



# Comparative study between coal tar pitch and lower polycyclic aromatic hydrocarbon (PAH) alternative binders for use in taphole clays

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## ABSTRACT

The use of alternative low polycyclic aromatic hydrocarbon (PAH) binders in taphole clays is essential due to health and environmental concerns associated with PAHs. Binders that could potentially substitute for highly-temperature coal tar pitch (CTPht) or coal tar (CTht) in taphole clays were investigated. These include coal tar pitch blend, low PAH coal tar pitch, petroleum-based binders and wood-based tars from various sources. The binders were characterized according to chemical composition, with an emphasis on the identification of 16-EPA-PAH (well-known carcinogens), as well as rheology and volatilization behaviour. The alternative binders were ranked according to the analytical results, with the coal tar reference binder, CTht, serving as the benchmark. Beechwood tar (Tar-BW) and crude waxy oil (CWO) showed the most favourable results for replacing CTht in taphole clay. Both have higher viscosities than CTht, lower BE-values (indicating lower toxicity), and higher degrees of mass loss over a wider temperature range.

## 1. Introduction

The use of high-temperature coal tar pitch (CTPht), or high-coking-value tar (HCVT), has been used as a binder in taphole clays for over 50 years. The binder is used either in conjunction with a temperature-curing resin, i.e., phenolic resole resin, or on its own [1–3]. The introduction of phenolic resin to the binder system started when strict casting times, drilling times, and holding times were required during furnace operations. These resins cure through heating at temperatures above the gelation temperature range (160–165 °C) until curing is complete (<200 °C) [4]. The curing occurs through a process called cross-linking between monomer and oligomer chains that results in an increase in molecular weight, which is facilitated by a cross-linking agent, typically hexamethylenetetramine (HMTA) [5]. The carbonaceous binder used in taphole clay is a viscoelastic liquid that ensures proper mixing of the taphole clay at low temperatures (<50 °C) during manufacturing (liquid viscous response) and allows for good plastic behaviour during use and aging of the clay (solid elastic response). The benefits of using CTPht or HCVT as binders for taphole clay are that a thermoplastic clay with high plasticity and improved strength is produced after heating the clay, a transition-free sinter is formed between the old clay in the taphole and the freshly rammed clay, and lastly, the plasticity of the clay adequately ages below 60 °C [1,6,7].

One of the major disadvantages of using CTPht or HCVT as binders in taphole clays is their toxicity due to the presence of carcinogenic compounds, including the 16-EPA-PAHs, that form part of the molecular composition of the pitch or tar [8]. The 16-EPA-PAHs are polycyclic aromatic hydrocarbons (PAH) that are most frequently found in environmental monitoring samples, as identified by the US environmental protection agency (EPA) [9]. The policies regarding exposure to PAH species support the global drive to lower or eliminate human exposure. In the USA, the aim during operating times with high levels of exposure is to eliminate all human exposure to volatile matter. If circumstances do not allow for complete elimination, the permissible exposure limit (PEL) in air during an 8-h period of 16-EPA-PAH is 0.2 mg/m<sup>3</sup> and for benzo(a) pyrene (BaP) it is 0.2 µg/m<sup>3</sup> [10]. In European countries, the Dangerous Substance Directive (DSD) legally classifies only eight PAH species as carcinogens (EU-PAH), most of which are included in the 16-EPA-PAH, except for benzo[e]pyrene (BeP) and benzo[j]fluoranthene (BjF) [11]. The toxicity classification of PAH-containing binders in Europe is based on the BaP content, although this classification does not include the other seven carcinogenic PAH-species. The exposure limits differ between countries. For example, during an 8-h exposure period, the exposure limit for BaP can be as low as 0.002 mg/m<sup>3</sup> in Poland or as high as 0.2 mg/m<sup>3</sup> in Denmark and Romania [12]. The general short-term (15 min) exposure limit for BaP is a maximum of 0.4 mg/m<sup>3</sup> [12].

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Therefore, for the purpose of this study, the 16-EPA-PAH species will be used as the basis for comparison and not only BaP will be considered. This approach accounts for the fact that certain binders classified as unsuitable for use according to the 16-EPA-PAH in USA will not be applicable in Europe due to fewer PAH species considered as carcinogenic according to EU-PAH. Considering the aforementioned legislative measures and the drive to replace toxic materials with more sustainable and health-friendly alternatives, the replacement of CTPht in taphole clay with a lower PAH alternative or a non-toxic (PAH-free) binder has become a matter of great urgency.

Low PAH coal tar pitch binders that contain fewer higher boiling point PAH species such as benzo(a)pyrene, B(a)P, are currently being used in taphole clays [13–16]. These pitches still exhibit similar properties to CTPht, but with a reduced benzene equivalent (BE) value, which is a measure of the toxicity of the binder [17,18]. As previously stated, BaP is conventionally used as a measure of the toxicity of PAH-containing binders. However, this approach does not generate a realistic picture of the overall toxicity, especially the contribution of higher boiling point PAH species from the 16-EPA-PAH group that also contribute towards the carcinogenic nature of the binders. The BE-equivalent calculation introduces coefficients of toxicity that rank the PAH species according to their contribution to overall toxicity. This method is a more realistic measure to evaluate carcinogenic toxicity than only using the BaP concentration. In this paper, the BE-equivalent will be used to evaluate the total toxicity of the binders under consideration.

Some petroleum-based alternatives with lower PAH content include low-temperature pitches and waxy oils that have long-chained paraffinic structures [19]. The petroleum pitches and waxy oils have a lower toxicity content, but usually suffer from a reduced carbon yield (related to the PAH species that carbonize during the polycondensation reaction during heating) [15]. The waxy oil binders also undergo a crystallization process within a specific temperature range, referred to as the waxy appearance temperature (WAT) [19]. This process can cause variability in the clay flow behaviour. Other potential alternatives include bio-pitches, fatty acid pitches and tars. However, these alternatives usually face similar challenges as the petroleum-based liquids, which include lower viscosity and viscoelastic properties, as well as the cost of production, which also make them unfavourable options.

The work reported in this paper describes the characteristics and behaviour of a model taphole clay binder and compares it to alternative coal tar pitch binders of lower PAH content. The focus is on their mechanical and thermal characteristics. Some alternative binders to coal tar-based binders, which were investigated and evaluated as potential replacements of the model taphole clay binder, include petroleum-based mesophase-forming pitch and waxy oils, as well as wood-based tars that generally have fatty acid structures.

## 2. Materials and methods

### 2.1. Starting materials – binders

The liquids evaluated as possible alternative binders in taphole clays were categorized as either coal-based, petroleum-based, or wood/vegetation (organic) based. The coal-based binder used as a reference is a high-temperature coal tar (CTht), also referred to as high-coking-value tar (HCVT). HCVT is a viscous liquid residue resulting from the destructive distillation of coal during the cokemaking process in coke ovens. The first alternative coal-based binder is a blended product of a high-temperature coal tar pitch (CTPht-B) and a PAH-containing oil, referred to as merisol oil. This blend was designed to lower the softening point of the pitch to 20–30 °C. The high-temperature coal tar pitch used in CTPht-B is a product obtained from the destructive distillation of the CTht sample. The third coal-based binder (EcoP) was a low PAH (BaP) pitch that is synthetically prepared from high volatile coal tar pitch by removing high temperature PAH species through a combination of

fractional distillation and chemical treatments.

The second category of binders, the petroleum-based binders, includes three different types. The first was a crude waxy oil (CWO), which is used as a feed stream to a medium-temperature pitch processing unit in a petroleum process that produces diesel as a final product. The second binder (PCWO), was a refined version of the crude waxy oil that has undergone temperature processing to remove some low-temperature volatile species, including moisture. The last of the petroleum-based binders was a phenolic-based mesophase-forming pitch (MP), which is the product of a primary depitcher in a petrochemical process.

The last three binders considered were wood/vegetation-based tars, referred to as wood-based binders. Each of these binders is a different by-product of the Kraft process, obtained from different sources. The first was a liquid by-product from a pine tree source (Tar-PW). The second was a liquid by-product from a beech tree source (Tar-BW). The last was a liquid by-product from an organic composting source, primarily vegetable discards (Tar-Veg). These three binders are also commonly used as conditioning liquids to soften the hooves of ungulates for treatment purposes [20].

