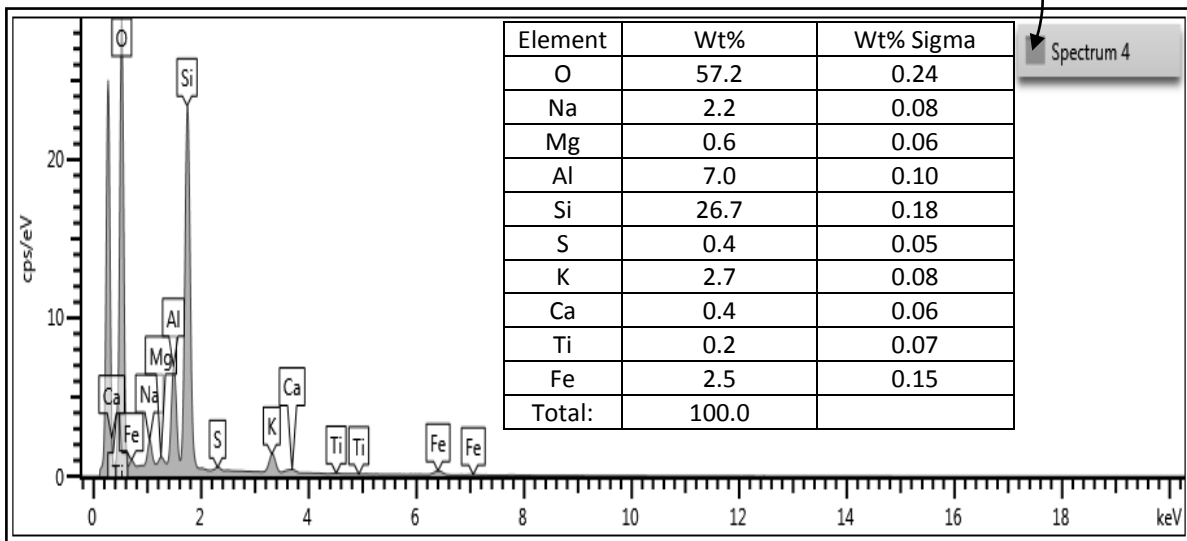
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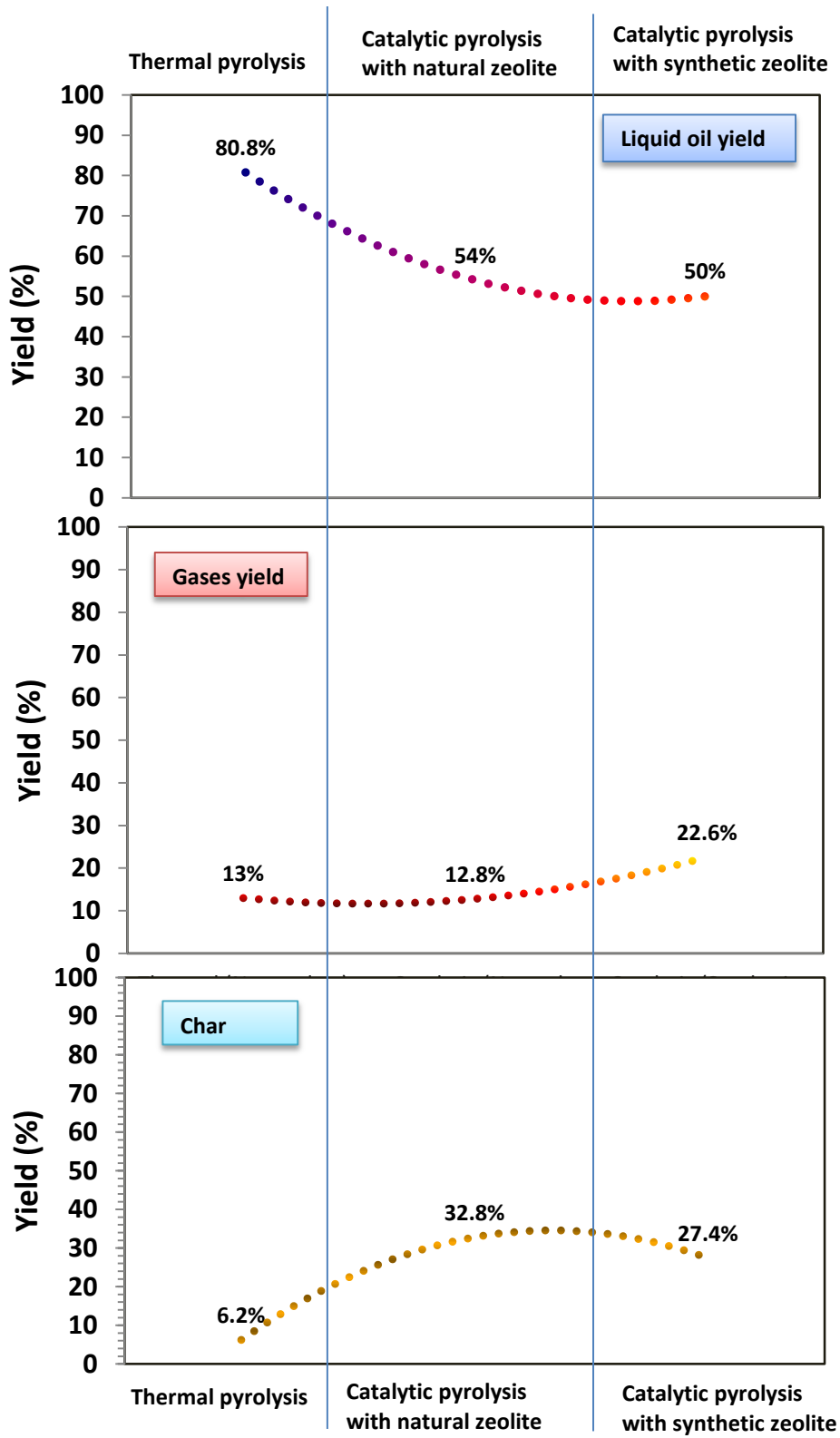


