Investigation of High-Density Polyethylene Pyrolyzed Wax for Asphalt Binder Modification: Mechanism, Thermal Properties, and Ageing Performance

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Highlights

- Thermal cracking of high-density polyethylene wax in a fixed bed reactor.
- Thermal ageing mechanisms in pyrolysis waxes for asphalt modification suitability.
- Loss of volatiles, oxidation, and polymerization ageing reactions in pyrolysis waxes.
- Optimal pyrolysis wax properties and blending for asphalt binder modification.

Abstract

The thermal pyrolysis of high-density polyethylene in a fixed bed reactor has been studied in the temperature range of 450-550 °C with two different nitrogen carrier gas flowrates, 2 and 4 L min^{-1}, to study the effect of these process parameters as well as the resultant vapour residence times on the formation of wax and its chemical and thermal properties. The technology had a high selectivity to waxes, with a yield of up to 91.87% wax from high-density polyethylene at 500 °C using a nitrogen carrier gas flowrate of 4 L min^{-1} and subsequent 1.76 second vapour residence time, calculated using the ideal gas law. The waxes were characterised using techniques including gas-chromatography-mass spectroscopy (GC-MS), Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The process operating temperature especially

and its subsequent effect on vapour residence times within the reactor had a considerable impact on both the chemical and thermal properties of the waxes. Higher operating temperatures yielded more olefinic waxes due to the promotion of degradation radical mechanisms such as β-scission. They were observed to have higher melting points and thermal stability. An investigation was conducted to assess the thermal properties and ageing performance of the waxes. Thermal conditioning in an ashing oven at 170 °C for 0-6 hours was conducted with a detailed analysis of GC-MS and FTIR at each stage of thermal exposure to further support thermal characterisation results. The changes in chemical composition were attributed mainly to oxidation and polymerisation ageing reactions and were seen to be more prominent in the more unsaturated waxes produced at higher pyrolysis temperatures. The wax produced at 550 °C was determined the optimal wax for binder modification in hot-mix asphalt pavement design due to lower volatile/mass loss. A lower temperature range was suggested for optimal blending conditions to further reduce loss of volatiles with initial blending and storage.

Keywords: Waxes; plastic pyrolysis; fixed bed reactor; ageing; asphalt; sustainable infrastructure

1. Introduction

High-Density Polyethylene (HDPE) is a polyolefin (PO) plastic that has contributed to the recent enormous rise in 'single-use' medical waste, generated from various sources during the COVID-19 pandemic (Dharmaraj et al. 2021). The majority of municipal plastic waste streams now comprise of polyethylene plastics such as this, which are typically treated through conventional methods like landfilling or incineration. However, these methods result in new environmental concerns, e.g., air pollution and dioxin emissions, land pollution and even ocean pollution (Onwudili et al. 2009; Tsai et al. 2009; Jambeck et al. 2015; R. Verma et al. 2016; Abdy et al. 2022). The drawbacks associated with these methods make them unsuitable to the goals for sustainable development and the current pressures on waste plastic management has made the development of more sustainable recycling infrastructure vital.

Currently, organic additives such as waxes have been broadly utilised as viscosity and workability improvers in asphalt binders of higher viscosity, such as rubberised and polymer modified asphalt. Also within warm mix asphalt (WMA) mixtures to achieve reduced process temperatures (100-140 °C) and thus lessen production energy, cost, and emission intensity (Zaumanis and Haritonovs, 2010; Ling et al. 2019; Sukhija and Saboo, 2021). Fischer-Tropsch (Sasobit) wax is a widely researched commercial wax additive studied in literature that is produced synthetically from syngas (Desidery and Lanotte, 2021). The wax reduces binder viscosity at mixing and compaction temperatures as well as produces stiffer mixtures at service conditions. Improved resistance to permanent deformation and interaction between the modifiers (for example, crumb rubber) and base asphalt has additionally been reported (Fazaeli et al. 2012; Yu et al. 2016; SASOL, 2018). Another lower molecular weight product of the polymerization process is polyethylene wax, which is as well largely studied for similar applications. The waxes have been reported to upgrade the rutting (controversial), fatigue, and temperature cracking resistances, as well as improve the moisture resistance of polymer modified WMA (Edwards, 2008; Kim et al. 2013; Nakhaei et al. 2016).

Alternatively, using PO plastics and plastic derived products as performance-enhancing materials in asphalt binders has also received focused attention for the possible recycling and reuse of this waste material (Leng et al. 2018; Ling et al. 2019). Grady, (2021) reviewed the potential of waste plastics in asphalt concrete and consider this as a practical and cost effective application with the large volumes of both waste and roads being produced. Additionally,

conventional asphalt binders are a by-product of the petroleum refining process with petroleum being a finite and highly impacting resource. A main effort within pavement engineering currently is to move towards “greener” alternatives such as this, aiming to align with sustainable development and circular economy goals (Su et al. 2018; Gaudenzi et al. 2021). PO plastics can be thermochemically treated via processes such as pyrolysis which crack the waste into smaller molecular products. This entails heating the materials from moderate to severe temperatures (<800 °C) in an inert atmosphere, the desired products typically being tars (oils and waxes), gaseous products and solid char (Al-Salem et al. 2009). Aliphatic waxes are the primary product of PO thermal pyrolysis at moderate temepratures (500 °C), with a high content of heavy wax hydrocarbons also obtained in the pyrolytic oil (Arabiourrutia et al. 2012; Quesada et al. 2020). Previous literature review work by the authors details the current scope of pyrolysis PO plastics in asphalt binder and hot mix asphalt (HMA) mixture modification (Abdy et al. 2022). It was particularly noted to demonstrate analogous results to binder modification with raw recycled plastics, in both neat and rubberised binders (reduction in penetration point, increase in binder stiffness, softening point, temperature susceptibility and stripping resistance, enhanced resistance to permanent deformation, etc (Al-Hadidy and Tan, 2009a, 2009b; Shang and Wang, 2011).) The use of lower mixing temepratures and times while achieving mixture homogeneity was concluded as a clear advantage in the review work, as these lower molecular weight and density products from pyrolysis can be more easily dissolved in bitumen binders (Abdy et al. 2022).

However, the product spectrum of polyethylene thermal pyrolysis is especially broad and is characterised by a skewed distribution. Due to the random chain scission mechanisms that occur during the primary cracking of thermal decomposition, the wax products that dominate the liquid yield composition at moderate process temperatures are comprised of a wide distribution of hydrocarbon aliphatic compounds, typically within the C_5-C_{40} range (Williams and Williams, 1997; Ragaert et al. 2017). This non-selectivity resulting in the generation of volatile components within the product waxes is important to consider when matching them to potential applications, such as within asphalt binder modification. Petroleum asphalt containing alternative materials obtained from depolymerisation processes such as pyrolysis, as reported in the case of bio-binders obtained from biomasses, can potentially exhibit quicker ageing when exposed to fresh air at high temperatures (Yang et al. 2015). The ageing of ‘bio-binders’ has been attributed to polymerization and oxidation reacitons, as well as the loss of volatiles; resulting in compositional changes, effecting the overall storage stability of the resultant

admixture (Hilten and Das, 2010). A high loss of volatiles especially indicates high emissions and therefore detailed information on the low molecular weight hydrocarbons should be evaluated with respect to influence on the environment and exposure in potential applications. The loss of modifier material may additionally result in it not fully imparting performance enhancing properties onto the asphalt binder admixture. Therefore, there is much significance in the optimisation of the pyrolysis process in obtaining waxes with optimal compositions for blending and reducing the volatiles present within the subsequent modified asphalt binders. Optimal wax modifiers should be able to exhibit both chemical and thermal stability when subjected to high-speed shear mixing with neat binders; in literature commercial waxes and waxes obtained from thermal degradation processes are typically blended between 115-180 °C for 10-30 minutes (Edwards, 2008; Dimondo and Guillon, 2017; Ling et al. 2019). Also during the thermal conditioning processes for long- and short-term ageing that are conducted on the modified binders; the rolling thin-film oven test (RTFOT) and pressure ageing vessel (PAV), allowing for full binder characterisation with respect to the main pavement failure modes such as fatigue and rutting (BSOL, 2012, 2014). Furthermore, optimisation to obtain a desired product decreases process uncertainty and increase the credibility and economic viability of the process for investment and commercialisation.

