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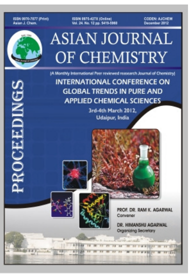

Thermo-catalytic Degradation of Thermocol Waste to Value Added Liquid Products†

ACHYUT K. PANDA[1,2,*], R.K. SINGH[1] and D.K. MISHRA[3]

[1]Department of Chemistry, School of Engineering and Technology Bhubaneswar Campus, Centurion University of Technology and Management, Ramchandrapur, Jatni, Khurda-752 050, India
[2]Department of Chemical Engineering, National Institute of Technology, Rourkela-769 008, India
[3]KMBB College of Engineering and Technology, Suryanagar, Bhubaneswar-751 003, India

*Corresponding author: E-mail: achyut.panda@gmail.com

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Kaolin clay and amorphous silica alumina have been studied as catalysts in the degradation of waste thermocol (expanded polystyrene) in a stainless steel autoclave surrounded by a furnace at different temperatures ranging from 350-550 ºC under partial oxidation condition. The major fraction of the pyrolysis reaction is an oily liquid, which is highly volatile. In the pyrolysis optimization studies, the highest yield of liquid product obtained is 93 % in thermal and 94.5 % in presence of kaolin at 500 ºC with 1:10 catalyst to plastic ratio. Although there is no considerable change in kinetics and yield of liquid products in the degradation reaction using the catalysts but they altered the product distribution. In thermal pyrolysis the amount of styrene is 78 %, which decreased in presence of both the catalysts and out of the two catalysts tested silica-alumina show the highest yield of ethyl benzene and the lowest of styrene.

Key Words: Thermocol, Polystyrene, Pyrolysis, Kaolin, Silica alumina, Styrene.

INTRODUCTION

Thermocol is the commercial name for the expanded polystyrene and is produced from a mixture of about 90-95 % polystyrene and 5-10 % gaseous blowing agent, most commonly pentane or carbon dioxide. This is one of the highest consumed polymers produced due to its versatile application in different fields particularly in packaging. Due to its non-biodegradability and high volume it constitutes a major fraction in municipality waste stream.

Chemical recycling of plastics has been recognized as one of the suitable method of plastic waste management and also to recover liquid fuel and valuable chemicals. In this process, the waste plastics are thermally or catalytically degraded into fuel and/or resources of chemicals. This process has also been commercially operated. In contrast to polyethylene and polypropylene, polystyrene can be thermally depolymerized to obtain the monomer styrene with a high selectivity. The oil, thus recovered, produces lots of carbon dioxide when burnt as fuel due to the high aromatic contents in it. Thus, several investigations have focused on the recovery of monomer when recycling of polystyrene is a question[1].

Technology has been developed for better pyrolysis with different reactors to achieve better yield of liquid product and monomers. Several pyrolysis processes were developed using fluidized bed and bubble fluidized bed reactors. Although these reactors performed well with heat transfer, they have a major disadvantage due to stickiness of sand particles coated with melted plastics, which results in defluidization and agglomeration. Conical spouted bed reactor, internally circulating fluidized bed reactor (ICFB), swirling fluidized bed reactor (SFB) are proposed to overcome the above stated problem including maintaining a uniform temperature inside the reactor. The conical spouted bed reactor enables vigorous gas-solid contact and, thus, reduces the segregation of particulates observed in the fluidized bed. However, this reactor suffers from the plastic particles after melting, which clogs and blocks particle circulation[2].

Different catalysts used in the catalytic pyrolysis of polystyrene are HMCM-41, HZSM-5, HY zeolites or REY zeolites, silica alumina[3], natural clinoptilolite[4], mordenite, BaO, MgO and Fe_2O_3[5]. Solvent addition helps in better heat and mass transfer and lowers operating temperatures. Further advantages of this approach are higher liquid yields and easier control[6].

This manuscript focuses on the research work related to the pyrolysis of waste thermocol in a fixed bed reactor in presence of kaolin and silica alumina catalyst and to optimize the reaction condition for enhanced yield of liquid fraction.

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This work also reports on the characterization of the liquid fraction using detailed hydrocarbon analyzer for composition.

EXPERIMENTAL

The waste thermocol in form of disposed off packaging material was collected from the waste yard of the National Institute of Technology, Rourkela Campus, India. The soft and high volume thermocol samples were first kept inside the oven at 80 ºC for 1 h resulting in a low volume hard brittle mass, which was then ground to powder. The powdered samples were subjected to pyrolysis. Commercial grade kaolin and silica alumina procured from Chemtex Corporation, Kolkata, India was used as catalyst in the pyrolysis reaction. The catalyst samples were characterized for their composition by XRF, acidity by ammonia temperature programme desorption, surface area by N_2 adsorption isotherm method.