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Figure 3. SEM-EDXS of Saudi Arabian natural zeolite showing elemental composition and quantities in wt% for certain location (Spectrum 4).



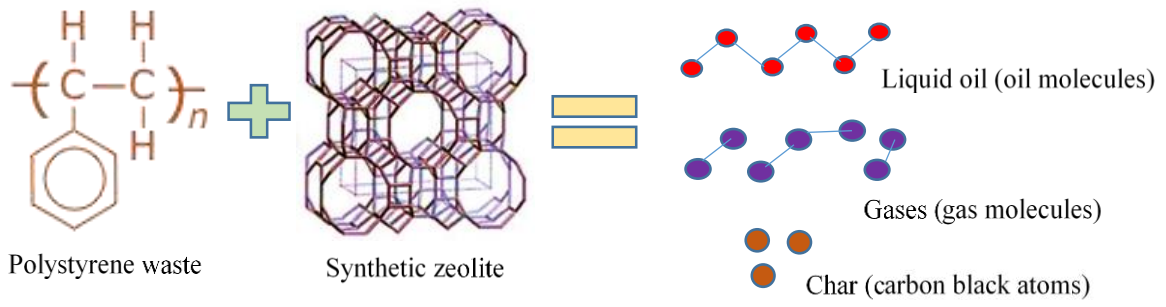
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881 Figure 4. The yield of liquid oils, gases and char from thermal and catalytic pyrolysis with

882 natural and synthetic zeolite.