A small portion of studies have used optimised experimental configurations (e.g., vacuum pyrolysis, conical spouted reactor) suitable for the selectivity of obtaining pyrolysis waxes, the primary devolatilization product in polymer degradation in pyrolysis. Through characterisation, the waxes presented as similar to commercial paraffin waxes and suitable for certain fuel and other applications (Aguado et al. 2002; Arabiourrutia et al. 2012). Yet a research gap identified in previous review work was the lack of extensive characterisation of the modifier materials derived from waste and the full determination of their suitability for asphalt binder modification prior to blending and binder analysis (Abdy et al. 2022). Therefore, no fully established relationships have been made between the thermal and chemical characteristics of the pyrolysis waxes from HDPE and the subsequent mechanical and rheological performance of the modified asphalt binders. Furthermore, without such relationships, optimal wax properties have not been identified for this application, leading to a lack of optimisation of the pyrolysis process for desired products.

Using a fixed bed reactor to obtain wax from the thermal pyrolysis of HDPE, this paper describes the first phase of a broader work, in which pyrolysis mechanisms and wax yields are

described, and relationships between the proccess operating parameters and resultant wax chemical and thermal properties are established. Its novelty is its focus on the thermal properties and ageing performance of the waxes, especially with regards to volatile loss and the proposed ageing mechanisms that occur. This can be linked to the chemical composition of the wax and thus the pyrolysis parameters utilised that result in certain pyrolysis reaction mechanisms. The techniques utilised to assist in this investigation include non-isothermal thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to examine the thermal degradation characteristics and melting point ranges of the unaged waxes. Gas Chromatography-Mass Spectroscopy (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) are used to quantitatively determine the chemical composition and distribution as well as qualitatively identify the chemical functional groups present in the pyrolysis waxes, respectively. The two latter techniques especially are used to comprehensively analyse the unaged and thermally ages waxes, in order to propose ageing mechanisms that take place. These techniques in conjunction can be used to assess the ageing performance of the waxes such that optimal waxes can be taken forward in later work for blending with asphalt binders.

2. Materials and Methods

2.1. Materials

High-density polyethylene (HDPE) was sourced from Sigma-Aldrich in the form of approximately 2 x 2 mm^2 clear round pellets (injection moulding grade). The materials physical properties were declared in the MSDS as density (ρ = 0.952 g/mL), melt index (MI; 12 g/ 10 min), visca softening point (125 °C), and melting point (125-140 °C).

2.2. Thermal Pyrolysis

The HDPE pellets were pyrolyzed using a bench scale system at 450-550 °C to examine the influence of operating temperature on product wax yield and properties. As seen in Figure 1, the system consisted of a fixed-bed reactor vessel containing a metal crucible that was first filled with 20 g of metal balls to provide improved heat transfer within the crucible, followed by 25 g of HDPE pellets for every batch pyrolysis reaction. The dimensions of the reactor tube were a 50.8 mm diameter and a 150 mm length. A Carbolite electric furnace model EVT 12/150B with a power capacity of 750 watts was used as the external heating source. Prior to each experimental run, the system was purged with nitrogen (N_2) gas to eliminate the presence of oxygen. Upon exiting the pyrolysis reactor, the gases passed through a 5 °C water condenser and further glassware for wax product condensation and collection. A cotton wool filter was in place to capture any escaping vapours and the non-condensbale gases were vented. Using this reactor configuration, the HDPE pellets were thermally degraded gradually, achieving the final temperature using a heating rate of 10 cm min^{-1}. Volatile products were purged from the reactor tube using two nitrogen flowrates (2 and 4 L min^{-1}) to additionally observe the influence of vapour residence time on the yield and properties of the pyrolysis wax products. The vapour residence times were estimated using the ideal gas law for the carrier gas and can be found in Table 1. The condensed wax product was collected after >2 hours of pyrolysis reaction time without separating the light and heavy fractions. All experiments were conducted in triplets. The product waxes were named according to the pyrolysis parameters used, for example the pyrolysis wax produced at 450 °C with a 2 L min^{-1} carrier gas flowrate is referenced to as sample 450-2, and so on.

Table 1: Pyrolysis conditions.

Pyrolysis Temperature (°C)	Nitrogen (N_2) Flowrate (L min^{-1})	Vapour Residence Time* (s)
450	2	3.76
	4	1.88
500	2	3.52
	4	1.76
550	2	3.30
	4	1.65

*Vapour residence time was estimated using Ideal Gas Law.

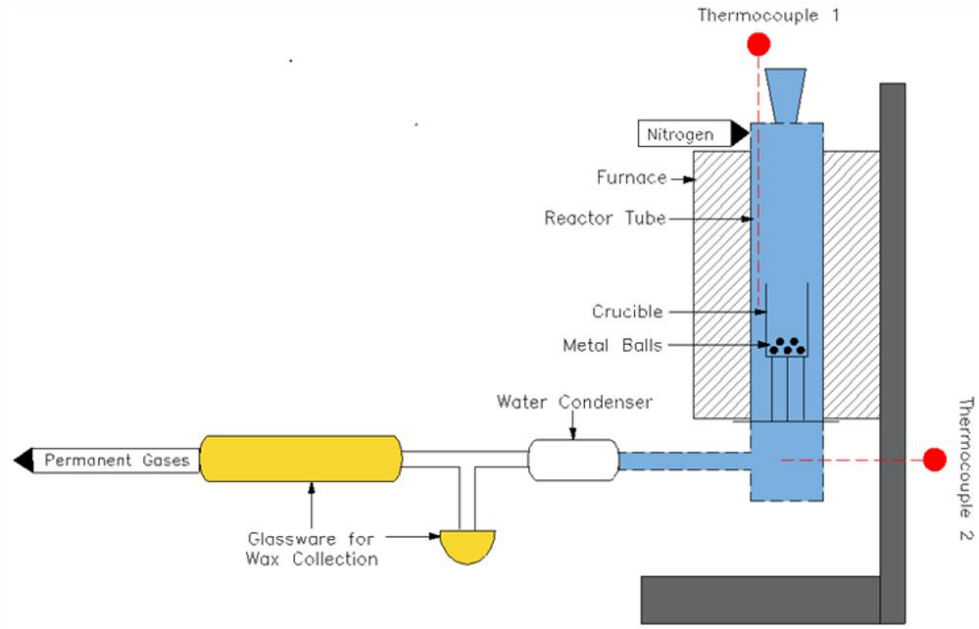

Figure 1. Schematic diagram of the bench scale pyrolysis reactor system used in this study.

2.3. Wax Characterisation

Fourier transform infrared (FTIR) spectroscopy was employed in attenuated total reflectance mode (ATR) for the chemical characterisation of the pyrolysis wax samples. The IR spectra of the waxes obtained were recorded on a PerkinElmer Frontier Spectrometer, with the wavelength range 400-4000 cm^{-1}, 32 scans and a 4 cm^{-1} resolution. This was as well used to demonstrate the repeatability of the waxes between pyrolysis runs.