### 2.2. Fourier-transform infrared spectroscopy

The Fourier-transform infrared spectroscopy (FTIR) setup was used in attenuated total reflectance mode for liquid samples to measure the absorption at different wavelengths. The equipment used was a PerkinElmer Spectrum 100, which utilized a UATR accessory with a diamond/ZnSe measuring system. Spectrum 10 software was used for control and data management. A wavelength range from 600 to 4000  $\text{cm}^{-1}$  was selected, with 32 scans per sample.  $\text{CO}_2$  and  $\text{H}_2\text{O}$  peaks were excluded from the analyses.

### 2.3. Gas chromatography mass spectroscopy

Gas chromatography mass spectroscopy (GC-MS) analysis was used to evaluate the volatile species in each of the binders. The GC-MS analysis included both targeted and untargeted analyses. In the targeted analysis, a pesticide standard containing the 16-EPA-PAH species was analysed, and concentration graphs were constructed for the standard. This facilitated the identification and quantification of each PAH in the examined liquid binders. In the untargeted analysis, the pesticide standard and three different standards (one for each type of binder: pitch, petroleum, and fatty acid-containing) were used to identify the species in each sample, excluding the 16-EPA-PAH species. For the untargeted analysis, only the identified species and isomers were recorded with pseudo-quantification.

The samples were dissolved in both hexane and toluene to determine which solvent dissolved the most species from the samples. For lower molecular weight samples, toluene and hexane performed similarly. However, for higher molecular weight binders such as coal tar pitches and some petroleum pitches, hexane did not dissolve all the sample, so toluene was used consistently throughout. To prepare the binders for analysis, a quantity of 300–1000 mg of sample was dissolved in toluene. The samples were then vortexed and sonicated for 30 min. After sonication, 5 mL of ultra-pure water was added to the tubes, which were then again vortexed and centrifuged for 1 min at 3000 rpm. The top layer of the sample (which was the toluene-dissolved layer) was transferred to a 2 mL vial. From this, 1  $\mu\text{L}$  was injected into the GC-MS with a split ratio of 1:20.

Sample separation was performed using a 6890 N Agilent Technologies inert XL EI/CI mass selective detector (MSD), coupled with a CTC Analytics PAL auto-sampler. The PAH samples were separated using a non-polar Rxi-5Sil MS capillary column, with helium as the carrier gas at a flow rate of 1 mL/min, injected into the column at 240 °C. The MSD was operated in SIM mode under electron impact (EI) mode at an ionization energy of 70 eV, scanning from 30 to 650  $m/z$ .

## 2.4. Thermogravimetric analysis

The thermogravimetric analysis was conducted with a Hitachi STA 7300 TGA, using TA 7000 measurement software. The samples were weighed to two decimal places and placed into 30  $\mu\text{L}$  alumina crucibles, with sample weights ranging from 5 to 10 mg. An automatic sampler was used. The binders were heated in a nitrogen atmosphere, starting from 50  $^{\circ}\text{C}$  and increasing up to 800  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ , with a gas flow rate of 20 mL/min. The setup also enabled DTG analysis, which was captured, and the DTA results were confirmed through manual calculations. Three experiments were performed on each binder and average values were reported.

## 2.5. Rheology

The rheology evaluations of the binders consisted of three different tests: (1) isothermal rotational test at 45  $^{\circ}\text{C}$ , (2) temperature sweep in rotation that evaluated the change in dynamic viscosity of the binders with an increase in temperature (thermal stability), and (3) determination of the wax appearance temperature (WAT) of the waxy oils. Before conducting these tests, the linear viscoelastic region (LVER) of each binder was determined and the critical shear rate that was identified was used in the subsequent tests to ensure all measurements were performed within the LVER. The rheometer used was an Anton Paar Physica MCR 501 equipped with a cone-plate measuring system that uses a 0.5 $^{\circ}$ , 50 mm diameter spindle. The rheometer was also equipped with a Peltier PTD 200 temperature control system that can heat the liquids up to 200  $^{\circ}\text{C}$  in air. The RheoCompass<sup>TM</sup> software was used for capturing and programming the rheometer. All the binders evaluated were used as received without any prior conditioning. The conditions for the isothermal rotation test at 45  $^{\circ}\text{C}$  with a shear rate range of 0,1 to 100  $\text{sec}^{-1}$ . For both the WAT and temperature sweep tests, a shear rate of 1  $\text{sec}^{-1}$  and a temperature ramp rate of 5  $^{\circ}\text{C}/\text{min}$  were used. In the WAT procedure, the temperature was cooled from 110 to 15  $^{\circ}\text{C}$  as opposed to heating up to 150  $^{\circ}\text{C}$ .

## 3. Results and discussion

### 3.1. Compositional and molecular structure analysis

The compositional and molecular structure analysis of the binders included both FTIR and GC-MS analyses. The goal was to determine the presence of the 16-EPA-PAH species in the binders, as well as the bulk molecular composition to establish correlations with other binder properties, such as thermal analysis and rheology.

#### 3.1.1. Fourier-transform infrared spectroscopy evaluation of binders

The identification of the major functional groups of the binders is given in Table 1. The FTIR results assisted in developing an understanding of whether the structure is aromatic or aliphatic (i.e., open vs closed chain structures) by providing information on the major functional groups. The importance of an aromatic structure of the binder lies in its role in the formation of residual carbon that remains after firing to high temperatures. This is achieved through condensation reactions of the PAH species to form a carbon skeleton that assists with high temperature strength of the clay. The downside of highly aromatic binders is the increased toxicity with regards to the 16-EPA-PAHs. The presence of aliphatic chains in the molecular structure inherently reduces the PAH species in the binder that volatilize during heating. The larger aliphatic species tend to decompose into smaller compounds at higher temperatures, which are consequently released as volatiles. As a result, the carbon yield of the sample decreases. This allows for a qualitative assessment of which of the binders are less aromatic, and consequently contain fewer PAH species. The identification of functional groups primarily focused on wavelengths between 1400 and 3600  $\text{cm}^{-1}$ . Peaks at wavelengths lower than 1400  $\text{cm}^{-1}$  are considered part of the

**Table 1**

Identification of functional groups in binders through FTIR analysis.

Binder	Wavelength ( $\text{cm}^{-1}$ )	Functional groups
CTht, CTPht-B	1444, 1592	C=C Stretch (aromatic)
	3040	SP2 hybridized C-H str. (aromatic)
	1643	C=O Stretch
EcoP	1185, 1236	C-O-C
	1446, 1593	C=C Stretch (aromatic)
	3038	SP2 hybridized C-H str. (aromatic)
	2912	SP3 hybridized C-H str. (aliphatic)
CWO, PCWO	1187	C-O (ester)
	1459, 1600	C=C Stretch (aromatic)
	2853, 2923	SP3 hybridized C-H str. (aliphatic)
MP	1443, 1520	C=C Stretch (aromatic)
	3334	O-H Stretch (alcohol)
	1100–1324	C-O Bond
	3040	SP2 hybridized C-H str. (aromatic)
Tar-PW	2831–2994	SP3 hybridized C-H str. (aliphatic)
	1180–1320	C-O-C Stretch
	1700	C=O Carbonyl (incl. OH)
	3398	O-H Stretch (alcohol)
	2950	SP3 hybridized C-H str. (aliphatic)
Tar-BW, Tar-Veg	1102, 1204	C-O-C Stretch
	1700, 1730	C=O Carbonyl
	2885, 2921, 2957	SP3 hybridized C-H str. (aliphatic)
	1456	C=C Stretch (aromatic)
	1162, 1373	C-O (ester)

fingerprint area and are usually disregarded unless they can help to better explain the molecular structure by complementing other functional groups.

The results presented in Table 1 indicate that CTht contains cyclic aromatic hydrocarbons in the form of benzene due to C=C aromatic and SP2 C-H stretch. The majority of molecules are benzene-like hydrocarbons with some ester functional groups, which indicate that the binder may have undergone some cross-linking [21]. Similarly, the CTPht-B binder has the same molecular composition, except for the less abundant C-O stretch (ester), indicating that the cross-linking in this pitch is less than that of the CTht. EcoP has a combined structure with both SP2 C-H stretch (benzene) and SP3 C-H stretch (aliphatic) functional groups present. The majority of molecules are benzene-like hydrocarbons, with either some chained hydrocarbons surrounding smaller structures, or which form part of the bulk aromatic hydrocarbon structure. The pitch also underwent cross-linking due to the presence of the C-O (ester) functional group.

