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Chemically accelerated stabilisation of a cellulose-lignin precursor as a route to high yield carbon fibre production

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Abstract

The production of carbon fibre from bio-based or renewable resources has gained considerable attention in recent years with much of the focus upon cellulose, lignin and cellulose-lignin composite precursor fibres. A critical step in optimizing the manufacture of carbon fibre is the stabilisation process, through which the chemical and physical structure of the precursor fibre is transformed, allowing it to withstand very high temperatures. In this work, thermogravimetric analysis (TGA) is used to explore and optimize stabilisation by simulating different stabilisation profiles. Using this approach, the influence of atmosphere (nitrogen or air), cellulose lignin composition and alternative catalysts on the carbon yield, efficiency and rate of stabilisation, is explored. Carbon dioxide and water vapour released during stabilisation are analyzed by Fourier Transform Infra-Red (FTIR) spectroscopy providing further information on the stabilisation mechanism and the accelerating effect of oxygen and increased char yield (carbon content), especially for lignin. A range of different catalysts are evaluated for their ability to enhance char yield and a phosphorus-based flame retardant (H_3PO_4) proved to be the most effective, in fact a doubling of the char yield was observed.

Introduction:

Low carbon footprint manufacturing is critical to reducing global CO_2 emissions and countering the growing threat of human induced climate change. In addition to the environmental benefits created by the promise of light-weight carbon fibre composites, bio-based carbon fibre enables the transition from fossil fuel derived to bio-based or renewably sourced precursors. Although other bio-based sources of precursor exist, such as chitosan and silk, cellulose and lignin are the first and second most abundant organic polymers on earth, with millions of tons produced by plants and vegetation every year [1,2]. Hence, the use of lignin or cellulose to make carbon fibre represents an enormous opportunity to begin a transformation of carbon fibre composites into a more sustainable industry.

The production of bio-based carbon fibre is not actually new at all, indeed cellulose derived carbon fibre was used in the first light bulb made by Thomas Edison in 1880[3]. However, the low char yield and inferior mechanical properties in comparison to PAN-based carbon fibre soon made cellulose-based carbon fibre uncompetitive, leading to the domination of the industry by PAN, which continues to this day. Cellulose-based carbon fibre is now a niche market product, destined for applications such as thermal ablation which require low thermal conductivity. Demand for carbon fibre in the electric vehicle market is increasing rapidly, however, providing cellulose and lignin-based carbon fibre another opportunity to regain some of their market share. Important factors determining demand are the lower mechanical property requirements and increased focus upon sustainability and functionality. The mechanical property requirements of automotive carbon fibre are low, with a tensile strength of 1.72 GPa and a tensile modulus of 172 GPa[4,5], often being referred to as the properties necessary to initiate wider uptake. These properties are significantly lower than a typical PAN-based carbon fibre, such as T300 which has a tensile strength of about

3 GPa [6] and tensile modulus of about 240 GPa. Carbon fibre made from cellulose and/or lignin has also been shown to have different stabilisation pathways than PAN due to different molecular structures, prompting research into better understanding the stabilisation mechanism. If disadvantages such as low char yield and long stabilisation times can be overcome, bio-based carbon fibre may again become an important part of the carbon fibre market[1,7].

As mentioned above, stabilisation is a critical step in the carbon fibre production process, where the precursor is converted into a thermally stable fibre prior to entering a high-temperature furnace for carbonization. Effective stabilisation not only prevents the deformation of the fibre during carbonization but importantly increases char yield during production[8,9]. The stabilisation of cellulose-based carbon fibre has been widely studied in the 60s and 70s of the 20th century when the production of cellulose-based carbon fibre was still strong, but the proprietary nature of the industry and the lack of suitable characterisation techniques, has resulted in the stabilisation of cellulose remaining not well understood. In contrast, lignin, although providing benefit through increasing char yield, brings more challenges due to its very slow rate of stabilisation[1,10]. Composite fibre based upon lignin and cellulose precursors, however, have been shown recently to overcome some of these challenges, but further improvements are necessary. In this work, the stabilisation of lignin cellulose composite precursor is explored using programmable thermogravimetric analysis (TGA) coupled with Fourier-transform infrared spectroscopy (FTIR) as a function of stabilisation time, atmosphere (nitrogen or air), lignin content and stabilisation catalysts. A variety of isothermal profiles were used in a TGA oven, allowing the fibre to be exposed to high temperature as rapidly as possible, so as to stimulate stabilisation in a continuous carbon fibre production line where the fibre enters the ovens and is instantly exposed to high temperature. Ultimately, the goal of the study was to improve char yield in the shortest possible time thereby promoting the value of an emerging low-cost carbon fibre manufactured from bio-based resources.

