Conversion of hazardous plastic wastes into useful chemical products

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ABSTRACT

Azoisobutylnitrile (AIBN) initiator was used in the treatment of most widely used domestic plastics in lieu of catalysts. The pyrolysis of low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), poly-ethylene terephthalate (PET) and polystyrene (PS) plastics with azoisobutylnitrile was carried out individually under nitrogen atmosphere. A series of single (plastic/AIBN) and binary (mixed plastics/AIBN) reactions were carried out in a 25-cm^3 micro-autoclave reactor. The optimum conditions selected for this study were: 5% AIBN by weight of total plastics, 60 min, 650 psi and 420 °C. It was found that HDPE, LDPE, PP underwent to a maximum cracking and produced highest amounts of liquid and gaseous products. Pyrolysis of PET and PS plastics with AIBN afforded comparatively significant amount of insoluble organic materials. In other reactions, fixed ratios of mixed plastics were pyrolyzed with AIBN that afforded excellent yields of liquid hydrocarbons. This result shows a very significant increase in the liquid portions of the products on using AIBN in the pyrolysis of plastics. The use of AIBN in the pyrolysis of plastics is seems to be feasible and an environmental friendly alternative to catalytic process for maximizing the liquid fuels or chemical feed stocks in higher amounts.

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1. Introduction

The huge population increase coupled with the improved living conditions of the people led to a dramatical increase of the consumption of plastics worldwide. The chief usages of polymeric materials are packaging, household and domestic products, electrical and electronic goods and also in building, construction and automotive industries. It has been estimated that almost 170 million tones of plastics were produced worldwide during the year 2003. Current statistics for Western Europe estimate the annual total consumption of plastic products at 48.8 million tons for 2003 and generating approximately 15 million tons of waste plastics throughout Europe [1]. In 2006, the United States generated about 14 million tons of plastics in the form of municipal solid waste (MSW) as containers and packaging, over 6 million tons as non-durable goods, and almost 9 million tons as durable goods. The total amount of plastics in MSW—almost 30 million tons—represented 11.7% of total MSW generation in 2006 [2].

Saudi Arabia is one of the major producers of plastic in the world with total production capacity of around six million tons per year. The amount of plastic wastes in Saudi Arabia is about 15-wt% in the composition of domestic municipality waste [3]. Approximately 40% of the waste plastics have life duration shorter than 1 month, thus there is a huge waste stream creating a serious environmental problem [1]. Thermoplastic polymers make up a high proportion of waste and this amount is continuously increasing, thus posing a more serious environmental challenge because of their huge quantity and disposal problem as thermoplastics do not biodegrade for very long time. The land filling of sites and incineration of waste plastics have serious drawbacks. Plastics are produced from petroleum derivatives and are composed primarily of hydrocarbons but also contain additives such as antioxidants, colorants and other stabilizers which are undesirable from environmental and pollution point of view [4].

As a result of the rush of legislation in recent years, recycling of plastics has become a major response to the environmental challenges facing the plastic industry [5,6]. Recycling has several meanings such as primary, secondary, tertiary and quaternary recycling. *Primary recycling* is the processing of scrap plastics into similar types of product from which it has been generated, using standard plastics processing methods. This process remains the most popular as it ensures simplicity and low cost, dealing however only with the recycling of clean uncontaminated single-type waste. *Secondary or mechanical recycling* where the polymer is separated from its associated contaminants and can be readily reprocessed into granules by conventional melt extrusion [7]. *Secondary recycling* includes the sorting and separation of the wastes, size reduction and melt filtration. The main disadvantage of this type of recycling is the deterioration of product properties in every cycle.

Tertiary or chemical or feedstock recycling involves the transformation of polymeric materials by means of heat or chemical agents to yield a variety of products ranging from the starting monomers,

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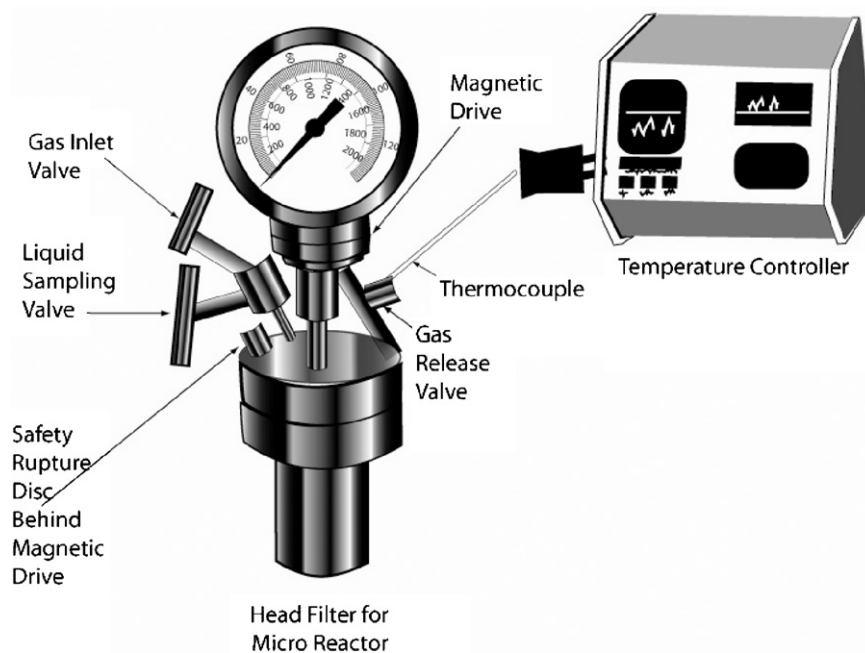*E-mail address:* mnahid@kfupm.edu.sa.

