

Conversion of waste polystyrene through catalytic degradation into valuable products

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Abstract—Waste expanded polystyrene (EPS) represents a source of valuable chemical products like styrene and other aromatics. The catalytic degradation was carried out in a batch reactor with a mixture of polystyrene (PS) and catalyst at 450 °C for 30 min in case of Mg and at 400 °C for 2 h both for MgO and MgCO₃ catalysts. At optimum degradation conditions, EPS was degraded into 82.20±3.80 wt%, 91.60±0.20 wt% and 81.80±0.53 wt% liquid with Mg, MgO and MgCO₃ catalysts, respectively. The liquid products obtained were separated into different fractions by fractional distillation. The liquid fractions obtained with three catalysts were compared, and characterized using GC-MS. Maximum conversion of EPS into styrene monomer (66.6 wt%) was achieved with Mg catalyst, and an increase in selectivity of compounds was also observed. The major fraction at 145 °C showed the properties of styrene monomer. The results showed that among the catalysts used, Mg was found to be the most effective catalyst for selective conversion into styrene monomer as value added product.

Keywords: Waste Polystyrene, Catalytic Degradation, Selective Conversion, Chemical Products, Styrene Monomer

INTRODUCTION

Plastic polymers make up a high proportion of waste, which is constantly increasing and causing serious pollution problems [1,2]. Amongst plastic polymers polystyrene (PS) is a widely used commodity thermoplastic [3-5]. EPS is used extensively for building insulating materials and as packaging materials [6]. It ranks fourth in the world consumption after polyethylene (PE), polypropylene (PP) and polyvinylchloride (PVC) [3]. In 2004 EPS total world production was 5 million tons, the average annual growth is expected to be 2.5% per annum through 2010, and according to expectations its total amount will be double within 25 years [6]. Disposal of waste EPS is becoming an extreme problem that has a high environmental impact. There has been increasing concern about the recycling of waste EPS, for which different options exist. An alternative way for handling waste polymers is tertiary recycling in which plastic waste is degraded/depolymerized into different materials like styrene, toluene and ethylbenzene to produce either new polymers or other substances [7-12]. Proper selection of catalyst and reactor design can decrease temperature for catalytic degradation as well as increase the selectivity of products. Most of the catalytic degradation of PS has been studied with solid catalysts such as zeolite, silica-alumina, fresh FCC catalyst, MCM-41, etc., which are expensive [13-15]. However, few studies have been conducted with solid base as catalysts such as alkali and alkaline earth metals oxides and salts [15-21].

70 weight percent (wt%) styrene has been recovered using a semibatch reactor with continuous flow of inert gas (N₂) at 350 °C from the degradation of PS [20]. With solid acid and solid base catalysts like magnesium oxide (MgO), calcium oxide (CaO), barium oxide (BaO), potassium oxide (KO), copper oxide (CuO), iron oxide

(FeO), titanium dioxide (TiO), chromium oxide (CrO), cobalt oxide (CoO), zinc oxide (ZnO), silica-alumina (SiO/AlO), zeolite (HZSM5) and active carbon (AC) catalysts were used separately and found that BaO was the most effective catalyst for the degradation of PS to styrene monomer and dimer at 350 °C [21]. On the other hand, another method with very low selectivity (above 5 wt%) of styrene in the degradation of PS was reported with solid acids such as silica-alumina and HY or REY zeolites at 350 °C [22].

Recently, the effect of metal oxides in the presence of hydrogen at elevated temperature and pressure using benzene as a solvent was studied for the degradation of PS. They found that alkali oxide shows higher reactivity towards PS as compared to transition metal oxides as catalyst except manganese (IV) oxide, which showed higher reactivity due to its reduction towards stable manganese (II) oxide under degradation environment [23].

The aim of the present study was to convert waste EPS into liquid products with selective hydrocarbons which could be used as a raw chemical, without the use of any solvent and other additives. The catalytic performance of Mg, MgO and MgCO₃ as catalysts was evaluated by catalytic degradation of EPS. The effects of temperature, contact time, catalyst to polymer ratio and pressure were studied on the catalytic degradation process.

EXPERIMENTAL

1. Materials and Methods

Waste EPS sample was collected from the refrigeration industry used for packing of refrigerators and freezers; EPS beads are manufactured with an average molecular weight between (Mw) 160,000 and 260,000 g/mol [6,24]. The sample was then ground into small granules and heated at 150 °C for 15-25 min to reduce its volume 20 times. Three catalysts were used for EPS degradation, i.e., magnesium powder (Mg) (Particle size: 0.06-0.3 mm, 98.5%) and magnesium oxide (MgO) (98.0-100.5%) that were obtained from Merck

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KGaA 64271, Darmstadt, Germany; while magnesium carbonate (MgCO_3) (99.87%) was purchased from BDH Laboratory Supplies, Poole, BH15 1TD, England. Both thermal and catalytic degradation experiments were conducted in an indigenously designed efficient Pyrex glass batch reactor (I.D. 7 cm and h 22 cm) provided with an external heating assembly that operates up to 1,000 °C. EPS samples in mixture with corresponding amount of catalyst were loaded into the reactor, a solid-solid blend without the use of any solvent and heated at a rate of 25 °C/min. All the experiments were performed using triplicate analysis; the results of the experiments are consistent and within the statistical acceptable range. The degradation of EPS gave off liquids, gases and residues - the carbonaceous compounds stuck to the reactor wall.