Experimental section:

Precursor Fibre:

Composite lignin-cellulose precursor fibres were provided by Aalto University, Finland prepared according to a wet spinning process reported elsewhere[11]. A succinct summary of the process consists of first dissolving the wood pulp and lignin in the ionic liquid 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc) which is then dry-jet wet spun using a piston-spinning unit (Fourné Polymertechnik, Germany), with an air gap of 1 cm prior to the aqueous coagulation bath. The cellulose component of the precursor fibre consisted of pre-hydrolysed kraft birch pulp (Stora Enso Enocell mill in Finland) while the lignin component was organosolv beech lignin powder (Lignocellulosic Biorefinery Pilot Plant, Fraunhofer CBP in Leuna, Germany). Several different precursor fibres with different cellulose lignin compositions including cellulose (100 wt% cellulose), 90-10 (90 wt% cellulose - 10 wt% lignin), 70-30 (70 wt% cellulose - 30 wt% lignin) and 50-50 (50 wt% cellulose - 50 wt% lignin) were prepared.

Preparation of fibres treated with flame retardants:

Table 1: List of flame retardants and soaking method

Number	Chemical	Supplier	Soaking method
1	H_3PO_4	Sigma-Aldrich	Soaking precursors in aqueous solution at a concentration of 3% wt at 80 °C for 5 min.
2	$KH_2PO_4.3H_2O$	Sigma-Aldrich	
3	H_3BO_3	Sigma-Aldrich	
4	Citric acid monohydrate	Sigma-Aldrich	
5	Bi-functional phosphaphenanthrene siloxane	Prepared in house according to method describe here[12]	Soaking precursors in acetone solution at a concentration of 3% wt at 50 °C for 5 min.
6	Hexa-phenoxy-cyclotriphosphazene	Shanghai Yuchuang Chemical Technology	

The chemicals used to evaluate the acceleration of stabilisation are: H_3PO_4, KH_2PO_4, H_3BO_3, citric acid, a bi-functional phosphaphenanthrene siloxane and a hexa-phenoxy-cyclotriphosphazene (HPCTP). Details of suppliers and preparation methods of chemicals are described in Table 1 above. The H_3PO_4, KH_2PO_4, H_3BO_3 and citric acid were dissolved in water at a concentration of 3%wt then heated to 80 °C before soaking in these solutions for 5 min. Bi-functional phosphaphenanthrene siloxane and hexa-phenoxy-cyclotriphosphazene (HPCTP) did not dissolve in water so acetone was used instead. A similar process was conducted but the soaking temperature reduced to 40 °C due to the low boiling point of acetone. After that, the fibres were wiped to any remove excess solvent and dried at 60 °C in an air circulating oven until the weight was unchanged. The final increase in the mass of the fibre was less than 2% regardless of the flame retardants and application process.

Thermogravimetric analysis (TGA):

Thermogravimetric analysis (TGA) was conducted using a Netzsch Libra TGA in the dynamic and isothermal mode to explore the effect of stabilisation and flame retardant on the char yield and overall degradation profiles. Typical TGA were performed by heating to 600 °C at a heating rate of 20 °C /min under nitrogen. Stabilisation was simulated by heating up samples of between 4 and 5 mg at a heating rate of 50 °C /min to 280 °C for unmodified fibres or 200 °C for the flame retardant modified fibres, then holding isothermally for 15, 30, 60 and 120 minutes under an atmosphere of nitrogen or air. The samples were allowed to cool to room temperature then heated to 600 °C at a heating rate of 20 °C /min under nitrogen.

Simultaneous thermal analysis - Fourier-transform infrared spectroscopy (STA-FTIR):

Investigation of the gas emissions during the isothermal stabilisation and dynamic measurements were conducted using a hyphenated simultaneous thermal analysis instrument (STA 8000, Perkin Elmer) connected to a Fourier-Transform Infrared spectrometer (Frontier, Perkin Elmer). Similar thermal methods as per the above TGA experiments were used while making continuous measurements an FTIR spectrum of the pyrolyzed gas over 500 to 4000 cm^{-1} at a resolution of 2 cm^{-1} and a scan rate of 3 s per spectrum. Samples of about 5 mg were performed to establish semi-quantitative comparison of the evolved gas during decomposition.

