

Thermo-catalytic degradation of thermocol waste to value added liquid products

Achyut K.Panda^{a,b*}, R.K.Singh^a, D.K.Mishra^c,

^aNational Institute of Technology Rourkela, Orissa,

^bCenturion Institute of Technology, Bhubaneswar, Orissa, India

^cJagannath Institute for Technology and Management, Parlakhemundi, Orissa, India

*Mobile Number: 09437132916, E-mail: achyut.panda@rediffmail.com. Fax: +91 674 2490480

Abstract

Kaoline 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 350-550⁰C under partial oxidation condition. The major fraction of the pyrolysis reaction is an oily liquid, which is highly volatile. The reaction time decreased and the yield of liquid fraction increased with the increase in temperature. In the pyrolysis optimization studies, the highest yield of liquid product obtained is 93% in thermal and 94.5% in presence of clay catalyst at 500⁰C with 1:10 catalyst to plastic ratio. Kaoline clay shows a slight increase in liquid yield whereas silica alumina gives the same with regard to the thermal cracking. The liquid product has been analysed using fourier transformation infrared spectroscopy and detailed hydrocarbon analyser. In addition to styrene the other major products present in the liquid fraction are benzene, ethyl benzene, toluene and methyl styrene. In thermal pyrolysis the amount of styrene is 78%. Both the catalysts altered the product distribution and out of the two catalysts tested, silica-alumina show the highest yield of ethyl benzene and the lowest one of styrene.

Keywords

Thermocol, polystyrene, pyrolysis, kaolin clay, silica alumina, styrene.

1. Introduction

Thermocol is the commercial name for the expanded polystyrene (EPS) 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 gases and oils, which can be used as fuel and/or resources of chemicals. Recycling of fuel oil from waste plastics has been attractive and also commercially operated. In contrast to polyethylene and polypropylene, polystyrene can be thermally depolymerised 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 (Panda et al., 2010).

Pyrolysis being an endothermic process, proper heat transfer and a uniform temperature inside the reactor is required for better pyrolysis. 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 defluidisation and agglomeration. Conical spouted bed reactor (CSB), 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 CSB 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 (Liu et al., 2000 and Chauhan et al., 2008). The performance of different reactors used by different investigators are summarised below.

Liu et al. (2000) developed a specially designed laboratory fluidized-bed reactor for the pyrolysis of polystyrene (PS) waste in the range 450–700°C with nitrogen as the carrier gas and 20–40 mesh quartz sand as the fluidization medium, operating isothermally at atmospheric pressure. The yield of styrene monomer reached a maximum of 78.7 wt.% at a pyrolysis temperature of 600°C. Some mono-aromatics with boiling point lower than 200°C is also obtained as high-octane gasoline fraction. Styrene monomer with 99.6 wt.% purity was obtained after vacuum distillation of the liquid products, which could be used as the raw material to produce high-quality Polystyrene circulation (Liu et al., 2000).

Lee et al. (2003) used a swirling fluidized-bed reactor to recover the styrene monomer and valuable chemicals effectively from the polystyrene waste, since it can control the residence time of the feed materials and enhance the uniformity of the temperature distribution. To increase the selectivity and yield of styrene monomer in the product, catalysts such as Fe₂O₃, BaO or HZSM-5 (Si/Al=30) were used. Effects of temperature, volume flow rate of gas, pyrolysis time and the ratio of swirling gas to the amount of primary fluidizing gas on the yields of oil product as well as styrene monomer are determined. It is found that the reaction time and temperature can be reduced profoundly by adding the solid catalyst. The swirling fluidization mode makes the temperature fluctuations more periodic and persistent, which can increase the uniformity of temperature distribution by reducing the temperature gradient in the reactor. The yields of

styrene monomer as well as oil products were increased with increasing the ratio of swirling gas, but exhibited their maximum values with increasing the total volume flow rate of gas (Lee et al., 2003) .

Aguado et al. (2003) used a conical spouted bed reactor (CSBR) for studying the degradation kinetics of polystyrene in the 500-600⁰C range. It is found that, heat and mass transfer limitations within the particle are important in the temperature range required for maximizing the yield of styrene, when polystyrene particles of 1 mm are fed into the reactor. A high yield of styrene is obtained (64.5 wt.%) in the 723–773 K range. A comparison with other reactor proves the advantages of the gas–solid contact of this reactor for the kinetic study of pyrolysis of plastics at high temperature, which stems from the high heat transfer rate between gas and solid and again from the fact that particle agglomeration is avoided (Aguado, 2003).