The wax samples were additionally submitted for gas chromatography-mass spectroscopy (GC-MS) chemical analysis. Prior to submission, the waxes were dissolved in toluene and filtered using PTFE 0.2µm filters. A Shimadzu GC-MS-QP2010 SE model was used for the analysis using a GC program of 50 °C to 300 °C with a heating rate of 10 °C/min (Al-Salem

et al. 2020). The method proposed by Szulejko et al. (2013) to predict gas chromatographic mass response factors (RF) based on the theory of effective carbon numbers (ECN) was used to interpret the experimental data.

Thermogravimetric analysis (TGA) was utilised to examine the thermal characteristics of the pyrolysis wax materials. Additionally, it was applied as an indicator for the thermal stability of the waxes for potential applications such as within asphalt pavements as alternative binder materials at 150-170 °C. A Perkin Elmer Pyris 1 TGA was used to analyse the pyrolysis waxes from 20-600 °C with a heating rate of 10 °C min^{-1} under a constant flow of pure nitrogen (N_2) gas at 30 mL min^{-1}. Differential Scanning Calorimetry (DSC) was carried out to measure the melting point of the pyrolysis waxes, using a Mettler Toledo DSC 1 from 25-200 °C with a heating rate of 5 °C min^{-1}, done in an inert atmosphere using aluminium containers.

2.4 Wax Ageing Experiment

To provide further interpretation of the results obtained from both TGA and DSC analyses, an additional experimental setup was arranged for the thermal conditioning of the waxes in an ashing oven set at 150 °C for 0, 1, 3, and 6 hours. From the mass loss, the total loss of volatiles could be determined. The GC-MS and FTIR techniques mentioned previously were utilised to show the effects of somewhat short-term ageing on the wax chemical composition. This was also utilised as an indicator for the suitability of pyrolysis waxes in asphalt pavement production, in which the bitumen binders are heated for prolonged times during mixing and storage. All ageing experiments were repeated three times.

3. Results and Discussion

3.1. Pyrolysis Yields

Polyolefin pyrolysis consists of a set of free-radical reaction mechanisms, predominantly yielding a broad product spectrum of lower molecular paraffins and α-olefins (C_1 to C_{50}). The plastic degradation mechanism has been previously described to involve three main steps that occur sequentially, being initiation, propagation, and termination (Horvat, 1999; Al-Salem et al. 2017). During the initiation reaction, the polymer chain undergoes a random homlytic scission, initiating the mechanism by producing primary radicals. Moreover, hydrogen

abstraction and β-scission are considered as the propagation steps and are associated particularly with the degradation of PO plastics [39]. Hydrogen abstraction (intermolecular) entails the transfer of hydrogen between the primary radicals and hydrocarbon chains to produce new hydrocarbon products as well as more stable radicals. β-scission involves the scission of paraffin, olefin and diolefin radicals to produce olefin or diolefin products, as well as a new radical. The thermal degradation is completed by a recombination reaction which generates a smaller residual polymer chain (Savage, 2000; Mastral et al. 2007). The radical chain mechanisms can be seen in Figure 2. Typically, waxy materials in the C_{20}-C_{50} range are produced in the primary devolatilization reaction of pyrolysis. These primary products are cracked further in secondary reactions to yield mainly olefinic hydrocarbons. Though, the gaseous products are highly reactive and thus further tertiary reactions take place to form more stable compounds, including aromatics. The process may also yield additional products such as hydrogen, methane and coke when the product stream undergoes a long resisence time (Aguado et al. 2002; Al-Salem and Dutta, 2021).

INITIATION: $\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\sim \rightarrow \sim CH_2\text{-}CH_2\text{-}\dot{C}H_2 + \dot{C}H_2\text{-}CH_2\text{-}CH_2\sim$

PROPAGATION: $CH_3\text{-}(CH_2)_n\text{-}CH_2\text{-}\dot{C}H_2 + \sim CH_2\text{-}CH_2\text{-}CH_2\sim \rightarrow CH_3\text{-}(CH_2)_n\text{-}CH_2\text{-}CH_3 + \sim CH_2\text{-}\dot{C}H\text{-}CH_2\sim$

(Hydrogen abstraction, alkane production)

$\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\dot{C}H_2 \rightarrow \sim CH_2\text{-}CH_2\text{-}\dot{C}H_2 + CH_2{=}CH_2$

(β-scission of the primary radical)

$\sim CH_2\text{-}CH_2\text{-}\dot{C}H\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow \sim\dot{C}H_2 + CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

(β-scission, alkene production)

TERMINATION: $\sim\dot{C}H_2 + \sim\dot{C}H_2 \rightarrow \sim CH_2\text{-}CH_2\sim$

(Recombination)

Figure 2. Radical mechanism of the thermal degradation of polyethylene, taken from (Bockhorn et al. 1999; Horvat, 1999).

In this study, the two controllable variables were the pyrolysis temperature and carrier gas flowrate. Figure 3 shows the wax yield with respect to the process conditions described in *Section 2.2*. The yield of wax obtained for HDPE pyrolysis is higher than that reported by Al-Salem and Dutta, (2021). in a fixed-bed reactor at 500 °C, which was 32 wt%. Nevertheless, Arabiourrutia et al. (2012) saw a similar yield in a conical spouted bed reactor at 450 °C of 80 wt%. A prominent trend reported in literature is the favouring of secondary cracking reactions at high operating temperatures, which generates more gaseous products and in turn reduces the formation of wax products (Williams and Williams, 1999a; Aguado et al. 2002; Arabiourrutia et al. 2012; Al-Salem et al. 2017). This is due to the increased concentration of short radicals from favouring the vaporisation of long chains and as a consequence increasing the rate of this process. In this study, the trend in wax yield with increasing pyrolysis temperature differs to this, such that the wax yield increases with temperature from 75.73-79.46 wt% at 450 °C to 86.53-87.86 wt% at 550 °C. The wax yield is only seen to decrease with temperature from 91.87 wt% at 500 ° to 86.53 wt% at 550 °C at the higher carrier gas flowrate of 4 L min^{-1}. For HDPE, an initial increase in wax yield at increasing low-moderate operating temperatures (500-600 °C), followed by a yield decrease at higher temperatures (600+ °C) was also reported by Al-Salem and Dutta, (2021). This result can be explained as a consequence of the low branched structure of HDPE. For polyolefins with a higher degree of branching (polypropylene), at lower temperatures (450-500 °C), cracking initially takes place in branched chains. At the short residence times achieved by reactor configurations designed for optimised wax production, the cracking of principal chains is low. At temepratures of 450-500 °C, the cracking of HDPE feedstock to gases is favoured, which may later be condensed to pyrolysis oils. Furthermore, it was reported that commingled plastic solid waste (PSW) consisting of mildly branched feedstock (such as HDPE) with 10 wt% of the higher branched PP yielded no wax at 500 °C and produced low yields at 600 and 800 °C (Al-Salem and Dutta, 2021). It was attributed to the mildly branched, more crystalline feedstock requiring higher temperatures and residence times (Aguado et al. 2002; Al-Salem and Dutta, 2021). This was consistent with their lower wax yield from HDPE pyrolysis at 500°C and agrees with this work at 450-500 °C. Another explanation is that a lower residence time as a result of increasing the temperature in the reactor reduces cracking of the feedstock, therefore higher molecular chain hydrocarbons are obtained (Adrados et al. 2012). One governing factor in the pyrolysis of PO polymers is the residence time of the feedstock material in the reactor; longer residence times increases the cracking of primary products to more thermally stable products, favouring the production of oils (Mastral et al. 2003). Moreover, Park et al.