XRF analysis of the catalyst samples was done using a Model-PW2400 of Phillips. The chemical composition of the kaolin sample was found to be SiO_2 43.12 %, Al_2O_3 46.07 %, Fe_2O_3 nil, MgO 0.027 %, CaO 0.030 %, ZnO 0.0064 %, K_2O 0.01 %, TiO_2 0.74, LOI at 1000 ºC 9.9 %. And that of silica-alumina was SiO_2 42.45 %, Al_2O_3 35.1300 %, Fe_2O_3 1.3100 %, MgO 1.1060 %, CaO 2.1430 %, ZnO 0.0064 %, K_2O 0.4410 %, TiO_2 0.5600, loss of ignition (LOI) at 1000 ºC 16.82 %. Nitrogen adsorption-desorption measurements (BET method) were performed with an autosorb BET apparatus from quantachrome corporation. The BET surface area of kaolin and silica alumina was found to be 23 m^2/g and 29 m^2/g respectively. The acid properties of the catalysts were probed by ammonia temperature programme desorption measurements in Micromeritics 2900 temperature programme desorption equipment. The acidity of the kaolin and silica alumina catalysts determined using this method are 0.04 mmol NH_3/g and 0.214 mmol NH_3/g respectively.

The decomposition pattern of powdered thermocol was carried out in a DTG-60/60 H of Shimadzu in a silica crucible with temperature ranging from 35 ºC to 600 ºC at a heating rate of 10 ºC/min operating in N_2 atmosphere with a flow rate of 40 mL/min. The detail composition of liquid product was analyzed using detailed hydrocarbon analyzer of Perkin-Elmer model Arnel 4050 detailed hydrocarbon analyzer.

The pyrolysis setup used in this experiment consists of a reactor made of stainless steel tube (length-145 mm, internal diameter-37 mm and outer diameter-41 mm) sealed at one end and an outlet tube at other end which was heated externally by an electric furnace and the temperature was measured using a Cr-Al: K type thermocouple fixed inside the reactor and temperature was controlled by external PID controller. 20 g of thermocol powder was loaded in each pyrolysis reaction. In the catalytic pyrolysis process, catalyst and thermocol power were mixed in different proportion (1:2.5, 1:5, 1:10 and 1:20) and were subjected to pyrolysis in the reactor set up and heated at a rate of 20 ºC/min. up to the desired temperature at different temperature range from 350 to 550 ºC. The condensable liquid products were collected through the ice water cooled condenser and weighed. After pyrolysis, the solid residue left out inside the reactor was weighed. Then the weight of gaseous product was calculated from the material balance.

RESULTS AND DISCUSSION

TGA analysis: The TG profile of impure polystyrene sample in nitrogen is presented in Fig. 1. The polystyrene degradation pattern (TGA) show a very deep diminution above 310 ºC (10 % weight loss) with weight loss of 50 % and 90 % taking place at 356 ºC and 388 ºC respectively.