Fig. 1. Schematic experimental setup of micro-reactor under N_2 gas pressure.

to oligomers or mixtures of other hydrocarbon compounds. The resulting raw materials are then reprocessed into plastics materials or other products of the oil refining process. *Quaternary recycling or energy recovery* is an effective way to reduce the volume of organic materials by recovering the latent energy content of plastic materials by incineration. Although polymers are actually high-yielding energy sources, this method has been widely accused as ecologically unacceptable owing to the health risk from air born toxic substances such as dioxins and hydrogen chloride, airborne particles and carbon dioxide [8].

The prime objective of waste plastic recycling should not only be the reuse of polymeric materials but also the production of raw or feedstock materials (monomers). In this context, among the techniques discussed for recycling of waste plastics, tertiary recycling is considered to be the most challenging and appropriate method. *Tertiary recycling* returns plastics to their constituent monomers or to their basic hydrocarbon feedstock [9,10]. Tertiary or feedstock recycling of waste plastics has an advantage over other recycling processes where sorting and separation of objects by plastic type, and also by color in some cases, is crucial to an economically viable plastics recycling chain. The most important and widely used tertiary recycling process is pyrolysis, where plastics are heated in the absence of oxygen. Pyrolysis provides an excellent alternative for the disposal of plastics wastes with the recovery of valuable transportation fuels like gasoline, kerosene and diesel. Thermal pyrolysis of plastic yields a very broad compositional range of low-value mixture of liquid hydrocarbons whereas catalytic pyrolysis yields a much narrower products range and most suitable for transportation fuels. Pyrolysis of waste plastic affords high rates of conversion into liquid fuels that can be used as feedstock in refinery [11].

The advantage of pyrolysis is that the waste plastics do not have to be separated ahead of time, thereby, eliminating the labor-intensive step as required in the hydrolysis and mechanical recycling methods. The production of transportation fuels from waste plastics is an emerging technological solution to the huge amount of waste plastics that cannot be economically recovered by conventional mechanical recycling processes. The pyrolysis of mixed plastics has been considered as an effective way to convert waste plastics into environmental and industrially useful hydrocarbon products. Pyrolytic process is therefore ideal for converting

waste plastics into liquid fuels as a productive alternative for plastic recycling. *Tertiary recycling* of waste plastics may not be considered as a solution for waste plastics disposal only: rather generating an environmentally acceptable transportation fuel or feed stock for the production of virgin plastics also [12].

There have also been reports on the pyrolysis of polyolefins to aromatic hydrocarbons with activated carbon-supported metal catalysts [13,14]; cracking of polystyrene and polyethylene on silica alumina [15] and reforming of heavy oil from waste plastics using zeolite catalysts [16,17] and other research work on the pyrolysis of individual and mixed plastics to get liquid fuels [18–21]. Pyrolysis of polyethylene produces olefins of varying chain length and aromatic polymers produces aromatic compounds such as benzene, toluene and styrene. Pyrolysis can tolerate mixtures of different plastic resins as well as high levels of organic contamination, which is also pyrolyzed [22–24]. Western Research Institute has developed an advanced tertiary plastics recycling process that produces a product in the gasoline and diesel fuel boiling range for use in the refining and petrochemical industries [25]. Pyrolysis of electronic and thermoset were also investigated for the recovery of useful liquid products [26,27]. Korea Institute of Energy Research has developed and demonstrated the performance of pilot plants for the pyrolysis process of mixed plastic wastes generated from household and industry. The liquid products obtained by pyrolysis at around 400 °C were used as an alternative fuel oil [28].

The above literature review indicates the importance of recycling of waste plastics around the globe. The present study is conducted to explore and develop a new, non-catalytic, free radical initialized method of pyrolysis of actual and post-consumer waste plastics. The prime objective of this study was not only the reuse of polymeric materials but also the production of monomers or feedstock materials using tertiary or feedstock recycling method.

2. Experimental

2.1. Materials

The model plastic compounds, LDPE (Density = 0.920–0.922, Mn = 80,000), HDPE (Density = 0.948, Mn = 85,000), PET (Den-

sity = 0.835 + 0.015, Mn = 32,500), PP (Density = 0.918, Mn = 75,000) and PS (Density = 1.05, Mn = 180,000) used in this study were obtained from Saudi Basic Industries Corporation (SABIC), Riyadh, Saudi Arabia, and were used as received. Some of the post-consumer plastics such as water bottles, their caps and cups were also studied by pyrolysis. Locally available 99.9% pure N_2 gas and HPLC grade hexane, toluene and tetrahydrofuran (THF) solvents from Fischer Scientific were used in the reactions.