Material balance calculations were performed using the following formula (Eq. (1)-(3)):

$$\% \text{ Conversion of Liquid} = \frac{\text{Wt. of Liquid obtained}}{\text{Wt of PS}} \times 100 \quad (1)$$

$$\% \text{ Conversion of Gas} = \frac{\text{Wt. of EPS} - (\text{Wt. of Liquid} + \text{Wt. of Residue})}{\text{Wt of EPS}} \times 100 \quad (2)$$

$$\text{Total \% Conversion} = \frac{(\text{Wt. of PS} - \text{Wt. of Residue})}{\text{Wt. of EPS}} \times 100 \quad (3)$$

After optimization of degradation conditions 100 g sample of EPS in a mixture with optimum amount of catalyst was loaded in the reactor and heated at their respective optimized temperature and time for both thermal and catalytic degradation. The reaction temperature was measured by a thermocouple that was in direct contact with the reaction mixture, and the liquid products from the reactor were collected in a cold trap over a period of time (optimum time). The liquid products collected at optimized parameters were used for fractional distillation, GC-MS analysis and selectivity of component products. The parent liquid was separated on the basis of boiling point, where each distillate was also analyzed for its composition using GC-MS.

2. Thermogravimetric Analysis

Thermogravimetric analysis of EPS sample was done in a Perkin-Elmer TG/DTA Diamond Series (USA) instrument in which about 7 mg of sample pieces was heated. The temperature was increased from 40 °C to final temperature 1,000 °C at a rate of 10 °C/min. The sample temperature was measured with a thermocouple attached directly at the crucible very close to the sample. The weight loss versus temperature curve for thermal decomposition of PS under a linear heating rate in oxidative (O_2) and inert (N_2) atmosphere is given in Fig. 1.

3. Physical Parameters Study

The parent liquid obtained from thermal and catalytic degradation of waste EPS was separated on the basis of boiling point of hydrocarbons by fractional distillation. The different fractions obtained were characterized using density (d), refractive index (n_D^{25}) and molar refraction (γM). For refractive index (n) Abbe's Refractometer (ATAGO DTM-1) was used.

4. GC-MS Analysis

The degraded products were analyzed with GC-MS (Shimadzu QP2010 Plus) fitted with a DB-5MS (J&W Scientific) fused silica capillary column (30 m×0.25 mm ID, 0.25 μm film thickness), hav-

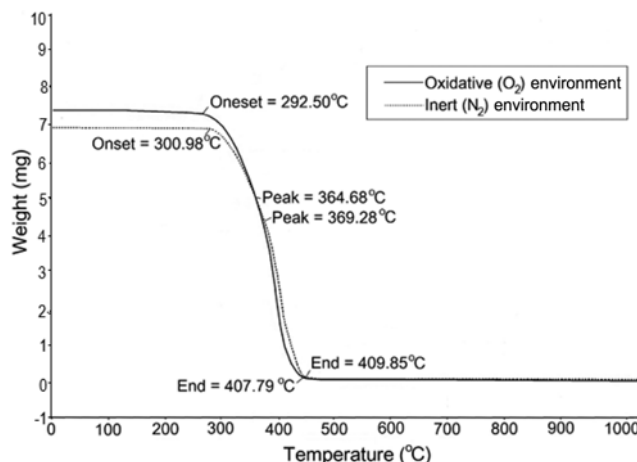


Fig. 1. TGA curves of PS in oxidative (O_2) and inert (N_2) environment.

ing a stationary phase of 95% dimethylpolysiloxane with 5% polyphenyl. Helium was used as carrier gas with a flow rate of 1.5 ml/min. The injection volume was 1 μL . The injector temperature was 300 °C. The temperature program applied was as follows: the oven was held at 35 °C for 5 min, then ramped to 100 °C at the rate of 5 °C/min, held for 1 min at 100 °C, then the temperature was ramped to 150 °C at the rate of 10 °C/min, held for 10 min at 150 °C, and again the temperature was ramped to 290 °C at 2.5 °C/min, which was held for 10 min at 290 °C. The ion source temperature was 280 °C and the interface temperature was 290 °C. The ion mass spectra were automatically compared to spectral libraries.

RESULTS AND DISCUSSION

1. Thermogravimetric Analysis

The weight loss versus temperature curves for thermal decomposition of PS under a linear heating rate in the inert (N_2) and oxidative (O_2) environment were made and the results are shown in Fig. 1. It can be seen that the decomposition is a single step process with the onset and end temperature of 300.98 °C and 409.85 °C, respectively, in case of N_2 environment and 292.50 °C and 407.79 °C, respectively, for oxidative environment. The curve shows that maximum weight loss related to volatilization of hydrocarbons occurred at 369.28 °C in inert atmosphere and 364.68 °C in case of oxidative atmosphere. In inert atmosphere 99.57% changes occurred from 300.98 °C to 409.85 °C. In case of oxidative environment 100% weight changes occurred from 292.50 °C to 407.79 °C. At these temperatures with the volatilization process, other reactions like cracking of side chain from aromatic rings, isomerization and poly condensation also occur. Therefore, one might think that all the volatile matter of PS has been decomposed to volatile hydrocarbons.

2. Catalytic Degradation of EPS

The aim of the current study is to increase the selectivity of liquid product yield with higher total percent conversion and minimum residue. The data obtained with thermal and catalytic degradation were compared for liquid product yield, total percent conversion and selectivity of aromatic compounds. The effect of different process parameters such as contact mode of catalyst, degradation temperature, residence time and polymer to catalyst ratio were opti-

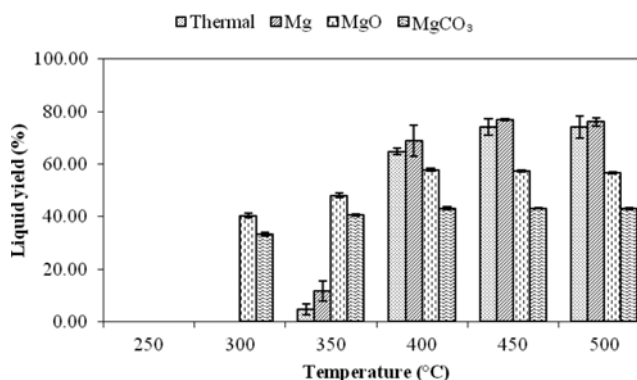


Fig. 2. Effect of temperature and comparison of liquid products yield using thermal degradation (degradation time, 120), Mg, MgO and MgCO₃ catalysts (time, 30 min; polymer to catalyst ratio, 1 : 0.3) for the degradation of EPS.

mized for maximum conversion of EPS into liquid products.