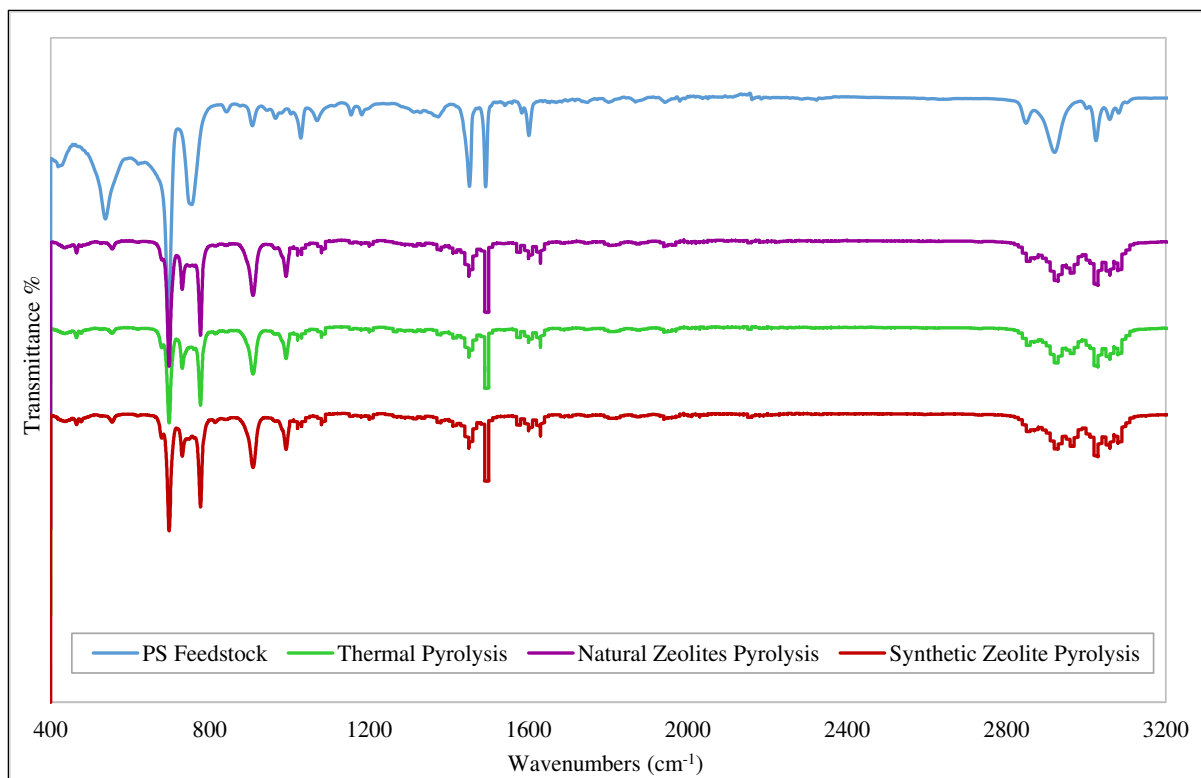
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887 Figure 5. Reaction of polystyrene plastic waste with synthetic zeolite