2.2. Analytical procedure

Azoisobutylnitrile (AIBN) initialized pyrolytic reactions were carried out in a 25-cm³ stainless steel tubular micro-autoclave reactor under certain conditions of weight of initiator, time duration, pressure and temperature with a programmable temperature controller purchased from the Parr Scientific, USA, as shown in Fig. 1. First, pyrolysis of HDPE, LDPE, PP, PS and PET was carried out individually in presence of azoisobutylnitrile in a micro-autoclave reactor under nitrogen atmosphere. In a second step, a series of pyrolytic reactions of three mixed plastics, HDPE/PP/PS, HDPE/PET/PS, LDPE/PET/PS, LDPE/PP/PS and PET/PP/PS were also conducted with azoisobutylnitrile under similar reaction conditions. The reactor was gradually heated at the rate of 5 °C/min and optimum conditions selected for this study were: 5% AIBN by weight of total waste plastics, 60 min duration, 450–650 psi pressure under nitrogen gas and evolved gases and 420–430 °C temperature. The micro-reactor was agitated by a built-in mechanical stirrer and heated with a temperature controlled built-in heater. After one hour, the reactor was cooled to room temperature. The nitrogen and the gases evolved during the pyrolysis were vented out. After the reaction, the liquid and solid products were separated and analyzed by the solvent fractionation methods to determine the amounts of liquid (fuel oil) products [12,19]. The liquid product was dissolved in three different solvents successively hexane, toluene and THF. The fractions obtained were hexane-soluble materials (HXs); toluene-soluble, hexane-insoluble material (TOLs); THF-soluble, toluene-insoluble material (THFs); and THF-insoluble material called as insoluble organic material (IOM). Analysis was performed using different analytical techniques on hexane soluble liquid fractions obtained from the pyrolysis reactions.
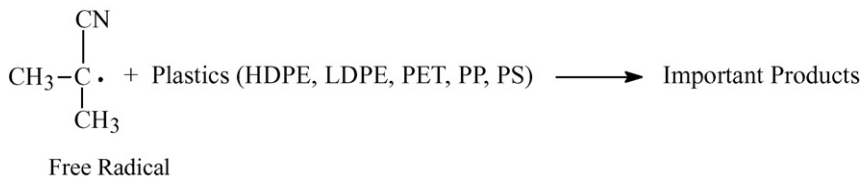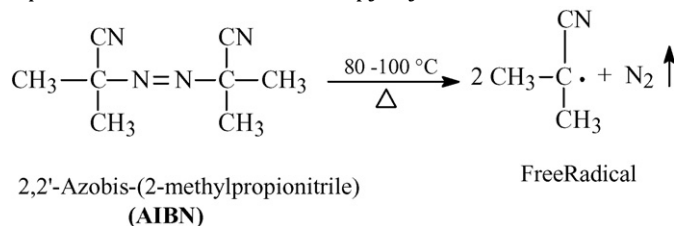
2,2'-Azobis-(2-methylpropionitrile)
(AIBN)

FreeRadical

Free Radical

After the reaction, the liquid and solid products were separated and analyzed by the solvent fractionation methods to determine the amounts of liquid products using previously reported methods [12,19].

2.2.1. Fourier transform-infrared (FT-IR) spectroscopy

The hexane soluble (HXs) obtained from different pyrolysis reactions were analyzed using infrared spectroscopy on a PerkinElmer Model 16F PC FT-IR spectrophotometer loaded with Spectrum v2.00 software (Massachusetts, USA). The thin film samples were pre-

pared in chloroform. The samples were analyzed using thin film on the KBr salt plate technique. The insoluble organic materials (IOM) were analyzed using KBr as a mulling agent.

2.2.2. Nuclear magnetic resonance (NMR) spectroscopy

Solutions for the measurement of ¹H NMR spectra were prepared by dissolving 1 g of sample in 2 ml of deuterated-chloroform. Spectra were recorded on a JEOL-500 pulse Fourier transform (PFT) spectrometer operating at 500 MHz using 5 mm sample tubes. ¹H NMR spectra were obtained and the experimental conditions were: spectrum width, 2800 Hz; data points, 15,680; pulse width, 3.5 ms (45°); pulse delay, zero; and number of transients, 64.

2.2.3. Simulated distillation

The boiling range distributions of hexane soluble fractions were determined using simulated distillation analyzer [ASTM method 5307]. The simulated distillation analyzer used for this study was a Hewlett Packard 5880A gas chromatograph equipped with automatic sampler model HP 7673A and a flame ionization detector (FID). The column used was 1/8 × 20 in. stainless steel, coated with 10% UCW-982 on 80/100 mesh chromosorb P-AW. The computer program calculates the data and produces a simulated distillation report in percent distilled versus temperature.

2.2.4. Gas chromatography

Agilent GC 6890 plus Series gas chromatograph equipped with a split–splitless injector (split ratios of 20:1) was used for the GC analysis. The temperature of the injector was 250 °C, with 10 psi constant pressure. The column was an HP-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness) consisting of Crossbond® (5% phenyl–95% dimethylpolysiloxane). Helium was the carrier gas at a flow rate of 15.8 ml/min and programmed temperature was applied to obtain the separation of the compounds; precisely the initial temperature was 50 °C, hold 2 min, then ramped at 10 °C/min to 140 °C (hold time 0 min), then finally ramped at 20 °C/min to 250 °C (hold time 20 min). The detector was flame ionization detector (FID), with hydrogen and air flow of 40.0 and 450.0 ml/min, respectively. Makeup flow was on with 45.0 ml/min of helium.

