Studies on Production of Valuable Aromatics Benzene, Toluene and Ethylbenzene Using Multiphase Catalytic Pyrolysis of Waste Expanded Polystyrene

Thesis submitted in partial fulfillment

For the Award of Degree

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By

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Dedicated to My Beloved

Parents &

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NOMENCLATURE

Abbreviation	Meaning
ANOVA	Analysis of variance
BBD	Box-Behnken Design
BET	Brunauer Emmett Teller
3D	Three-dimensional
DF	Degree of freedom
EDX	Energy dispersive X-ray spectroscopy
EPS	Expanded polystyrene
FTIR	Fourier transform infrared spectroscopy
GCV	Gross calorific value
HDPE	High density polyethylene
LDPE	Low density polyethylene
MPW	Municipal plastic waste
MSW	Municipal solid waste
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
RSM	Response surface methodology
SEM	Scanning Electron Microscopy
TGA	Thermogravimetry analysis

WEPS	Waste expanded polystyrene
XRD	X-Ray Diffraction

Greek Symbols	**Meaning**
δ_o	Linear parameter
δ_{ii}	Quadratic parameter
δ_{ij}	Interaction parameter

PREFACE

The production of plastics is rapidly increasing due to its low manufacturing cost, various applications, development and modernization of society. The drastic increase in the plastic production naturally has led to large amount of plastic waste generation that is deteriorating the environment because of proper disposal plastic waste. A few options that have been considered for plastic waste management were recycling and energy recovery technique. However, several obstacles of recycling techniques such as the need of sorting process that is labour intensive and also polluting environment. Thus, the recycle process is not sustainable. In view of this, the plastic waste conversion into energy and valuable chemicals via pyrolysis process was considered in the present study to develop an economical and sustainable process through extensive research.

Recently, pyrolysis of waste expanded polystyrene (WEPS) gained much attention because of its high energy content, chemical value and low recycling rate. The polystyrene is a non-biodegradable aromatic plastic which can convert in to valuable aromatics such as benzene, toluene and ethylbenzene (BTE) via pyrolysis followed by *in-situ* hydrogenation at a moderate temperature. Thus, in the present research work, catalytic pyrolysis of waste expanded polystyrene (WEPS) followed by *in-situ* hydrogenation was conducted in three different reactor arrangements i.e., liquid phase/A-type, vapour phase/B-type and multiphase/AB-type for the production of valuable aromatics benzene, toluene and ethylbenzene (BTE) and reduction of unwanted styrene in the pyrolysis oil. The thermal pyrolysis process was also performed for comparison in terms of product yield and composition.

The raw material waste expanded polystyrene (WEPS)/thermocol was collected from the waste yard of Indian Institute of Technology (BHU), Varanasi. First of all, the large sheets of

thermocol were manually cut into small pieces of size 80 mm x 80 mm using a cutter. Thereafter, the volume was reduced by placing the cut pieces of WEPS in an oven at a temperature of 85 ^{o}C for 1 hr which resulting in brittle mass of average size 40 mm x 40 mm. Three different types of catalysts i.e., ZSM-5 ammonium powder, Nickel on silica-alumina and synthesized catalyst from natural red clay were used for the catalytic pyrolysis of WEPS for each type of reactor arrangement. First two catalysts were commercial and last one was synthesized catalyst from natural red clay. The catalyst Zeolite ZSM-5 ammonium powder of surface area 400 m^2/g with SiO_2 to Al_2O_3 mole ratio of 200-400:1 was procured from Alfa Aesar, USA. The commercial catalyst ammonium ZSM-5 (SiO_2:Al_2O_3 =200-400:1) powder was used in the present study due to its excellent catalytic activity towards the formation of better liquid yield containing aromatics hydrocarbons. The ammonium type ZSM-5 also provides Bronsted acid sites NH_4^+ which helps in selective cracking. The Nickel on silica-alumina powder with 66 ± 5 % Ni was also procured from Alfa Aesar, USA. The nickel on silica-alumina catalyst improves the hydrogen production during the pyrolysis process which, may use in *in-situ* hydrogenation reaction for the production of ethylbenzene. Furthermore, the Nickel on silica-alumina catalyst shows higher selectivity towards the gasoline range hydrocarbon molecules. The natural red clay was selected as the catalyst because of high silica (41.10 wt.%) and alumina content (31.48 wt.%) as these are responsible for the catalytic properties of red clay. The natural red clay was collected from Chandauli district of Uttar Pradesh near Devdari and Rajdari waterfall which is situated 60 km away from IIT (BHU) campus, Varanasi. Five different catalysts were synthesized from the eco-friendly and non-toxic red clay i.e., red clay in natural from (RC), red clay calcined at 600 ^{o}C (RC-600), red clay calcined at 700 ^{o}C (RC-700), red clay calcined at 800 ^{o}C (RC-800), red clay calcined at 900

^{o}C (RC-900). The raw and calcined red clay catalysts were characterized by various characterization techniques such as scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area, Fourier transformed infra-red spectroscopy (FTIR).