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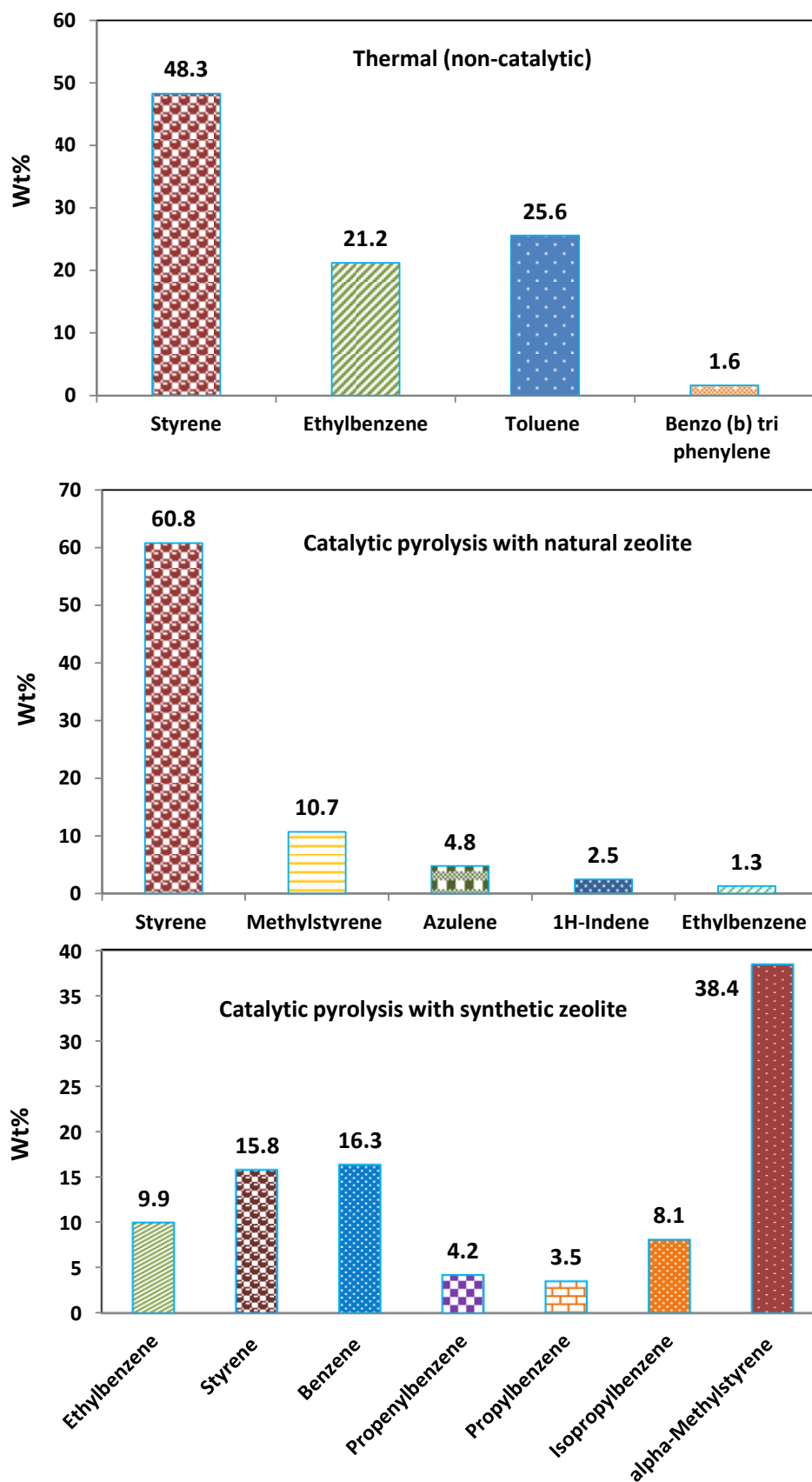
Frequency cm^{-1}	Bond	Functional group
3020, 3030, 3070	=C-H stretch	Aromatics
2850, 2920, 2940	C-H stretch	Alkanes
1450, 1490	C-C stretch (in-ring)	Aromatics
905, 989	=C-H bend	Alkenes
697, 775	C-H "oop"	Aromatics
533.71	C-Br stretch	Alkyl halides

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890 Figure 6. FT-IR spectrum of PS plastic raw material and thermal and catalytic pyrolysis liquid
 891 oils.