The crude waxy oil (CWO) and processed version of the CWO (PCWO) have similar compositions characterised by the presence of aromatic species (probably to a lesser extent) and a predominantly aliphatic bulk composed of chained hydrocarbons, such as alkanes. These aliphatic structures are commonly found in the source of these binders [22]. The mesophase pitch (MP) is also a combination structure of aromatic benzene hydrocarbons (SP2 C-H stretch) and aliphatic chained hydrocarbons (SP3 C-H stretch). The presence of the SP2 C-H stretch, together with the C-O/O-H peaks, indicates the presence of a phenolic functional group, which is expected as the source of this binder is phenol.

The wood-based tar binders have complex structures, although it does not seem that all of them have fatty acid-chained structures as expected. Pinewood tar (Tar-PW) seems to have a saturated fatty acid structure, as evidenced by the presence of the SP3 C-H stretch and carboxyl functional group (C=O carbonyl together with O-H stretch). The absence of C=C aromatic peaks indicates that the binder is not aromatic in nature. Tar-BW has a carbonyl functional group with no O-H stretch, indicating that the structure is not carboxyl. The presence of the SP3 C-H stretch and C=O carbonyl suggests the presence of a type of ketone structure or that some esters are present in the bulk structure of the material. The last binder, Tar-Veg, has the same structure as that of the beechwood tar (Tar-BW) of which the bulk of the binder is ester-based.

The binders that, according to the FTIR results, are expected to have lower PAH concentrations compared to the reference binder, are the aliphatic petroleum binders (CWO, PCWO), as well as the wood-based binders (Tar-PW, Tar-BW and Tar-Veg). The coal-based binders are high in aromatic structures, with MP also having some degree of aromaticity, which could directly correlate with the presence of polycyclic aromatic species present in the sample. To confirm and determine the concentrations of the 16-EPA-PAH species in the binders, a more quantitative approach was required, using gas chromatography mass spectroscopy (GC-MS).

### 3.1.2. Gas chromatography mass spectroscopy evaluation of binders

**3.1.2.1. Toxicity coefficients (benzene equivalents) for the different binders.** GC-MS analysis was performed to identify the organic molecules that constitute the different binders. The 16-EPA-PAH contents of each binder was determined through a targeted analysis. This PAH analysis was used to calculate the toxicity coefficient or benzene equivalent (BE) according to equation (1), which is adapted to exclude benzo(e)pyrene as this compound was not part of the 16-EPA-PAH list was also absent from the calibration standard for the GC-MS targeted analysis [23].

$$BE = 1,00C_{BaP} + 0,034C_F + 0,033C_{BaA} + 0,26C_C + 0,10C_{BbF} + 0,10C_{IP} + 1,40C_{DBA} + 1,00C_{BP} \quad (1)$$

where C refers to concentration in mass%, BaP refers to benzo(a)pyrene, F refers to fluoranthene, BaA refers to benzo(a)anthracene, C (as a subscript) refers to chrysene, BbF refers to benz(b)fluoranthene, IP refers to ideno(1,2,3,c,d)pyrene, DBA refers to dibenz(a,h)anthracene, and BP refers to benz(g,h,i)perylene.

The higher boiling point PAHs such as BaP, DBA, IP and BP are more carcinogenic molecules based on the concentration contribution of each of these species towards the BE equivalent in equation (1). The CDC/ATSDR (Centers for Disease Control and Prevention/Agency for Toxic Substances and Disease Registry) stipulates an occupational permissible exposure limit for total PAH species of 0,2 mg/m<sup>3</sup> (~0,04 ppm) per 8-h period [10,24].

The results of the targeted analysis of each binder were first used to determine the total 16-EPA-PAH content in ppm before calculating the mg/kg ratio to determine the BE-values. The results of the PAH content are shown in Fig. 1. However, it should be noted that these concentrations are not for an 8-h exposure time and will be higher due to the short volatilization time used in the GC-MS. Also, the concentrations in Fig. 1 are only for the identified 16-EPA-PAH species and not all the species considered in the PEL by ATSDR. The results for the pinewood and beach wood tar are not considered due to the absence of PAH species in these

fluids.

Based on the results in Fig. 1, all the binders have PAH levels above the PEL as defined by the ATSDR. Due to the difference in exposure time between the on-site situation (during ramming) and the GC-MS analysis time, the GC-MS result of the reference binder was used as the benchmark to which the alternative binders were compared. An increase in PAH levels, however, implies more difficulties in complying with PEL regulations. This value would be higher if there are additional PAH species in the sample that are not part of the 16-EPA-PAH group of species. The pitch blend (CTPht-B) shows the highest total PAH content among the coal-based binders, with the coal tar (CTht) as second highest. The petroleum-based fluids have a substantially lower PAH content, with the PCWO having the lowest PAH content in this category. Its crude counterpart (CWO) has the fifth highest concentration overall, indicating the effect of processing on crude waxy oil. The mesophase-forming pitch (MP) has the highest PAH content among the petroleum-based binders. However, when comparing it to the coal-based pitch with the lowest PAH content (EcoP), there is an order of magnitude difference between these two different pitch sources.

The targeted analysis of the 16-EPA-PAH species are shown in Table 2. All 16-EPA-PAH species were detected in two of the coal-based binders (CTht, CTPht-B). The EcoP and MP binders contained all of the 16-EPA-PAH species, except for acenaphthylene in EcoP and benzo(a)pyrene in MP. The remaining petroleum wax oils (CWO, PCWO), and the wood-based binder (Tar-Veg) had lower aromaticity and a reduced number of EPA-PAH species. Tar-BW and Tar-PW did not contain any of the 16-EPA-PAH species, and consequently are not listed in Table 2. The boiling point of each compound is given in brackets below the name for comparison purposes.

The reference sample consists of an abundance of different PAH species, of which naphthalene is in the highest concentration. The benzene equivalent is a measure of the toxicity of the binders and can be used to compare samples that have high aromaticity or concentrations of 16-EPA-PAH species. The benzene equivalent for the reference sample in Table 2 (CTht) is above 1.67. When compared to published values from the literature, the result is in line with the values obtained for similar coal tar liquids, with calculated BE values of 1.05–1.75 [23]. For the coal tar pitch blend (CTPht-B), the benzene equivalent is 1.92, which is slightly lower than the typical range of 2.1–2.5 found in the literature [23]. The coal tar pitch values published in the literature are however, for processed pitches with higher softening points (90–105 °C), whereas the CTPht-B is a pitch-oil blend, designed to lower the softening point from 150 °C to between 20 and 30 °C, as evaluated with a ring and ball apparatus. The slightly lower BE value of CTPht-B, when compared to the values in the literature, can therefore be attributed to the pitch-oil blend having a different composition from the processed pitches.

The PAH species of lower molecular mass (naphthalene,

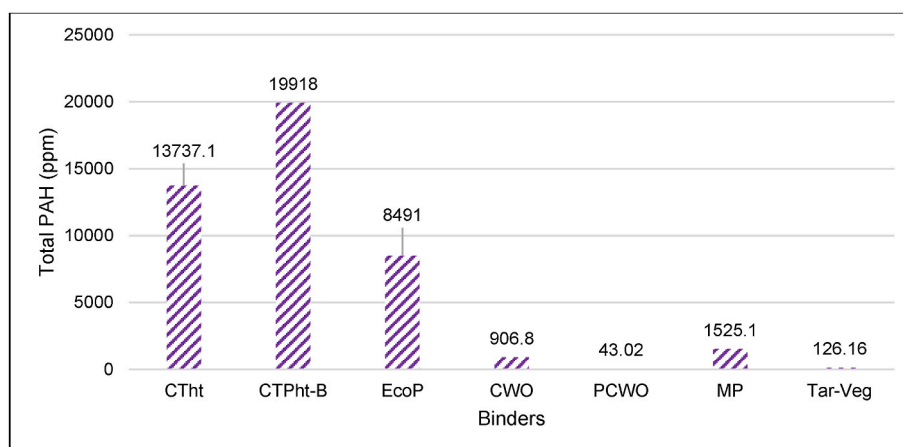


Fig. 1. Total PAH content of each binder, determined using GC-MS.

**Table 2**

Targeted analysis of 16-EPA-PAH in binders investigated (%wt); BP = Boiling point [23].