(2002) reported the non-isothermal pyrolysis of low-density polyethylene (LDPE) at 440 °C in a semi-batch reactor, noting that the retention time increased in the low temperature region and a subsequent increase in ratio of lower molecular weight products.

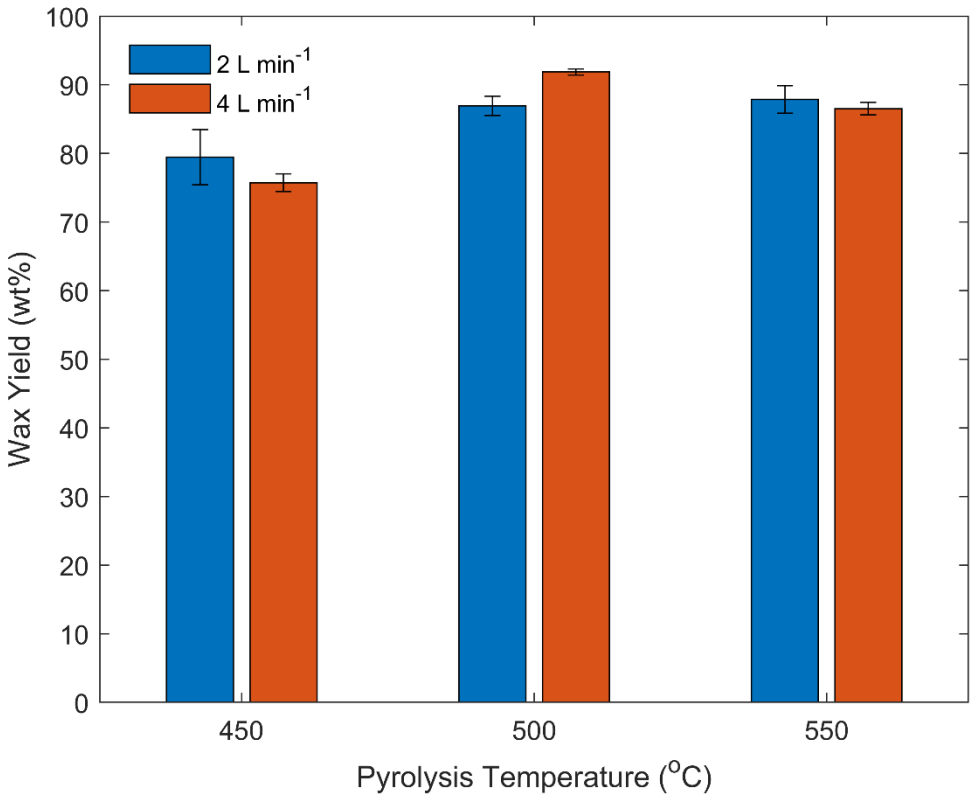

Figure 3. Yields (wt%) of wax with respect to the reactor operating conditions.

In terms of the effect of the carrier gas flow rate and subsequent vapour residence times calculated at each temperature, a faster nitrogen flowrate decreased the yield of wax at 450 °C, which could be attributed to a cooling effect, as the nitrogen was not preheated prior to entering the reactor system and it has been established that due to the structure of HDPE, it may require more elevated temperatures for higher wax yields. The only increase in wax yield with an increase carrier gas rate is at 500 °C, whereas the yields are somewhat similar at each flowrate at 550 °C. It can be comprehended that the effect of the operating temperature and its subsequent vapour residence time had a lager effect on the resultant wax yields. The predominant influence of reactor temperature on the resultant spectrum of pyrolysis products, more so than other process parameters, has been reported by other authors. This is due to the temperature being the key parameter in controlling the cracking mechanisms of the polymer chains (Westerhout et al. 1998; Kumar and Singh, 2011).

3.2. Wax Chemical Characterisation

Infrared spectra of the waxes obtained at the pyrolysis parameters studied are shown in Figure 4. The spectra are analogous to each other and it is noted that they are also comparable to those obtained by (Chaala et al. 1997). for commercial paraffinic wax as well as pyrolysis wax obtained from the vacuum pyrolysis of polyethyelene based electric cables. There are two bands corresponsing to the stretching of $-CH_2-$ groups at 2920 and 2850 cm^{-1}, as well as a doublet seen at 725 cm^{-1} which relates to the skeletal vibrations of these C-H groups. Two shoulders are observed at 2960 and 2900 cm^{-1} which correspond to $-CH_3$ terminal bond groups. Aguado et al. (2002) noted that these are much weaker for pyrolytic waxes than for commercial waxes, inferring that the alkyl chains of waxes obtained from pyrolysis are less branched than those produced commercially. Deformation vibrations of these C-H alkyl groups are additionally observed by the bands at 1465 and 1380 cm^{-1}. When comparing the spectra of this study with those produced by (Chaala et al. 1997). for commercial waxes, it is noticed that the waxes obtained from plastic pyrolysis are more unsaturated, the generation of -C=C- olefinic groups explained by the occurrence of radiacal degradation mechanisms such as β-scission. The bands located at 3040, 1645 and in the 890-995 cm^{-1} range correspond to C-H deformation vibrations of olefinic bonds, stretching of conjugated alkene groups and $R-CH=CH_2$, trans -CH=CH- and $R_1R_2C=CH_2$ groups, repsectively (Aguado et al. 2002).

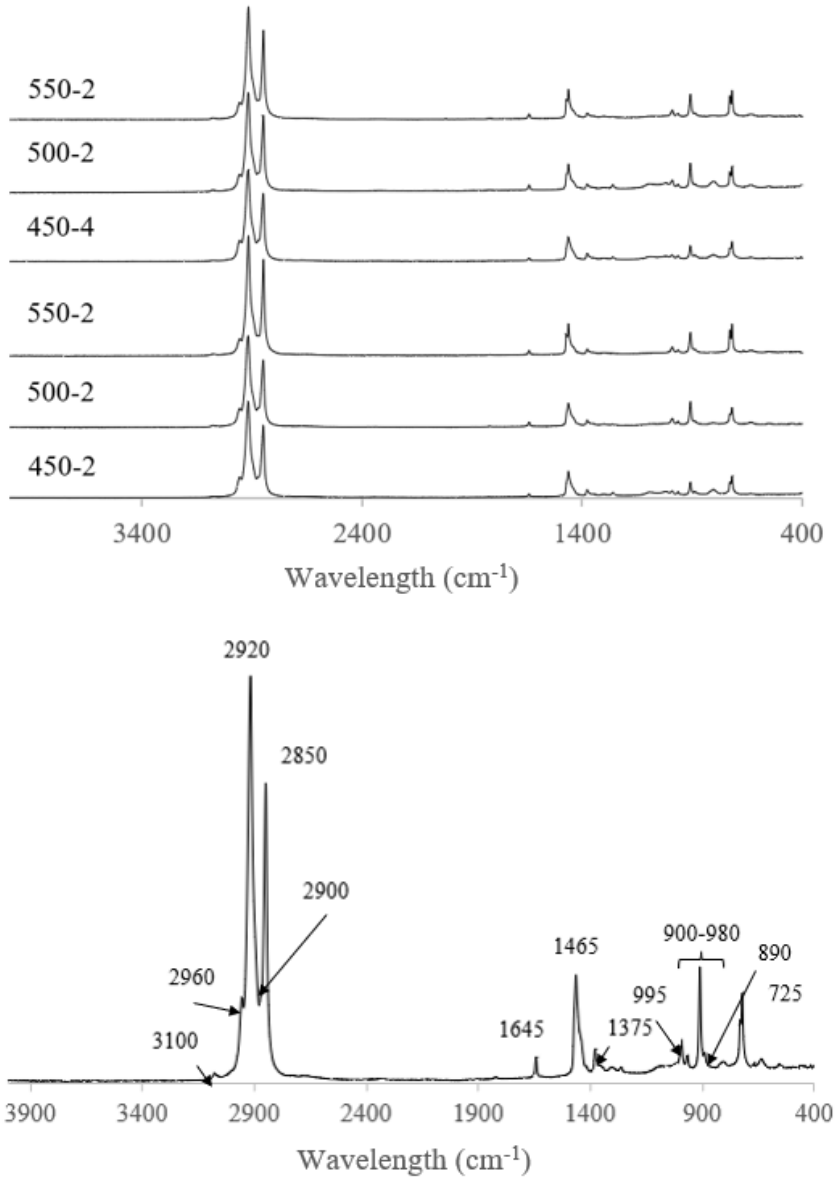

Figure 4. FTIR Spectra for HDPE Pyrolysis Waxes.