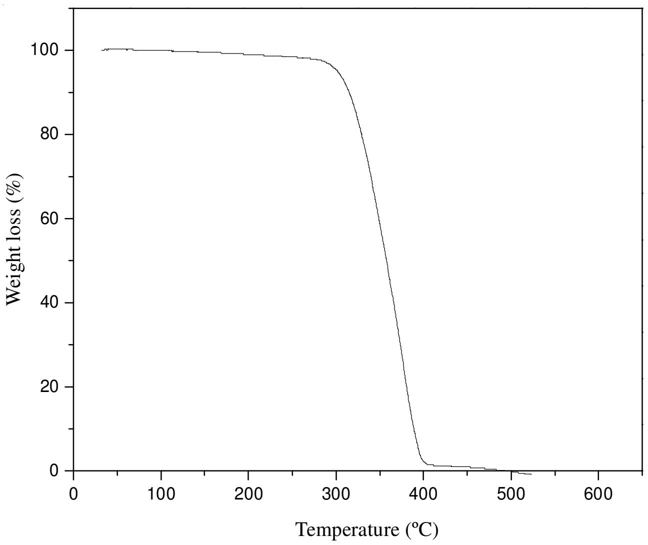

Fig. 1. TGA of thermocol waste

Effect of temperature: The effect of temperature on the polystyrene degradation was studied in absence of catalyst. Fig. 2 represents product distribution for thermal pyrolysis of waste thermocol at different temperatures ranging from 350 to 550 ºC. The results show that the liquid yield increased from 50 to 93 wt. % as the temperature increased from 350 to 500 ºC then decreased to 89 wt. % when the reaction temperature was increased to 550 ºC. The gas/volatile fraction and solid residue yield decreased from 39 to 4 wt. % and 11 to 2.5 wt. % respectively when the pyrolysis temperature was increased from 350 to 500 ºC. Comparatively, the residue amount was higher at lower temperature and less at higher temperature indicating that product formed at lower temperature could not get enough energy to come out of the reactor and thus stays for more time inside it. This leads to competitive cross linking reactions resulting in cross linked hard polymer residue and so the cracking of the resulting cross-linked polymer becomes more difficult. The increase of gas yield at higher temperature above 500 ºC was due to secondary cracking of the pyrolysis liquid into gaseous product.

Effect of catalyst: Catalytic pyrolysis of polystyrene was carried out using different plastic to catalyst ratio at different temperatures. Fig. 3 shows the effect of catalysts on product distribution with 1:10 kaolin catalyst to thermocol ratio. From the figure it is observed that presence of Si-Al has no effect on the yield of reaction where as kaolin slightly increased the yield of liquid fraction to 94.5 wt. % (from 93 wt. % in thermal pyrolysis) with kaolin catalyst to thermocol ratio 1:10 at 500 ºC. The reaction time slightly increased in presence of catalysts. The enhancement of the yield of the liquid product in presence of kaolin is for the promoted cracking reactions by its low acid strength distribution, where as the low effectiveness of

Si-Al for liquid yield is due to promotion of cross linking reaction among adjacent polymeric chains or even inside the same polymer leading to slightly more residue formation owing to higher acidity compared to kaolin[7]. However cross linking reaction is not much significant due to non-availability of sufficiently high acid sites. So the residue amount is not much higher as compared to the other two reactions.