2-1. Effect of Catalyst Contact Mode

In EPS catalytic degradation process, two modes of catalyst introduction to the EPS were studied. In a batch reactor MgO and MgCO₃ were introduced as a solid and liquid form for catalytic degradation experiments. In batch cases the catalysts were mixed with polymer, placed in the reactor and heated at 400 °C for 2 h. The volatile products were cooled and analyzed. It has been observed that liquid phase of catalyst retards the escape of products, and the yield of liquid from catalytic degradation of EPS was lower as compared to solid catalyst.

2-2. Effect of Temperature

The effect of temperature on thermal and catalytic degradation of EPS was studied in the range of 250 °C to 500 °C (Fig. 2). Most of the previous studies reported the degradation of PS with fixed temperature [19,24] or with low limits of the reactor temperature, for example, most autoclaves can be operated up to a certain temperature like 250 °C and 427 °C [23,25]. Our preliminary experiments and literature survey show that the yield of styrene monomer and associated component products like benzene, toluene and ethylbenzene increased with the increase of degradation temperature [26-29]. Where further increase from 500 °C showed decrease in the yield of styrene monomer as well as benzene, toluene and ethylbenzene products [26]. Some studies have reported decrease of styrene monomer with thermal degradation in the presence of benzene or toluene as solvents [30,31], but for cost effective methods low cost catalyst must be preferred. Therefore, the acceptable and most observed temperature range from 250-500 °C was selected for cost-effective method in order to yield maximum liquid products and high selectivity of the product contents. In the current study thermal degradation was carried out in 120 min, while with catalysts each reaction was carried out in 60 min degradation time using polymer to catalyst ratio 1 : 0.3. The amount of liquid increased with increase in temperature and maximum yield of liquid obtained at 500 °C with thermal degradation (74.13±4.05 wt%) and using Mg as catalyst (76.87±0.50 wt%). The maximum amount of liquid 57.80±0.53 wt% and 43.27±0.42 wt% was obtained at 400 °C with MgO and MgCO₃ catalysts, respectively. Further increase in temperature did not show any increase in the yield of liquid but the amount of residue was decreased with the increase of gases in case of Mg and

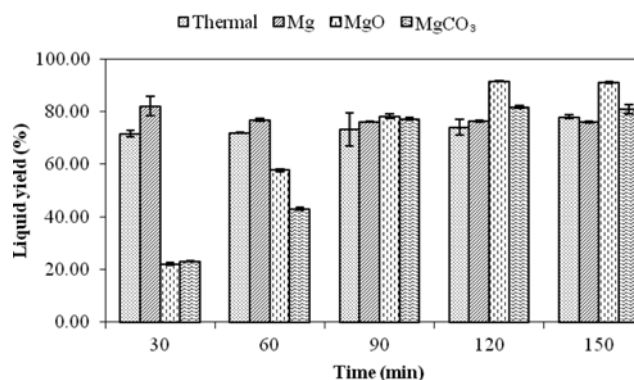


Fig. 3. Effect of time and comparison of liquid products yield using thermal degradation (temperature, 450 °C), Mg (temperature, 450 °C; polymer to catalyst ratio, 1 : 0.3), MgO (temperature, 400 °C; polymer to catalyst ratio, 1 : 0.3) and MgCO₃ (temperature, 400 °C; polymer to catalyst ratio, 1 : 0.3) catalysts for the degradation of EPS.

MgO catalysts. At lower temperature the residue formation indicated competitive crosslinking reaction, which produced hurdles in the degradation of PS and its resulting products [27].

2-3. Effect of Time

The Effect of heating time on thermal and catalytic degradation

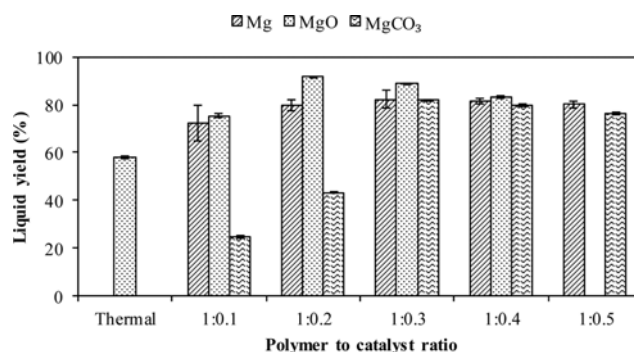


Fig. 4. Effect of polymer-to-catalyst ratio and comparison of liquid products yield using Mg (temperature, 450 °C; time, 30 min), MgO (temperature, 400 °C; time, 120 min) and MgCO₃ (temperature, 400 °C; time, 120 min) catalysts for the degradation of EPS Thermal degradation means no catalyst was used (temperature, 450 °C; time, 150 min).

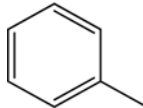
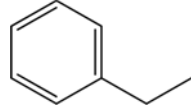
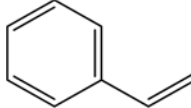
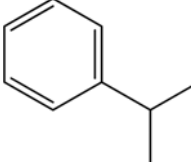
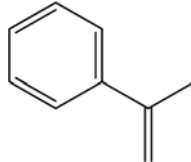
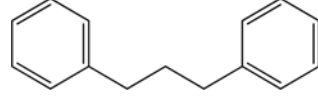
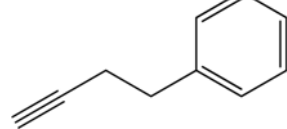
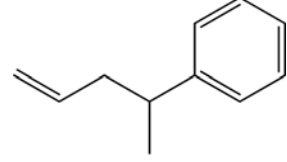
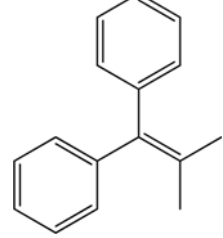
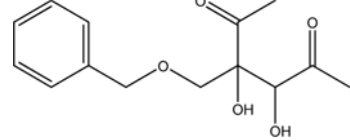
Table 1. Major compounds in the degradation liquid from EPS at 1.47 MPa and 400 °C (wt%)

