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

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By

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CHAPTER 6
CONCLUSIONS

In this chapter, the major findings on thermal and catalytic pyrolysis of waste expanded polystyrene (WEPS) have been incorporated. The thermal pyrolysis of WEPS was investigated in detail in liquid phase only to find out the liquid yield and BTE content. However, the catalytic pyrolysis followed by *in-situ* hydrogenation were carried out in three different reactor arrangements i.e., A-type/liquid phase, B-type/vapour phase and AB-type/multiphase for the production of target molecules benzene, toluene and ethylbenzene (BTE). Two commercial catalysts i.e., ZSM-5 ammonium powder, Nickel on silica-alumina and one synthesized catalyst from natural red clay were used for the catalytic pyrolysis. The low cost natural red clay catalyst RC-800 shown excellent performance for the production of BTE and comparable with commercial catalysts ZSM-5 ammonium powder and Nickel on silica-alumina. The experimental results obtained from catalytic pyrolysis of WEPS followed by *in-situ* hydrogenation shows that the catalytic pyrolysis of WEPS could be a good option for the production of pyrolysis oil rich in valuable aromatic hydrocarbons BTE suitable for the internal combustion (IC) engine, cooking stoves, and generator sets.

6.1 Thermal pyrolysis

The maximum liquid yield of 94.37 wt..% was obtained at a reaction temperature of 650 ^oC, and heating rate of 15 ^oC/min. The gaseous yield of 5.55 wt.% and solid yield of 0.08 wt.% was obtained at the same pyrolysis temperature of 650 ^oC and heating rate of 15 ^oC/min. The pyrolysis oil mainly composed of styrene monomer of 84.74 wt.%. However, the benzene (0.62 wt.%), toluene (10.21 wt.%), and ethylbenzene (0.55 wt.%) were also found very low amount in the thermal pyrolysis oil.

The gross calorific value (GCV) of thermal pyrolysis oil obtained at optimum conditions was found to be 9816 Cal/g. The carbon residue of thermal pyrolysis oil was 1 wt.% due to presence of high boiling range aromatic hydrocarbons. Moreover, the flash and fire point of pyrolysis oil obtained at optimum conditions were 58 ^{o}C and 62 ^{o}C, ensure the easy storage and transportation. The calorific value of thermal pyrolysis oil (9816 Cal/g) was lesser than the commercial fuels gasoline (11315 Cal/g) and kerosene (11052 Cal/g).

6.2 Catalytic pyrolysis of WEPS using ZSM-5 ammonium powder catalyst

The catalytic pyrolysis of WEPS using ZSM-5ammoium powder enhances the valuable aromatic hydrocarbons benzene, toluene, ethylbenzene (BTE) and reduce the styrene content. The optimum conditions for A-type/liquid phase catalytic pyrolysis were reaction temperature of 600 ^{o}C, heating rate of 15 ^{o}C/min and feed to catalyst ratio of 20:1. Whereas, the optimum conditions for B-type/vapour phase and AB-tpe/multiphase catalytic pyrolysis were reaction temperature of 550 ^{o}C, heating rate of 15 ^{o}C/min and feed to catalyst ratio of 20:1. The BTE content of 18.98 wt.% was obtained for A-type catalytic pyrolysis at optimized conditions. However, the styrene content of 55.78 wt.% was found in the pyrolysis oil obtained at optimized conditions. The vapour phase/B-type and multiphase/AB-type catalytic pyrolysis obtained BTE content of 24.28 wt.% and 28.12 wt.%, respectively at the optimized conditions. The styrene content of 46.42 wt.% and 46.30 wt.% were found for the vapour phase/B-type and multiphase/AB-type catalytic pyrolysis at the optimized conditions. The calorific value of pyrolysis oil (12685 Cal/g) obtained from AB-type/multiphase catalytic pyrolysis at the optimized conditions was highest among all types of catalytic pyrolysis oil even higher than the commercial gasoline indicates the presence of lighter molecules. The carbon reside of 0.6

wt.% was found for the AB-type catalytic pyrolysis oil. Moreover, the flash and fire point of AB-type catalytic pyrolysis were 38 ^oC and 42 ^oC, lower than commercial kerosene and slightly higher than the gasoline. It should also be noted that catalyst ZSM-5 successfully decrease the reaction temperature and improve the quality of pyrolysis oil. Thus, good quality of fuel can be achieved in less time at low temperature.