The GC-MS chromatograms produced for the pyrolysis waxes are appended in Figure S1 (a-g) and show homologous series of triplets that are typical of HDPE depolymerisation. (Lund et al. 2008). Within the spectrum, each triplet is comprised of an α,ω-diene, olefin and paraffin for each carbon number (Al-Salem et al. 2020). In addition, trace amounts of branched and cyclic hydrocarbons between the triplets as well as noticeable peaks for aromatic components, such as benzene and xylene, can be seen at the lower retention times within the spectrum. The mass response factors and thus percentiles were calculated for each component and the peak areas were integrated and totalled for representative categories: gasoline range ($<C_{12}$) and high molecular weight (MW) hydrocarbon ($C_{13}<$) components, as

well as the class of hydrocarbons (aromatic, paraffinic, olefinic and diene) present in each sample, as shown in Table 2.

Table 2: Distribution of hydrocarbons in each pyrolysis wax sample and percentile distribution in gasoline and high MW categories, as well as class of components.

	450-2	500-2	550-2	450-4	500-4	550-4
Gasoline Range ($<C_{12}$)	25.87	25.76	26.37	22.92	29.93	30.18
High MW ($C_{13}>$)	74.13	74.24	73.63	77.08	70.07	69.82
Aromatic	3.38	3.48	2.91	2.45	1.83	2.38
Paraffinic	57.53	39.57	36.70	61.83	38.11	35.53
Olefinic	36.03	49.65	51.38	35.72	54.53	54.79
Diene	3.06	7.29	9.00	0.00	5.53	7.30

The wax samples were extremely viscous (semi-solid) at room temperature, and the majority of each sample eluted in the higher molecular weight carbon range ($C_{13}>$). It is observed that heavy hydrocarbons did not elute with a considerable differentiation from the baseline due to the GC-MS program utilised, as also observed by Al-Salem et al. (2020). This should be considered when the heavy components are analysed. However, this program is still considered as suitable as it meets the criteria previously outlined by Lund et al. (2008) for the analysis of plastic depolymerisation. Kumar and Singh, (2013) reported the characteristivs of heavy hydrocarbon thermal degradation to include poor gasoline selectivity, with a wide distribution of light molecular weight products. The results and chromatograms show that this work is in agreement mainly due to the reactor system operating under thermal (non-catalytic) pyrolysis conditions, therefore fuel production is not favoured. Furthermore, it can be seen that the operating temperature has the most significant effect on the cracking and wax product composition, rather than the effect of the carrier gas flow rate on volatile residence times in the reactor system.

It is generally established that increasing the pyrolysis temperature results in a reduction of residence time, lowering the cracking reaction rates and thus a generating higher molecular weight compounds (oils and waxes (Adrados et al. 2012)). Noticeably in this work, with the increase in pyrolysis temperature, the percentage of gasoline range hydrocarbons is seen to rise. Specifically, the increased generation of C6-C8 aliphatic compounds is noted, such as 1-hexene, 1-heptene and 1-octene. Similar observations have been made; Hernández et al. (2007) conducted thermal pyrolysis of HDPE in a fluidised bed reactor. Yields of these compounds (especially *n*-hexane) were reported to have increased due to the extension of

secondary propagation reactions of intermediate compounds, facilitated by high operating temperatures and low resisence times.

Al-Salem, (2019) saw an initial increase in high molecular weight compounds in the product oil with increasing operating temperature (500-600 °C), for the thermal cracking of HDPE in a fixed bed reactor. However, the authors also saw an increase in gasoline range compounds with the further elevation of bed temperatures (600 °C+) as a consequence of further cracking reactions. In this work, the pyrolysis temperature is seen to have a dominating impact in promoting secondary cracking reactions to generate smaller compounds (C_6-C_8) within the gasoline range, that are too promoted (to an extent) at higher temperatures with lower residence times, thus reducing the mass% of C_{13}< wax compounds somewhat. Williams and Williams, (1999b) summarised their analysis of the oil and wax products from the thermal pyrolysis of mixed plastic waste, solely confirming aliphatic products comprising of paraffins, olefins and diolefins. The latter possibly a result of propagation intramolecular hydrogen transference and β-scission mechanisms (as described in Figure 2). Ghasr and Abedini, (2017) produced a mechanistic model to predict the product distribution of HDPE pyrolysis in a conical spouted-bed reactor, based on the radical mechanisms previously discussed. The results showed that the fastest reaction and controlling propagation stage in cracking is β-scission for the production of olefins and dienes. The importance of other stages was also emphasised, such as hydrogen abstraction in the role of paraffin and diene production. The main product was olefin, while the amount of diene production increased significantly with increasing temperature. Other authors have reported similar for the thermal pyrolysis of HDPE (Mastral et al. 2007; Kumar and Singh, 2013). This work is mainly in agreement with the findings of the mechanistic model, with the exception of paraffinic compounds being the main product at the lower pyrolysis temperature of 450 °C, which generated trace-small amounts of diene compounds.

Aromatics such as benzene belong to a group of compounds which yield increases by increasing the residence time and temperature (Hernández et al. 2007). Jung et al. (2010) suggested that the Diels-Alder reaction mechanism followed by dehydrogenation may result in aromatic production from the catalytic pyrolysis of polypropylene/polyethylene. Generally, raising the pyrolysis temperature increases the formation of aromatic hydrocarbons as it promotes the rapid release of radicals which undergo intramolecular exchanges to produce cyclic compounds (Seeger and Barrall, 1975; Al-Salem, 2019). Additionally, high residence times and temperatures favour secondary reactions that produce highly reactive gaseous

products, allowing for tertiary reactions to form more stable aromatics compounds. In this study, small amounts of benzene, ethyl benzene and xylene were seen in the lower region of the chromatograms. The amount of aromatics in the wax samples varies between 1.83-3.48%, the carrier gas flowrate does not largely affect the yield of cyclic compounds present, however, it is observed that the aromatic yield is higher for the reactions with a 2 L/min carrier gas flowrate, corresponding to slightly higher residence times. Overall, a slight decrease in aromatics can be seen as the temperature parameter is increased, suggesting that the effect of temperature on volatile residence times within the reactor has a larger influence on aromatic production in this reactor system.