The treated waste expanded polystyrene (WEPS) of 50 g fed to the primary reactor made of mild steel of 99.3 mm inner diameter and 155 mm height. The thermal and catalytic pyrolysis of WEPS were performed at different temperatures in the range between 400 ^{o}C to 700 ^{o}C, under inert atmosphere of nitrogen (200 mL/min). The catalytic pyrolysis was performed using all three selected catalysts i.e., ZSM-5 ammonium powder, Nickel on silica-alumina and synthesized catalyst from natural red clay for each type of reactor arrangement. The catalytic pyrolysis was performed at different feed to catalyst ratio of 10:1, 20:1, 30:1 and 40:1.

Scanning electron microscopy (SEM) confirms that the calcination temperature greatly influenced the surface morphology and surface area of the red clay catalysts. The surface morphology of calcined red clay catalyst RC-800 shows nano cluster form of particles with very high porosity. The highest surface area of 29.25 m^2/g and highest silica content of 56.82 wt.% were found for the RC-800 catalyst. Furthermore, the XRD analysis ensured the presence of illite-micas, α- quartz, κ- kappa alumina, δ- delta alumina, and θ- theta alumina in the RC-800 catalyst only. The presence of strong Bronsted acid sites in RC-800 catalyst was confirmed by the Fourier transform Infrared spectroscopy (FTIR) analysis. Thus, the optimum calcination temperature for red clay was found to be 800 ^{o}C, as RC-800 catalyst showed excellent catalytic activity for *in-situ* hydrogenation to obtained target molecules benzene, toluene and ethylbenzene (BTE).

The compositional analysis of pyrolysis oil was evaluated by gas chromatograph (NUCON 5765) using flame ionization detector (GC-FID). The bomb calorimeter (IP 12/63 T) was used to determine the gross calorific value (GCV) of pyrolysis oil. The carbon residue of pyrolysis oil was obtained using Rams bottom carbon residue apparatus (IP 14/65). The flash and fire point of pyrolysis oil were obtained using Cleveland open cup apparatus (ASTM D 92).

The valuable aromatics benzene, toluene, and ethylbenzene (BTE) were significantly increased and styrene got reduced by many folds when AB-type/multiphase catalytic pyrolysis was performed for each type of catalyst i.e., ZSM-5 ammonium powder, Nickel on silica-alumina and best red clay catalyst RC-800. However, the highest amount of BTE content was found in the case of Nickel on silica-alumina catalyst.

Thermal pyrolysis produced maximum liquid yield of 94.37 wt.% at a temperature of 650 ^{o}C and at a heating rate of 15 ^{o}C/min. On the other side, the catalytic pyrolysis using ZSM-5 ammonium powder produced maximum liquid yield of 88.05 wt.%, 78.85 wt.%, and 75.11 wt.% for the A-type, B-type, and AB-type catalytic pyrolysis at the temperature of 600 ^{o}C, 550 ^{o}C and 550 ^{o}C, respectively using the same heating rate of 15 ^{o}C/min. The liquid oil of thermal pyrolysis contains very low amount of valuable aromatic hydrocarbons BTE of 11.38 wt.% and the highest amount of styrene (84.74 wt.%). The BTE content of pyrolysis oil obtained using ZSM-5 ammonium powder increased progressively in the order of 18.98 wt.% (A-type) < 24.27 wt.% (B-type) < 28.12 wt.% (AB-type). The styrene content significantly decreased to a very low value of 46.30 wt.% for AB-type/multiphase pyrolysis at a reaction temperature of 550 ^{o}C, heating rate of 15 ^{o}C/min, feed to catalyst ratio of 20:1 using ZSM-5 ammonium powder catalyst.

The liquid phase/A-type, vapour phase/B-type and multiphase/AB-type catalytic pyrolysis using Nickel on silica-alumina catalyst produced a highest liquid yield of 88.54 wt.%, 83.21 wt.%, and 81.15 wt.% at the same heating rate of 15 ^{o}C/min and at a reaction temperature of 600 ^{o}C, 550 ^{o}C, and 550 ^{o}C, respectively. Among, the all types of reactor arrangements, AB-type/multiphase pyrolysis produced pyrolysis oil with highest amount of BTE content of 28.56 wt.% using Nickel on silica-alumina catalyst. Furthermore, the pyrolysis oil obtained from A-type, B-type and AB-type catalytic pyrolysis contains low styrene content of 69.94 wt.%, 65.67 wt.% and 55.55 wt.%, respectively as compared to thermal pyrolysis (84.74 wt.%).