Compound	Thermal	Catalyst		
		Mg	MgO	MgCO ₃
Benzene	1.27	1.27	1.32	1.0
Toluene	27.0	27.6	35.0	34.0
Ethylbenzene	39.0	28.0	40.0	45.0
Styrene	21.0	25.0	10.0	5.0
Isopropylbenzene	0.9	2.5	0.9	2.6
Alpha methyl styrene	0.33	1.2	1.0	2.1
1,3-Diphenyl-propane	0.6	2.56	1.2	2.5
Others	9.9	11.87	10.58	7.8

of EPS was studied from 30 min to 150 min at optimum temperature (Fig. 3) using polymer-to-catalyst ratio of 1:0.3. The effect of

time has not been studied in most of the studies and the degradation of PS has been carried out for a fixed reaction time [19,23].

Table 2. List of component products formed using thermal degradation (temperature, 450 °C; time, 150 min), Mg (temperature, 450 °C; time, 30 min), MgO (temperature, 400 °C; time, 120 min) and MgCO (temperature, 400 °C; time, 120 min) catalysts

S. No.	Product name	Structure	Percent composition			
			Thermal	Mg	MgO	MgCO ₃
1	Toluene		2.6	2.7	4.1	6.3
2	Ethylbenzene		1.1	1.0	2.2	7.6
3	Styrene		50.4	66.6	54.5	55.2
4	Benzene, (1-methylethyl)-		0.06	0.34	0.15	1.28
5	Alpha.-Methylstyrene		1.7	1.5	3.7	5.7
6	Benzene, 1,1'-(1,3-propanediyl)bis		2.5	2.4	5.4	6.3
7	Benzene, 3-butynyl		22.5	0.0	17.1	8.6
8	Benzene, (1-methyl-3-butenyl)		1.5	1.5	2.2	1.0
9	Benzene, 1,1'-(2-methyl-1-propenylidene)bis		0.0	0.0	0.0	0.7
10	1,2-Propanediol, 3-benzyloxy-1,2-diacetyl		12.9	19.2	5.0	2.6
11	Other hydrocarbons	-	4.7	3.8	5.7	4.7

The effect of reaction time has a profound effect on the degradation of EPS and reaction products, i.e., liquid products. In the current study, the effect of time was checked for the degradation at a fix optimized temperature. The yield of liquid products was 78.07 ± 0.64 wt% with thermal degradation time (150 min) as compared to thermal degradation; the liquid yield was 82.20 ± 3.80 wt% with 30 min heating using Mg as a catalyst, and with MgO and MgCO_3 catalyst maximum liquid obtained was 91.60 ± 0.20 wt% and 81.80 ± 0.53 wt%, respectively for 120 min heating time. Negligible amount of residue 0.60 ± 0.40 wt% was obtained using Mg catalyst with 99.40 wt% total conversion. The yield of liquid products was high and low cost with all catalysts as compared to previous studies. Ukei et al. [21] reported catalytic degradation of PS with maximum liquid

yield 93.4 wt% producing 76.4 wt% styrene at 450°C for 180 min and Lee et al., [14] found $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst with maximum 83.5 wt% of liquid products at 400°C for 120 min.

2-4. Effect of Polymer-to-catalyst Ratio

All the three catalysts, Mg, MgO and MgCO_3 , were used in polymer-to-catalyst ratio of 1 : 0.1 to 1 : 0.5 for the catalytic degradation of EPS at optimum temperature and time (Fig. 4). It is evident from the previous studies that catalyst selection has a profound role in the degradation of polymer and as well for the selectivity of products. Many researchers have reported the impact of polymer-to-catalyst ratio on the degradation of EPS [25,28]. In the current study the effect of polymer-to-catalyst ratio was checked for the degradation of EPS, for all catalysts the liquid yield was increased with in-

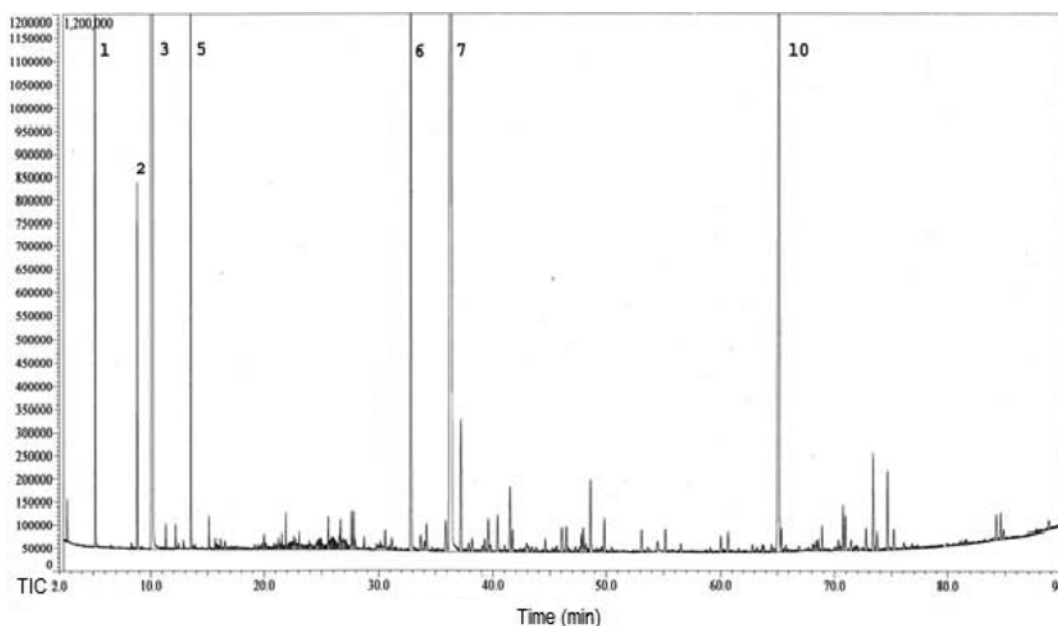


Fig. 5. Chromatogram of the liquid products obtained with thermal degradation at 500°C and 120 min reaction time.