3.2 Wax Thermal Characterisation

Representative TGA and DTG thermograms for each pyrolysis wax thermal degradation as a function of pyrolysis conditions (temperature, carrier gas flowrate) are presented in Figure 5. HDPE typically shows a two-stage decomposition process; the initial degradation starts at a lower temperature and propagates gradually until the second degradation stage is reached in which a sharp degradation is observed (Miandad et al. 2019). The pyrolysis of HDPE significantly shortens the initial stage of thermal decomposition in the wax products and the rapid weight loss of hydrocarbons now happens over a wider temperature range, as the pyrolysis has yielded a broad spectrum of small molecular weight hydrocarbons. The maximum degradation of PE is typically achieved within 420-490 °C, whereas this can be seen to happen between 90-460 °C for the pyrolysis waxes. As the temperature was increased for the pyrolysis, an increase in thermal stability, or a decrease in volatility, of the pyrolysis waxes was observed. This infers that heavier hydrocarbon chains are generated and distilled during the chain scission mechanism at higher pyrolysis temperatures. The effect of carrier gas flowrate on vapour residence time is also seen to influence the thermal properties of the waxes, with the waxes produced using a faster nitrogen flowrate having a slightly higher thermal stability, for the same reason as the higher temperature conditions. These results for thermal stability of the waxes indicate their potential suitability in asphalt pavement applications such as alternative binder materials, as these are incorporated into bitumen at temperatures of 150-170 °C.

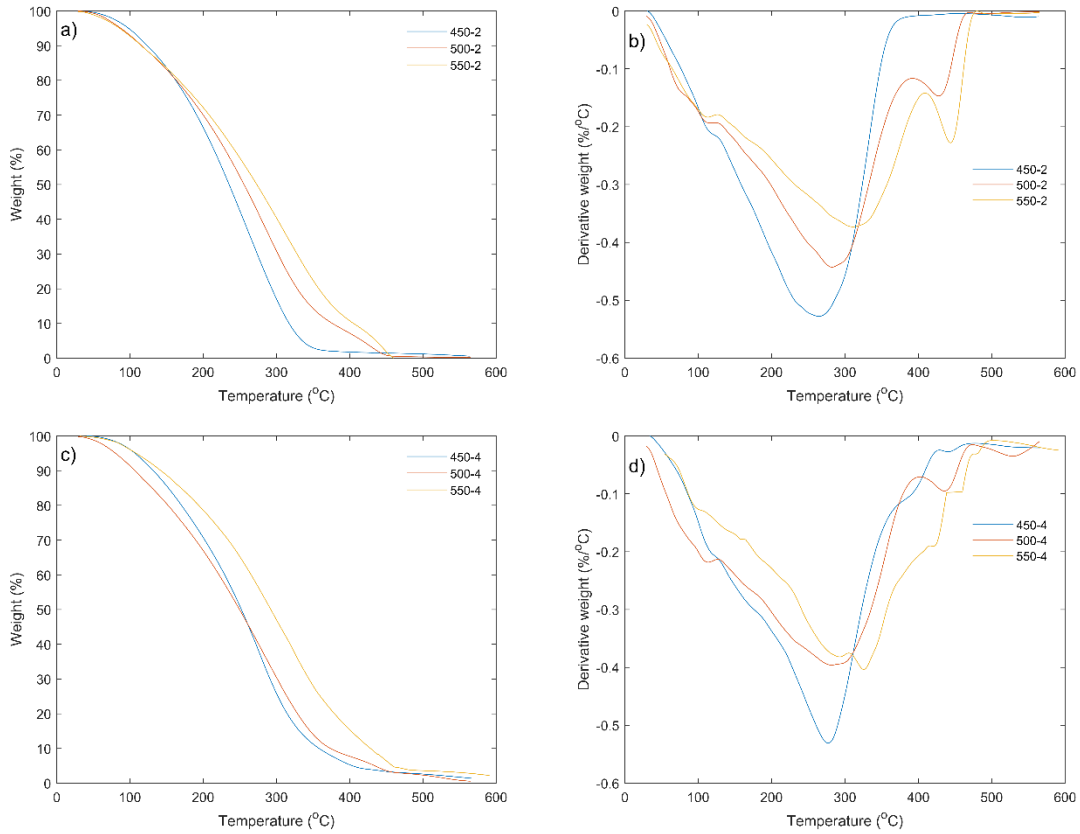

Figure 5. Representative TGA and DTG thermograms for the pyrolysis waxes as a function of pyrolysis conditions (temperature, carrier gas flow rate.)

Waxes are mixtures of different size and nature molecules and therefore do not have a defined characteristic melting point that pure substances have (Dwivedi, 2017). Therefore, when investigating the melting points of the pyrolysis waxes with DSC, a temperature from which the samples start to melt (onset temperature) and a highest peak indicating the point at which the samples have melted completely were recorded. The onset and peak melting temperatures are recorded in Table 3, taken from the endothermic peak identified for the melting of the wax on the DSC thermograms. The melting point values obtained for the HDPE pyrolysis waxes can be compared to commercial paraffin (50-70 °C), microcrystalline (60-91 °C), barnsdall (70-74 °C) and beeswax (63-70 °C) waxes, as observed by Arabiourrutia et al. (2012) when characterising waxes produced from the pyrolysis of polyolefins in a conical spouted bed reactor. The same trend in influence of the pyrolysis parameters is seen in these results as those for the TGA analysis. The pyrolysis temperature is seen to have a more definitive impact on the thermal properties of the waxes (as with chemical characterisation.) With increasing process temperature, higher peak melting points can be observed. Additionally, the waxes produced using a higher carrier gas flowrate and thus lower vapour residence time, also have slightly higher melting points than those

produced with the lower nitrogen flowrate. In Section 3.2 it was discussed that the rise of process temperature results in an increase gasoline range ($<C_{13}$) compounds, therefore, containing more lower melting point compounds. The higher melting points seen in the waxes produced at the higher pyrolysis temperatures (500 and 550 °C) may be explained in Section 3.3, in which further GC-MS and FTIR analysis of the waxes at different stages of thermal (and oxidative) ageing are investigated. The waxes produced at higher temperatures are more olefinic in nature, containing more unsaturated compounds as a result of the influence of process temperature on the radical mechanisms involved in pyrolysis. Not only do alkenes have slightly higher melting points than alkanes due to stronger intermolecular forces, but they are also more prone to oxidation reactions, as indicated by the number of compounds containing hydroxyl and carbonyl functional groups in Table 4, even at the unconditioned stage. The hydroxyl and carbonyl groups present within alcohol molecules require a greater energy to overcome the stronger intermolecular forces of hydrogen bonding, therefore the melting point of alcohols is higher than that of alkanes with the same chain length (Purohit and Pradhan, 2013). Additionally, when further exposed to elevated temperatures in analysis, the more unsaturated waxes may take part in polymerization reactions to form heavier molecules.

Table 3: Onset and peak melting points of the pyrolysis waxes using DSC.

Sample	Onset (°C)	Peak (°C)
450-2	46.84	49.26
500-2	85.25	88.92
550-2	71.22	78.25
450-4	48.02	49.75
500-4	82.21	86.42
550-4	74.18	87.67

3.3 Thermal Ageing of Waxes

In this study, it has been established that the pyrolysis operating temperature is the dominant parameter that influences the chemical and thermal properties of the wax products in the thermal pyrolysis of HDPE. To further support the thermal characterisation results within this section and to assess the suitability of the waxes for applications that may involve their incorporation at temperatures above their melting points, such as in asphalt road construction, three of the waxes (450-2, 500-2 and 550-2) were selected for thermal conditioning/ageing and analysis. A further detailed analysis of GC-MS chromatograms was conducted at each

stage of the thermal conditioning, including further representative categories for the different molecular weight components within the waxes; diesel (C_4-C_9), gasoline (C_{10}-C_{19}) and wax (C_{20+}) fractions, as seen in Table 4. A focus on compounds that are present in trace-small amounts and therefore overlooked in the initial analysis by the peak width integration and identification are also examined to identify possible oxidation products. FTIR analysis was additionally utilised to examine the change in functional groups present at each stage.