6.3 Catalytic pyrolysis of WEPS using Nickel on silica-alumina catalyst

The nickel on silica-alumina catalyst was another commercial catalyst used for the catalytic pyrolysis of waste expanded polystyrene (WEPS). The maximum liquid yield of 88.54 wt.% was obtained for the A-type/liquid phase catalytic pyrolysis at the optimum conditions i.e., reaction temperature of 600 ^oC, heating rate of 15 ^oC/min and feed to catalyst ratio of 20:1. Whereas, the maximum liquid yield of 83.21 wt.% and 81.15 wt.% were obtained for B-type/vapour phase and AB-type/multiphase catalytic pyrolysis at the optimum conditions i.e., reaction temperature of 550 ^oC, heating rate of 15 ^oC/min and feed to catalyst ratio of 20:1.

The maximum BTE content of 13.99 wt.% and 21.38 wt.% were obtained for A-type and B-type catalytic pyrolysis at the optimized conditions. Whereas, AB-type/multiphase catalytic pyrolysis of WEPS produced highest amount of target molecules BTE of 28.56 wt.% and the styrene content of 55.55 wt.% at the optimum conditions. Thus, the multiphase pyrolysis oil can be used as rich source of benzene, toluene and ethylbenzene. In addition, the calorific value of pyrolysis oil obtained from multiphase/AB-type was found to be highest among all types of pyrolysis oil and higher than the gasoline because of high content of lower molecular weight hydrocarbons. On the other hand, low flash point (40 ^oC) of multiphase pyrolysis oil indicates the easy ignition in IC engines. Similarly, less carbon residue of 0.45 wt.% indicates the less formation of carbon deposit inside the engine surface. Thus, the AB-type pyrolysis oil could be recommended as an alternative of commercial fuels like gasoline and kerosene. It should be noted that benzene and styrene should be separated from the product oil to have the desired specification of fuel as per the need of IC engines.

6.4 Catalytic pyrolysis of WEPS using synthesized red clay catalyst RC-800

The catalytic pyrolysis of waste expanded polystyrene (WEPS) followed by *in-situ* hydrogenation of pyrolysis oil were successfully performed on red clay synthesized catalyst RC-800 in three different reactor arrangements viz liquid phase/A-type, vapour phase/B-type and multiphase/AB-type as per requirement. The low cost red clay RC-800 catalyst enhanced the production of valuable lower aromatics BTE and significantly reduced styrene content in the pyrolysis oil. The RC-800 catalyst exhibited the best performance in terms of quality of pyrolysis oil because of its highest surface area of 29.25 m^2/g and highest surface concentration of silica (Si) (56.82 wt.%).

The maximum liquid yield of 88.82 wt.% was obtained for A-type catalytic pyrolysis using RC-800 catalyst at the optimum temperature of 600 ^oC, heating rate of 15 $^oC/min$ and feed to catalyst ratio of 20:1. Whereas, maximum liquid yield of 80.81 wt.% and 79.47 wt.% were obtained for B-type and AB-type catalytic pyrolysis at the optimum temperature of 550 ^oC, heating rate of 15 $^oC/min$ and feed to catalyst ratio of 20:1. The AB-type/multiphase catalytic pyrolysis produced the highest lighter aromatic hydrocarbons i.e., benzene, toluene, ethylbenzene (BTE) of 27.62 wt.% and lowest styrene content of 60.75 wt.% at the optimum conditions. The GCV of AB-type/multiphase pyrolysis oil was highest (12810 Cal/g) among all types of catalytic pyrolysis oil, even higher than the commercial fuels such as gasoline and kerosene. Moreover, the lowest carbon residue (0.35 wt.%) of AB-type pyrolysis oil, indicates the less possibility of formation of carbon shoot in IC engines. The pyrolysis oil of AB-type could also be used as a source of valuable chemicals BTE. The laboratory synthesized red clay catalyst RC-800 effectively reduces the cost of the pyrolysis process by replacing the costly commercial catalysts. Thus, the pyrolysis of WEPS using red clay catalyst RC-800 found to be a promising method for the management of WEPS via *in-situ* hydrogenation. The developed process could be scaled up for commercial production of BTE and reduce environmental pollution by reducing WEPS via conversion of waste to energy.