Compound	Formula	CTht	CTPht-B	EcoP	CWO	PCWO	MP	Tar-Veg
Naphthalene (BP = 218 °C)	C10H8	4,75	6,73	2,99	0,25	–	0,45	–
Acenaphthylene (BP = 270 °C)	C12H8	1,20	0,07	–	–	–	0,02	–
Acenaphthene (BP = 279 °C)	C12H10	0,07	1,95	1,95	0,37	–	0,42	–
Fluorene (BP = 295 °C)	C13H10	1,03	1,67	1,81	0,28	–	0,40	–
Phenanthrene (BP = 338 °C)	C14H10	2,58	3,08	1,24	0,15	0,01	0,25	–
Anthracene (BP = 340 °C)	C14H10	0,79	3,02	1,21	0,04	–	0,10	–
Fluoranthene (BP = 383 °C)	C16H10	1,64	1,95	0,38	0,03	–	0,09	–
Pyrene (BP = 393 °C)	C16H10	0,95	1,29	0,31	0,02	–	0,07	–
Chrysene (BP = 441 °C)	C18H12	1,11	0,78	0,04	–	–	0,08	–
Benzo(a)anthracene (BP = 435 °C)	C18H12	0,47	0,46	0,03	–	–	0,05	–
Benzo(b)fluoranthene (BP = 481 °C)	C20H12	1,11	0,82	0,03	–	–	0,06	0,06
Benzo(k)fluoranthene (BP = 481 °C)	C20H12	0,19	0,15	0,01	–	–	0,05	0,03
Benzo(a)pyrene (BP = 496 °C)	C20H12	0,65	0,73	0,02	–	–	–	0,01
Indeno(1,2,3-cd)pyrene (BP = 524 °C)	C22H12	0,35	0,49	0,06	–	–	0,06	–
Dibenzo(a,h)anthracene (BP = 539 °C)	C22H14	0,16	0,22	0,04	0,02	0,02	0,15	–
Benzo(ghi)perylene (BP = 545 °C)	C22H12	0,29	0,35	0,07	–	–	0,05	–
BE	–	1,67	1,92	0,66	0,03	0,03	0,24	0,02

acenaphthene, fluorene, phenanthrene, anthracene) are more concentrated in the pitch blend sample (CTPht-B), with higher molecular mass species (chrysene, benzo(b) fluoranthene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene) still present, as seen by the increased BE value. The higher BE value of the CTPht-B, as compared to the coal tar (CTht), which is generally higher in PAH as previously mentioned, suggests that the increase in the BE value of the pitch blend (CTPht-B) is possibly due to the composition of the oil, which might have a higher PAH content than the coal tar pitch it is mixed with. Naphthalene, phenanthrene, and anthracene are the most abundant EPA-PAH species in CTPht-B. Of all the binders being considered, the CTPht-B has the highest toxicity, with the highest BE value.

From the alternative binders being evaluated, the ones that are considered more environmentally friendly, with regards to emissions from 16-EPA-PAH, are the wood-based tars, both Tar-PW and Tar-BW, followed by the processed crude waxy oil (PCWO), the vegetable tar (Tar-Veg) and then the crude waxy oil (CWO). The mesophase-forming pitch (MP) and all the coal-based alternative binders (CTPht-B, EcoP) are better alternatives than the reference. However, the use of these binders in taphole clay materials will still be considered unfavourable due to its toxicity to both humans and the environment, as they contain higher levels of PAH, as indicated by the results from the 16-EPA-PAH with regards to the PEL.

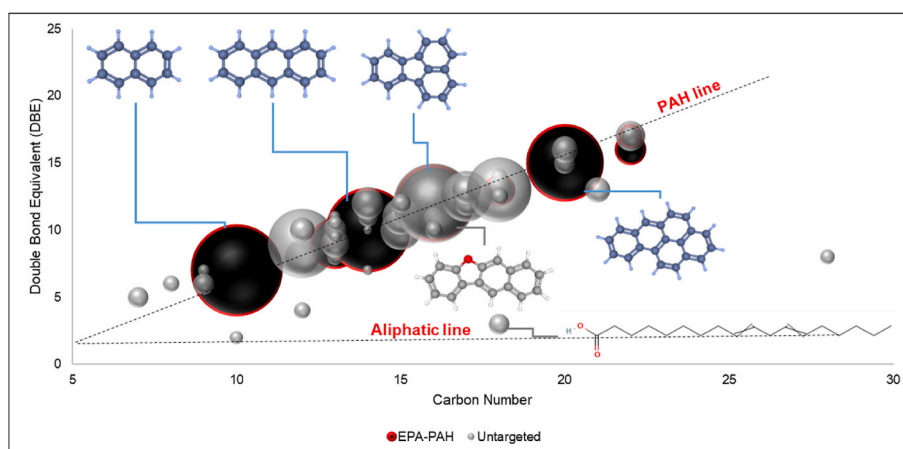
**3.1.2.2. Double bond equivalent vs. carbon number of the organic molecules that constitute the binders.** The goal was not only to identify the 16-EPA-PAH species in each of the binders but to also identify the molecular

composition of each binder whereby they could be ranked in terms of their associated health risks. Other species (non-16-EPA-PAH) in the binders were identified through a pseudo- or untargeted analysis. The untargeted analysis results are schematically represented by bubble plots, in which the double bond equivalent (DBE) is plotted against the carbon number (CN) (Fig. 2). The untargeted analysis serves as a guide to understand which alternative species are present in the samples, mainly to illustrate that besides the 16-EPA-PAH species present in the samples, there are additional aromatic species present in some samples. These species may be toxic and are not considered as part of the 16-EPA-PAH species. The untargeted analysis also gives an indication of the distribution to higher aromaticity species as compared to targeted aromatic species. The carbon number was determined from the theoretical stoichiometry of each molecule which is used to calculate the level of unsaturation (DBE) for that specific molecule. Each of the individual bubbles represent a type of organic molecule in the sample with a specific DBE and CN. The size of each of the bubbles is an indication of the relative concentration of that species in the sample. The DBE (also called the degree of unsaturation) is the level of unsaturation present in an organic molecule and can be calculated from the following equation [25]:

$$DBE = C + 1 - (H/2) - (X/2) + (N/2) \quad (2)$$

where C = number of carbon atoms, H = number of hydrogen atoms, X = number of halogen atoms and N = number of nitrogen atoms.

The enlarged graphical representation of both targeted and untargeted analysis of the reference binder (CTht) is shown in Fig. 2. The EPA-



**Fig. 2.** Untargeted analysis results depicting the relationship between double bond equivalent (DBE) and carbon number for CTht.

PAH species identified through targeted analysis are represented as dark spheres in Fig. 2, whereas the untargeted analysis of the remaining species in the binder is depicted as light spheres. The conjugated double bond PAH species follow a linear trend ( $DBE/CN = 2/3$ ), as indicated by the dashed PAH line in Fig. 2. The line for aliphatic species is at a DBE of zero with a zero-slope line for pure aliphatic species, moving to higher carbon number as the chains become longer. Because the aim is to identify low-PAH alternative binders, the fewer species that follow the PAH line, and closer to the X-axis, the more aliphatic the structure is. Reducing the PAH species and consequently the 16-EPA-PAHs, the less toxic the binder would be, but at the cost of a lower carbon yield that will result after firing.

The combination of targeted (Table 2) and untargeted (Fig. 3) analyses reveals that the reference binder (CTht) is primarily composed of aromatic benzene-based species, with some benzo(b)naphtho(2,3-d) furan ( $DBE = 12$ ,  $CN = 16$ ), biphenylene ( $DBE = 9$ ,  $CN = 12$ ), and a few minor aliphatic species, such as octadecadienoic acid ( $DBE = 3$ ,  $CN = 18$ ). The CTPht-B binder also mostly consists of aromatic benzene-based species, with azulene ( $DBE = 7$ ,  $CN = 10$ ) and benzo(b)naphtho [2,3-d] furan ( $DBE = 12$ ,  $CN = 16$ ) in addition to the identified PAH species. The FTIR results of this material does not highlight the presence of any aliphatic species, but this can be due to the nature of the sample and the test method. Generally, high molecular weight liquids that are not opaque which result in complex compositions, wherein the detection limit of infrared spectroscopy may not be able to detect all functional groups. This might be the case for this sample. The EcoP contains benzene-like molecules, but with a lower BE-value, indicating that the PAH species are of the low boiling point type (targeted). The CWO is a combination of aromatic and aliphatic species as shown by the GC-MS results, similar to that shown from the FTIR results. The PCWO composition consists mainly of linear chained hydrocarbons, indicating that the processing of the CWO has removed the majority of aromatic hydrocarbons it contained. The mesophase-producing pitch (MP) is phenol-based, with identified PAH species and other aromatic species such as 2,4-dimethylphenol ( $DBE = 4$ ,  $CN = 8$ ), 3-ethyl-4-methylphenol ( $DBE = 4$ ,  $CN = 9$ ), azulene ( $CBE = 7$ ,  $CN = 10$ ), and 4-ethylbenzaldehyde ( $DBE = 5$ ,  $CN = 9$ ), which confirms the higher aromaticity of this binder as compare to the other petroleum-based binders.

