CHAPTER 5
CONCLUSIONS

In this chapter, a summary of the main investigation and their implications and recommendations for future experiments are presented. Thermal and catalytic pyrolysis of polyethylene were thoroughly and systematically investigated in nitrogen environment. The pyrolysis and in-situ aromatization of waste plastics polyethylene, polypropylene and polystyrene using three different types of catalyst arrangements A-type/vapor phase, B-type/liquid phase and C-type/multiphase were performed to obtain optimum conditions for maximum BTEX yield. The commercial catalyst ZSM-5 and synthesized catalyst from waste fly ash were use as catalyst for the comparison of their performance in terms of BTEX yield. The fly ash synthesized catalyst showed excellent and comparable performance for the plastics pyrolysis and aromatization in the reactor.

5.1 Thermal pyrolysis

The experimental results of pyrolysis of waste plastics polyethylene, polypropylene and polystyrene and analyses of product yield show that the process could be a very good option for production of valuable liquid hydrocarbon suitable for diesel engine as fuel, after removal of benzene via suitable process. In addition, this method may possibly reduce the plastic waste load to municipal dumping ground. The maximum liquid yield of 68.02 wt. %, 80.56 wt. % and 96.0 wt. % were obtained by thermal pyrolysis of waste plastics polyethylene, polypropylene and polystyrene, respectively at a temperature of 700 ^{o}C. However, the maximum liquid yield of 72.66 wt. %, 87.62 wt. % and 91.6 wt. % were obtained by thermal pyrolysis of waste plastics polyethylene, polypropylene and polystyrene, respectively at a temperature of 800 ^{o}C, which is waxy at room temperature. The maximum aromatic content/BTEX of 10.75 wt. %, 30.91 wt. % and 13.58 wt. % were obtained at a temperature of 700 °C for liquid yield by thermal pyrolysis of waste plastics polyethylene, polypropylene and polystyrene, respectively. The flash point and fire point of pyrolysis oil were found to be in the range of diesel and kerosene irrespective of pyrolysis temperature. Lower amount of carbon residue in the pyrolysis oil of i.e., 0.28 wt. %, 0.24 wt. % and 0.86 wt. % obtained from PE, PP and PS, is an indication of low amount aromatic content. The maximum calorific value of 10982 Cal g^{-1}, 9015.48 Cal g^{-1} and 7073.37 Cal g^{-1} were obtained for the pyrolysis oil obtained at the temperature of 700 °C from the thermal pyrolysis for PE, PP and PS, respectively. Although, the BTEX content of pyrolysis oil were low, the calorific value and low carbon residue advocate the pyrolysis oil for the use as domestic fuel.

5.2 Catalytic Pyrolysis Using Commercial ZSM-5 Catalyst

The experimental results of PE, PP and PS pyrolysis and analyses of products show that the developed process could be a very good option for production of aromatics mainly benzene, toluene, ethylbenzene and xylene (BTEX). Among all type of reactor arrangements, C-type/ multiphase catalytic pyrolysis resulting in highest amount of aromatics of 39.47 wt.%, 53.12 wt. % and 26.86 wt. % for PE, PP and PS, respectively. The optimum process conditions i.e., temperature of 700 °C, reaction time of 30 min and feed to catalyst ratio of 20:1 were obtained for the maximum BTEX yield. Physicochemical properties of the pyrolysis oil (C-type) show that it can be used as alternative fuels and as a source of valuable chemicals such as benzene, toluene, ethylbenzene or xylene. Gases product can also be used to supply energy in process industry and the surplus may be used for additional power generation. These indicate that waste plastic pyrolysis via this novel approach C-type/multiphase catalytic arrangement which is energetically and economically viable and sustainable process. As mentioned earlier, the use of ZSM-5 catalyst decreases the quantity of pyrolysis oil but enhanced the quality of pyrolysis oil. The flash point and fire point of pyrolysis oil were found to be in the range of kerosene irrespective of pyrolysis process used. Liquid fuel obtained by catalytic pyrolysis (C-type) of waste PE has maximum GCV of 11230 Cal/g which is in the range of gasoline and diesel. However, the GCV of pyrolysis oil obtained from catalytic pyrolysis of PE for A-type and B-type were 10996 Cal/g and 11090 Cal/g, respectively. The maximum GCV of pyrolysis oil obtained from waste PP and PS were 9914 Cal/g and 9268 Cal/g, respectively. Lower amount of carbon residue of the pyrolysis oil i.e., 0.234 wt. % for waste PE, 0.23 wt. % for waste PP and 0.64 wt. % for waste PS indication of good fuel property, as they are less than 1 wt.%. This confirms the presence of low molecular weight aromatics in the oil. From this result, it is observed that this could be possible feedstock for further upgrading to use in the diesel engine besides recovery of BTEX as a valuable product from the pyrolysis of waste PE, PP and PS.