Polystyrene wastes were degraded in a free-fall reactor under vacuum to regain the monomer at varied temperature between 700°C and 875°C and determined its effects on the phase yields, the benzene, styrene, toluene, and naphthalene distribution of the liquid output and C₁–C₄ content of the gaseous output. The liquid yield maximized at around 750°C and the styrene yield, at 825°C. In general, operating at higher temperatures lessened the solid residue and increased the gaseous yield and total conversion. Employing waste particles in four different size ranges, it was observed that, the finer the waste particles fed the higher the gaseous yield and total conversion (Karaduman et al., 2001).

In the thermal degradation of polyolefins, many hydrocarbons having a wide range of distribution of carbon atom members have been found. However, use of suitable catalysts enhances the rate of reaction, and narrows the product distribution in the liquid fraction. Most commonly used catalysts in the catalytic degradation of polymers are solid acids and bases

(Panda et al., 2010). Different catalysts used in the catalytic pyrolysis of polystyrene are HY zeolites (Protonated Y zeolite) or REY zeolites (Rare earth Y zeolite), silica alumina, HMCM-41 (Protonated MCM-41), natural clinoptilolite, ZSM-5 (Zeolite Sieve of Molecular porosity or Zeolite Socony Mobil-5), mordenite, BaO, MgO and Fe₂O₃.

Audisio et al. (1990) reported very low selectivity of the styrene in polystyrene degradation with solid acids such as silica–alumina and HY or REY zeolites at 350°C. The main products in their study were benzene, ethyl benzene and cumene [9]. Polystyrene catalytic cracking over amorphous silica alumina (SA) and HZSM-5 zeolite results in a lower conversion than the thermal degradation under the same reaction conditions. Decreasing the plastic to catalyst mass ratio over HZSM-5 leads to a reduced cracking activity. In contrast to HZSM-5 and amorphous silica alumina, HMCM-41 has shown enhanced polystyrene conversion compared to the thermal degradation. The main products resulting from the catalytic cracking over HMCM-41 and SiO₂–Al₂O₃ are benzene, ethyl benzene and cumene (Audisio et al., 1990).

The natural clinoptilolite zeolite (HNZ) show good catalytic performance for the catalytic degradation of polystyrene, without much formation of residues or cokes at 400°C for 2 h. All the catalysts tested (HNZ, HZSM-5, SA) produced aromatic liquid oils with over 99% of selectivity. While styrene is the major product in both thermal and catalytic degradation over the solid acid catalysts, significant differences are observed in the aromatic products distribution in presence of each catalyst. HNZ and HZSM-5 show a decrease of styrene and an increased selectivity towards ethyl benzene and propyl benzene compared to thermal degradation (Serrano et al., 2000).

The application of basic catalyst to degrade polystyrene is an attractive alternative to acid catalysis. In the presence of acid catalysts, polystyrene affords low-valued indane derivatives, other polycyclic compounds, benzene, and only minor yields of styrene monomer. In contrast, studies suggested that basic catalysts enhanced the yield of styrene monomer from polystyrene compared to thermal and acid-catalyzed degradation (Woo et al., 2000). Ukei et al. (2000) reported that solid bases, especially BaO, were more effective catalysts than solid acids for the degradation of polystyrene to styrene monomer and dimer at 350°C (Ukei et al. 2000).

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. Sato et al. (1990) studied thermal degradation of polystyrene using two different solvent groups at temperatures between 300°C and 450°C. The first solvent group comprised of tetralin and 9,10 dihydroanthracene, which are both hydrogen donors. The solvents in the second group were phenol, 2-naphtol and diphenylamine, all with easily removable hydrogen atom. Higher styrene yield was claimed in the second group. Heavy oil was the medium used in another thermal degradation research on polystyrene, the temperature ranging from 370 °C to 415 °C. Nitrogen was employed to carry the products which were mainly styrene, toluene, methyl styrene, ethyl benzene and cumene (Sato et al. 1990). Ali Karaduman (2002) studied the thermal degradation of Polystyrene with various organic compounds, such as phenol, quinone, naphthalene, and diphenylamine at varied temperature range from 350°C to 450°C. The main products of Polystyrene waste pyrolysis were mainly styrene monomer, ethyl benzene, toluene, and methyl styrene. The product spectrum can be described as a function of pyrolysis temperature and used organic compounds. The yield of styrene in liquid products at various temperatures with different organic compounds varies from 60 to 74%. The optimum pyrolysis temperature to maximize

styrene monomer yield (about 60%) was 400°C, and the maximum styrene yield was obtained with naphthalene, 74% as found in this study. The amount of styrene was found to increase in the order: diphenylamine < thermal < phenol < quinone < naphthalene (Karaduman, 2002).