The wood-based tars have different species, some of which are

complex in nature. The Tar-PW contains mainly methoxybenzene species, with the bulk (>85%) of the sample not being fatty acid, as indicated by the FTIR results. Upon further investigation into the fingerprint area of the FTIR results of this binder, a co-elution peak at  $1250\text{ cm}^{-1}$  was identified, showing similar characteristics to compounds like methoxybenzene [26]. This confirms the GC-MS untargeted analysis. There are also some alkanes present in the sample but in trace amounts. The beechwood tar (Tar-BW) has a long-chained fatty acid structure (aliphatic structure), with the predominant species in the binder being 9-octadecenoic acid ( $DBE = 3$ ,  $CN = 36$ ). The remaining identified species highlight a ketone structure, as indicated by the FTIR results. The vegetable tar (Tar-Veg) is a complex binder, consisting of different organic species, including both cyclic aromatic hydrocarbons and chained hydrocarbons. Some of the major species identified include peri-xanthenoxanthene-4,10-dione, 2-,8-bis(1-methylethyl)-quinone ( $DBE = 16$ ,  $CN = 20$ ), 9,17-octadecadienal (Z), which is a chained hydrocarbon ( $DBE = 3$ ,  $CN = 18$ ), and 1,2,4-methenoazulene, decahydro-1,5,5,8a-tetramethyl-, [1S-(1 $\alpha$ ,2 $\alpha$ ,3 $\alpha$ ,4 $\alpha$ ,8 $\alpha$ ,9R\*)]- ( $DBE = 15.5$ ,  $CN = 15$ ), which has a cyclic hydrocarbon structure but not a benzene structure. The presence of methenoazulene is hazardous to the environment and aquatic life, making the use of this binder dangerous. Analysing the results from the untargeted analysis, binders with a more aliphatic structure such as PCWO and Tar-BW would be the preferred alternatives to CTht. These binders have all shown low BE values in the targeted analysis.

### 3.2. Thermogravimetric analysis of binders

It is important to use a binder in taphole clays that has a large volatilization temperature range, gradual release of volatiles over the wide temperature range, and allows for a high concentration of the organic material to be transformed into carbon, that can aid in the strength of the clay after firing. Thermal analysis of the binders was therefore conducted in an inert environment with the aim of evaluating the volatilization behaviour of each binder as it was heated from 50 to 800 °C. The volatilization behaviour was used to highlight the rate of mass loss, the temperature range of bulk mass loss, and the inflection points where the highest degree of mass loss would occur. The carbon yield, calculated as a percentage of the remaining mass of the sample

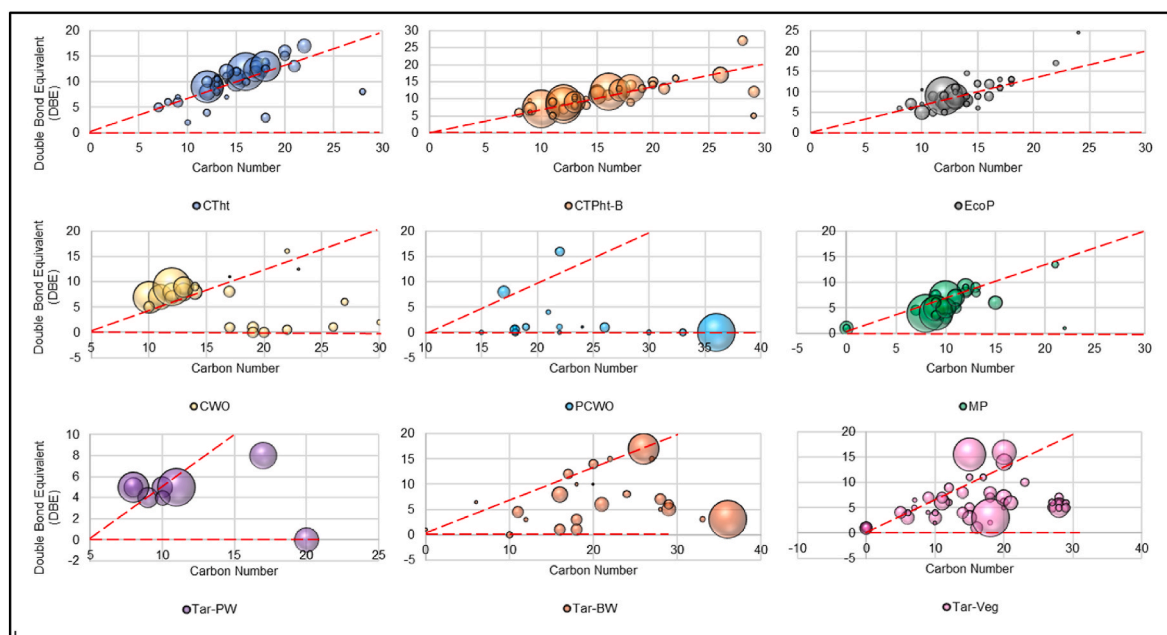


Fig. 3. Untargeted analysis results depicting the relationship between double bond equivalent (DBE) and carbon number for the different binders (fine dashed line – PAH line with slope  $DBE/CN = 2/3$ ; thick dashed line – aliphatic line with slope  $DBE/CN = 0$ ).

after heating to 800 °C, was also recorded for each binder.

The TGA summary graph that shows the cumulative mass loss in mass % of each binder, is shown in Fig. 4. The curves in Fig. 4 were used to obtain the mass loss temperature range for each sample; this is calculated as the difference between the volatilization end and start temperatures. These temperatures are determined as the temperature at which the mass loss starts to plateau (end temperature) and the onset temperature of the critical mass loss fractions (start temperature). This accounts for the majority of the mass loss of the sample. The average gradient of this mass loss over the temperature range was determined for each curve in mass %/°C. The carbon yield is determined as mass % of the residue at 800 °C. The average gradient, mass loss temperature range, as well as carbon yield of each binder are given in Table 3. The temperature range given in Table 3 represents only the start and end temperatures (range) for the linear slope calculation and does not encompass the entire volatilization range.

The reference binder, CTht, EcoP, and Tar-PW are the only binders that exhibited a mass loss at temperatures below 100 °C (less than 10% mass loss) which is likely due to evaporation of moisture or low temperature volatile species from the sample. The inflection points at 113.5 °C and 150.1 °C (CTht) are due to the volatilization of lower molecular weight species. The subsequent total mass loss (75.4% mass) between 150.1 and 380.4 °C is due to the volatilization and decomposition of PAH species present in the sample. Close to the mesophase formation temperature, i.e., 380–450 °C [27], the binder starts to phase separate into mesophase and amorphous fractions. The phase separation is liquid-liquid separation into an emulsion. The solid carbon will start forming between 450 and 500 °C during coking. Upon further heating, the binder attains a carbon yield of 10.6% mass. The average mass loss per temperature change is 0.28 mass loss/°C between 70.8 and 380.4 °C with a total  $\Delta T$  of 309.6 °C and a carbon yield of 10.6% mass. From the mass loss results in Table 3, the reference sample shows the second-lowest degree of mass loss. The closest alternative binder that shows a similar degree of mass loss is the EcoP binder, although with a higher carbon yield. The mass loss at lower temperatures, <100 °C, is possibly due to species that volatilised at lower temperatures, as opposed to moisture in some of the other binders, as this is a refined fluid.