6.5 Optimization of effective parameters by RSM

The detailed study of catalytic pyrolysis using three different reactor arrangement confirms the multiphase catalytic pyrolysis found to be best, as it produced the maximum BTE content. Thus, process parameters temperature, heating rate and feed to catalyst ratio were optimized for multiphase catalytic pyrolysis only. The main findings for optimization of process parameters using RSM-BBD tool are presented below.

6.5.1 Optimization of process parameters using ZSM-5 ammonium powder

The higher F-value (11989.41) and low P-value (<0.0001) obtained from ANOVA analysis proved that the model was significant and applicable. The optimum value of temperature (A_1), heating rate (B_1) and feed to catalyst ratio (C_1) suggested by model were 566.62 ^{o}C, 15.41 ^{o}C, and 20.80:1, respectively. The predicted (Y_1) and experimental value of liquid yield were 74.73 wt.% and 74.04 wt.%, respectively at the optimized condition. As per ANOVA, the F-value for linear term A_1, B_1 and C_1 were 8.90, 556.64 and 23793.22, respectively. Thus, feed to catalyst ratio (C_1) has highest effect among three independent variables i.e., temperature (A_1), heating rate (B_1) and feed to catalyst ratio (C_1). It could be concluded that the optimization of the effective operating parameters by RSM-BBD is important to achieve the maximum liquid yield by conducting the lesser number of experiments which reduces the wastage of resources and time. The BTE content of 27.86 wt.% was found in pyrolysis oil obtained at optimized process conditions.

6.5.2 Optimization of process parameters using Nickel on silica-alumina catalyst

The predicted (Y_2) and experimental values of maximum liquid yield were of 81.10 wt.% and 80.85 wt.%, respectively which were obtained for the optimum temperature of 536.04 ^oC, heating rate of 15.02 ^oC/min and feed to catalyst ratio of 20.54:1 using Nickel on silica-alumina catalyst. As per ANOVA, the F-value for linear term A_2, B_2 and C_2 were 315.92, 42.13 and 3392.52, respectively. It can be concluded that the feed to catalyst ratio has larger effect on liquid yield obtained from the multiphase catalytic pyrolysis using Nickel on silica-alumina catalyst, as compared to the heating rate and temperature. However, temperature is the second effecting factor after feed to catalyst ratio. Only 0.41 % error was found between the predicted (81.10 wt.%) and experimental value (80.85 wt.%) ensured the developed RSM-BBD model is significant and applicable. The BTE content of 28.44 wt.% was obtained at the optimized conditions using Nickel on silica-alumina catalyst.

6.5.3 Optimization of process parameters using red clay catalyst RC-800

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. The F-value for linear term A_3, B_3 and C_3 were 8523.38, 3859.06 and 38895.34, respectively. Thus, based on the F-value for linear terms A_3, B_3 and C_3, it could be concluded that the liquid yield obtained from multiphase catalytic pyrolysis using natural red clay catalyst RC-800 catalyst strongly affected by the feed to catalyst ratio (C). However, heating rate (B) has least effect on response liquid yield. Moreover, only 0.77 % error was found between the predicted (79.49 wt.%) and experimental value (78.88 wt.%) confirms the developed RSM-BBD model is significant and applicable.