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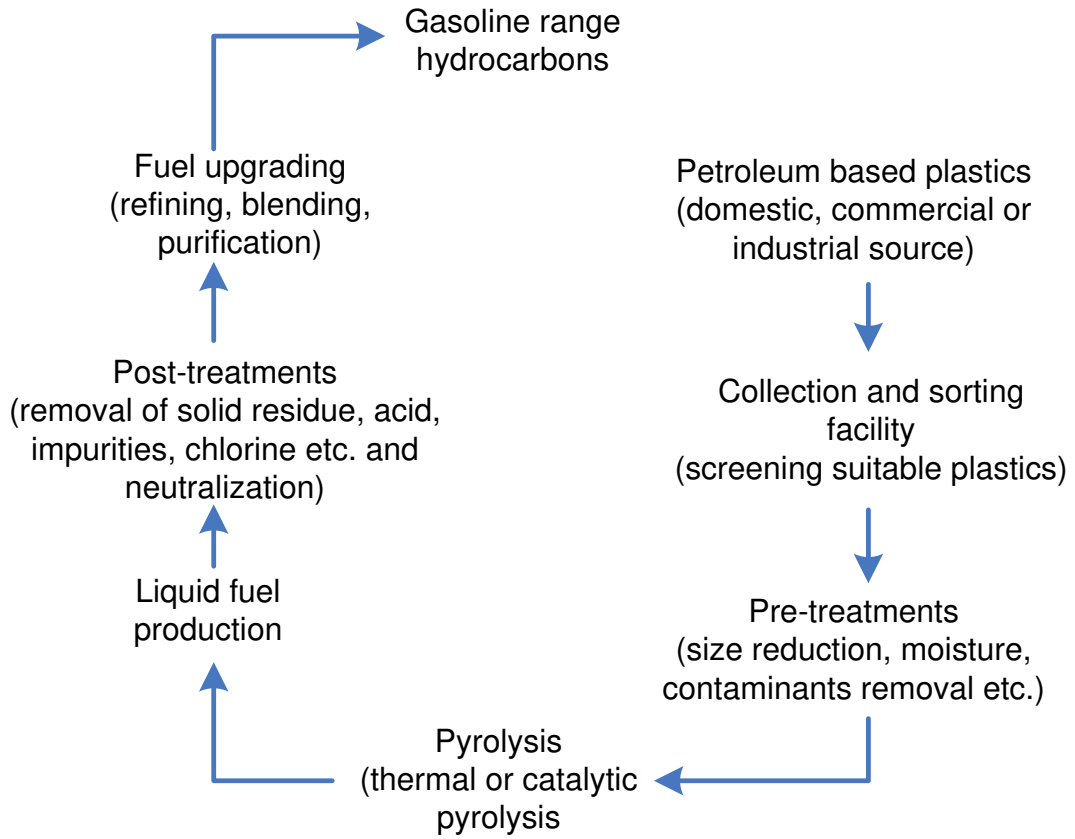
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895 Figure 7. GC-MS analysis showing the effect of thermal and catalytic pyrolysis on liquid oil

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Figure 8. Recovery of petroleum based plastics into gasoline range hydrocarbons

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901 Table 1. Technical and economical comparison of pyrolysis with others WTE technologies (Ouda et
 902 al., 2016a, Nizami et al., 2015c; Sadeh et al., 2016; Rahmanian et al., 2015; Eqani et al., 2016; Munir
 903 et al., 2016)

WTE technologies	Capital cost/ton/year	Net operational cost /ton	Merits	Limitations
Incineration	\$14.5-\$22	\$1.5-\$2.5	<ul style="list-style-type: none"> - Up to 80% of volume reduction - Up to 70% of mass reduction - Large amounts of waste can be treated - Fast treatment 	<ul style="list-style-type: none"> - Air and water pollution - Carcinogenic chemical (dioxins) release - Public opposition - Produce solid waste (slag)
Pyrolysis	\$17-\$25	\$2-\$3	<ul style="list-style-type: none"> - Up to 80% energy recovery from waste - Reduced land requirement - High calorific value products - Liquid products easily separated from vapor phase - Up to 50-90% reduction in MSW volume 	<ul style="list-style-type: none"> - Lower liquid products yields - Moisture produced from organic matter - Coke formation from liquid products - By-products cleaning - Corrosion of pyrolysis metal tubes
Plasma arc gasification	\$19.5-\$30	\$2.5-\$4	<ul style="list-style-type: none"> - No GHG emissions - All waste types can be treated - Easy technology expansion 	<ul style="list-style-type: none"> - Higher energy consumption - High capital and operating cost
Refuse derived fuel (RDF)	\$7.5-\$11.3	\$0.3-\$0.6	<ul style="list-style-type: none"> - Stabilized waste - Reduced waste volume - RDF pellets having high calorific values 	<ul style="list-style-type: none"> - Air pollution by RDF fuel - Ash formation - Land requirement
Anaerobic digestion (AD)	\$0.1-\$0.14	Minimal	<ul style="list-style-type: none"> - Lower solid produced - High rate anaerobic composting with energy - Nutrient rich digestate as an organic fertilizer - Cost effective technology 	<ul style="list-style-type: none"> - Impurities - Not suitable at larger scale - Vulnerability to overloads and shocks - Space requirement

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907 Table 2. Comparison of thermal and catalytic pyrolysis and their impacts on fuel characteristics