On the other side, the highest liquid yield of 88.82 wt.% was obtained for the A-type pyrolysis at the optimum temperature of 600 ^{o}C and heating rate of 15 ^{o}C/min using red clay catalyst RC-800. The B-type and AB-type pyrolysis produced maximum liquid yield of 80.81 wt.% and 79.47 wt.% respectively, at the optimum temperature of 550 ^{o}C and at heating rate of 15 ^{o}C/min using the same red clay catalyst RC-800. However, the multiphase/AB-type pyrolysis produced highest BTE content of 27.62 wt.% and lowest styrene content (60.75 wt.%) at a temperature of 550 ^{o}C using RC-800 catalyst among all types of pyrolysis. The maximum BTE content of 23.51 wt.% and 18.58 wt.% were obtained for vapour phase/B-type and liquid phase/A-type catalytic pyrolysis at their respective optimum conditions. The styrene content got reduced significantly from 68.83 wt.% to 60.75 wt.% when the reactor arrangement was changed from A-type to AB-type.

The effective process parameters such as feed to catalyst ratio, heating rate and temperature were also optimized by ESM for the best reactor arrangement AB-type using each type of catalyst i.e., ZSM-5 ammonium powder, Nickel on silica-alumina and synthesized catalyst from natural red clay via RSM-BBD technique. The optimum value of temperature (A_1),

heating rate (B_1) and feed to catalyst ratio (C_1) suggested by model were 566.62 ^oC, 15.41 ^oC, and 20.80:1, respectively for AB-type pyrolysis using ZSM-5 ammonium powder catalyst. The predicted (Y_1) and experimental value of liquid yield were 74.73 wt.% and 74.04 wt.%, respectively at the optimized condition for the same ZSM-5 ammonium powder catalyst. However, the predicted and experimental values of maximum liquid yield (Y_2) were of 81.10 wt.% and 80.85 wt.%, respectively were obtained for the multiphase/AB-type pyrolysis at the optimum temperature (A_2) of 536.04 ^oC, heating rate (B_2) of 15.02 ^oC/min and feed to catalyst ratio (C_2) of 20.54:1 using Nickel on silica-alumina catalyst. The predicted maximum liquid yield (Y_3) of 79.49 wt.% was obtained for the optimum temperature (A_3) of 536.51 ^oC, heating rate (B_3) of 15.15 ^oC/min and feed to catalyst ratio (C_3) of 20.33:1 using best red clay catalyst RC-800. Whereas, the experimental value of response (liquid yield) was found to be 78.88 wt.% at the same optimized conditions (A_3, B_3, and C_3) using RC-800 catalyst.

In addition, the reusability assessment was performed using best Nickel on silica-alumina catalyst only for the best reactor arrangement multiphase/AB-type. The experiments were performed at the reaction temperature of 550 ^oC, heating rate of 15 ^oC/min and feed to catalyst ratio of 20:1. The fresh Nickel on silica-alumina catalyst produced the liquid yield of 81.15 wt.% and gaseous yield of 17.14 wt.% for AB-type catalytic pyrolysis in Run-1. Whereas, the liquid yield decreased to 87.15 wt.% at the fifth run using used/spent Nickel on silica-alumina catalyst. The surface area of fresh catalyst decreased from 96.60 m^2/g to 6.35 m^2/g and 7.00 m^2/g for liquid phase (primary reactor) and vapour phase catalyst (secondary reactor), respectively. However, the surface area increased to 82.70 m^2/g for liquid phase catalyst and 86.20 m^2/g for vapour phase catalyst after the regeneration process. The BTE content of 28.56 wt.% was found for the pyrolysis oil obtained from fresh Nickel on silica-alumina catalyst at

a temperature of 550 ^{o}C, heating rate of 15 ^{o}C/min and feed to catalyst ratio of 20:1. Whereas, the BTE content was reduced to 14.27 wt.% at the fifth run (5^{th}) of experiment. The regenerated Nickel on silica-alumina catalyst produced BTE content of 28.44 wt.% in the pyrolysis oil which is similar to the BTE content obtained using fresh catalyst.

The pyrolysis oil obtained from AB-type/multiphase reactor arrangements using Nickel on silica-alumina catalyst highest BTE content and fuel range hydrocarbon and thus, the gross calorific value of the pyrolysis oil for this catalyst was found to be highest (12750 Cal/g). The other physicochemical properties were also satisfactory for the use in IC engine, diesel generator set or cooking stoves.