This manuscript focuses on the research work related to the pyrolysis of waste thermocol in a fixed bed reactor in presence of kaoline clay and silica alumina catalyst and to optimize the reaction condition for enhanced yield of liquid fraction. This work also reports on the characterization of the liquid fraction using FTIR and detailed hydrocarbon analyser for composition.

2. Materials and methods

2.1 Samples for pyrolysis

The waste thermocol in form of disposed off packaging material was collected from the waste yard of the National Institute of Technology Rourkela campus. The soft and high volume thermocol samples were first kept inside the oven at 80⁰C for one hour resulting in a low volume hard brittle mass which was then ground to powder. The powdered samples were subjected to pyrolysis.

Commercial grade kaoline clay 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 (TPD), surface area and pore structure by N₂ adsorption isotherm method.

2.2 Pyrolysis apparatus and procedure

The pyrolysis setup used in this experiment (Figure 1) mainly consists of a reactor made of stainless steel (SS) tube (length- 145 mm, internal diameter- 37 mm and outer diameter- 41 mm)

sealed at one end and an outlet tube at other end. The SS tube 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. 20g of thermocol powder was loaded in each pyrolysis reaction. In the catalytic pyrolysis process, catalyst and thermocol powder 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 20⁰C/min. up to the desired temperature. 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. Reactions were carried out at different temperature range from 350⁰C to 550⁰C. The reaction time was calculated from the start of reaction (when the feed is taken in the reactor and temperature raised from the room temperature) till its completion (the time when no more oil comes through outlet tube).

2.3 Analysis Methods

XRF analysis of the catalyst samples were done using a Model-PW2400 of Phillips make, with X-ray tube of rhodium anode and scintillation detector with a current 40mA and voltage 40mV. Nitrogen adsorption–desorption measurements (BET method) were performed at liquid nitrogen temperature (–196⁰C) with an autosorb BET apparatus from Quantachrome Corporation. The analysis procedure is automated and operates with the static volumetric technique. Before each measurement, the samples were outgassed first at 200⁰C for 2 hours, at 5×10^{-3} torr and then at room temperature for 2 hours, at 0.75×10^{-6} torr. The isotherms were used to determine the specific surface areas using the BET equation. The acid properties of the catalysts were probed by ammonia TPD measurements in Micromeritics 2900 TPD equipment. Previously, the samples were outgassed under He flow (50Nml/min) by heating with a rate of 15⁰C/min up to 560⁰C and

remaining at this temperature for 30 min. After cooling to 180⁰C, the samples were treated with a 30Nml/min ammonia flow for 30 min. The physisorbed ammonia was removed by passing a He flow at 180⁰C for 90 min. The chemically adsorbed ammonia was determined by increasing the temperature up to 550⁰C with a heating rate of 15⁰C/min, remaining at this temperature for 30 min, and monitoring the ammonia concentration in the effluent He stream with a thermal conductivity detector.

The decomposition pattern of powdered thermocol was carried out in a DTG-60/60H of SHIMADZU in a silica crucible with temperature ranging from 35⁰C to 600⁰C at a heating rate of 10⁰C/min operating in N₂ atmosphere with a flow rate of 40ml/min.

FTIR of the pyrolysis oil obtained at different temperatures were taken in a Perkin-Elmer Fourier transformed infrared spectrophotometer with resolution of 4 cm⁻¹, in the range of 400-4000 cm⁻¹ using Nujol mull as reference to know the functional group composition.

The detail composition of liquid product was analysed using Detailed Hydrocarbon Analyser (DHA) of Perkin Elmer Model Arnel 4050 DHA. This analyzer is an engineered chromatography system based on the PerkinElmer Clarus 500 Gas Chromatograph (GC) with programmable pneumatic control (PPC) which comes standard with DHA software completely integrated with PerkinElmer's TotalChrom Workstation used to characterize hydrocarbon samples through high-efficiency capillary gas chromatography and Flame Ionisation Detector (FID). The column consists of tuned 100m x 0.25mm x 0.5µm polydimethylsiloxane and the carrier gas used in this process was Helium. The oven programme starts with initial temperature 5.0⁰C/min (cryogenics: LN₂), initial hold for 10.00min, (maximum temperature 350⁰C and equilibration time 5.0 min) then, 5.0 ⁰C/min to 48⁰C, hold for 53.4 min, then 1.4 ⁰C/min to 200⁰C hold for 18.0 min.

