

THE FORMATION OF AROMATIC HYDROCARBONS DURING THE PYROLYSIS OF POLYETHYLENE

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ABSTRACT

Plastics see very widespread use in modern society. The properties of many plastics can be modified relatively easily to fit a wide variety of applications. However, the disposal of waste plastics presents a significant environmental challenge. Recently, there has been considerable interest into tertiary recycling of waste plastics to produce liquid fuel. This project focuses on the formation of aromatic hydrocarbons during thermal pyrolysis of plastics. Several reactor configurations have been suggested for the pyrolysis of plastics. The reactor configuration used in this study consists of a stirrer tank reactor coupled with a reflux column and a condenser.

The effect of varying operating temperatures on the aromatic content of the product was investigated. It was found that the mono-aromatic and di-aromatic hydrocarbon concentration in the liquid product is essentially independent of the reaction temperature and reflux temperature in the temperature range investigated. On the other hand, it is possible to regulate the tri+aromatic content of the product by varying reactor and reflux temperatures. An increase in either the reaction temperature or the reflux temperature results in a significant increase in tri+aromatic concentration in the fuel.

The insensitivity of mono- and di-aromatic content to changes in operating temperatures and the very low concentrations of tri+aromatics present in the fuel would suggest that it is not possible to regulate the aromatic content to a significant extent by varying operating conditions alone.

INTRODUCTION

While plastics play an integral role in modern society, there are well publicised issues regarding the disposal of plastics at the end of their useful lifetime. The chemical stability of plastics renders it very resistant to degradation and hence their disposal to landfills poses a very significant environmental problem. Primary recycling of plastics, in which the original plastic is melted and reformed into useful products, poses a very attractive alternative but has limited application. This has resulted in significant interest in other forms of recycling in which plastic is utilised as a feedstock to produce other useful materials. Two methods which have received a lot of interest from the research community are monomer recycling and thermal depolymerisation. Monomer recycling is

a process in which the plastics are “depolymerised” to reclaim the initial monomers which are then utilised to reform to original polymer.

Thermal depolymerisation is the process of interest in this research. Here, the plastics undergo thermal pyrolysis to break down the polymer chains into hydrocarbons similar to that found in petroleum. These hydrocarbons can then be utilised for other purposes. The main focus of the current research is the production of liquid fuel, mainly of the diesel fraction, from pyrolysis of plastics commonly found in waste. The 3 most common plastics found in waste are polyethylene (PE), polypropylene (PP) and polystyrene (PS) (Pinto *et al*, 1999). Of these, PE is the most prevalent – municipal waste consists of approximately 70% PE. The current research focuses on the pyrolysis of PE.

It is known that during the pyrolysis of plastics, aromatic hydrocarbons are formed (Blazso, 1993, Lee & Shin, 2007). Aromatic hydrocarbons are detected in fuel generated from the pyrolysis of plastics such as PE and PP, even though the chemical structure of the polymer does not contain any aromatic or even cyclic groups. It is important that the content and type of aromatic hydrocarbons present in the fuel is regulated. Sufficient quantities of these aromatic compounds have a very significant effect on both the chemical and physical properties of the fuel. The pyrolysis of PE predominantly produces straight chain hydrocarbons which have a low density and relatively high cloud point. The presence of aromatic hydrocarbons in this fuel will have the combined effect of raising the density and lowering the cloud point, which is essential to meet the automotive fuel specifications set out by the various governments. Mono-aromatics in the fuel also have a positive effect on the energy density of the fuel. On the other hand, the presence of polycyclic aromatic hydrocarbons (PAHs) is a cause for concern because these compounds lead to the formation of soot in engines. The soot and PAHs are discharged into the atmosphere and poses a health risk to the general public. For this reason it is important to understand the factors which affect aromatic formation and how changing these conditions might affect other aspects of fuel quality. This paper presents the results of an investigation into the effect of varying reactor and reflux temperatures on the aromatic content in fuel from low-density polyethylene (LDPE).