The waxy crude oil has the highest mass loss over a small temperature range with some moisture release close to 100 °C. The mesophase-forming pitch (MP) has a slightly higher mass loss over a similar temperature range as the CTPht-B binder. The pinewood tar binder (Tar-PW) has a higher mass loss over the same temperature range as the reference sample. The vegetable tar (Tar-Veg) loses mass over a larger temperature range than most of the samples, with a similar mass loss per temperature change to the pinewood tar (Tar-PW) sample. From the TGA results, the binders that are closest to the reference binder and that

**Table 3**

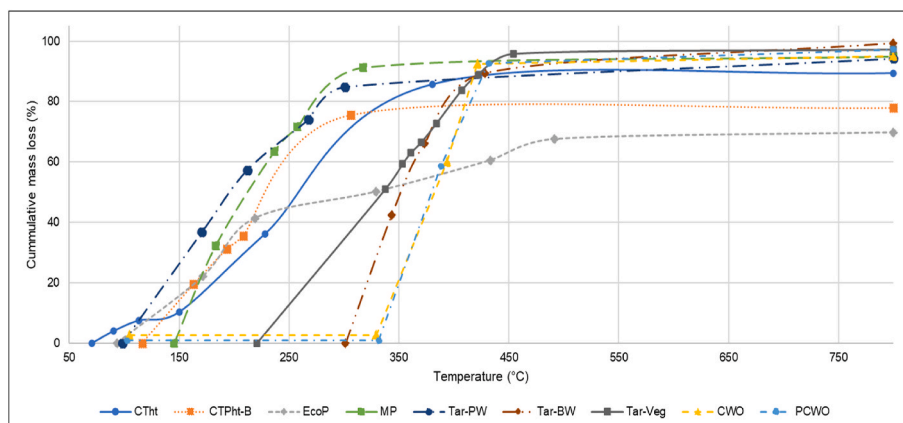
Summary of the TGA results of the binders that were examined (temperature range indicates the start temperature of volatilization and the end bound represents the final volatilization temperature).

Binder	Inflection points (°C)	Average mass loss per temperature change (g/°C)	Temperature range (°C) ( $\Delta T$ , °C)	Carbon yield (%)
CTht	70,8; 90,5; 113,5; 150,1; 228,2; 380,4	0,28	70,8–380,4 ( $\Delta T \sim 310$ )	10,6
CTPht-B	116,4; 163,3; 193,6; 208,3; 306,1	0,40	116,4–306,1 ( $\Delta T \sim 190$ )	22,1
EcoP	93,4; 171,6; 219; 329,2; 433,4; 491,6	0,21	93,4–491,6 ( $\Delta T \sim 398$ )	30,2
CWO	101,3; 329,3; 393,8; 421,6	0,96	329,3–421,6 ( $\Delta T \sim 92$ )	4,9
PCWO	102,9; 331,8; 388,3; 431,5	0,92	331,8–431,5 ( $\Delta T \sim 100$ )	2,7
MP	145,6; 183,3; 236,9; 257,8; 317,3	0,53	145,6–317,3 ( $\Delta T \sim 172$ )	5,1
Tar-PW	98,6; 170,8; 212; 267,6; 300,8	0,42	98,6–300,8 ( $\Delta T \sim 202$ )	5,8
Tar-BW	301,5; 343,4; 373,3; 428,3	0,70	301,5–428,3 ( $\Delta T \sim 127$ )	0,7
Tar-Veg	220,8; 337,5; 353,5; 360,6; 370,1; 384; 407; 422; 454,4	0,45	220,8–422,0 ( $\Delta T \sim 201$ )	2,7

would be ideal for taphole clay use are coal-based alternatives (CTPht-B and EcoP), and to some extent the mesophase-forming pitch (MP) and the pinewood tar (Tar-PW). For CTPht-B and EcoP this is due to the wide range of volatilization temperatures, the low degree of volatilization (close to that of the reference binder), and the high carbon yield. Although the volatilization temperature range is wide for MP and Tar-PW, and the degree of volatilization low, the carbon yield is also lower.

### 3.3. Rheological evaluation of binders

The results of the isothermal rotational test at 45 °C, which evaluated the Newtonian behaviour of the liquids, are shown in Fig. 5. The chosen test temperature was 45 °C, as this is generally the mixing temperature of the taphole clay, for optimal binder usage and distribution of fluid throughout the clay matrix during manufacturing. Based on the results of the isothermal rotation, it is evident that all the binders exhibited Newtonian behaviour, with the exception of CWO. This enhanced shear-thinning at lower shear-rate was probably due to higher residual moisture content in the binder as this is the unrefined version of the waxy oil.



**Fig. 4.** Thermal gravimetric analysis (TGA) of the examined binders.

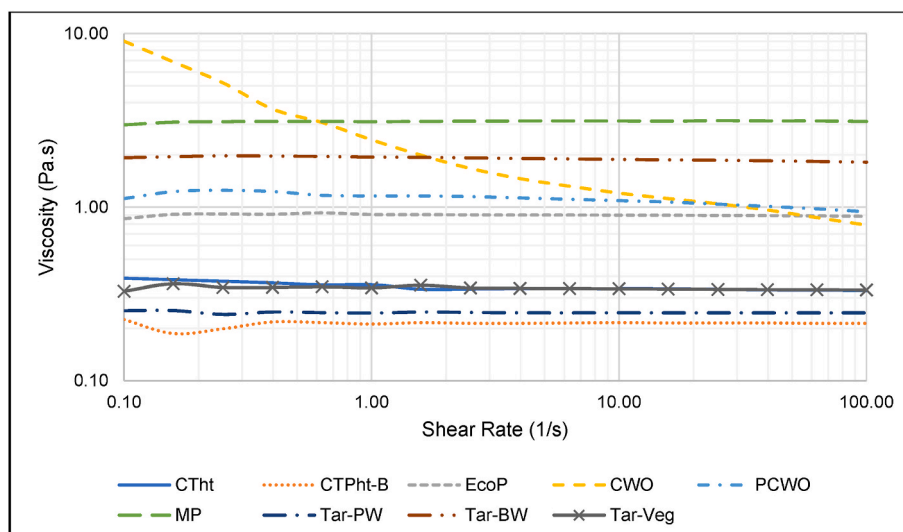


Fig. 5. Graphical presentation of the isothermal rotational test at 45 °C, aimed at determining the Newtonian behaviour of the binders.

In this manner, the water in the emulsion, likely in the form of droplets, is being deformed or are coalescing. The reference binder has a starting dynamic viscosity of 0.40 Pa s, which was maintained throughout the shear-rate range. The binders that exhibit Newtonian behaviour similar to that of the reference binder are the vegetable tar (Tar-Veg), the pinewood tar (Tar-PW), and the low softening point pitch blend (CTPht-B). The latter two having a slightly lower viscosity compared to the CTht. The remaining binders have higher viscosities than the reference binder, with EcoP and PCWO the closest alternatives that could still be used in the clay. The beechwood tar (Tar-BW) and mesophase-forming pitch (MP) have the highest viscosities of the binders. The rheological behaviour of the binders is related to their molecular composition. Higher average molecular weight binders show a higher viscosity (assuming a similar type of molecules in the sample), while larger molecules result in increased inter- and intra-compound interactions, which increase the force needed to overcome internal resistance and initiate flow of the fluid [28].

The thermal stabilities of the binders, as depicted by a change in dynamic viscosity (threshold to overcome internal friction) as the temperature increases, are shown in Fig. 6. The results from Figs. 5 and 6 are inconsistent due to variations in the nature of the samples as well as the sampling process. The results are solely used to observe trends and for

comparison. For the fluid samples being evaluated, thermal stability is described as the tendency for the fluid to approach a viscosity limit (plateau) and how easily this happens with an increase in temperature. For CTht, CTPht-B, and EcoP, the decrease in viscosity will occur over a larger temperature range. The viscosity of the CTht decreases up to 80 °C, after which it shows a sudden increase between 80 and 93 °C and then decreases again. As the temperature increases past 93 °C, the viscosity remains constant up to 150 °C. The sudden increase in viscosity between 80 and 93 °C could be due to a sudden mass loss, probably due to lower temperature volatiles, that affects the manner in which the rheometer measures viscosity. The low softening point pitch blend, CTPht-B, has a starting viscosity slightly lower than that of the reference sample at 0.78 Pa s and shows a similar rate in reduction in viscosity as the temperature increases. The viscosity decreases up to 90 °C, after which it remains constant up to 140 °C.

The EcoP has the highest starting viscosity of the coal-based binders, and the degree of change in dynamic viscosity between the starting and final viscosity at 150 °C is lower compared to the reference and CTPht-B binders. The higher viscosity indicates that the binder has a larger attractive binding energy between the molecules.