3 Results and Discussion

3.1 Catalyst characterisation

The composition, surface area and acidity of the catalysts are summarised in the Table 1. The major components of both the catalyst are SiO₂ and Al₂O₃ with nearly same SiO₂ content and different Al₂O₃ content. The surface area and acidity of Silica alumina are higher to that of kaoline.

3.2 TGA analysis

The TG profile of impure polystyrene sample in nitrogen is presented in Figure 2. The polystyrene degradation pattern (TGA) show a very deep diminution above 310°C (10% weight loss) with weight loss of 50% and 90% taking place at 356⁰C and 388⁰C respectively, which is comparatively lesser than the pure polystyrene as reported by Pierella et al. (Pierella et al., 2005) [16]. This slight difference in the degradation pattern may be explained due to the presence of some components other than styrene added during manufacture of the product and decrease in bond strength during processing.

3.3 Effect of temperature

The effect of temperature on the polystyrene degradation was studied in absence of catalyst. Figure 3 shows that the reaction time decreased with the increase in temperature. Figure 4 represents product distribution for pyrolysis of waste thermocol at different temperatures ranging from 350⁰C to 550⁰C in absence of the catalyst. The results show that the pyrolysis liquid yield increased from 50 wt.% to 93 wt. % as the temperature increased from 350⁰C to 500⁰C then decreased to 89 wt. % when the reaction temperature was increased to 550⁰C. The gas/volatile fraction and solid residue yield decreased from 39 wt.% to 4 wt.% and 11 wt.% to 2.5 wt.% respectively when the pyrolysis temperature was increased from 350⁰C to 500⁰C. 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 500⁰C was due to secondary cracking of the pyrolysis liquid into gaseous product.

3.4 Effect of Catalyst

To determine the effect of catalyst on the pyrolysis of thermocol, the experiments were conducted using two catalysts, silica alumina and kaoline clay using different plastics to catalyst ratio in solid phase contact mode and at different temperatures. The reaction time increased in presence of catalysts as observed from the Figure 3. Figure 5 shows the effect of catalysts on product distribution with 1:10 kaoline clay catalyst to thermocol ratio. From the figure it is observed that presence of Si-Al did not alter the yield of reaction where as kaoline clay slightly increased the yield of liquid fraction to 94.5wt.% from 93wt.% in thermal pyrolysis reaction. Figure 6 indicates that the highest yield of liquid product is obtained in catalyst to thermocol ratio 1:10 at 500⁰C. The enhancement of the yield of the liquid product in presence of kaoline clay is for the promoted cracking reactions by its low acid strength distribution and surface area. 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 kaoline (Nanbu et al., 1987 and) Lee et al., 2001). 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.

Table 2 shows the comparison of liquid fraction yield during the study with that observed during previous research work. The yield of the liquid fraction is found the same or slightly more in the present study as compared to the work done by Chauhan et al. (Chauhan et al., 2008) at 500⁰C using the similar experimental set up.

3.5 Compositional analysis of Pyrolysis oil

Figure 7 is the FTIR spectrum of the pyrolysis oil at 500⁰C with some significant assignments. The presences of functional groups corresponding to different peaks in the spectra are summarized in Table 3. The table indicates that most of the components of the oil are aromatic in nature. Table 4 shows the PIONA (paraffins, isoparaffins, olefins, naphthenes, aromatics) distribution of liquid products. This shows that the major component in the liquid is aromatics. Slight increase in the aliphatic component is observed in silica alumina catalysed reaction due to severe cracking.

Table 5 shows the detail composition of the oil obtained in DHA. 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.

Thermal degradation shows the highest selectivity of styrene (77.58 wt.%) which has been reduced to 63.65 wt.% in presence of kaolin clay and 48.85 wt.% in presence of Si-Al. Silica-alumina show a considerable increase in the amount of isoparaffins compared to thermal and kaoline clay catalysed pyrolysis. The amount of ethyl benzene is the lowest in thermal degradation (5.1wt.%) and increased to 12.71 wt.% and 24.73 wt.% using kaoline clay 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 (Audisio et al., 1992, Jellinek ,1949 and Guyot, 1986). The main products are styrene and its corresponding dimers and trimers. Where as, the acid catalyzed cracking of polystyrene is of carbenium nature (Audisio et al., 1992). 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.(Audisio et al., 1990). 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 (Puente and Sedran, 1998). Secondly, high acidity also accelerates the hydrogenation styrene to ethyl benzene (Lee et al. 2002 and Chumbhale et al, 2005). As Si-Al has high acidity and surface area compared to kaoline, 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 kaoline clay catalysed reaction compared to thermal and silica alumina catalysed reaction is due to its low acidity which favors oligomerization of styrene and subsequent cracking to toluene.