EXPERIMENTAL

Pyrolysis Reactor

Figure 1 is a schematic representation of the apparatus used to carry out the pyrolysis experiments. The pyrolysis was carried out in a stainless steel batch reactor. The reactor is equipped with a mechanical agitator and an inert gas supply. Heat is supplied to the reactor using a fluidised sand bed. The use of a fluidised sand bed allows more uniform heat transfer to the reactor. The combination of this all-round heating and agitation attempts to overcome the heat transfer problems commonly encountered when attempting to heat a high viscosity fluid with low thermal conductivity such as a plastic melt.

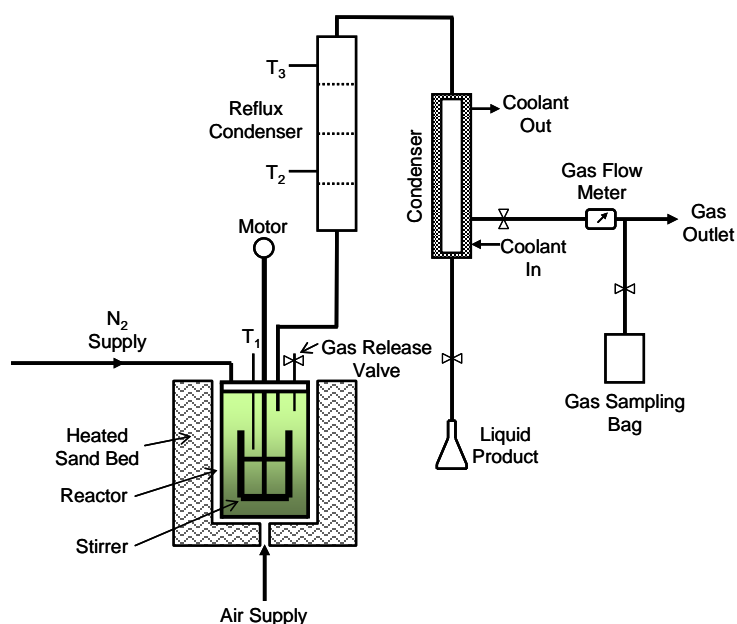


Fig. 1: Schematic representation of the thermal pyrolysis system.

The gaseous products from this reactor are passed through a reflux condenser. The reflux column is maintained at a lower temperature than the reactor which results in the heavier (i.e. high boiling point) components of the vapour being recycled back to the reactor for further cracking. Heating tapes are used to pre-heat the reflux column and supply additional heat when necessary. Lighter compounds will escape the reflux column and enters a condenser unit. The condenser system used here is a simple coil in column design. Silicone oil is used as the heat transfer media and the temperature in condenser is controlled using a heating/cooling bath.

Experimental Method

The LDPE used was sourced locally. For these experiments, virgin plastic powder was used to eliminate interferences from fillers, additives and contaminants. A fixed amount of plastic was fed into the reactor at room temperature at the start of the experiment. The system was then heated from ambient temperature to the desired reaction temperature. During the first 60 minutes of the heating period, nitrogen gas was continuously flowed through the system to eliminate the presence of oxygen from the system. The agitator was not started until the temperature reaches 200 °C as the viscosity of the melt was initially too high and places too much strain on the motor.

The reflux column and condenser were pre-heated to approximately 220 °C and 50 °C, respectively. A relatively high condenser temperature was chosen as certain operating conditions result in the generation of waxes which could solidify and clog the condenser at lower temperatures. The temperature of the reflux column varies slightly depending on the quantity of vapour being produced in the main reactor and the temperature has to be monitored constantly throughout the experiment.

Unless otherwise specified, the pyrolysis of LDPE was carried out at 440 °C and the reflux column was maintained at 280 °C. At regular time intervals, the oil produced was collected and weighed and a small sample was collected for analysis. The oil sample was tested for aromatics using the methods described in the following sections.