Results and discussion:

Impact of atmosphere on stabilisation for the 90/10 composite fibre:

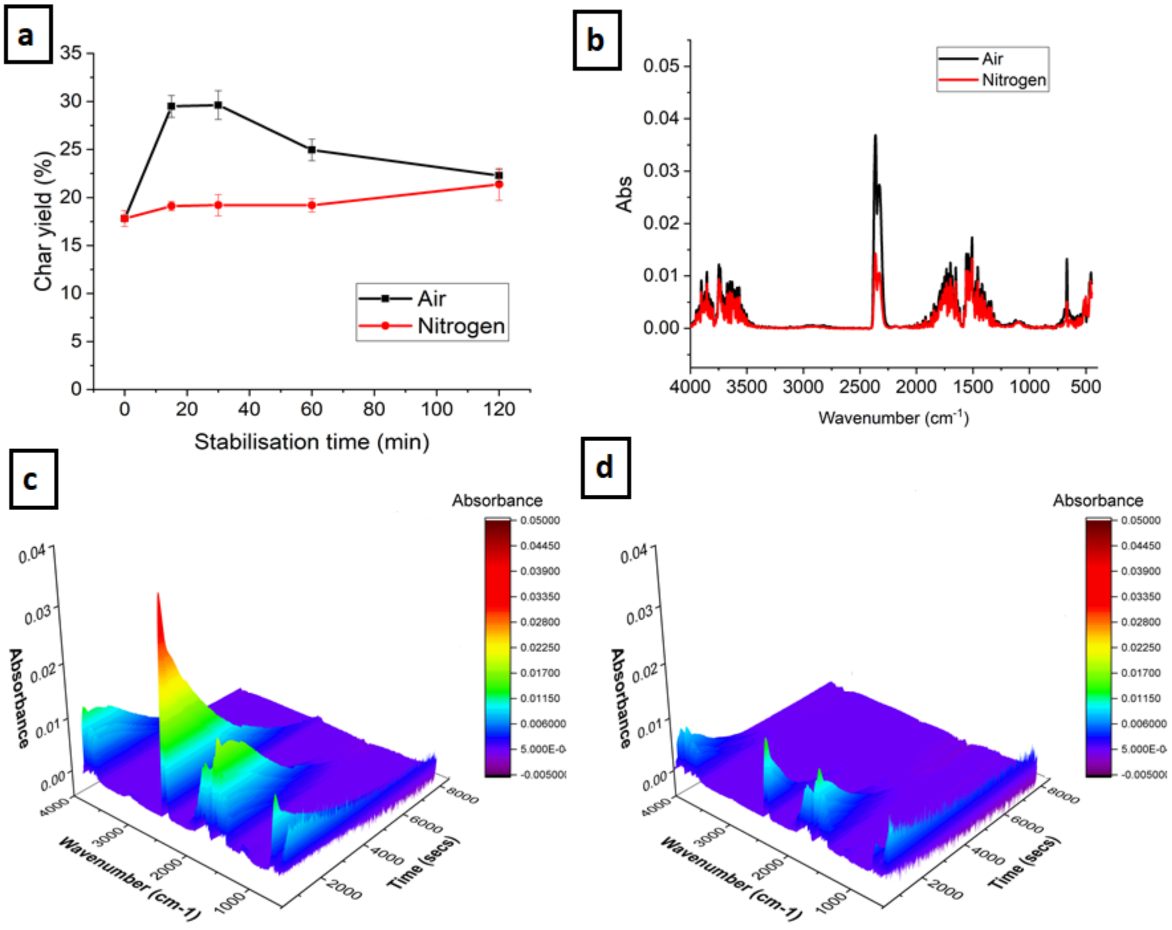

Figure 1: a) Char yield as a function of stabilisation time in air and nitrogen at 280 °C; b) FTIR spectrum at peak emission; gas emission of stabilisation in c) air and d) nitrogen

Air is typically used as the primary atmosphere for stabilisation because it induces crosslinks between polymer chains[8,13], it is inexpensive, safe and available. However, while air has traditional been used, the use of an inert atmosphere for stabilisation warrants exploring. Traditionally stabilisation of PAN is conducted in air, but recent research has shown that a nitrogen pre-treatment can significantly increase the rate of oxidation due to catalysis of cyclization[14]. In contrast, preliminary studies for cellulose have shown that the rate of stabilisation in oxygen is much faster than nitrogen although it reduces the mechanical properties of the fibre[15]. For lignin, there is still a lack of direct comparison between the use of an oxidative and non-oxidative atmosphere since most studies have used oxygen to stabilise the precursor [8,13].