2.2.5. Gas chromatography–mass spectrometry

A Trace GC–MS 2000 Series (Varian Inc. USA) gas chromatograph equipped with a split–splitless injector (split ratios of 20:1) was used for the GC–MS analysis. The column was a Cp-Sil low bleed®-5 MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness) consisting of Crossbond®. Helium was the carrier gas at a flow rate of 1.0 ml/min and programmed temperature was applied to obtain

the separation of the compounds; precisely the initial temperature was 50 °C, hold 2.0 min, then ramped at 10 °C/min to 140 °C (hold time 0 min), then finally ramped at 20 °C/min to 250 °C (hold time 20 min). The gas chromatograph was interfaced with a GCQ Plus mass detector operating in the EI mode (70 eV), under autotune conditions. The temperatures of injector, transfer line and ionization source were 250, 225 and 270 °C, respectively. The mass spectra were recorded within 50–450 amu in full scan mode to collect the total ion current (TIC) chromatograms; NIST MS search was used for compound identification.
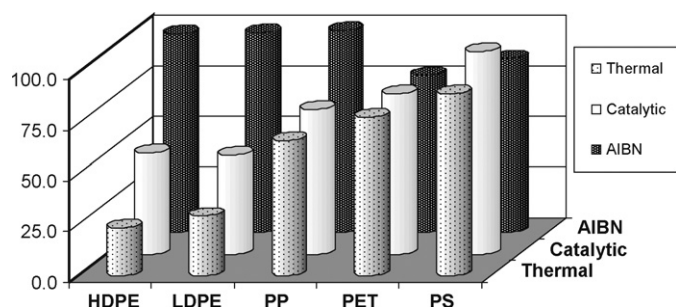
Fig. 2. Percent conversion of single plastics in thermal, catalytic and AIBN pyrolysis.

Table 1
Pyrolysis of mixed plastics with AIBN.

Plastics	Temperature, °C	Pressure, psi	% Conversion	% IOM
HDPE/LDPE/PS	440	500	95.0	5.0
HDPE/LDPE/PP	422	500	97.8	2.3
HDPE/LDPE/PET	426	700	90.3	9.8
LDPE/PP/PET	425	650	91.5	8.5
LDPE/PP/PET	410	800	88.0	12.0
PS/PP/PET	410	600	83.8	16.3
PS/LDPE/PET	420	500	84.0	16.0
PS/HDPE/PET	428	550	75.0	25.0
WCUP/BCUP/BOTTLE	405	450	85.8	14.3

3. Results and discussion

HDPE, LDPE, PP, PS and PET polymers used in this study were individually pyrolyzed with azoisobutylnitrile (AIBN) at optimal reaction conditions. The liquid and solid products were separated by the solvent fractionation methods described previously [12,19]. The percent conversion of these plastics obtained from the pyrolysis in presence of AIBN was compared with thermal [12] and catalytic [19] pyrolysis conversions carried out by us as shown in Fig. 2. Pyrolysis of individual plastics with AIBN shows that under similar conditions of temperature and nitrogen pressure, PP underwent a complete conversion whereas LDPE and HDPE yielded near complete conversions and PS and PET afforded in the moderate to high conversions. It is observed with great interest that the percent conversions of plastics obtained by thermal and catalytic pyrolysis were far less than AIBN pyrolysis. In thermal pyrolysis, HDPE and LDPE conversions increased from less than 25% to close to 100% while PP converted increased from around 40% to 100% [12]. Though there was increase in the percent conversions of PS and PET with AIBN pyrolysis, these plastics were significantly converted in thermal pyrolysis as shown in Fig. 2. The main purpose of using catalysts in pyrolysis study is to increase the cracking and degradation of plastics more than thermal pyrolysis. The result shows that all plastics appreciably converted more in catalytic pyrolysis than thermal pyrolysis [19]. However, on comparing the catalytic pyrolysis with AIBN pyrolysis, the results give a very promising and significant data. HDPE, LDPE and PP plastic conversions with AIBN increased to almost double than that of catalytic pyrolysis conversion. The AIBN pyrolysis conversion of PET was also increased but slightly than that of catalytic pyrolysis. However, in case of PS, AIBN pyrolysis could not convert higher than that of catalytic pyrolysis and this reaction need to be investigated further.

It is important to discuss the role of azoisobutylnitrile and possible reaction mechanism. The use of azoisobutylnitrile as an initiator for the purpose of depolymerization or liquefaction in pyrolysis of plastics has not yet been reported. Most of the plastic such as LDPE, HDPE and PP are polymers of alkanes' monomers while PS and PET contains additional aromatic benzene rings in their structures. These alkanes are derived from petroleum hydrocarbons and are used to produce energy by combustion but a few percent are converted to industrially useful compounds by controlled reactions. The alkanes are inert to attack by most chemical reagents and reacts only under the special conditions of high temperature, in presence of catalysts and/or radical initiated reactions. In our study, radical initiated degradation were found to be more effective from chemistry point of view and should be adopted from the environment point of view because there is no spent catalyst in insoluble organic material (IOM) fractions. In a second process, a series of pyrolytic reactions of three different plastics in one batch was conducted with azoisobutylnitrile under similar conditions and results are given in Table 1. The result indicates that maximum conversion is obtained where both HDPE and LDPE are pyrolyzed together with other plas-

tics. These results are in agreement with the individual plastic AIBN pyrolysis where HDPE and LDPE were almost completely converted. The conversion includes conversion of total charge of plastics into gases and liquids products that is called pyrolysis oils. Analysis was performed on hexane soluble liquid fractions using different analytical techniques.