Analytical Methods

High Performance Liquid Chromatography (HPLC)

A Waters HPLC system that consists of an in-line degasser, 600E multisolvent delivery system, 717plus autosampler and 2414 refractive index (RI) detector was used to determine the aromatic content of the samples. The testing method used conforms to European Standard EN12916:2006. All the analyses were carried out using a solvent flowrate of 1ml/min of heptane and both the column and detector were heated to 30 °C. Due to the lower concentration of aromatics in diesel from plastics as compared to diesel from petroleum, undiluted samples were used. 10 microliter of neat sample was injected for each analysis and calibrations were carried out at the beginning and end of each series of tests. All calibration standards were made up using high purity reagents purchased from Sigma-Aldrich.

A Waters Spherisorb NH2 column was used to perform the separation. This column retains aromatic hydrocarbons with larger ring sizes more effectively resulting in longer retention times for heavier aromatics. However, separation of individual aromatic compounds is not achieved, nor is it required for this analysis. The standard only requires that the aromatics in the fuel be separated into three groups, namely mono-aromatics, di-aromatics and tri+-aromatics (where tri+-aromatics refer to aromatics with 3 or more rings). The concentrations of aromatic hydrocarbons in each of these groups are calculated based on calibration curves generated using 1,2-dimethyl benzene, fluorene and phenanthrene for the mono-, di- and tri+-aromatics respectively.

UV-Visible Fluorescence Spectroscopy

A Perkin-Elmer LS-50B luminescence spectrometer was also used to investigate the fuel obtained from the multi-phase reactor. This testing method takes advantage of the fact that aromatic hydrocarbons absorb and fluoresce ultra-violet (UV) radiation at a wavelength which is quite different to that of other hydrocarbons within the fuel (predominantly alkanes and alkenes). The waveform of the absorption and emission spectra of the sample provides valuable information regarding the aromatics present within the sample (Han *et al*, 2006, Li *et al*, 1994). In fuel produced from the pyrolysis of LDPE, the concentration of large aromatic species (tri+-aromatics) is generally extremely low. So, while a HPLC with a RI detector is an indispensable tool for determining the mono- and di-aromatic content of the fuel, its sensitivity is usually insufficient to detect the larger poly-aromatics in these fuels. UV fluorescence analysis complements the HPLC in that the fluorescence response of aromatics with 3-5 rings is much higher than that of both mono- and di-aromatics.

Constant energy difference synchronous fluorescence spectroscopy was used to analyse the samples generated. An energy difference (ΔE) of 2800 cm^{-1} was used and the peaks at 300 nm and 340 nm, which correspond to the fluorescence of 1-2 ring aromatics and 3 ring aromatics (Benkhedda *et al*, 1992) respectively, were evaluated. A scan rate of 200 nm min^{-1} and slit width of 2.5 nm was used for all analyses. It should be noted that the ring sizes corresponding to these peaks are just approximations. Also, the peaks in the UV-fluorescence spectra can be related to the presence of an aromatic species or a group of similar species. These groups indicate aromatics with similar ring structures but different substitutional groups. The compounds within these groups are physically different but behave similarly with respect to UV fluorescence due to their very similar aromatic ring structures. Analysis was carried out on samples which were diluted to

200 ppm with chloroform. While the variation of signal intensity versus concentration was not perfectly linear at this concentration, the choice of 200 ppm was a compromise between linearity of response and a high signal to noise (SNR) ratio. It is also necessary to note that in UV-fluorescence analysis, only comparisons of relative concentrations at a particular wave are possible. Fluorescence intensities should not be compared across different wavelength.