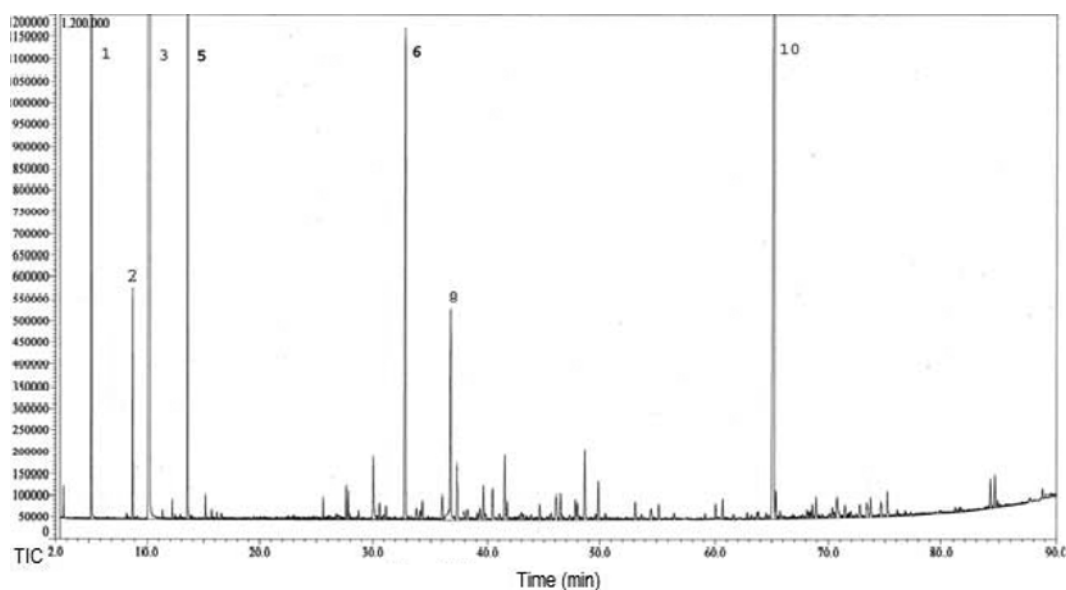


Fig. 6. Chromatogram of degraded products using Mg catalyst at 450°C , 30 min reaction time and 1 : 0.3 polymer-to-catalyst ratio.

crease in feed ratio from 1 : 0.1 to 1 : 0.3 and small decrease was observed with further increase in feed ratio. Therefore, polymer-to-catalyst feed ratio of 1 : 0.3 was used in further degradation process.

At optimum conditions maximum liquid yield and gas was obtained with minimum residue using all the three catalysts. The total percent conversion was 99.40 wt%, 98.60 wt% and 94.87 wt% with Mg, MgO and MgCO₃ catalysts, respectively.

2-5. Effect of Pressure

The catalytic degradation experiments were performed in a closed batch reactor equipped with internal pressure measurement gauge. The reactor vessel was fitted with a gas inlet and gas outlet valve (served for volatile components sampling). Each experiment was conducted with an initial nitrogen pressure of 0.3 MPa. Due to the experiments being in a closed batch reactor, hot gases from the cata-

lytic degradation process increased internal pressure. The catalytic degradation experiments were subjected to pressure produced by the gases from degradation process whose extend depends on the amount of gas produced and the reaction temperature. At the end of the experiment, the pressure was measured, the reactor was cooled rapidly until room temperature and again the pressure was measured. The experiment was performed at optimum conditions of the batch reactor without adjusting initial pressure by nitrogen. The results are given in Table 1. The major compounds include benzene, toluene, ethylbenzene, and styrene. It appears that with increase in pressure, light aromatic hydrocarbons dominate the liquid fraction. Styrene monomer decreased from 50 wt% to 20 wt% in thermal degradation with increase in pressure. The same trend in decrease of styrene monomer was also observed with Mg, MgO and MgCO₃

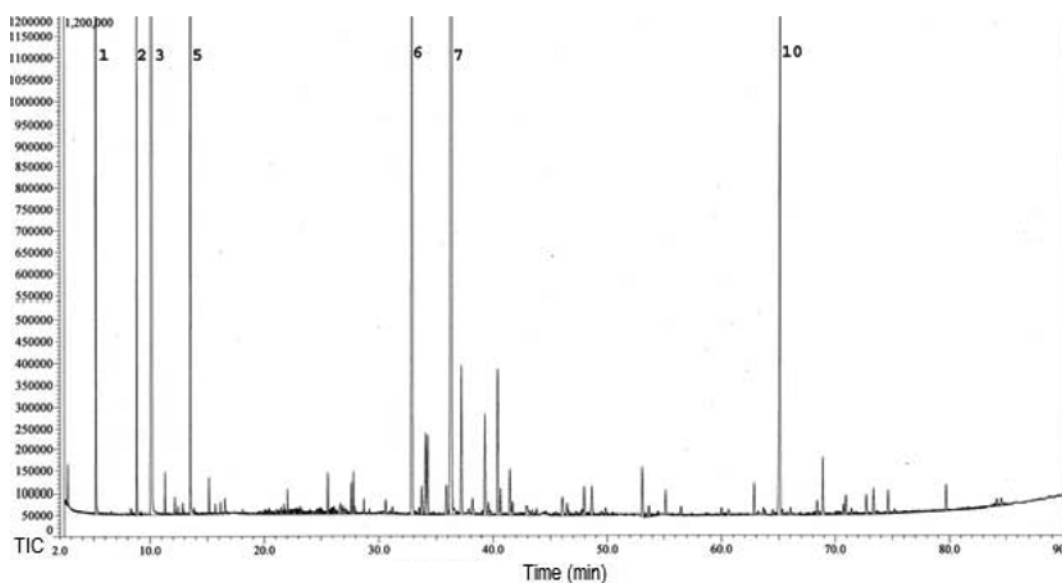


Fig. 7. Chromatogram of degraded products using MgO as catalyst at 400 °C, 120 min reaction time and 1 : 0.3 polymer-to-catalyst ratio.