3.1. FT-IR spectroscopy analysis

The polyalkene plastics, HDPE, LDPE, and PP, gave very similar FT-IR spectra since their polymer structures are very similar and their thermal degradations are likely to produce similar compounds in the derived oil/wax. The medium sharp peak at $3084\,cm^{-1}$ and strong sharp peak at $3025\,cm^{-1}$ is due to the presence of alkene —C—H stretching vibrations. The peaks between 3000 and $2800\,cm^{-1}$ indicate the presence of —CH_3, —CH_2, and C—H functional groups, which are indicative of aliphatic species such as alkanes. The sharp strong peak at $2919\,cm^{-1}$ is indicates asymmetrical —CH_2 stretch and broad medium peak at $2870\,cm^{-1}$ is represents a symmetrical —CH_2 stretch. The C=C absorbance peak between 1625 and $1675\,cm^{-1}$ confirms that alkene groups are present in the hexane soluble fractions. The presence of peak in the region from 1350 to $1500\,cm^{-1}$ due to the deformation vibrations of C—H bonds confirms the presence of aliphatic groups. A weak and sharp peak located at $894\,cm^{-1}$ represent C—H out-of-plane bending vibration of alkene structures. Two sharp strong peaks at 699 and $730\,cm^{-1}$ indicate C—H cyclic deformations which suggest either aromatic or more likely —CH_2 bending which has spilt due to interaction in long molecular chains, representing the presence of long oligomer chains. The overall FT-IR spectra of the liquid product obtained from the various pyrolysis processes is, therefore, dominated by the presence of alkane and alkene functional groups.

The presence of mono, polycyclic and substituted aromatic groups were clearly observed at lower wavelengths. Naphthalene and benzene have been identified as the major constituents in hexane soluble fractions derived from the pyrolysis of PS, while other aromatic compounds identified included alkylated benzenes and other polycyclic aromatic hydrocarbons. The liquid products obtained from the pyrolysis of HDPE, LDPE, PP and PS gave very similar FT-IR spectra, which consist essentially of the mixed spectra from each component. Each spectra contain the dominantly alkane and alkene peaks derived from the HDPE and LDPE plastics and the mainly aromatic peaks derived from the PS. The aromatic structures present in the hexane soluble fractions from the mixtures are clearly indicated by the strong peaks from 3000 to $3050\,cm^{-1}$, medium sharp peaks at 1080 and $1029\,cm^{-1}$ due to aromatic in-plane bending and group of peaks between 675 and $900\,cm^{-1}$. The following prominent peaks were observed in FT-IR spectra of the liquid products obtained from various pyrolysis processes. These peaks are attributed to the degradation of PET plastics because it contains C=O groups in its structure. The small sharp peaks at 2733, 1941, 1857, $1801\,cm^{-1}$ are due to carbonyl overtones. A strong sharp peak at $1729\,cm^{-1}$ and another sharp but weak peak at $1178\,cm^{-1}$
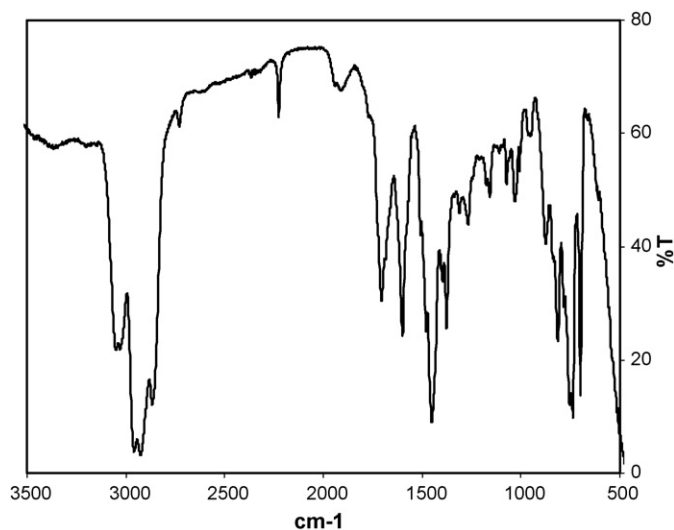
Fig. 3. FT-IR spectrum of hexane soluble obtained from AIBN pyrolysis of HDPE–LDPE–PET mixed plastics.

are due to carbonyl groups. Fig. 3 shows FT-IR spectrum of hexane soluble obtained from AIBN pyrolysis of HDPE–LDPE–PET mixed plastics.

3.2. NMR spectroscopy analyses

The proton NMR analyses of the liquid products derived from AIBN pyrolysis of individual and few mixed plastics are given in Table 2. The integrated area of H NMR spectra illustrates the presence of $-CH_3$, $-CH_2$ and $C-H$ functional groups in the aliphatic region between 0:00 and 4.00 ppm. The aromatic structures present in the liquid portion obtained from AIBN pyrolysis of individual and mixed plastics clearly indicated by the strong peaks $C=C$ absorbance in the region between 6:00 and 8.00 ppm. NMR spectra of the liquid products derived from AIBN pyrolysis of LDPE, HDPE and PP contained predominant aliphatic peaks indicating the liquid products derived from the alkane polymers. PP has an additional CH_3 group than HDPE and LDPE polymers so it was expected to give lower content of aromatic hydrogen. The liquid product obtained from PS and PET plastics AIBN pyrolysis contains major portion of aromatic hydrogens. The higher aromatic content of hydrogen indicates the presence of aromatic ring structures in the PS and PET plastics under study.