RESULTS AND DISCUSSION

Effect of Reactor Temperature on the Pyrolysis of Polyethylene

The first parameter under investigation was the effect of reaction temperature. As is expected, an increase in reactor temperature results in an increase in the rate of plastic pyrolysis (Westerhout *et al*, 1998). However, there is very little known about the effect of varying pyrolysis temperature on the formation of aromatics. Several mechanisms have been suggested for the formation of aromatics during pyrolysis of plastics in the literature (Richter & Howard, 2000), and it is generally believed that the dominant pathway is dependent on the pyrolysis temperature.

Figure 2 shows the mono-aromatic concentration of the oil collected from the pyrolysis of LDPE at different temperatures. The samples were analysed by HPLC in accordance with EN12916:2006. Although there is considerable scatter in the results, it can be seen that there does not appear to be any particular trend in the results as the temperature is varied from 420 °C to 470 °C. Regardless of the temperature, approximately 9,000 ppm of mono-aromatics was detected in the fuel. However, a three-fold increase in the rate of plastic pyrolysis was measured as the temperature was increased from 420 °C to 470 °C - i.e the time required to pyrolyse the quantity of plastic in the reactor was reduced by a factor of three. The fact that the final mono-aromatic concentration in the product is approximately equal despite this increase in the rate of pyrolysis suggests that the increase in the rate of mono-aromatic production and rate of plastic pyrolysis in the same in the temperature range 420 °C to 470 °C. This would tend to indicate that the sensitivity of both reactions (the cracking of LDPE and the formation of mono-aromatics) to the reaction temperature are very similar in this temperature range. It could be possible that the Arrhenius plots for the two reactions either intercepts (or approaches an intercept) in this temperature range. In order to determine if this is occurring, it would be necessary to isolate the two reactions and determine their changes in reaction rate with temperature. This was not possible with the current set-up.

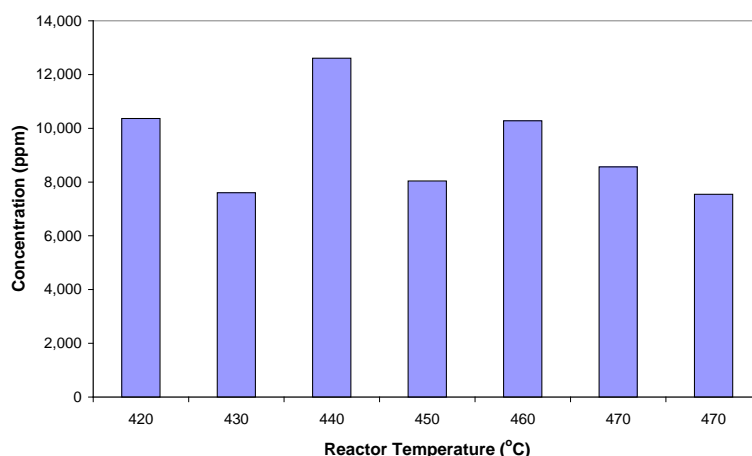


Fig. 2: Concentration of mono-aromatics in oil produced from LDPE at different temperatures.

One explanation for such a result is that the rate limiting step for both reactions is the same. One such possibility is that the formation of mono-aromatics relies on the formation of an intermediate which is the result of the cracking of LDPE. If the formation of this intermediate is rate limiting (possibly due to heat-transfer limitations), then it is conceivable that the rate of formation of mono-aromatics and the rate of plastic pyrolysis are very similar.

Figure 3 shows the concentration of di-aromatics in the samples as determined by HPLC. As is the case with mono-aromatics, there does not appear to be a correlation between the di aromatic content in the fuel and the reaction temperature; approximately 700 ppm of di aromatics were detected in the fuel generated from pyrolysis of LDPE. The concentration of tri-aromatics has not been reported as they are below the detection limits of the HPLC.