4 Conclusion

Study shows that a simple batch pyrolysis method could convert the waste thermocol between 350-550⁰C using kaoline clay and silica alumina catalyst to value added liquid products. The

reaction was affected by temperature, type of catalyst and amount of catalyst. The optimum temperature for obtaining highest yield of liquid fraction (93 wt.%) in thermal pyrolysis is 500⁰C. The liquid fraction further increase to 94.5 wt. % by the addition of kaoline clay as catalyst in the 1:10 catalyst to polymer ratio at 500⁰C. The yield of liquid fraction is unaffected by the presence of silica alumina. FTIR and DHA 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. Both the catalysts show a decrease of styrene and an increased selectivity towards ethyl benzene compared to thermal degradation. Silica alumina shows the lowest amount of styrene and a high increase of ethyl benzene. The liquid product obtained in the thermal pyrolysis thus may preferably be used for styrene monomer recovery, where as the oil obtained in catalytic pyrolysis which contain less amount of styrene and comparatively higher amount of other components (such as ethyl benzene etc.) may be used to obtain these components along with the styrene monomer. The oil obtained from both the thermal and catalytic process may also be used as a blended fuel or feedstock to petrolium refining industry.

5. References

Panda, A.K., Singh, R.K., Mishra, D.K., 2010. Thermolysis of waste plastics to liquid fuel; a suitable method for plastic waste management and production of value added products- A World prospective. *Renew Sustain. Energ. Rev.* 14, 233-248.

Liu, Y., Qian, J., Wang, J., 2000. Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction. *Fuel Process Tech.* 63, 45–55.

Aguado, R., Olazar, M., Gaisan, B., Prieto, R., Bilbao, J., 2003. Kinetics of polystyrene pyrolysis in a conical spouted bed reactor. *Chem Eng J.* 92, 91–99.

Audisio, G., Bertini, F., Beltrame, P.L., Carniti, P., 1992. Catalytic degradation of polyolefins, *Makromol Chem Macromol Symp.* 57, 191-196

Audisio, G., Bertini, F., Beltrame, P.L., Carniti, P., 1990. Catalytic degradation of polymers: Part III -.Degradation of polystyrene. *Polym Degrad Stab.* 29, 191-198.

Catalytic degradation of polystyrene over zsm-11 modified materials. Proceedings 2nd Mercosur Congress on Chemical Engineering, 4th Mercosur Congress on Process Systems Engineerin. Pierella et al., 2005.14-18.

Chauhan, R.S., Gopinath, S., Razdan, P., Delattre, C., Nirmala, G.S., Natarajan, R., 2008. Thermal decomposition of expanded polystyrene in a pebble bed reactor to get higher liquid fraction yield at low temperatures. *Waste Manage.* 28, 2140–2145.

Chumbhale, V.R., Kim, J.S., Lee, W. Y., Song, S.H., Lee, S.B., Choi, M.J., 2005. Catalytic degradation of expandable polystyrene waste (EPSW) over HY and modified HY zeolites, *J. Ind. Engg. Chem.* 11, 253-260.

de la Puente, G., Sedran, U., 1998. Recycling polystyrene into fuels by means of FCC: performance of various acidic catalyts, *Appl Catal. B.* 19, 305-311

Guyot, A., 1986. Recent Developments in the Thermal Degradation of Polystyrene A Review *Polym Degrad Stab.* 15, 219-235

Jellinek, H.G., 1949. Thermal degradation of polystyrene. Part II. *J. Polym Sci.* 4, 13-19.