The proton NMR results obtained from the pyrolysis of three mixed plastics were also analyzed. The AIBN degradation of PS–HDPE–PET mixed plastics produces liquid that contains major portion of aromatic hydrogens. Thermal and catalytic pyrolysis afforded almost same results with not much significant changes in the hydrogen contents of the liquid products. However, AIBN pyrolysis of mixed waste plastics (WP-Cup-Cap) gave different results. WP is a waste plastic (PET bottle), cup is polystyrene waste cup and cap is the drinking water cap (HDPE). The liquid

Table 2
Percent hydrogen obtained from the proton NMR spectra of hexane solubles.

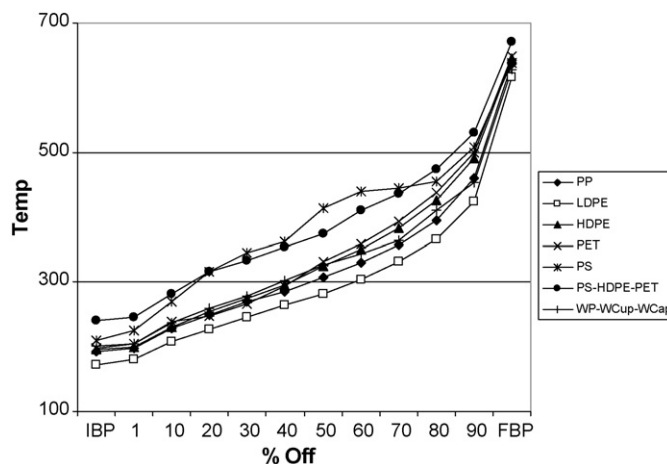| Plastics	Aliphatic	Aromatic
PP	90.10	9.90
LDPE	92.22	7.78
HDPE	80.69	19.31
PET	25.93	74.07
PS	23.08	76.92
PS–HDPE–PET	31.03	68.97
WP-Cup-Cap	55.36	44.64

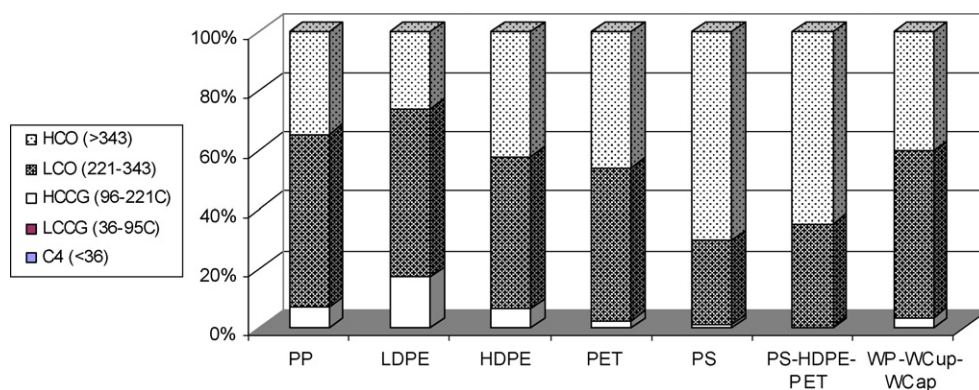**Fig. 4.** SIM distillation of hexane solubles obtained from AIBN pyrolysis of plastics.

product obtained from AIBN pyrolysis of mixed waste plastics (WP-Cup-Cap) has more aliphatic hydrogen than model mixed plastics (PS–HDPE–PET). This could be due to the presence of some additives and stabilizers in the processed and waste plastics which are missing in model and virgin plastics. These additives and stabilizers might be hindering the degradation process.

### 3.3. SIM distillation of liquid products

The hexane soluble fractions of the different reaction systems were analyzed using simulated distillation (SIM). The results from the analysis regarding the recovery temperatures of HXs at initial boiling point (IBP) shows 10%, 50%, 90% and final boiling point (FBP). In addition, the amount of LCCG (light catalytically cracked gasoline, light naphtha), HCCG (heavy catalytically cracked gasoline, light naphtha), LCO (light cycle oil) and HCO (heavy cycle oil) were also determined. The SIM results show a general decrease in IBP recovery temperature for the liquid products. The low boiling fraction materials were not found and cuts were obtained only after 96 °C+ boiling point. It could be due to the vaporization of highly volatile components quickly. In AIBN pyrolysis of individual HDPE, LDPE, PP and PET plastics, LCO fractions have high recovery than HCO fractions with the exception of PS where HCO is higher. PS–HDPE–PET mixed plastics have high HCO fractions whereas WP-WCup-Wcap missed plastics have high LCO recovery. Percent product distribution of different hydrocarbons obtained from the SIM distillation of hexane soluble portion of individual and mixed plastics are given in Figs. 4 and 5. The proportion of material that boiled in the range 200–300 is found to be low and 300 °C+ was found to be relatively larger. The mixed plastics show the recovery of high boiling fractions than individual plastics as can be clearly inferred from the figures. LDPE has shown the maximum contents of the low boiling fractions.