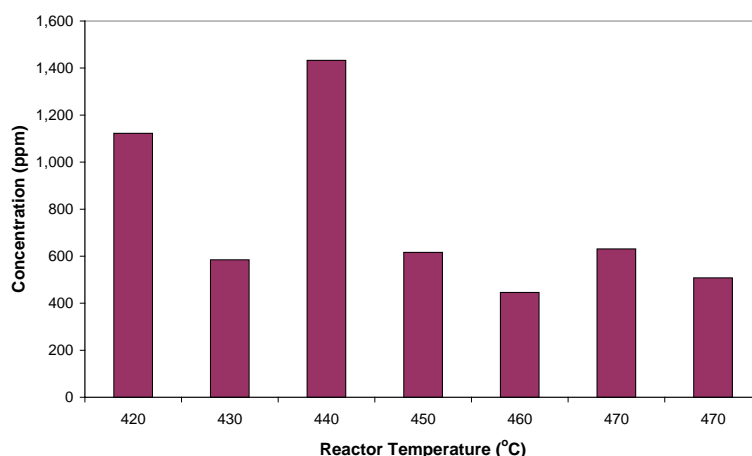


Fig. 3: Concentration of di-aromatics in oil produced from LDPE at different temperatures.

Figure 4 shows the peak intensities corresponding to the mono- and di-aromatics in the fuel as determined using UV-fluorescence. As pointed out above, these peak intensities should only be used to indicate relative changes in concentration (instead of absolute concentration). As in figures 2 and 3, there does not appear to be any relationship between temperature and mono- and di-aromatic concentration. These results support the finding of the HPLC analysis.

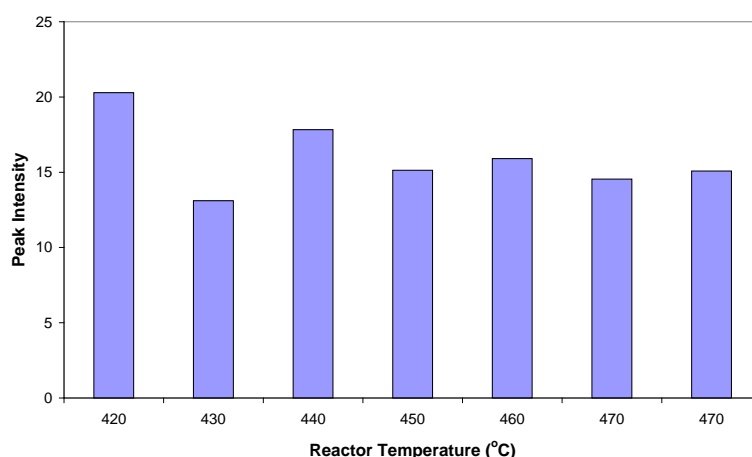


Fig. 4: UV-fluorescence peak intensities at 300 nm ($\Delta E = -2800 \text{ cm}^{-1}$) of the oil samples produced from LDPE at different temperatures.

UV-fluorescence analysis of the larger PAHs in the samples indicates that there is a relationship between the concentration of these species and the reaction temperature. Figure 5 shows the concentration of 3-ring aromatics as determined using UV fluorescence. Allowing for some scatter in the results, it can be seen that increasing the temperature from 420 °C to 470 °C results in a three-fold increase in the tri-aromatic concentration.

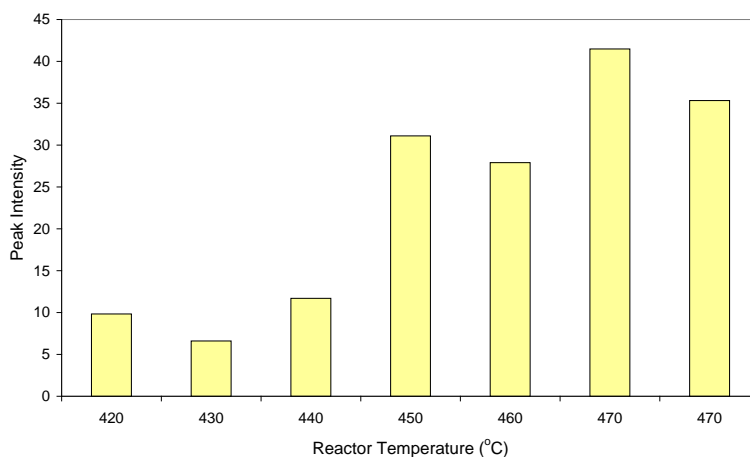


Fig. 5: UV-fluorescence peak intensities at 340 nm ($\Delta E = -2800 \text{ cm}^{-1}$) of the oil samples produced from LDPE at different temperatures.