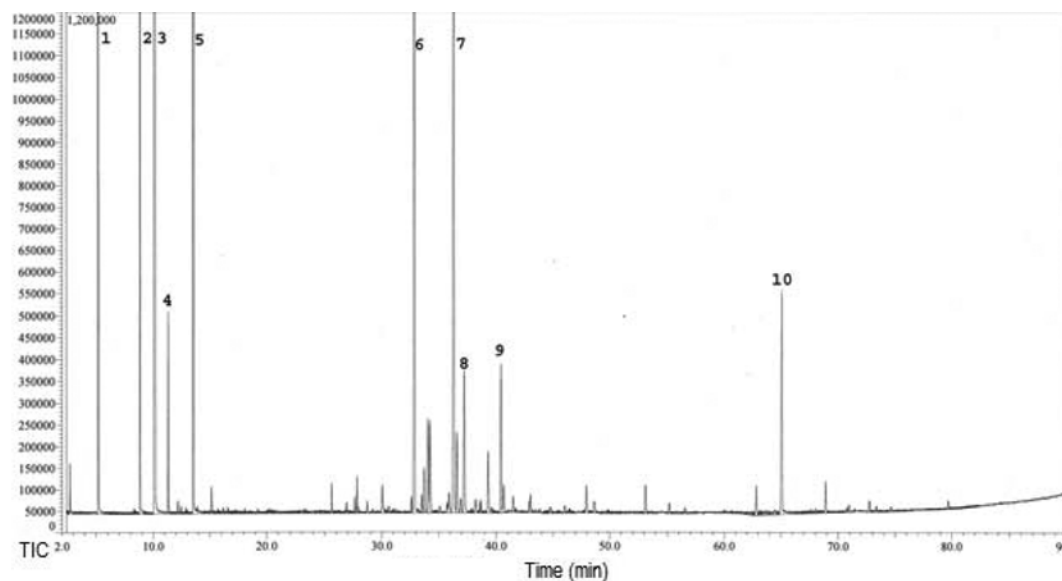


Fig. 8. Chromatogram of degraded products using MgCO₃ as catalyst at 400 °C, 120 min reaction time and 1 : 0.3 polymer-to-catalyst ratio.

Table 3. Comparison of reaction conditions, reaction products and its composition of the current study with literature reported work

Catalyst	Current methods				Literature methods	
	Thermal	Mg	MgO	MgCO ₃	BaO [21]	SiO ₂ /Al ₂ O ₃ [22]
Reaction conditions						
Temperature (°C)	500	450	400	400	450	400
Time (min)	150	30	120	120	180	120
Pol. to Cat. ratio	-	1 : 0.3	1 : 0.3	1 : 0.3	-	-
Contents of products (wt%)						
Liquid yields	78.07	82.20	91.60	81.80	93.40	83.5
Gas and cokes yields	20.40	17.20	7.00	13.07	-	11.70
Residue	1.53	0.60	1.40	5.13	3.20	4.80
Contents of liquid (wt%)						
Benzene	0.06	0.06	0.08	-	-	1.90
Toluene	2.64	2.73	4.05	6.28	1.60	4.70
Ethylbenzene	1.09	0.88	2.23	7.59	0.20	22.60
Styrene	50.36	66.56	54.53	55.23	76.40	36.00
Isopropylbenzene	0.06	0.34	0.15	1.28	-	0.04
α -Methylstyrene	17.02	1.52	3.74	5.72	1.40	7.60
1,3-Diphenyl-propane	2.53	2.42	5.40	6.30	18.30	-
Other	26.24	25.49	29.82	17.60	2.10	27.16

catalysts. However, significantly increased concentration of toluene and ethylbenzene was observed with increase in pressure. A decrease in styrene and increase in ethylbenzene concentration in the liquid product indicates that ethylbenzene formed from the hydrogenation of styrene. Styrene the degraded product of EPS is known to be very reactive and may be the reason for low levels of styrene in the liquid product at higher pressure.

3. Composition of Liquid Products

The liquid products obtained from thermal and catalytic degradation at optimum conditions were dissolved in acetone and analyzed for their chemical composition by GC-MS. The results of analysis are given in Table 2 in terms of weight percent of liquid products analyzed, and GC-MS spectra are shown in Figs. 5-8 for thermal degradation, Mg, MgO and MgCO₃ catalysts, respectively.

GC-MS analysis of the liquid consisted entirely of aromatic compounds and the content of any aliphatic compounds was below the detection limits in the presence of their predominant aromatic counterparts. These hydrocarbons included toluene, ethylbenzene, styrene, α -methyl styrene and benzene, 1,1'-(1,3-propanediyl)bis. Basic catalysts like BaO have been reported as having good selectivity for styrene monomer [21], whereas metal catalysts have also been reported for the efficient, rapid degradation of polystyrene [5,32]. Mg metal catalyst was used to act as synergist as well as catalyst with its basic compounds i.e. MgO and MgCO₃ using indigenously designed glass reactor and heating assembly in order to compare the composition of yielded products. Percent composition of liquid showed that styrene monomer is the predominant compound in the liquid obtained from different catalytic as well as thermal degradation process. Maximum amount of styrene (66.6 wt%) was obtained from Mg catalytic degradation, while with MgO (54.4 wt%) and MgCO₃ catalysts (55.2 wt%) almost the same amount of styrene was formed. The presence of high molecular weight aromatic hydrocarbons like benzene, 3-butynyl in case of base catalysts indicates that along with depolymerization processes, ring opening, dehydrogenation,

hydrogenation and cyclization processes also took place [18,21]. The yield of oxygen-containing compounds might be formed with the reaction of atmospheric oxygen and any residue present in the waste EPS samples [5]. The reaction conditions and components of liquid products were also compared with each other and previous reported methods and presented in Table 3.