Figure 1a shows the char yield as a function of stabilisation time in both air and nitrogen illustrating the increased char yield regardless of atmosphere and emphasizing the role of stabilisation in converting the precursor into a more thermally stable fibre which increases char yield. However, stabilisation in air has a greater increase in char yield and requires a shorter time to achieve the maximum yield compared with nitrogen. Clearly, the presence of oxygen facilitates thermal degradation at a faster rate than in nitrogen. The oxygen in air more easily attacks C-H and C-OH bonds in the lignin and cellulose polymer structure promoting precursor degradation. As a consequence, more carbonyl groups (C=O) are introduced into the precursor which encourages crosslinking via condensation reactions[16,17] and creates a higher char yield. However, at longer oxidation times, the char yield decreases as carbon is lost through increasing CO_2 emission (peak at 2361 cm^{-1} in Figure 1c).

The gas emissions, during the 120 min stabilisation experiment in air, primarily carbon dioxide and water vapour (H_2O), are shown in Figure 1c, while the corresponding nitrogen experiment is shown in Figure 1d. High concentrations of CO_2 and H_2O are emitted immediately once stabilisation begins, simulating entry into a stabilisation zone on a carbon fibre production line. The emission of both gases reduces over time reflecting the transformation of the precursor into a more thermally stable structure which inhibits volatile evolution. Comparison of Figure 1c and 1d, however, clearly illustrates the overall higher volatile evolution in air compared to nitrogen, but also the more rapid reduction in volatile production under nitrogen. In nitrogen, both CO_2 and H_2O cease being emitted after about 4000 s, whereas in air, H_2O stops at about 6000 s, while CO_2

evolution continues to at least 8000 s. These observations confirm that oxidation/degradation is more efficient and continuous in air compared to nitrogen, complementing other research studies already mentioned[15]. Furthermore, CO_2 emission, when compared to H_2O during oxidation is much higher than under nitrogen, where the evolution of H_2O and CO_2 appear relatively similar. The reason for this is likely because oxidation will preferentially increase the formation of carbonyl groups compared with a nitrogen environment, which in turn facilitates increased CO_2 via decarboxylation during stabilisation[18,19]. In contrast, dehydration would be expected to be less affected by atmosphere due to the high concentration of hydroxyl groups already present in cellulose.

Figure 1b shows the FTIR at the peak of emission in Figure 1c and 1d. The FTIR spectrum contains mostly H_2O (at 1250-1500 cm^{-1} and 3500-4000 cm^{-1}) and CO_2 (at 2300-2400 cm^{-1}) [20,21]. A small peak at 1160 cm^{-1} accounts for C-O-C bonds, while another small band around 2700-3000 cm^{-1} accounts for C-H bonds[22,23]. Both peaks suggest the existence of trace amounts of cellulose or lignin monomers[11,20]. With negligible other pyrolysis products observed, other than H_2O and CO_2, it can be proposed that stabilisation was conducted at a temperature that avoided severe pyrolysis and a reduction in char yield. Importantly, this temperature which is typically chosen from the onset of degradation from the TGA curve, is still able to achieve a comparatively high stabilisation rate[24].

Impact of lignin content on stabilisation:

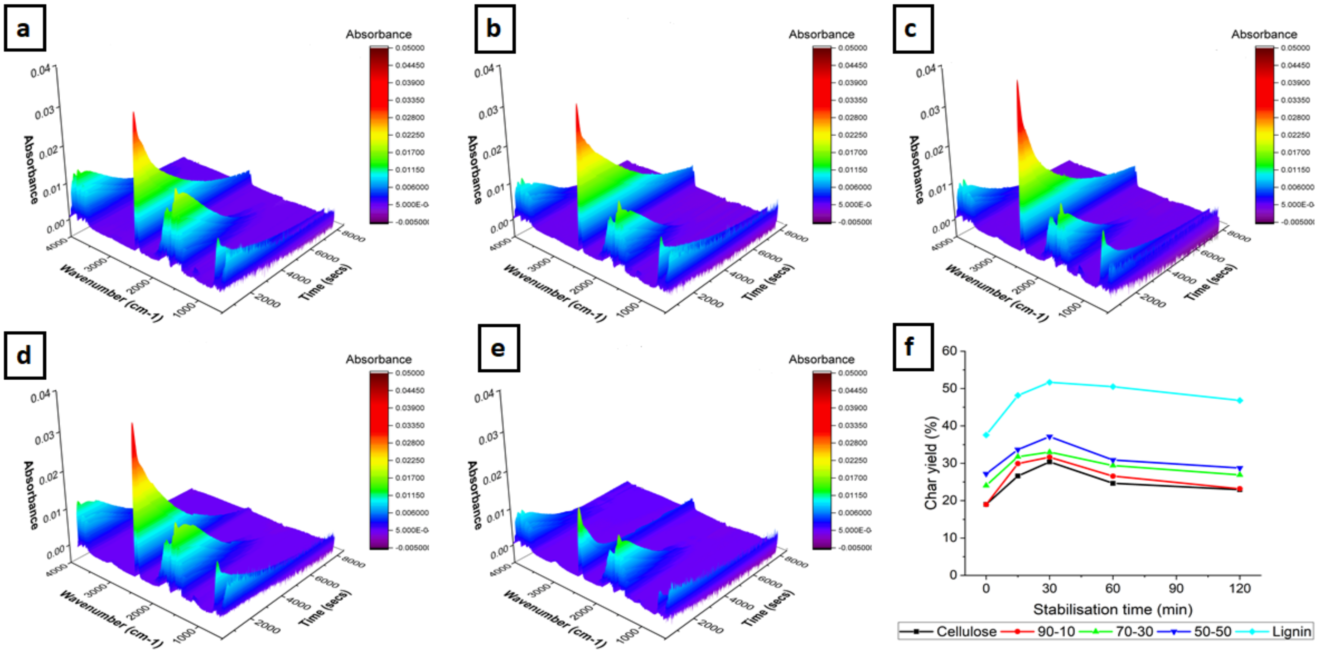

Figure 2: Gas emission for a) cellulose, b) 90-10, c) 70-30, d) 50-50, e) lignin; f) Char yield as a function of stabilisation time in air.

In here, cellulose fibres, composite fibres (90-10, 70-30 and 50-50) and lignin powder were stabilised in air for 120 min. The emission gas during the stabilisation is shown from Figure 2a to 2e. Similar to 90-10 precursor, CO_2 and H_2O are the primary gases emitted during stabilisation, but the increasing lignin content significantly impacted the emission of CO_2. Having an aromatic structure, lignin is harder to be oxidized and therefore will release less CO_2 than cellulose (Figure 3). Indeed, the lower CO_2 emission for 50-50, also significantly reduces overtime, unlike other cellulose-lignin composite fibres.