6.6 Reusability assessment using best Nickel on silica-alumina catalyst

This reusability assessment demonstrated the regeneration and reuse of nickel on silica-alumina catalyst for the multiphase catalytic pyrolysis of waste expanded polystyrene (WEPS) at a temperature of 550 ^oC, heating rate of 15 ^oC/min and feed to catalyst ratio of 20:1. The quantitative and qualitative results obtained from multiphase/AB-type catalytic pyrolysis of WEPS using fresh and regenerated nickel on silica alumina catalyst confirms the recovery of cracking ability after regeneration process. The liquid yield of 81.15 wt.% and gaseous yield of 17.14 wt.% were obtained for AB-type catalytic pyrolysis using fresh nickel on silica-alumina catalyst (Run-1). Whereas, the liquid yield of 87.15 wt.% was obtained at the fifth run using used/spent catalyst. It may be due to the coke deposition over the surface of the catalyst, which reduced the surface area and cracking ability of the catalyst. The BET surface area of fresh catalyst was found to be 96.60 m^2/g. Whereas, surface area decreased to 6.35 m^2/g and 7.00 m^2/g for liquid phase and vapour phase catalyst, respectively. The surface area was 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. Moreover, SEM images of regenerated catalyst was found to be same as the fresh Nickel on silica-alumina catalyst.

The BTE content of 28.56 wt.% was found in 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 get reduced from 28.56 wt.% to 14.27 wt.% after fifth run. However, the BTE content of 28.44 wt.% was found in the pyrolysis oil obtained using regenerated catalyst shows that, after regeneration process Nickle on silica-alumina catalyst could effectively produce the BTE content similar to the fresh catalyst.

6.7 Future scope

This developed process on pyrolysis of waste expanded polystyrene (WEPS) using specially designed reactor and *in-situ* hydrogenation could help in handling and conversion of a large amount of waste polystyrene to valuable fuel range hydrocarbon benzene, toluene and ethylbenzene (BTE) after scale-up of the laboratory scale reactor followed by commercialization.

The future scope of the present work on the pyrolysis of WEPS for the production of BTE is very promising, as this type of research work has never been performed earlier.

In the present study, three different reactor arrangements like A-type, B-type and AB-type were used for the catalytic pyrolysis of WEPS followed by *in-situ* hydrogenation to enhance the BTE content and reduce unwanted styrene content in the pyrolysis oil. In B-type and AB-type reactor arrangement only four layer catalytic bed was used for the interaction between hydrocarbon molecules and catalyst particles. Thus, in the future work some more layers of catalyst can be added to the catalytic bed for enhancing the interaction between catalyst particles and hydrocarbon molecules. Furthermore, some other modification in reactor arrangements could be done for the more production of target aromatic hydrocarbons benzene, toluene and ethylbenzene (BTE).

In the present research work, only pyrolysis oil is analyzed by various characterization techniques like GC-FID, FTIR and physicochemical properties. Thus, in the future work, pyrolysis gas as well solid should be analyzed using various techniques. Furthermore, self-sustained pyrolysis process can be developed using product gas as a source of heat for the pyrolysis process.

The developed catalyst from natural clay is very promising and low cost which, reduces the overall cost of the entire pyrolysis process for the production of valuable aromatic hydrocarbons BTE.

The red clay catalyst RC-800 obtained BTE content of 27.62 wt.% at a moderate temperature of 550 ^{o}C and heating rate of 15 ^{o}C/min using feed to catalyst ratio of 20:1 for multiphase/AB-type catalytic pyrolysis process. The BTE content obtained using RC-800 catalyst was comparable but lower than the BTE content obtained from the commercial catalysts ZSM-5 ammonium powder (28.12 wt.%) and Nickel on silica-alumina catalyst (28.56 wt.%). Thus, RC-800 catalyst needs some additional modifications as it gives the lower BTE content as compared to the commercial catalysts. In addition some new low cost catalyst should be developed for the production of valuable hydrocarbons BTE and reduction of unwanted styrene.

In the present work, thermal and catalytic pyrolysis both contains the various components other than target molecules BTE. Thus, in the future work, all components of pyrolysis oil should be measured and undesired compounds should be removes for better performance of IC engines.

The designed experimental setup used in the present study is semi-batch type and fully manual. Thus, in the future study, a continuous reactor setup should be used to make the process faster.