	Thermal pyrolysis	Catalytic pyrolysis	Impact on fuel
Classification	Classification is simple	Technology classification is unclear	Poor market acceptance
Temperature	High temperature demand leads to production of some diolefins	Decomposition of feedstock at low temperature	Effect fuel cost on product selectivity
Reaction time	High reaction time	Low reaction time is required	Effect on fuel cost
Gas formation	Increase production of CH ₄ and C ₂ H ₆	Increase the concentration of C ₃ and C ₄ hydrocarbons	Effect the quantity and quality of gas production
Solid residue	High solid residue production	Less solid residue production	Effect the quality and quantity of oil
Impurities	High impurities in the form of S, N, P, and acid	Impurities removed via adsorption	Effect on the quality of liquid oil
Aromaticity	Less aromatic hydrocarbon formation	High aromatic hydrocarbon formation	Aromatic cyclization
Paraffins formation	Less formation of paraffin	Paraffin production via hydrogen transfer	Effect on the gasoline selectivity
Reactivity	Less reactivity	More reactive especially for larger molecules	Effect on radical formation
Distribution of molecular weight	Large distribution of hydrocarbon with less short chain hydrocarbon	High production of short chain hydrocarbons	Effect on gasoline selectivity

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922 Table 3. Pyrolysis reactor features

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Heating tank (height)	360 mm
Heating tank (diameter)	310 mm
Catalytic chamber (height)	200 mm
Catalytic chamber (diameter)	165 mm
Reactor (total capacity)	20 L
Catalytic chamber (total capacity)	1 L
Condenser (length)	860 mm
Condenser (diameter)	147 mm
Temperature (maximum)	600 °C

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927 Table 4. Pyrolysis products yield and liquid oil composition of thermal and catalytic pyrolysis

Pyrolysis type	Pyrolysis products (%)			Liquid oil (Composition %)
	Liquid oil	Gases	Char	
Thermal pyrolysis	80.8	13	6.2	<ul style="list-style-type: none"> • Styrene (48.3) • Ethylbenzene (21.2) • Toluene (25.6) • Benzo (b) tri phenylene (1.6)
Catalytic pyrolysis (natural zeolite)	54	12.8	32.8	<ul style="list-style-type: none"> • Styrene (60.8) • Methylstyrene (10.7) • Azulene (4.8) • 1H-Indene (2.5) • Ethylbenzene (1.3)
Catalytic pyrolysis (synthetic zeolite)	50	22.6	27.4	<ul style="list-style-type: none"> • Ethylbenzene (9.9) • Styrene (15.8) • Benzene (16.3) • Propenylbenzene (4.2) • Propylbenzene (3.5) • Isopropylbenzene (8.1) • Alpha-Methylstyrene (38.4)

929 Table 5. Higher heating value (HHV) in MJ/kg of the feedstock and produced liquid oil and
 930 char

Feedstock (PS plastic)	Thermal pyrolysis		Catalytic pyrolysis			
	Liquid	Char	Natural zeolite		Synthetic zeolite	
	Liquid	Char	Liquid	Char	Liquid	Char
39.3	41.6	20.1	41.7	11.1	40.6	9.7

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933 Table 6: Comparison of present study liquid oil with conventional diesel

Parameters	Our results	Conventional diesel	Reference
Dynamic viscosity (mPa.s)	1.8	1-4.1	Wongkhorsub and Chindaprasert, 2013
Density@15 °C (g/cm ³)	0.9	0.8-0.9	Syamsiro et al., 2014
Kinematic viscosity @40 °C (cSt)	1.9	2.0-5.0	Syamsiro et al., 2014
Pour point (°C)	-60	Max 18	Syamsiro et al., 2014
Flash point (°C)	30.2	Min 55-60	Syamsiro et al., 2014

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937 Table 7. Heating value of different fuel types according to their hydrocarbon chains (Lee et al.,
938 2015).

Fuel type	Hydrocarbons	HHV (MJ/kg)
LPG	C ₃ - C ₄	46.1
Petrol	C ₄ - C ₁₂	44.0
Kerosene	C ₁₂ - C ₁₅	43.4
Diesel	C ₁₂ - C ₂₄	43.0
Heavy fuel oil	C ₁₂ - C ₇₀	41.1

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