4. Selectivity of Compounds

After the characterization data of GC-MS, the liquid obtained with thermal and catalytic degradation was separated into different fractions using fractional distillation to recover the hydrocarbons selectively. Fractions obtained by the fractional distillation of parent liquids derived from the degradation of waste EPS were characterized by different parameters like density (d_{25}), refractive index (n_D^{25}), and molar refraction (γ_M) for the identification of different fractions whose results are given in Table 3.

As can be seen from Table 3 data, during fractional distillation the residence time of liquid increases and further degradation occurs in the liquid with the decrease in percentage of styrene from 50.4 wt% to 35.0 wt%, α -methyl styrene from 1.7 wt% to 0.0 wt% and other compounds also. While, increase of toluene from 2.6 wt% to 51.0 wt% was observed, which confirms further degradation into low molecular weight hydrocarbons with increase of time. The thermal degradation process could be used selectively for recovery of toluene (51.0 wt%) and styrene monomer (35.0 wt%). During fractional distillation the percentage of styrene in liquid derived from Mg catalytic degradation, decreased from 66.6 wt% to 43.0 wt%. In the liquid derived from MgO and MgCO₃ catalytic degradation also decreased in styrene wt% which is less with the use of MgCO₃ catalyst. The study reveals that Mg catalytic process could be used for styrene monomer recovery (43.0 wt%), benzene (1-methyl-3-butynyl) (14.0 wt%) and 1,2-propanediol, 3-benzoyloxy-1,2-diacetyl (18.0 wt%), MgO catalyst for toluene (11.5 wt%), ethylbenzene (35.0 wt%), styrene monomer (23.8 wt%) and α -methylstyrene (11.0 wt%), while MgCO₃ catalyst mainly for toluene (15.8 wt%) and

Table 4. Physical parameters of the fractions obtained by fractional distillation of the liquid derived from thermal, Mg, MgO and MgCO₃ catalytic degradation of EPS

Compound name	Thermal					Mg					MgO					MgCO ₃				
	%age	d ₂₅ (g/ml)	η_D^{25}	γ M	%age	d ₂₅ (g/ml)	η_D^{25}	γ M	%age	d ₂₅ (g/ml)	η_D^{25}	γ M	%age	d ₂₅ (g/ml)	η_D^{25}	γ M	%age	d ₂₅ (g/ml)	η_D^{25}	γ M
Benzene	1.0	0.8770	1.5223	27.18	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2-Phenone, 4-hydroxy-4-methyl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Toluene	51.0	0.9293	1.5363	30.93	9.0	0.9020	1.5334	31.72	11.5	0.8768	1.5086	31.36	15.8	0.9005	1.5097	30.59	-	-	-	-
Ethylbenzene	2.0	0.8731	1.5051	36.07	-	-	-	-	35.0	0.8909	1.5084	35.55	-	-	-	-	-	-	-	-
Styrene	35.0	0.9115	1.5510	36.45	43.0	0.9165	1.5421	35.77	23.8	0.9082	1.5470	36.37	51.9	0.9013	1.5463	36.60	-	-	-	-
Cumene	-	-	-	-	-	-	-	-	6.0	0.8802	1.5102	40.85	-	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	-	-	1.5	0.8802	1.5455	38.15	-	-	-	-	-	-	-	-
alpha.-Methylstyrene	-	-	-	-	4.0	0.9004	1.5496	41.79	11.0	0.9037	1.5329	40.58	3.0	0.9166	1.5347	40.12	-	-	-	-
Benzene, 1,1'-(1,3-propanediyl)bis	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Phenanthrene	6.0	0.9910	1.5999	61.52	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, 3-butynyl	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Benzene, (1-methyl-3-butynyl)	-	-	-	-	14.0	0.9022	1.5285	49.95	-	-	-	-	-	-	-	-	-	-	-	-
1,2-Propanediol, 3-benzoyloxy-1,2-diacetyl	3.0	0.9320	1.5273	87.88	18.0	1.2095	1.5396	69.04	-	-	-	-	-	-	-	-	-	-	-	-

Where %age (Percentage of the Fraction), d₂₅ (g/ml) (density), (Refractive Index), and γ M (Molar Refraction)

Table 5. Physical parameters of standard compounds

Compound name	Density (d) g/ml	Refractive index (η)	Molar refraction (γ M)
Benzene	0.873	1.5010	26.253
Toluene	0.872	1.4967	31.078
2-Phenone, 4-hydroxy-4-methyl	0.868	1.4970	35.802
Ethylbenzene	0.868	1.4970	35.802
Styrene	0.903	1.5460	37.177
Cumene	0.862	1.4910	40.438
Benzaldehyde	1.050	1.5450	33.006
alpha.-Methylstyrene	0.872	1.5450	42.002
Benzene, 1,1'-(1,3-propanediyl)bis	0.984	1.5600	64.922
Phenanthrene	1.130	1.7150	61.938
Benzene, 3-butynyl	0.936	1.5290	42.896
Benzene, (1-methyl-3-butynyl)	0.872	1.5020	49.429
1,2-Propanediol, 3-benzyloxy-1,2-diacetyl	1.225	1.5420	68.393

styrene monomer (51.9 wt%). The decrease of styrene monomer in case of Mg catalyst might be because of the recombination of styrene and/or condensation and degradation to new high molecular weight aromatic hydrocarbons via H-abstraction followed by cyclization or leading the formation of head-to-head structures [33], while the formation of toluene and ethylbenzene in case of liquids obtained with Mg, MgO and MgCO₃ catalysts is because of further cracking of styrene or dimers and hydrogenation [21,27].

Refractive index and density of each fraction from fractional distillation was measured for calculation of molar refraction given in Table 4. The molar refraction values of standard compounds used for comparison are given in Table 5. The molar refraction values of aromatic compounds from different catalytic degradation of EPS are in close agreement with the standard compounds molar refraction values which confirm the compounds.