Table 4: Distribution in weight percentage of molecular weight and class of hydrocarbons in pyrolysis waxes (450-2, 500-2 and 550-2) after thermal conditioning at 170 °C from 0-6 hours.

	450-2				500-2				550-2			
Ageing time (hour)	0	1	3	6	0	1	3	6	0	1	3	6
Diesel (C_4-C_9)	7.19	3.41	6.30	6.19	7.87	3.54	7.56	10.96	10.42	3.18	7.99	15.57
Gasoline (C_{10}-C_{19})	62.0	44.89	20.31	1.76	56.89	37.11	10.46	1.15	54.38	31.92	10.54	0
Wax (C_{20+})	30.81	51.70	73.39	92.04	35.24	59.36	81.98	87.89	35.20	64.90	80.92	84.43
Paraffinic	55.76	59.60	58.95	72.46	34.65	41.35	46.29	61.69	35.89	37.84	42.04	49.49
Olefinic	35.92	31.34	29.35	17.41	48.31	45.73	38.90	23.01	50.24	47.12	40.83	28.68
Diene	2.96	2.64	1.55	0.25	7.09	6.79	4.27	0	8.80	8.68	5.96	0
Aromatics	3.27	3.57	6.30	6.19	3.39	3.78	8.71	12.86	2.85	3.18	7.99	18.48
Alcohols	2.08	2.30	3.09	2.61	2.52	2.08	1.59	2.45	2.10	2.43	2.83	2.46
Carbonyls	0	1.39	0.75	1.07	0.16	0.27	0.24	0	0.13	0.74	0.36	0.89

Due to the wax fractions being cooled swiftly from hot vapors to a low temperature (5 °C) after leaving the pyrolysis reactor vessel, they contain lightweight components (<C_{10}) that have boiling points lower than the chosen condition temperature of 170 °C. Significant mass losses from 15.96-21.61% at 1 hour to 28.2-41.49% at 6 hours were observed (Figure 6) as a result of the loss of volatiles. A high mass loss indicates high emissions and therefore detailed information on the low molecular weight hydrocarbons should be evaluated with respect to influence on the environment and exposure. If the effects are substantial, further efforts to reduce this should be considered for potential applications. At all time periods, the mass loss surpasses the initial percentage of compounds with a boiling point below 170 °C, indicating thermal decomposition taking place of the decreasing gasoline range (C_{10}-C_{19}) to lower molecular weight components (C_4-C_9), which are emitted by the samples. In all waxes, an initial significant decrease in diesel (C_4-C_9) fractions is observed within the first hour as the low boiling point components are emitted and lost from the samples. The fractional category is then seen characteristically to increase, assumed to be a result of the gasoline (C_{10}-C_{19}) fractions beginning to thermally decompose upon extended thermal exposure. The diesel

fractions again begin to incrementally decrease at 6 hours as the produced lower molecular weight products of thermal decomposition begin to be emitted and lost from the samples.

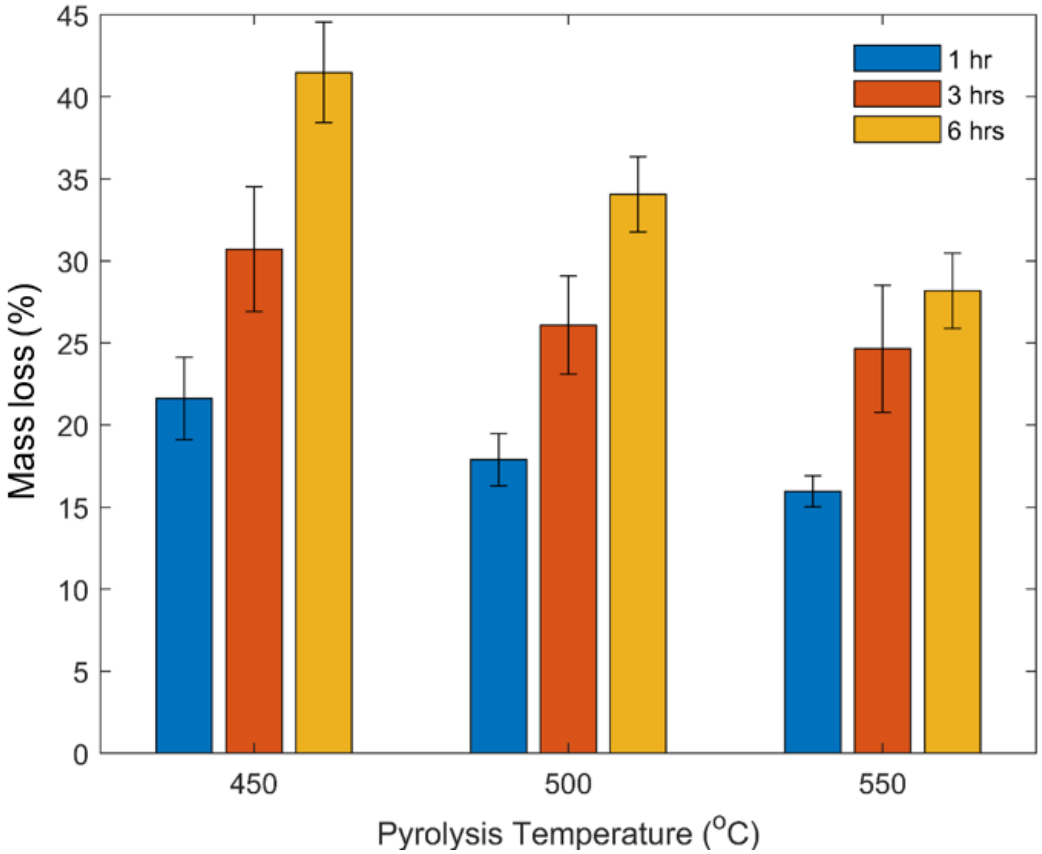

Figure 6. Mass loss of pyrolysis waxes with thermal conditioning.

The heavier wax fraction (C_{20+}) is seen to significantly increase, obviously due to the mass % decrease of the diesel and gasoline fractions. However, the increase in wax components is larger than the overall reductions in the other fractional categories and the total mass loss in the wax samples at the end of the thermal conditioning. Thermal hydrocarbon chemistry involves the degradation of large molecules into smaller ones, but it can also involve the production of heavier molecules (Savage, 2000). The thermal polymerisation of alkenes within the wax may be a contributing reaction to the substantial increase in heavier molecular weight fractions. A reaction such as this can be evident by the sizable drop in percentage of unsaturated (alkene and diene) compounds present in the waxes from the non-conditioned state to 6 hours of thermal conditioning, and the subsequent increase in mass percentage of larger paraffinic hydrocarbons. The peaks in the GC-MS chromatograms were seen to shift to the right, as seen in S3 (a-j.) Additionally, the bands corresponding to olefinic bonds in the FTIR spectra (890, 900-980, 995, 1645 and 3040 cm^{-1}) are all seen to decrease or disappear entirely from the spectra throughout the stages of thermal exposure. In the case of not all

unsaturated bonds being located at the terminal position of the hydrocarbon chains, this could contribute to the reduction in the two bands at 2960 and 2900 cm^{-1} that correspond to $-CH_3$ terminal groups. The C-H bond stretching of $-CH_2-$ groups at 725, 2850 and 2920 cm^{-1} are seen to be slightly more elongated in shape but are not significantly changed.