Several explanations can be suggested to rationalise this trend which is not seen with the smaller aromatic species. The first is that the formation of these larger PAHs follows a different mechanism which is not dependent on the formation of the intermediate suggested above. It is possible that these larger aromatics are formed from the polymerisation of the smaller aromatic species, which would follow a different pathway to that of the formation of mono-aromatics. It is expected that the temperature dependence of these reaction mechanisms would be substantially different to that of the formation of mono-aromatics.

The fact that 3-ring aromatics have boiling points similar to the temperatures used in the reflux column (e.g. anthracene boils at 340 °C) suggests another possible explanation for this trend. The higher vapour flowrates generated at higher temperatures might not allow sufficient residence time in the reflux column for the vapour to reach equilibrium with the refluxed liquid. Hence, some of the higher molecular weight species could be “pushed” out of the reflux condenser and appears in the product. Further analysis of the oil samples are required to determine if this is the cause of the trend seen.

From an industrial perspective, the fact that the mono- and di-aromatic concentration appears to be independent of reaction temperature means that it is not possible to regulate the aromatic concentration using the reactor temperature. For this reason, it would appear it is not possible for the aromatic content to modify the physical properties of the fuel to a significant extent if the feedstock is predominantly LDPE.

Effect of Reflux Column Temperature on the Pyrolysis of Polyethylene

Several experiments were carried out in which the temperature of the top of the reflux column was varied. As discussed above, the reflux column temperature effectively controls which species are able to leave the reactor system. Species with a much lower boiling point (than the reflux temperature) would leave the column in the vapour stream whereas those with much higher boiling points would be condense and flow back into the reactor. Compounds with boiling points close to the operating temperature of the reflux column would be partially refluxed, the extent of which would depend on the vapour pressure of the species at the temperature of the column. The HPLC analysis results of fuel produced using 3 different reflux temperatures are shown in figure 6.

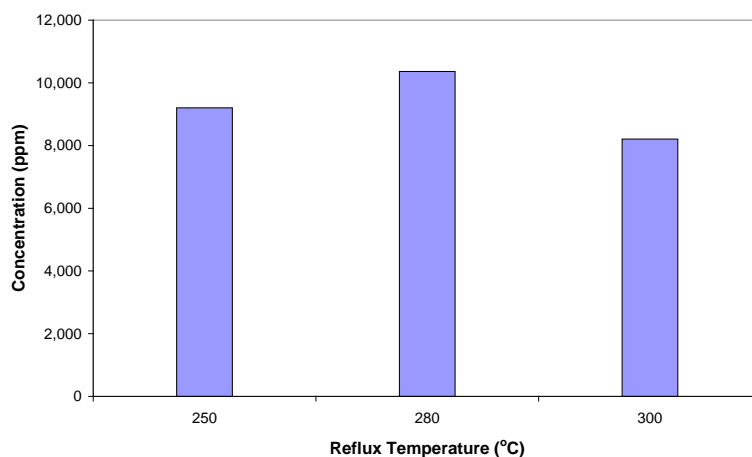


Fig. 6: Concentration of mono-aromatics in oil produced from LDPE as a function of reflux column temperature.