The petroleum-based waxy oils, CWO and PCWO, exhibit similar behaviour to the reference sample (CTht). Both binders show a

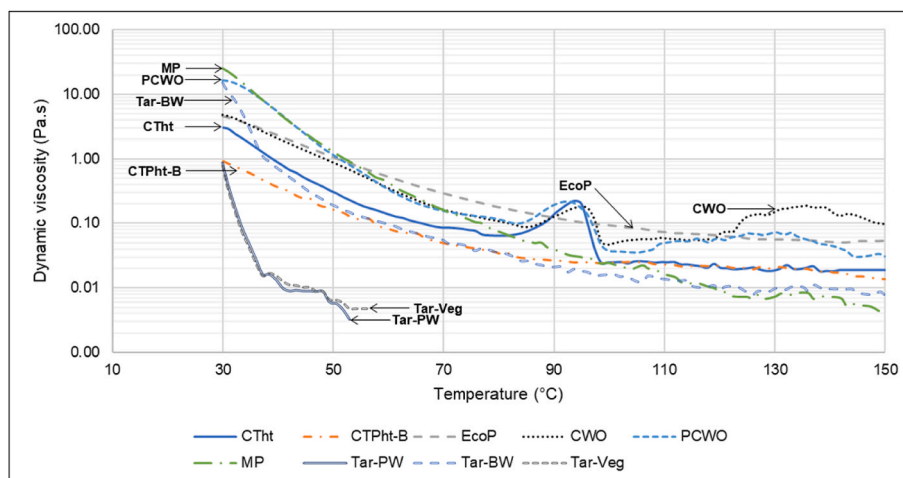


Fig. 6. Graphical presentation of the temperature sweep results of the binders between 30 and 150 °C and the influence of changes in temperature on dynamic viscosity.



reduction in viscosity up to 85 °C, with a small increase between 85 and 96 °C, which is possibly attributed to the release of lower temperature volatiles, which could include moisture in the case of the CWO binder. The increase in viscosity over this temperature range may, similar to the CTPht, be due to erroneous measurements caused by mass loss. The mesophase-forming pitch (MP) experiences a higher degree of reduction in viscosity. With this binder, viscosity continues to decrease with an increase in temperature. The thermal stability of this binder is not comparable to the reference binder.

The waxy oils were also heated and then slowly cooled (5 °C/min) to determine the WAT temperature [29]. This is important as the precipitation of wax crystals can cause a sudden increase in viscosity. In applications such as with taphole clays, this may affect the extrusion pressure and the plastic behaviour of the clay [30]. Both CWO and PCWO have similar WATs of between 58 and 65 °C. Precipitation of the paraffin crystals begins at 65 °C (liquidus temperature) and melting of the crystals (with a reduction in viscosity) occurs at 55 °C (solidus temperature). The values from the viscosity measurements for WAT are only indicative of changes in viscosity that are an order of magnitude within a short temperature range (~5 °C).

The last set of samples, which are the wood-based tars, exhibit considerably lower viscosity and thermal stability compared to all other samples, except for the beech tree tar (Tar-BW). Starting with the pinewood tar, the viscosity at 0.78 Pa s reduces significantly as the temperature increases up to 35 °C, after which the rate at which the viscosity decreases slows down (Fig. 6). The same behaviour is observed in the vegetable tar (Tar-Veg) as in the pinewood tar sample (Tar-PW), where the starting viscosity and reduction in viscosity with temperature are similar. Both of these samples reach extremely low viscosities after which no further data could be obtained. This is due to the low torque region that was reached and is a limitation of the equipment. The beechwood tar (Tar-BW) binder has a starting viscosity of 15.1 Pa s, which decreases significantly up to 38 °C and then gradually continues to decrease with further increases in temperature. The sample exhibits reduced internal friction up to ~110 °C, with the viscosity remaining constant up to 150 °C. The beechwood (Tar-BW) binder has better thermal variability due to its higher molecular weight compared to the other two samples as shown by the plateau in viscosity up to 150 °C. The thermal stability of the beechwood tar (Tar-BW) sample is comparable to that of the reference sample (CTht).

#### 4. Summary of results

This investigation aimed to identify suitable alternative binders to replace CTht in taphole clays. The binders were subsequently ranked based on their suitability to replace CTht, considering specific requirements and their evaluated properties. The requirements related to the binder include low BE-equivalent (toxicity), good viscoelastic behaviour, low softening point of the binder, high plasticity, gradual volatilization between 25 and 400 °C, reduced overall volatility to limit porosity, and sufficient residual carbon after firing [1,31–33].

##### 4.1. GC-MS

The ranking of the binders was based on their molecular compositions and structures, considering the total 16-EPA-PAH values, as well as the results from the untargeted GC-MS analysis and FTIR results. The two binders, Tar-BW and Tar-PW, have a zero BE-value and a total PAH content of zero based on the targeted species (16-EPA-PAH). However, the untargeted analysis of the Tar-PW revealed strong aromaticity with benzene-like compounds. This binder is not considered non-toxic according to the GC-MS analysis. The Tar-BW is considered the most favourable to replace CTht based on the holistic GC-MS analysis. The following suitable binder candidates were ranked according to their total PAH content and BE-equivalent: PCWO, followed by Veg-Tar, with Veg-Tar ranked lower than PCWO due to the presence of some aromatic

species in the binder. Next, the two remaining petroleum fluids, first CWO and then MP due to the difference in total PAH. Thereafter, the coal-based fluids were ranked, first EcoP and lastly CTPht-B, due to their high total PAH values and BE-equivalent.

##### 4.2. Thermal analysis

The ranking of the binders based on thermal analysis results were determined by considering first the mass loss per temperature change of the binder and secondly the carbon yield. In addition to the mass loss, the temperature range of volatilization, the starting volatile temperature, and the temperature over which the largest portion of the binder volatilised were also considered. The most suitable alternative binder was found to be EcoP due to its low average mass loss per temperature change, wide temperature range of volatilization, and high carbon yield. Pinewood-based tar (Tar-PW) was ranked second with a slightly higher rate of mass loss but a larger volatilization temperature range. Tar-Veg was ranked lower than CTPht-B, despite the relatively similar rate of mass loss and volatilization temperature range between these binders. However, these two binders have lower carbon yields as compared to the reference binder. This should be taken into account in the design of the taphole clay to ensure high temperature strength is maintained. When looking at the remaining material after carbonization, CTPht-B was ranked higher than both Tar-PW and Tar-Veg. The MP binder was still considered favourable despite having a slightly elevated mass loss, because this mass loss occurred over a wide temperature range. The last three binders, i.e., the beechwood-based tar and the waxy oils, were considered the least favoured due to their high rate of mass loss within a narrow temperature range. This abrupt or high mass loss will cause turbulence inside the taphole, which can increase the corrosion of the taphole if bypass occurs [1]. The high mass loss may also result in an increase in the porosity of the clay, which can lower its strength [34].

##### 4.3. Rheology

The rheological requirements of the binder system include: 1) allow for continuous flow of the clay with minimal variability in extrusion pressure and maintain a low extrusion pressure, 2) form a homogeneous mixture, and not an emulsion that will separate during ageing when strengthening agents such as phenolic resin are added, 3) maintain its molecular structure when heated. Taphole clays exhibit shear-thinning behaviour [35] due to the aggregate in the material that will rearrange to orient with the flow during extrusion. Any non-Newtonian behaviour will favour both the extrusion and quantity of binder that will be used. The non-Newtonian, shear-thinning, behaviour of binders is favourable if the viscosity is high, as it results in a lower extrusion pressure needed to extrude the clay. In the case of taphole clays, there is a correlation between workability and extrusion pressure, wherein an increase in workability results in a decrease in extrusion pressure and vice versa [30]. The increase in binder viscosity during aging reduces workability and consequently increases extrusion pressure. Therefore, binders with high viscosities will require higher extrusion pressures [30]. This can be alleviated by using a low viscosity, non-Newtonian, shear-thinning liquid to assist with increased flow during extrusion.