3.4. Gas chromatography and mass spectrometry analysis

Gas chromatography analysis of all liquid products was carried out to identify the types of industrial and environmentally useful components obtained from AIBN pyrolysis of plastics. Table 3 shows most of the compounds identified in liquid products obtained from the various pyrolysis processes using gas chromatography with flame ionization detection. The liquid products gave almost exclusively substituted aromatic products without any alkanes, alkenes and alkadienes. A wide spectrum of hydrocarbon fragments containing many number of carbon atoms were obtained from AIBN pyrolysis of the mixed plastics. Thermal pyrolysis occurs through

Fig. 5. Percent product distribution from the SIM distillation of hexane solubles obtained from AIBN pyrolysis of plastics. LCCG = light catalytically cracked gasoline (light naphtha); HCCG = heavy catalytically cracked gasoline (light naphtha); LCO = light cycle oil; HCO = heavy cycle oil.
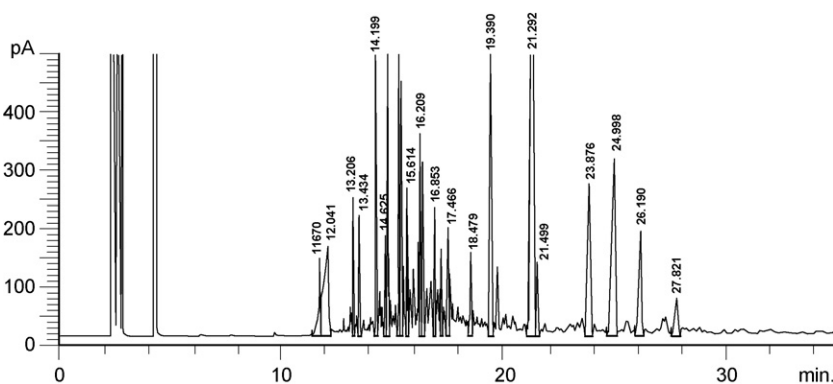
Fig. 6. Gas chromatogram of hexane soluble fraction obtained from the AIBN pyrolysis of plastics.

random scission of C—C bonds and yields a very broad range of liquid hydrocarbon mixture, whereas catalytic pyrolysis occurs at selective C—C positions yielding a much narrower range of liquid products. The AIBN pyrolysis occurs through free radical initiation and breaks C—C bonds on the basis of free radical stability and affords a massive range of products. The C—C bond is the weakest in the polyalkene structure and during the degradation process, the stabilization of the resultant radical after chain scission leads to the formation of C=C, carbon double bounds, in the structure. Consequently, a large number of compounds with carbon double bonds, as shown by the higher concentration of alkenes in the resultant pyrolysis oil, are obtained. However, because of the presence of the CH_3

side chain in the PP structure, different hydrocarbons may also form in addition to those found with other polyalkenes pyrolysis. The liquid product from the pyrolysis of PS mixed plastic chiefly gives aromatic product dominated by styrene and styrene derivatives. Polycyclic aromatic hydrocarbons, including naphthalene, benzoic acid, biphenyl, fluorine, diphenylmethane and phenanthrene and their alkylated derivatives, were also detected. Substituted aromatic compounds such as butylbenzyl phthalate1,1,3,1-terphenyl, biphenyl, 1,1,3,1-terpheyl-5-phenyl, m-ter phenyl and many compounds were analyzed in a moderate amounts.

Mass spectra of the liquid product obtained from AIBN pyrolysis of mixed plastics gave very important organic compounds.

Table 3
Chemical compounds identified by GC in the liquid product of AIBN pyrolysis.