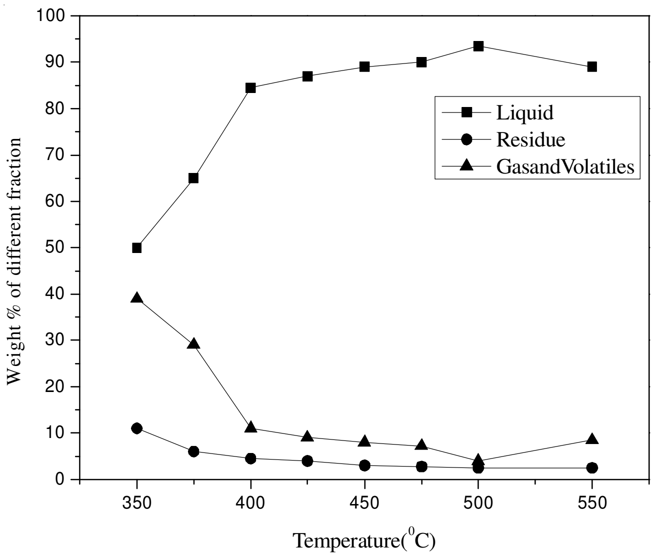

Fig. 2. Effect of temperature on the product distribution

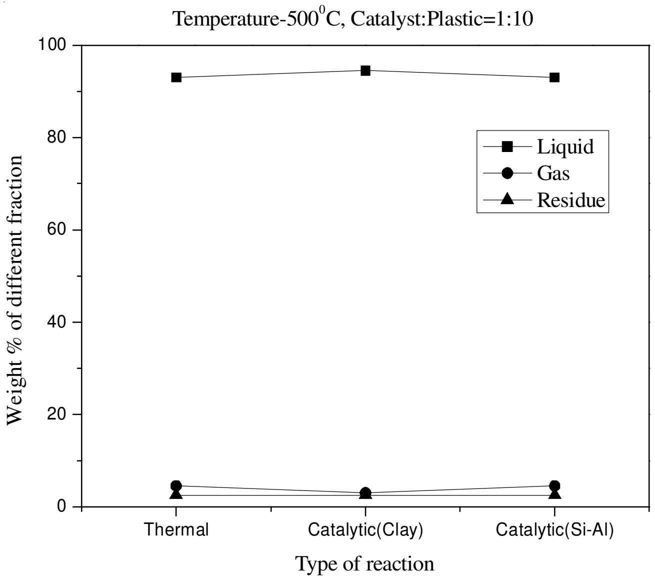

Fig. 3. Distribution of product in thermal and catalytic reaction

Compositional analysis of pyrolysis oil: Table-1 shows the *n*-paraffins, isoparaffins, olefins, naphthalenes and aromatics (PIONA) distribution of liquid products obtained in thermal and catalytic pyrolysis. This shows that the major component in the liquid is aromatics. Slight increase in the aliphatic component is observed in silica alumina catalyzed reaction due to severe cracking. Table-2 shows the composition of the oil obtained in hydrocarbon analyzer. Both thermal and catalytic degradation are shown mostly aromatic compounds, as they are stable enough and difficult to be further cracked or hydrogenated to paraffins or olefins.

TABLE-1
PIONA DISTRIBUTION IN LIQUID PRODUCTS OBTAINED AT 500 °C

Type of reaction	Distribution of different component in liquid (wt.%)				
	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics
Thermal	0.01	0.29	0.27	0.18	99.25
Catalytic (Clay)	0.06	0.98	0.12	0.20	98.64
Catalytic (Si-Al)	0.16	2.56	0.81	0.82	95.65

TABLE-2
DETAIL COMPOSITION OF LIQUID PRODUCT OBTAINED AT 500 °C

Composition (wt. %)	Thermal	Catalytic kaolin	Catalytic silica alumina
Benzene	1.48	3.64	7.06
Toluene	2.9	8.1	7.21
Ethyl Benzene	5.1	11.71	24.73
Styrene	77.58	64.65	48.85
Methyl styrene	8.62	9.13	9.1
Xylene	0	0	0.4
C9- aromatics	1.12	0.2	1.3
C10+-aromatics	3.2	2.52	1.35

Thermal degradation shows the highest selectivity of styrene (77.58 wt. %), which has been reduced to 64.65 wt. % in presence of kaolin and 48.85 wt. % in presence of Si-Al. Silica-alumina show a considerable increase in the amount of isoparaffins compared to thermal and kaolin catalyzed pyrolysis. The amount of ethyl benzene is the lowest in thermal degradation (5.1 wt. %) and increased to 11.71 wt. % and 24.73 wt. % using kaolin and silica alumina respectively. Thermal degradation of polystyrene starts with a random initiation to form polymer macro-radicals followed by different secondary reactions such as β-session, intermolecular transfer, intramolecular transfer (competing backbiting) and disproportionation reactions, which depends on the temperature[8]. The main products are styrene and its corresponding dimers and trimers. Where as, the acid catalyzed cracking of polystyrene is of carbenium nature[9]. The most likely reaction pathway involves the attack of proton associated with different acid sites to the aromatic rings of polystyrene, due to the reactivity of its side phenyl groups towards electrophilic reagents. The resulting carbenium may undergo β-scission followed by a hydrogen transfer. The possible production pathways of benzene, styrene, methyl styrene, toluene, ethyl benzene, *etc.* are reported by Audisio *et al.*[3]. The lower yields of styrene obtained on solid acids than those obtained by simple thermal degradation are partially due to its oligomerization reactions and the resulting oligomeric cations, in turn, would be cracked; thus, depending on the relative importance of the various alternatives of the catalytic cracking pathways, some of the main reaction products (benzene, toluene, styrene, indane and derivatives) obtained[10]. Secondly, high acidity also accelerates the hydrogenation styrene to ethyl benzene[11]. As Si-Al has high acidity compared to kaolin, the cracking and hydrogenation of styrene over its surface is more, which is less achievable on kaolin clay surface. This leads to the increased production of ethyl benzene and low selectivity of styrene. The high selectivity of toluene in kaolin catalyzed reaction compared to thermal and silica alumina catalyzed reaction is due to its low acidity which favours oligomerization of styrene and subsequent cracking to toluene.

Conclusion

Study shows that a simple batch pyrolysis method could convert the waste thermocol between 350-550 ºC using kaolin and silica alumina catalyst to value added liquid products. The reaction was affected by temperature, type of catalyst and amount of catalyst. Detailed hydrocarbon analyzer analysis of the liquid showed that the liquid products consist of mostly aromatic hydrocarbons. The product distribution of the liquid fraction is significantly affected by the presence of both the catalysts. While styrene is the major product in both thermal and catalytic degradation over the solid catalysts, significant differences are observed in the different aromatic products distribution in presence of catalysts. Thus the oil obtained from both the thermal and catalytic process may be used for monomer/chemical recovery and also be used as a blended fuel or feedstock to petroleum refining industry.

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