CONCLUSION

The catalytic degradation of waste EPS with different forms of magnesium as a catalyst was carried out with the aim to use a low cost catalyst for selective conversion of waste EPS into valuable hydrocarbons and resource recovery. The present method gave more selective products with good yield. The compounds with higher yields are mostly low molecular weight aromatic compounds instead of high molecular weight polyaromatic hydrocarbons, which indicates that the method is environment friendly. The degradation resulted in selective production of aromatic hydrocarbons. Maximum recovery of styrene (43.0 wt%) could be achieved with Mg (metal) catalyst, styrene (23.8 wt%) and ethylbenzene (35.0 wt%) with MgO catalyst while 51.87 wt% styrene and 15.81 wt% toluene with MgCO₃ catalyst.

REFERENCES

1. J. A. Onwudili, N. Insura and P. T. Williams, *J. Anal. Appl. Pyrolysis*, **86**, 293 (2009).
2. P. T. Williams, *Waste treatment & disposal*, Wiley, Chichester, UK, 390 (2005).
3. Z. Ahmad, F. Al-Sagheer and N. A. Al-Awadi, *J. Anal. Appl. Pyrolysis*, **87**, 99 (2010).
4. J. M. Arandes, J. Ereña, M. J. Azkoiti, M. Olazar and J. Bilbao, *J. Anal. Appl. Pyrolysis*, **70**, 747 (2003).
5. Z. Hussain, K. M. Khan and K. Hussain, *J. Anal. Appl. Pyrolysis*, **89**, 39 (2010).
6. R. S. Chauhan, S. Gopinath, P. Razdan, C. Delattre, G. S. Nirmala and R. Natarajan, *Waste Manage.*, **28**, 2140 (2008).
7. M. Blazsó, *J. Anal. Appl. Pyrolysis*, **39**, 1 (1997).
8. C.-G. Lee, J.-S. Kim, P.-S. Song, G.-S. Choi, Y. Kang and M.-J. Choi, *Korean J. Chem. Eng.*, **20**, 133 (2003).
9. K. Huang, L.-h. Tang, Z.-b. Zhu and W.-y. Ying, *J. Anal. Appl. Pyrolysis*, **76**, 186 (2006).
10. N. Kiran, E. Ekinci and C. E. Snape, *Resour. Conserv. Recycl.*, **29**, 273 (2000).
11. P. Layman, in *Chemical and Engineering News*, 4 (1993).
12. Z. Zhibo, S. Nishio, Y. Morioka, A. Ueno, H. Ohkita, Y. Tochihiro, T. Mizushima and N. Kakuta, *Catal. Today*, **29**, 303 (1996).
13. K. H. Lee, *Polym. Degrad. Stab.*, **93**, 1284 (2008).
14. S.-Y. Lee, J.-H. Yoon, J.-R. Kim and D.-W. Park, *J. Anal. Appl. Pyrolysis*, **64**, 71 (2002).
15. A. Marcilla, J. C. García-Quesada, S. Sánchez and R. Ruiz, *J. Anal. Appl. Pyrolysis*, **74**, 387 (2005).
16. A. Corma, S. Iborra, S. Miquel and J. Primo, *J. Catal.*, **173**, 315 (1998).
17. M. R. Jan, J. Shah and A. Rahim, *American Laboratory*, **4**, 12 (2008).
18. O. S. Woo, N. Ayala and L. J. Broadbelt, *Catal. Today*, **55**, 161 (2000).
19. C. Xie, F. Liu, S. Yu, F. Xie, L. Li, S. Zhang and J. Yang, *Catal. Commun.*, **9**, 1132 (2008).
20. Z. Zhang, T. Hirose, S. Nishio, Y. Morioka, N. Azuma, A. Ueno, H. Ohkita and M. Okada, *Ind. Eng. Chem. Res.*, **34**, 4514 (1995).
21. H. Ukei, T. Hirose, S. Horikawa, Y. Takai, M. Taka, N. Azuma and A. Ueno, *Catal. Today*, **62**, 67 (2000).
22. G. Audisio, F. Bertini, P. L. Beltrame and P. Carniti, *Polym. Degrad. Stab.*, **29**, 191 (1990).
23. P. Tiwary and C. Guria, *J. Polym. Environ.*, **18**, 298 (2010).
24. J. Kronholm, P. Vastamäki, R. Räsänen, A. Ahonen, K. Hartonen and M.-L. Riekkola, *Ind. Eng. Chem. Res.*, **45**, 3029 (2006).
25. H. Y. Shin and S. Y. Bae, *J. Appl. Polym. Sci.*, **108**, 3467 (2008).

26. A. Karaduman, E. H. Şimşek, B. Çiçek and A. Y. Bilgesü, *J. Anal. Appl. Pyrolysis*, **60**, 179 (2001).
27. S. Y. Lee, J. H. Yoon, J. R. Kim and D. W. Park, *Polym. Degrad. Stab.*, **74**, 297 (2001).
28. V. R. Chumbhale, J. S. Kim, W. Y. Lee, S. H. Song, S. B. Lee and M. J. Choi, *J. Ind. Eng. Chem.*, **11**, 253 (2005).
29. J.-W. Tae, B.-S. Jang, J.-R. Kim, I. Kim and D.-W. Park, *Solid State Ionics*, **172**, 129 (2004).
30. H.-Y. Shin and S.-Y. Bae, *J. Appl. Polym. Sci.*, **108**, 3467 (2008).
31. H. Ke, T. Li-hua, Z. Zi-bin and Z. Cheng-fang, *Polym. Degrad. Stab.*, **89**, 312 (2005).
32. Z. Hussain, K. M. Khan, N. Basheer and K. Hussain, *J. Anal. Appl. Pyrolysis*, **90**, 53 (2011).
33. Y. Hu and S. Li, *J. Anal. Appl. Pyrolysis*, **78**, 32 (2007).