In the case of self-initiated polymerization, the initiating radicals and mechanisms by which they are formed can be unclear. However, it is noted that the primary and secondary products of paraffin and alkene oxidation, as will be discussed, include hydroperoxides and acids. Hydroperoxide groups are largely used as initiators in radical polymerization reactions with alkenes as these functional groups can break easily, generating free radicals. Acidic reagents are also typically used in cationic polymerization by donating a proton to an alkene to yield long-chain carbocations (Moldoveanu, 2019; Liu, 2021). In the unconditioned waxes, small amounts (2.08-2.52 %) of primary alcohols were detected. This may be attributed to oxidation processes during the cooling of the waxes within the glassware in the instance of oxygen entering the system and upon wax storage prior to analysis. It can be observed in Table 5 that when subjected to heat in oxygen for prolonged times, the number of primary alcohols (C_{10}<) as well as diols are increased, which is supported by the FTIR spectra in S2 (a-i.) With increased time of thermal conditioning, the band at 1076 cm^{-1} for primary alcohols significantly increases, while the bands at 2960 and 2900 cm^{-1} for $-CH_3$ terminal bond groups are decreased. Some cycloalkanes with alcohol substituents such as methanol were also identified, such as Cyclododecanemethanol ($C_{13}H_{26}O$.) Additionally, trace amounts of compounds containing carbonyl functional groups were detected, increasing with conditioning time from the initial unconditioned waxes and including larger chain esters and acids especially. Products such as this are common in the thermal oxidation of paraffin wax conducted at 110-140 °C, however, typically with an appropriate catalyst present. This is reported to lead predominantly to the formation of alcohol isomers with the same number of carbon atoms as the initial hydrocarbon moleculs, as well as other secondary products including acids, esters, and ketones (Purohit and Pradhan, 2013). The oxidation products identified may also be a result of the oxidation of alkene molecules within the pyrolysis waxes. Alkenes are more susceptible to reactions with oxygen, with the addition of O_2 molecules most commonly occurring to the carbon atom adjacent to the double bond (Liu, 2021). This produces unstable hydroperoxide molecules that decompose to form two aldehyde or carboxylic acid groups (Liu 2021). This can be observed in the FTIR spectra as the reduced CH_3 band, as previously discussed, and the growing band at 1650-1800 cm^{-1} with

conditioning time that corresponds to conjugated and aliphatic aldehydes, carboxylic acids, esters, and ketones.

4. Potential of Pyrolysis Wax in Bitumen Modification

Asphalt pavement is the most common paving material for highways and urban roads, being a complex mixture comprising of aggregates, filler, bitumen binder, and air voids. Conventional bitumen binders are a by-product of the petroleum refining process with petroleum being a finite and highly impacting resource. A main effort within pavement engineering currently is to move towards “greener” alternatives, aiming to align with sustainable development and circular economy goals (Su et al. 2018; Gaudenzi et al. 2021). Pyrolysis has commonly been used by authors in literature to thermochemically treat waste materials such as biomasses, cooking oils and crumb rubber and study their derived products for the partial replacement and modification of hot mix asphalt (HMA) binders (Kolokolova, 2013; Dong et al. 2019). As discussed in previous work by the authors, through concepts such as Design from Recycling, pyrolysis could also be readily applied in the upgrading of waste plastics for such applications (Abdy et al. 2022). Furthermore, the addition of waxes as viscosity and workability improvers in asphalt binders has caught recent interest, with the aim to reduce mixing and compaction temperatures, thus reducing energy consumption, cost, and emission intensity (Edwards, 2008). PE waxes have especially been observed to offer higher softening points, improved chemcial stability, distribution, fluidity and water resistance (Prajapati et al. 2021). Authors have noted in particular that the addition of thermally degraded PO polymers such as polypropylene and low-density polyethylene results in an enhanced resistance to permanent deformation, as well as an increase in binder stiffness, temperature resistance, Marshall stability and stripping resistance (Al-Hadidy and Tan, 2009a, 2009c). Further exploration into this area of research that can provide detailed and optimisable pyrolysis processes and in-depth product characterisation for this applciation is still needed.

5. Conclusions

The findings in this paper show that the fixed-bed reactor vessel produced for this study was efficient for the thermal pyrolysis of HDPE at moderate temperatures (450-550 °C), which allowed for obtaining (in batch mode) a yield of up to 91.87% wax at 500 °C. The waxes

produced at higher temperatures were mainly olefinic, due to higher temperatures promoting certain thermal degradation radical mechanisms, such as β-scission. The melting points of the waxes were within the range of 49-89 °C, corresponding to commercial waxes that are typically used as flow improvers and performance enhancers in hot-mix asphalt, or as low temperature additives in warm-mix asphalt.

Relationships between the proccess operating parameters and resultant waxes were established, with a novel focus on the thermal properties and ageing performance of the waxes, especially with regards to volatile loss and ageing mechanisms that occur. The more olefinic waxes produced at higher temperatures and higher nitrogen flowrates (having the lowest vapour residence times) saw the lowest volatile mass loss. They were observed to be more prone to oxidation and polymerization reactions, the products from each supporting the higher melting point and thermal stability of these waxes. The lowest loss in volatiles was seen for the wax produced at 550 °C, inferring that it would be the optimal wax to blend with asphalt binders. For HMA modification purposes, blending at temperatures lower than 170 °C should be considered to lessen the volatile loss with initial blending and storage of the wax modified binders. In the case of significant volatile loss, further efforts to reduce this should be considered for potential applications. The relationship between pyrolysis parameters, resultant wax properties and their subsequent performance and compatibility as binder modifiers in hot-mix asphalt is not yet fully realised and will be investigated in following papers.

6. Supplementary Materials

Figure S1: GC-MS chromatograms for (a) 450-2 (450 °C, 2 L/min N_2 flowrate) wax, (b) 500-2 (500 °C, 2 L/min N_2 flowrate) wax, (c) 550-2 (550 °C, 2 L/min N_2 flowrate) wax, (d) chromatogram depicting homologous series of triplets which is indicative of PE depolymerisation, (e) 450-4 (450 °C, 4 L/min N_2 flowrate) wax, (f) 500-4 (500 °C, 4 L/min N_2 flowrate) wax, (g) 550-4 (550 °C, 4 L/min N_2 flowrate) wax. **Figure S2**: FTIR spectrum for (a) 450-2 wax, 1 hour @ 170°C, (b) 500-2 wax, 1 hour @ 170 °C, (c) 550-2 wax, 1 hour @ 170 °C, (d) 450-2 wax, 3 hours @ 170 °C, (e) 500-2 wax, 3 hours @ 170 °C, (f) 550-2 wax, 3 hours @ 170 °C, (g) 450-2 wax, 6 hours @ 170 °C, (h) 500-2 wax, 6 hours @ 170 °C, (i) 550-2 wax, 6 hours @ 170 °C. **Figure S3:** GC-MS chromatograms for (a) 450-2 wax, 1 hour @ 170 °C, (b) 500-2 wax, 1 hour @ 170 °C, (c) 550-2 wax, 1 hour @ 170 °C, (d)

Chromatogram depicting the alcohol and carbonyl containing compounds between triplets as a result of oxidation reactions, (e) 450-2 wax, 3 hours @ 170 °C, (f) 500-2 wax, 3 hours @ 170 °C, (g) 550-2 wax, 3 hours @ 170 °C, (h) 450-2 wax, 6 hours @ 170 °C, (i) 500-2 wax, 6 hours @ 170 °C, (j) 550-2 wax, 6 hours @ 170 °C.

7. Acknowledgements

The authors would like to acknowledge the financial support of a PhD studentship provided by Aggregate Industries UK Ltd. and Aston University. The author Jiawei Wang would also like to acknowledge the support from Guangdong Science and Technology Program, No. 2021A0505030008.

8. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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