The results shown in figure 6 indicate that the mono-aromatic concentration is independent of reflux temperature. This result is expected as mono-aromatics generally have boiling points well below the temperature of the reflux column. As such, small changes to the reflux temperature should not have any effect on the mono-aromatic content of the fuel. On the other hand, tri-aromatics have boiling points slightly above the reflux temperature. For this reason, small changes in the temperature of the reflux column are expected to result in very significant increases in the tri-aromatics concentration. This can be seen in the results shown in figure 7. A 30 °C increase in the reflux temperature shows a five-fold increase in tri-aromatic concentration of the product. While only two experimental results are shown here, preliminary experiments into the effect of reflux temperature on the reaction kinetics show a similar trend.

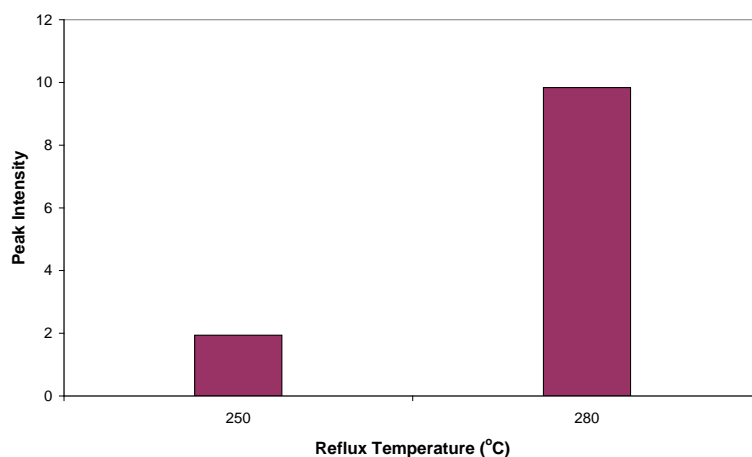


Fig. 7: Variation in the concentration of tri-aromatics in oil produced from LDPE as a function of reflux column temperature.

While the results shown here might tend to indicate that the reflux column temperature could be used to control the concentration of the larger aromatic species in the final product, it is important to remember that the reflux column temperature is adjusted based on the desired distribution of hydrocarbon chain lengths in the final product. Therefore, only relatively small temperature adjustments can be applied to the temperature of the reflux column without detrimentally affecting the overall quality of the fuel.

CONCLUSIONS

Pyrolysis of low-density polyethylene was carried out in a batch stirred tank reactor system. It was found that the concentration of mono- and di-aromatics in the fuel is effectively independent of the reaction temperature. In the temperature range investigated, the concentration of mono-aromatics and di-aromatics in fuel generated from the pyrolysis of LDPE is approximately 9,000 ppm and 700 ppm, respectively. Results obtained using UV-fluorescence analysis for 1-2 ring aromatics verify the results obtained using the HPLC. UV-fluorescence analysis indicates that tri+aromatics concentration vary significantly with changes in reaction temperature. However, it is not clear if this effect is due to a change in reaction mechanism or overloading of the reflux column due to the geometry of the experimental setup.

The temperature at the top of the reflux column was found to have essentially no effect on the concentration of mono- and di-aromatics in the fuel. While a higher top reflux column temperature produces fuel with a higher tri+aromatics concentration, regulating the concentration of these species using the reflux column is hindered by the fact that altering the reflux column temperature will also significantly alter the molecular weight distribution of the hydrocarbons in the product.

These results indicate that it is not possible to regulate the aromatic content to a significant extent by controlling the reaction and/or reflux temperatures. It is believed that more effective control of the aromatics content could be achieved by other means (e.g. control of the feedstock composition). This is the focus of another study and will be reported in a future publication.

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BRIEF BIOGRAPHY OF PRESENTER

Dr Wei Lit Choo is currently a research fellow with the Energy, Fuels and Reaction Engineering Research Group in the Department of Chemical Engineering, Monash University. He holds a Bachelor of Science and Bachelor of Engineering, as well as a PhD in Chemical Engineering from Monash University. His previous projects include investigations into the recovery of gold using ammoniacal sodium thiosulfate solutions as an alternative to cyanidation and the formation of sulphur compounds during the pyrolysis of plastic waste.