5.3 Catalytic Pyrolysis Using Synthesized Fly Ash Catalyst

The pyrolysis and in-situ aromatization of waste plastics PE, PP and PS on synthesized FA catalyst using reactor arrangements A-type, B-type and C-type were studied for the first time and has never been reported before in the available published literature. The optimum calcination temperature for the synthesis of catalyst from fly ash was 800 ^oC, as FA-800 catalyst showed excellent performance for aromatization of pyrolysis product in the reactor. The maximum surface area and (Si/Al) ratio of FA-800 catalyst were 310 m^2/g and 16.03, respectively. C-type/ multiphase catalytic pyrolysis on FA-800 catalyst at a temperature of 700 ^oC resulted in the highest amount of aromatics/BTEX of 22.10 wt.% for PE, 43.43 wt. % for PP and 20.92 wt. % for PS, respectively to any other process and catalysts tested in this study. The maximum GCV of 11786 Cal/g was obtained for the catalytic pyrolysis

(C-type) of waste PE using FA-800 catalyst. However, maximum GCV of pyrolysis oil for C-type catalytic pyrolysis obtained from waste PP and PS were 9625 Cal/g and 8953 Cal/g, respectively. The GCV of pyrolysis oil obtained from PP and PS are lower in comparison to waste PE. Lower amount of carbon residue of the pyrolysis oil i.e., 0.38 wt. % for waste PE, 0.24 wt. % for waste PP and 0.69 wt. % for waste PS indication of good fuel property, as they are less than 1 wt.%. This confirms the presence of low molecular weight aromatics in the oil. Lower amount of carbon residue of pyrolysis oil indicates that the possibility of carbon soot formation is negligible in IC engine. The experimental results on catalytic pyrolysis of PE, PP and PS and analyses of products show that the developed process could be a very good option for production of mainly aromatics BTEX.

The detailed study on the reactor using laboratory synthesis FA-800 from waste fly ash shows that the reactor arrangement C-type/ multiphase (vapor and liquid phase) catalytic pyrolysis is a state-of-the-art process for the production of aromatics/BTEX from waste plastics polyethylene, polypropylene and polystyrene. The developed process (C-type/ multiphase pyrolysis) can be scaled up to handle large amount of municipal waste polyethylene on law cost fly ash synthesized catalyst which ultimately transforms waste to energy material.

5.4 Future Scope

The developed process on the pyrolysis of waste plastics mainly polyethylene, polypropylene and polystyrene and in-situ aromatization for the BTEX is a new and innovative in nature. The future scope of the thesis work on the pyrolysis of waste plastics PE, PP and PS for BTEX production is very promising, as this type of process work has never been performed earlier. This work can be taken as road map for further development to increase the BTEX yield. The process is very simple, low cost and using waste materials fly ash synthesized catalyst and waste plastics. Thus, protecting nature from both the waste.

It is seen from the analysis of liquid yield that the maximum amount of BTEX, i.e., only 22.10 wt. % is present when PE is used as raw material in C-type catalytic pyrolysis on FA-800 catalyst. Whereas, for the same condition the BTEX yield of 43.43 wt. % and 20.92 wt. % are found in the liquid yield for PP and PS, respectively. Thus, there is a huge scope to make the process better by designing an ideal catalytic bed for maximum interaction between hydrocarbon molecules and catalyst particles resulting in faster and efficient aromatization. This also need modification of FA-800 catalyst, as it gives little lower BTEX yield than the commercial ZSM-5 irrespective of type of reactor arrangements and temperature.

The product oil contain multi components, however, only four major components benzene, toluene, ethylbenzene and xylene (BTEX) were evaluated. Thus, in future work, all other hydrocarbon molecules should be detected by GC-MS for further selective conversion of those molecules to BTEX using suitable catalyst and this could be ex-situ process.

There are certain issues need to be addressed and resolve before recommendation for commercialization of such process for BTEX production from waste plastics. The developed process is semi-batch type, little slow and no automation is there. Thus, a continuous packed bed process could be studied as future work plan using laboratory synthesized low cost green catalyst FA-800 for commercial production of BTEX. The coke deposition on catalyst resulting in deactivation of catalyst which gives low BTEX yield after 2nd cycle. Thus, stability and reusability of catalysts needs to be improved to make the process more attractive and draw attention of scientific community and industry people for future collaboration and true commercialization of the developed process.

In reality feed may come in mixture of waste plastics mainly PE, PP and PS with some inorganic additives. In such case the pyrolysis process will be more complex due to the different molecular structure of feed. The pyrolysis kinetics and reaction process will be more complicated for blended or mixed feed which will results in different liquid yield composition. Thus, a detailed study is required for mixed/ blended form of plastic feed to obtain higher BTEX yield along with lighter hydrocarbons. It should be noted that the mixed plastics waste must be segregated first to remove dirt and other inorganic additives which could hinder the pyrolysis process by blocking the catalyst pores (Zhang et al., 2018).

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