The ranking of the binders on the rheology results (Table 4) was done based on their thermal stability and Newtonian behaviour. Thermal stability is a critical property and is considered in preference to Newtonian behaviour, where shear-thinning is favoured. EcoP has an iso-viscous and thermally predictable behaviour, followed by low softening point pitch blend (CTPht-B) due to the smaller decrease in viscosity with temperature. CWO shows good thermal stability and a shear-thinning behaviour compared to its processed version, PCWO. The processed crude wax oil (PCWO) is ranked lower due to its high viscosity that will make it more difficult to extrude as compared to the crude version. Tar-BW and MP are ranked 4th and 5th (before PCWO), respectively, where the Tar-BW has a lower viscosity and will result in a

**Table 4**  
Ranking of alternative binders based on molecular structure, thermal analysis, and rheology.

Rank	Molecular composition (total PAH) $S_1 = 2$	Thermal analysis (volatilization) $S_2 = 1$	Rheology (viscosity & thermal stability) $S_3 = 2$	Overall rank
1 <sup>a</sup> ( $n_1 = 0.8$ )	Tar-PW	EcoP	EcoP	EcoP ( $C_1 = 2.8$ )
2 ( $n_2 = 0.7$ )	Tar-BW	Tar-PW	CTPht-B	Tar-BW ( $C_1 = 2.7$ )
3 ( $n_3 = 0.6$ )	PCWO	CTPht-B	CWO	CTPht-B ( $C_1 = 2.2$ )
4 ( $n_4 = 0.5$ )	Tar-Veg	Tar-Veg	Tar-BW	CWO ( $C_1 = 2.1$ )
5 ( $n_5 = 0.4$ )	CWO	MP	MP	PCWO ( $C_1 = 2.0$ )
6 ( $n_6 = 0.3$ )	MP	Tar-BW	PCWO	MP ( $C_1 = 1.8$ )
7 ( $n_7 = 0.2$ )	EcoP	PCWO	-	Tar-PW
8 <sup>b</sup> ( $n_8 = 0.1$ )	CTPht-B	CWO	-	Tar-Veg

<sup>a</sup> Best.

<sup>b</sup> Worst.

lower extrusion pressure. Tar-PW and Tar-Veg are not ranked in the rheology section of Table 4 due to their limited thermal stability that will not function well as binders for taphole clays.

#### 4.4. Overall ranking

Individual rankings of the examined binders, based on molecular composition, thermal analysis, and rheology, as well as the overall ranking, are summarised in Table 4. The criterion for determining the overall ranking was a combination of the lowest total PAH value, good dynamic viscosity and thermal stability suitable for manufacturing and green strength development, compared to the CTht reference binder. To select the most suitable binder for replacement of CTht, contribution calculation ( $C_1$ ) was done for ranks 1–8, using Equation (2):

$$C_1 = \sum S_n * n_n \quad (2a)$$

where  $S_n$  is the significance coefficient according to the most critical features required from the binder and  $n_n$  is the weighted coefficient based on the ranking position. For both the total PAH and rheology, the significance coefficient ( $S_n$ ) is 2, as both are considered equally important for the purpose of this study, while the thermal stability is denoted with a  $S_n$  value of 1. The weighted coefficients are only based on the position in ranking, meaning if a binder is ranked in the first position of a group, then the  $S$  value is multiplied by 0.8. The calculated contribution ( $C_1$ ) is the sum of all the products ( $S_n n_n$ ).

Based on the ranking from the three groups, i.e., molecular composition, structure and toxicity (PAH content), thermal analysis, and rheology as shown in Table 4, the most favourable binder according to

the investigation is the low PAH pitch (EcoP). The bio-based binder, Tar-BW is ranked second, and both Tar-PW and Tar-Veg are ranked in the last two positions. These two binders have  $C_1$  values of 2.3 and 1.5, respectively, but due to their failure to maintain thermal stability, they are consequently ranked in the last two positions. This is a critical property for use in taphole clay, as low viscosity would not only impede clay flow and compromise the integrity of the clay but also result in the clay not maintaining its shape during extrusion. The coal-based binder (CTPht-B) is placed third primarily because of their high total PAH. These binders, including EcoP, are conventionally used, but they present the well-known dilemma associated with the use of coal-based tars as binders, as indicated by the total PAH results in Table 4. Their high carbon yield, wide volatilization temperature, rheology (viscoelasticity), and thermal stability make them excellent binders for use in taphole clay. However, they have a disadvantage of high total PAH content, which is the reason behind their high carbon yield and good rheological characteristics. The industrial use of CTPht-B can be justified due to its excellent thermal and rheological characteristics. However, the aim of this exercise is to identify suitable non-toxic (zero 16-EPA-PAH) or lower toxicity binders as alternatives to conventional CTht. When compared to other alternatives such as the petroleum-based fluids, they are considered less favourable.

The first petroleum-based binder that is ranked in Tables 4 and is CWO in the fourth position. The MP and PCWO fluids are ranked lower than the coal-based binders. The decision regarding the ranking of the three petroleum-based fluids was done by first examining which consistently received a higher ranking among the three. The crude wax oil (CWO) was consistently ranked higher than the mesophase-forming pitch and PCWO as it has a lower total PAH than the MP and a more shear-thinning liquid compared to PCWO. Similarly, the ranking of PCWO was determined by comparing its performance in thermal analysis and rheology to that of MP, which showed better results and served as a favourable alternative.

If all the above is considered, the top three non-toxic alternative binders to CTht are Tar-BW, CWO and PCWO. Although EcoP is a refined version of normal coal tar pitch, the objective of this study was to investigate the best-suited non-toxic binders (zero 16-EPA-PAH) or the closest possible replacements for conventional CTht. The three non-toxic binders (Tar-BW, CWO, PCWO) derived from this selection process all have low carbon yields, which, when considering the function of a binder, lacks the property of having residual solid material (generally carbon) after heating at high temperature compared to conventional CTht. However, the non-toxic liquid binders are used together with a phenolic resin [36], such as resole, which has a significantly higher carbon yield [37]. This type of resin is one of the main reasons for binder strength when used in taphole clay. The binding liquid (without resole) serves as a binding agent up to the polymerization temperature of the resin (~200 °C), after which the polymerization of the phenolic resin results in low-temperature strength for the clay, which is maintained up to the sintering temperature of the ceramic components in the taphole clay. Various ratios of phenolic resin to liquid binder can be implemented to ensure that the change from a high carbonizing liquid binder such as CTht to a lower carbonization liquid binder such as Tar-BW, CWO, PCWO will attain the same low temperature strength of the taphole clay.

## 5. Conclusions

The selection of alternative binders to CTht for use in taphole clays was carried out using compositional analysis (GC-MS, FTIR/ATR), TGA, and rotational rheology. A group of binders was selected for evaluation and compared to the reference binder, CTht. The results were divided into three groups: molecular composition and structure (toxicity), thermal analysis (degree of volatilization), and rheology (viscosity and thermal stability). Toxicity in this investigation was assessed based on 16-EPA-PAHs, which serves as an indicator of general toxicity. The

volatilization and carbon yield of the fluids were considered as secondary properties during the ranking. The main conclusions drawn from these results are.

- The FTIR data highlighted differences among the aromatic hydrocarbon fluids (CTht, CTPht-B), linear chained hydrocarbon fluids (Tar-PW, Tar-BW, Tar-Veg), and a mixture of both aromatic and aliphatic species (EcoP, MP, CWO, PCWO).
- The analysis of the molecular compositions and structures of the binders showed that the binder with the highest BE-value and total PAH (toxicity) is the low softening point pitch blend (CTPht-B). The binders that have been found to be less toxic are the wood-based tars (Tar-PW, Tar-BW) as well as the petroleum waxy oils (CWO, PCWO). These binders have BE-values below 0.1 compared to the reference binder (BE = 1.65), and their total PAH content is an order of magnitude smaller than the coal-based fluids. The Tar-PW and Tar-BW binders are non-toxic, with a total PAH (16-EPA-PAH) value of zero.
- The thermal analysis results showed variations in the rate of mass loss for each binder, ranging between 0.21 and 0.96 g/°C. The EcoP binder exhibited the highest carbon yield and the lowest degree of mass loss. The petroleum-based oils and mesophase-forming pitch showed reduced carbon yields (below 6% mass). The wood-based tars also had reduced carbon yields, with higher degrees of mass loss, due to their primary aliphatic structures.
- All of the alternative binders exhibited Newtonian behaviour, except for CWO, which could be attributed to the presence of lower density liquids such as moisture in the sample. The dynamic viscosity thermal stability indicated that all binders, except Tar-PW and Tar-Veg, had good thermal stability. The wax oils exhibited a wax appearance temperature between 58 and 65 °C.
- The beechwood tar (Tar-BW) was selected as the most suitable non-toxic binder for replacing CTht in taphole clays, followed by the petroleum-based fluids.

## Declaration of 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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