| Peak #	RetTime [min]	Area %	Name of compounds
1	11.7	4.9	Naphthalene
2	11.8	4.1	Benzoic acid
3	13.4	2.7	1-Methyl naphthalene
4	14.2	11.1	Biphenyl
5	14.4	2.4	1-Ethyl naphthalene
6	14.7	6.1	Diphenylmethane
7	15.2	5.9	1,1′-Biphenyl-3-methyl
8	15.3	5.7	1,1′-Biphenyl-4-methyl
9	15.6	2.7	Bibenzyl
10	16.1	3.1	4-Ethylbiphenyl
11	16.3	5.5	2,2′-Dimethyl biphenyl
12	17.4	2.3	Naphthalene 2 (phenylmethyl)
13	18.5	3.7	p-Ter phenyl
14	19.4	7.5	m-Ter phenyl
15	21.2	15.5	Butybenzzyl phthalate1,3′,1″-terpheyl
16	23.8	4.7	Methanone (1,1′-biphenyl)-4-YLPhenyl
17	24.9	7.5	1,1′,3′,1″-Terpheyl-5′phenyl
18	26.1	4.3	1,1,3,1,3,1′-Quaterphenyl
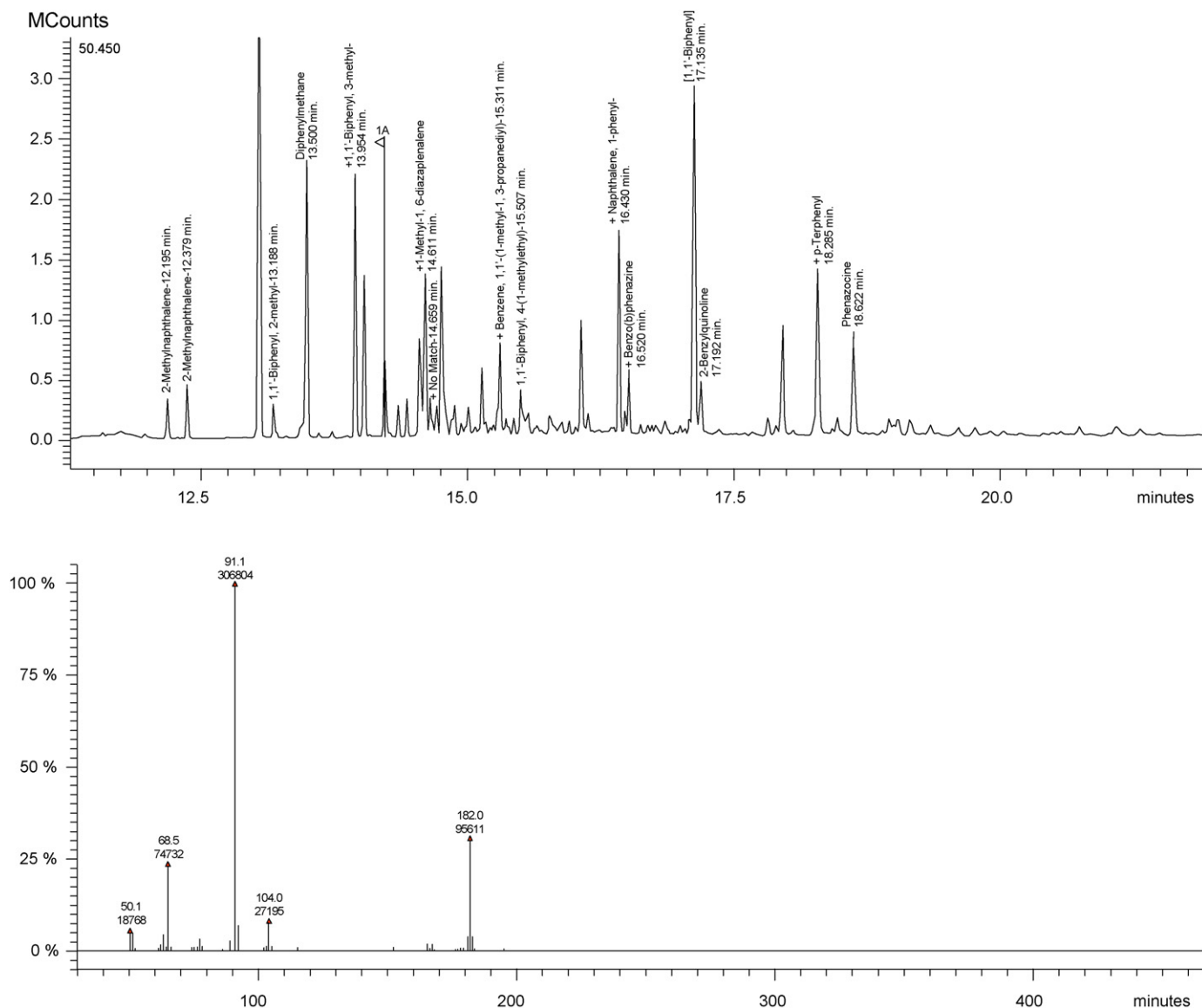
Fig. 7. GC–MS chromatogram of hexane soluble fraction obtained from the AIBN pyrolysis of plastics.

Some of the compounds searched through the GC–MS library identified: biphenyl, diphenylmethane, bibenzyl, 4-ethylbiphenyl, 1,1-diphenyl-2-ethyl, benzene-1-1-(1-methyl-1,3-propanediyl)bis, phenanthrene, 1-phenyl naphthalene, m-terphenyl, 2-phenylnaphthalene, 2-(phenylmethyl)-naphthalene, p-terphenyl, methanone (1,1′-biphenyl)-4-yl phenyl, 1,1,3,1,3,1′-quarterphenyl and many more. Fig. 6 shows the GC and Fig. 7 shows the GC–MS chromatogram of the liquid products obtained from AIBN pyrolysis.

4. Conclusions

The pyrolysis of mixed plastics has been considered as an effective way to convert waste plastics into environment friendly and industrially useful hydrocarbon liquid products. The main purpose of using catalysts in pyrolysis study is to increase the cracking and degradation of plastics more than thermal pyrolysis. Our study shows that all plastics appreciably converted more in catalytic pyrolysis than thermal pyrolysis. However, on comparing the results of catalytic pyrolysis with AIBN pyrolysis, a very promising and significant data is obtained. Pyrolysis of individual plastics with AIBN shows that under similar conditions of temperature and

nitrogen pressure, PP underwent a complete conversion whereas LDPE and HDPE yielded near complete conversions and PS and PET afforded in the moderate to high conversions. In a series of pyrolytic reactions of three different plastics in one batch with azoisobutyl-nitrile afforded maximum conversion where HDPE and LDPE both were pyrolyzed together with other plastics. It is observed with great interest that the percent conversions of plastics obtained by thermal and catalytic pyrolysis were far less than AIBN pyroly-sis. The use of AIBN in the depolymerization studies has several advantages over catalytic pyrolysis. First, AIBN is cheap, cost wise, in comparison to any catalyst used in such studies. Secondly, the amount of IOM in the reactor drastically decreased with AIBN. There is no problem of managing spent catalyst as AIBN completely disso-ciates into nitrogen gas and organic compounds during the pyrolysis process. Therefore, the use of AIBN for pyrolysis process is very environmental friendly. SIM distillation of hexane soluble portion showed that the low boiling fractions were not found and fractions were obtained only after 96 °C+ boiling point. GC identified some very important chemical compounds present in the liquid products obtained from the pyrolysis of individual and mixed plastics. These compounds are of great importance to the industry and environ-

ment as well. Pyrolysis of waste plastics in presence of AIBN is seen to be a feasible process by which waste plastics can be converted into liquid fuels or chemical feed stocks.

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