Lee, C.G., Cho, Y.J., Song, P.S., Kang, Y., Kim, J.S., Choi, M.J., 2003. Effects of temperature distribution on the catalytic pyrolysis of polystyrene waste in a swirling fluidized-bed reactor. *Catal Today*, 453–464

- Lee, S.Y., Yoon, J.H., Kim, J.R., Park, D.W., 2001. Catalytic degradation of polystyrene over natural clinoptilolite zeolite. *Polym. Degrad. Stab.* 74, 297–305.
- Lee, S.Y., Yoon, J.H., Kim, J.R., Park, D.W., 2002. Degradation of polystyrene using clinoptilolite catalysts. *J. Anal. Appl. Pyrolysis.* 64, 71–83.
- Nanbu, H., Sakuma, Y., Ishihara, Y., Takesue, T., Ikemura, T., 1987. Catalytic Degradation of Polystyrene in the Presence of Aluminum Chloride Catalyst. *Polym Degrad Stab.* 19, 61-72.
- Sato, S., Murakata, T., Baba, S., Saito, Y., Watanabe, S., 1990. Solvent effect on thermal degradation of polystyrene. *J Appl Polymer Sci.* 40, 2065–2071
- Serrano, D.P., Aguado, J., Escola, J., 2000. Catalytic conversion of polystyrene over HMCM-41, HZSM-5 and amorphous $\text{SiO}_2\text{-Al}_2\text{O}_3$ comparison with thermal cracking. *Appl. Catal. B.* 25, 181–189.
- Ukei, H., Hirose, T., Horikawa, S., Takai, Y., Taka, M., Azuma, N., Ueno, A., 2000. Catalytic degradation of polystyrene into styrene and a design of recyclable polystyrene with dispersed catalysts, *Catal. Today.* 62, 67–75.)
- Woo, O.S., Ayala, N., Broadbelt, L.J., 2000. Mechanistic interpretation of base-catalyzed depolymerization of polystyrene. *Catal. Today.* 55, 161–171.

Table 1 Properties of catalysts

| Properties | Kaoline | Silica Alumina |
|----------------------------------|---|---|
| Composition | SiO ₂ 43.12%, Al ₂ O ₃ 46.07%, Fe ₂ O ₃ nil, MgO 0.027%, CaO 0.030%, ZnO 0.0064%, K ₂ O 0.01%, TiO ₂ 0.74%, LOI at 1000 ⁰ C 9.9%. | SiO ₂ 42.45%, Al ₂ O ₃ 35.13%, Fe ₂ O ₃ 1.31%, MgO 1.10%, CaO 2.1430%, ZnO 0.0064%, K ₂ O 0.441%, TiO ₂ 0.56%, LOI at 1000 ⁰ C 16.82% |
| Surface area (m ² /g) | 23 | 29 |
| Acidity (mmol/g) | 0.04 | 0.214 |

| Pyrolysis mode | Reactor type | Weight % of liquid product | Reference |
|-----------------------|--|----------------------------|---------------------|
| Thermal/Catalytic | | | |
| Thermal | Semi batch reactor (atmospheric pressure) | 93 | Present study |
| Catalytic (Clay) | Semi batch reactor (atmospheric pressure) | 94.5 | Present study |
| Thermal | Pebble bed reactor (atmospheric pressure) | 85.0 | Chauhan et al.[5] |
| Thermal | Pebble bed reactor (vacuum) | 91.7 | Chauhan et al.[5] |
| Catalytic (H-ZSM-11) | Continuous-flow reactor(atmospheric pressure) | 99.46 | Pierella et al.[16] |
| Catalytic (Zn-ZSM-11) | Continuous-flow reactor(atmospheric pressure) | 99.67 | Pierella et al.[16] |
| Thermal | Laboratory fluidized-bed reactor(atmospheric pressure) | 96.4 | Liu et al.[4] |

Table 2 Comparison of yield liquid product in the pyrolysis of polystyrene at 500⁰C

| Wave number cm^{-1} | Band Assignments |
|------------------------------|---|
| 2857, 2930 | C-H _{stretching} Alkane |
| 3026, 3060, 3082 | C-H _{stretching} Aromatic ring |
| 1452, 1494 | C=C _{stretching} Alkene |
| 899, 965 | C-H _{bending} Aromatic ring |
| 689, 746, 776 | C-H _{bending} Aromatic ring |

Table 3 FTIR assignments of pyrolysis oil.

| Type of Reaction | Distribution of different component in liquid (wt.%) | | | | |
|-------------------|--|---------------|---------|------------|-----------|
| | n-Paraffins | Iso paraffins | 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 4 PIONA Distribution in liquid products obtained at 500⁰C

| Composition in wt % | Thermal | Catalytic | |
|---------------------|---------|-----------|----------------|
| | | Kaoline | 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 |

Table 5 Composition of pyrolysis oil at 500^oC