Separation of short carbon-chain precursor molecules from post-consumer plastic pyrolysis oil using fractional distillation

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Introduction

Pyrolysis oil derived from post-consumer polyolefins plastic typically of complex hydrocarbon mixture and some impurities (Al-Salem *et al*, 2017). However, pyrolysis oil has characteristically poor quality parameters such as high density, high viscosity, too high concentrations of trace metals and heteroatoms such as oxygen and chlorine. This makes pyrolysis oil unsuitable for their further applications for example in steam cracking, as it results in high coke formation amongst others, while oxygenated and chlorinated compounds result in unwanted acids (Diaz *et al*, 2018). Another problem is the wide carbon distribution, which causes by-product formation in case of conversion to valuable chemicals (Dao Thi *et al*, 2021).

On the other hand, from literature, it is known that pyrolysis of polyolefins results in formation of unsaturated terminal alkenes that are abundantly present (Tsug *et al*, 2011). These alkenes can be used as precursors molecules for preparation of chemicals by hydroformylation (Sharma *et al*, 2015). Therefore, valorisation of pyrolysis oil as precursors to precious chemicals is an interesting pathway. Yet, this would require efficient downstream process such as fractional distillation to separate short carbon-chain molecules of interest from pyrolysis oil. Distillation of pyrolysis oil has been discussed recently by researchers for its application as transportation fuel (Lee *et al*, 2021). Yet, research on the isolation of short carbon-chain molecules with narrow carbon cuts from waste plastic pyrolysis oil towards use as chemicals is scare. This presentation will show how to isolate three carbon-chain molecules from HDPE pyrolysis oil. Furthermore, insights will be provided on yields and purities of the initial oil and distillation cuts.

Materials and methods

The post-consumer HDPE pyrolysis oil investigated in the present study was obtained from a Belgian waste management company, Belgium. Pyrolysis process was carried out at 450 °C and 1 bara. Distillation was conducted in a batch setup consisting of a boiling flask having capacity of 5L. The distillation column has high efficiency structured packing: Montz-Pak Type B1-350 (Germany) corresponding to eight theoretical plates. The column is also provided with adjustable reflux splitter, cooling traps and a vacuum pump. Process conditions such as calculation of boiling point at reduced pressure, setting up of chiller temperature, boil-up ratio and selection of optimum reflux ratio for obtaining clean and sharper fractions was according to ASTM D2892-19. Gas chromatography - mass spectrometry (GC-MS) was tentatively applied to analyze hydrocarbons present in the pyrolysis oils and its distilled fraction.

Results and discussion

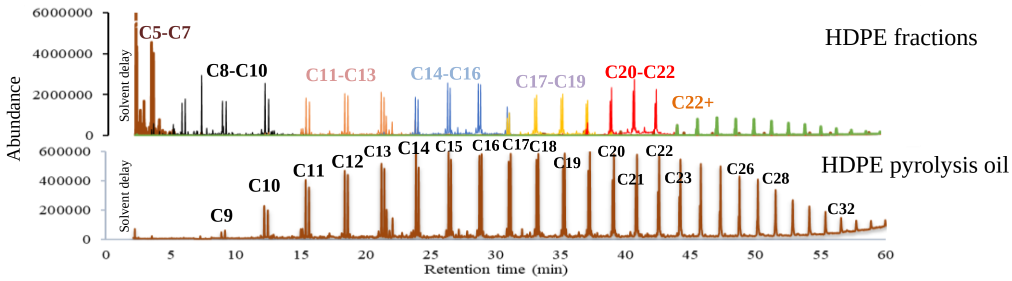

Fig. 1 : Comparison of GC chromatogram for HDPE pyrolysis oil and its derived fractions

Figure.1 shows comparative peaks from GC-MS for HDPE pyrolysis oil and its derived fractions. The GC chromatogram for HDPE pyrolysis oil represents sequence of carbon number in ascending order similar to those discussed by Tsug *et al*, 2011. Distillation allows the separation of three carbon-chain molecules such as C_5-C_7, C_8-C_{10}, C_{11}-C_{13}, C_{14}-C_{16}, C_{17}-C_{19}, C_{20}-C_{22} and C_{22+}. It can be observed that fractional distillation sharply isolate three carbon-chain hydrocarbons from HDPE pyrolysis oil. The fractions are cleaner with fewer overlap.

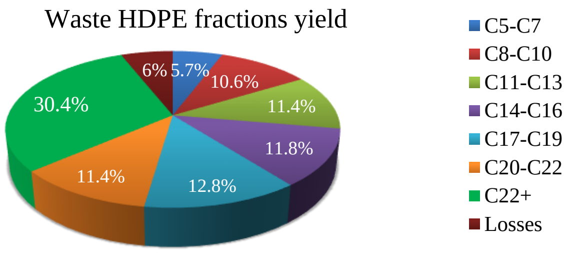

Fig. 2: Fractional distillation yield for HDPE pyrolysis oil & its derived fractions

Fig.2 represents distillation yields for HDPE pyrolysis oil. It can be seen that the yield of C_5-C_7 fraction is 5.7 %, which is significantly lower than C_8-C_{10} fraction at 10.6 % while variation in the yield of heavier fractions such as C_{11}-C_{13}, C_{14}-C_{16}, C_{17}-C_{19} and C_{20}-C_{22} was comparably small. The C_{22+} left in the distillation flask was 30.4 %.

Due to the presence of abundant alkenes in plastic pyrolysis oil, the short-carbon chain distilled fractions can be used as potential precursor for production of chemicals. For example by hydroformylation, the reaction of alkenes with syn-gas produces aldehydes. C_6-C_{13} aldehydes are used for the production of perfumery chemicals while C_6–C_{13} alcohols for the preparation of plasticizers. Linear C_{12}–C_{18} aldehydes find their applications in the detergent industries and many more (Sharma *et al*, 2015) .

Conclusion

Fractional distillation of pyrolysis oil resulted in separation of short carbon-chain molecules. GC-MS analysis showed that isolation of three carbon molecules from HDPE pyrolysis oil gives fewer overlaps. This depicts that pure molecules of minimum three carbon number can be obtained by fractional distillation of HDPE pyrolysis oil.

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