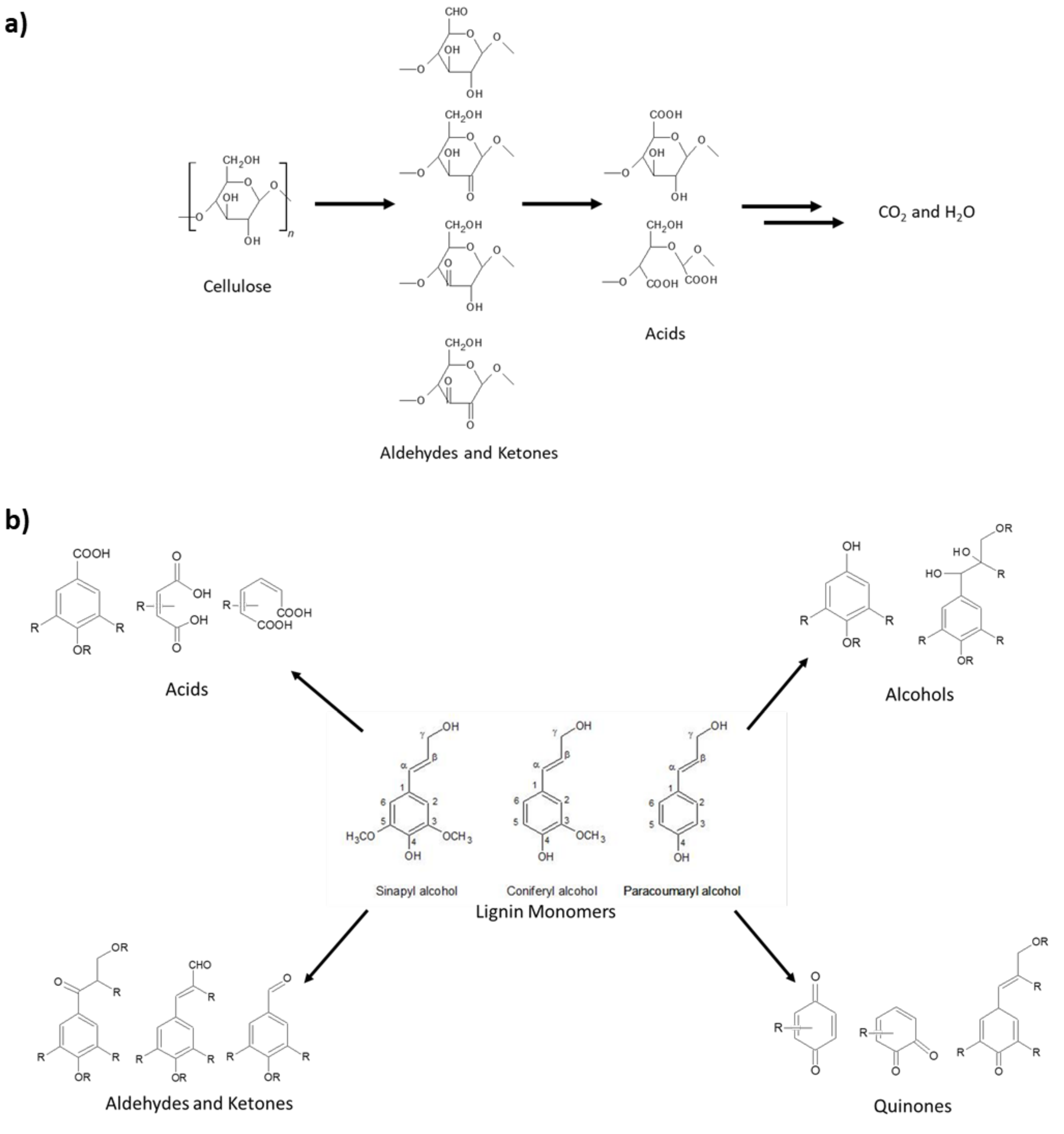

Figure 3: Proposed oxidised products of a) Cellulose; b) Lignin

As shown in Figure 2f, in the absence of any stabilisation, the char yield results are in accord with previous studies investigating the influence of lignin which show that the higher the content of lignin, the higher the observed char yield[11,25]. During stabilisation, similar trends are observed with stabilisation boosting char yield for all samples regardless of lignin and cellulose composition even at short stabilisation times (15 min). This is particularly important because it provides insight into the comparative acceleration of the stabilisation of bio-derived precursors and informs the overall potential economics of carbon fibre production using these bio-fibres. The 90-10 and 70-30 blends appear to display a faster rate of increase in char yield compared with the 50-50. This can be attributed to the higher concentration of cellulose producing more carboxylic acid groups during oxidation which can then react with hydroxyl groups in the lignin to enhance network formation and thus stabilisation. In addition to this, free radical degradation of the cellulose would also produce reactive species likely to react rapidly with the highly aromatic lignin, again enhancing the rate of crosslinking and therefore stabilisation of lignin[10]. After 30 minutes of stabilisation however, the char yield decreases as oxidation produces more CO_2 which weakens the thermal stability of the stabilised precursor. Additionally, stabilisation does not change the impact of lignin content as higher lignin content still achieves a higher char yield regardless of stabilisation time. The increase in char yield is also higher for lignin compared to cellulose, further indicating the dependency of lignin stabilisation on oxygen. Unlike cellulose, lignin is a complex mixture of polyphenolic polymers containing three basic aromatic monomer units as shown in Figure 3[1,24]. Therefore, due to the more thermally stable aromatic structure, oxygen is needed to transform these aromatic rings to aldehydes, ketones, quinones or acids which are able to form a crosslinked network during stabilisation[17,26].

Investigation on stabilisation catalysts for cellulose-lignin composite fibres:

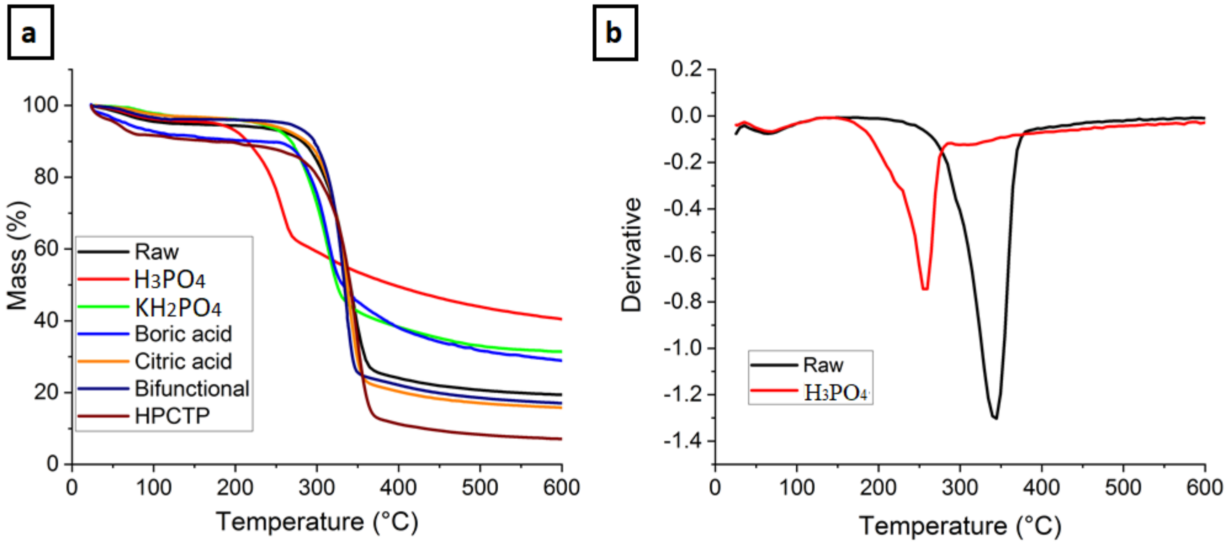

Figure 4: a) Char yield of 90-10 treated with different flame retardants b) Derivative thermogravimetric (DTG) results

The use of flame retardants is an established strategy to improve the char yield in stabilisation for cellulose [27–29] which has also proven successful with cellulose-lignin composite fibres[20,30]. In here, several flame retardants which would be expected to enhance the char yield of a polymer network, have been evaluated on the 90-10 cellulose and lignin composite fibres in this work including: phosphate-based (H_3PO_4, KH_2PO_4)[31,32], boric based (boric acid)[20,33], a common flame retardant (hexa-phenoxy-cyclotriphosphazene- HPCTP)[34], a bio-based flame retardant (citric acid[35–37]) and a phosphorus silicone flame retardants (bi-functional phosphaphenanthrene siloxane[12]).

Common flame retardants such as HPCTP and bi-functional phosphaphenanthrene siloxane did not work well with the composite fibres, most likely due to their lack of solubility in water. Also, given their hydrophobic nature, they do not bind with the cellulose and lignin precursor fibre further reducing their effectiveness. Citric acid, despite being a water-soluble compound, also had no influence on the composite fibres even though it has excellent proven flame retardant ability on other cellulose-based materials such as lyocell[35], aerogel[36] and cotton[37]. The flame-retardant ability of citric acid is based on its ability to crosslink the cellulose via the high concentration of available hydroxyl groups [36,37] which prevent the formation of volatile compounds entering the gaseous phase. Long soaking times are typically used to promote crosslinking with cellulose (24 h)[36] and compared with the short soaking time used here (5 min), it is not surprising that citric acid did not enhance the char yield.

In contrast, simple compounds such as H_3PO_4, KH_2PO_4 and boric acid (H_3BO_3) exhibit excellent ability to improve the char yield with H_3PO_4 being the best followed by KH_2PO_4 and boric acid displaying similar improvements. The solubility in water appears to be the dominant factor in controlling the char yield. For example, H_3PO_4 is miscible in water[38], the solubility of KH_2PO_4 is 208 g/l[39] and H_3BO_3 is 49.2 g/l, respectively, both at 20 °C[40]. Since hydroxyl groups are abundant in cellulose and lignin water-soluble flame retardants would penetrate the composite fibres more readily and thus enhance degradation and therefore char yield.

The onset of pyrolysis happened at a much lower temperature for the H_3PO_4 treated sample compared with the other additives. The pyrolysis temperature reduces from around 280 °C for untreated sample to around 200 °C for H_3PO_4 treated sample. The samples treated with H_3BO_3 and KH_2PO_4 show a slight decrease while others do not change. This reduction of pyrolysis temperature has a significant benefit since it may reduce the energy consumption during stabilisation, an important goal of the work. Further important results disclosed in Figure 4b compares the derivative of the TGA (DTG) result of the raw and H_3PO_4 treated samples. As shown here, the pyrolysis of the H_3PO_4 treated sample occurs at a lower temperature compared to the untreated sample, illustrating the role of H_3PO_4 in promoting degradation. Also, the rate of mass loss of the untreated sample is higher than the treated sample accounting for a faster and more severe degradation of the untreated sample. This suggests a potential sudden release of a high volume of volatile compounds over a small temperature range from 300 °C to 350 °C, which is important as it may lead to the often observed fibre fusion[20,24].

Investigation on the catalytic ability of H_3PO_4:

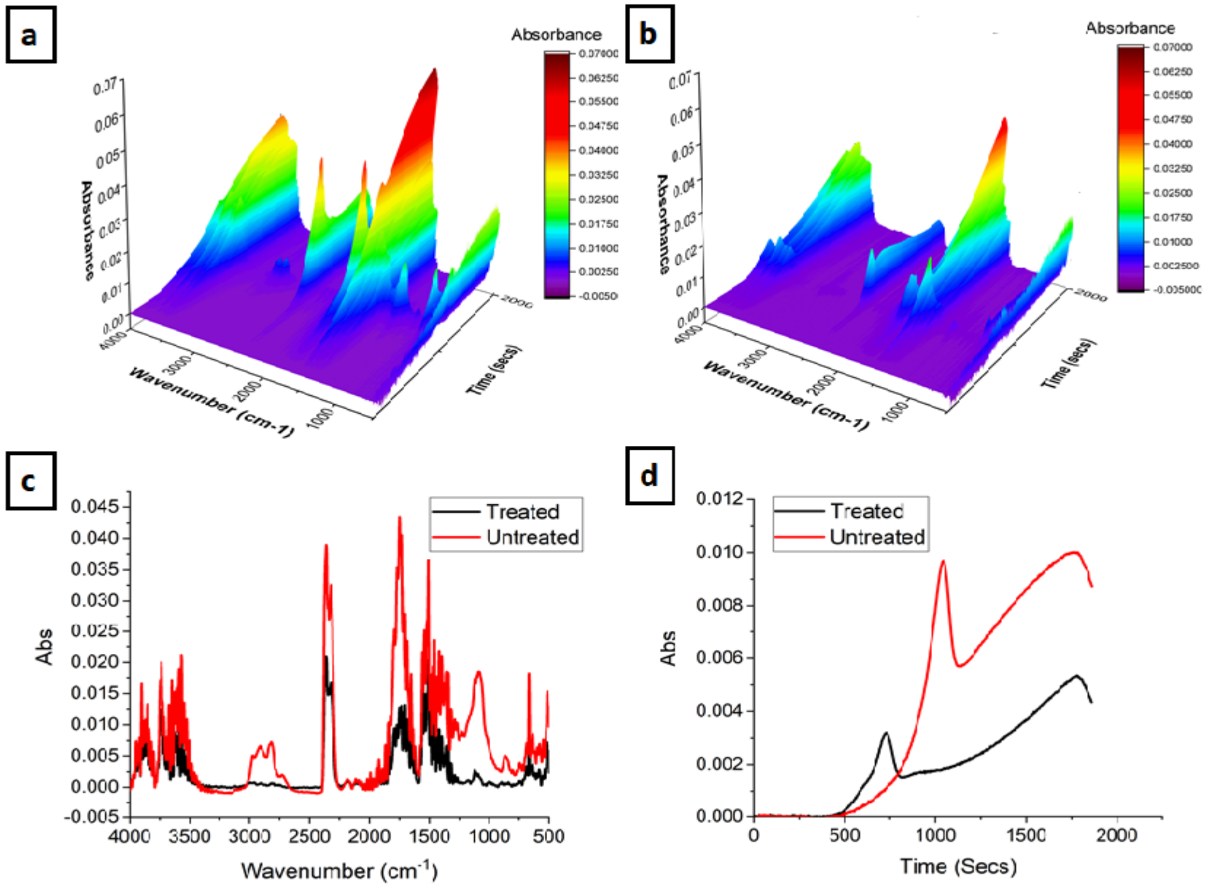

Figure 5: Gas emission overtime for TGA of a) untreated fibres b) treated fibres; c) FTIR at peak of emission; d) Absorbance intensity overtime

The gas emission of precursor fibre (90-10) during TGA measurement shown in Figure 4 is compared with the sample treated with H_3PO_4 in Figure 5a and b, respectively. Overall, the untreated sample has a significantly higher amount of gas emission with complex pyrolysis gas products. To further analyse, the FTIR spectrum at the peak of emission for both samples is compared in Figure 5c. The FTIR spectrum for the gas emission of the treated sample is simple with CO_2 and H_2O as the main products, whereas the FTIR pattern for untreated sample reveals more complex pyrolysis gas products with FTIR peaks from 2700 cm^{-1} to 3000 cm^{-1} which can be attributed to C-H [23], 1122 cm^{-1} for aromatic skeletal and C–O stretch in lignin monomers [41], 1080 cm^{-1} C-O-C pyranose ring skeletal vibrations in cellulose monomers [42]; 870 cm^{-1} C–H out-of-plane deformation vibrations for cellulose pyrolysis products [21,23]. Overall, the untreated sample shows the release of cellulose and lignin monomer units as pyrolysis products causing a significant loss of char yield. In contrast, the use of H_3PO_4 prevents this release with only a small peak at 1122 cm^{-1} for lignin monomers. The main reason is that H_3PO_4 alternates the pyrolysis pathways by accelerating the dehydration and therefore char formation [21,31]. The alternative pyrolysis pathway, significantly reduces the amount of gas pyrolysis as shown in Figure 5d. Moreover, the peak of emission also happens earlier with the catalytic of H_3PO_4 which complements the above DTG results.

Impact of lignin on the catalytic ability of H_3PO_4

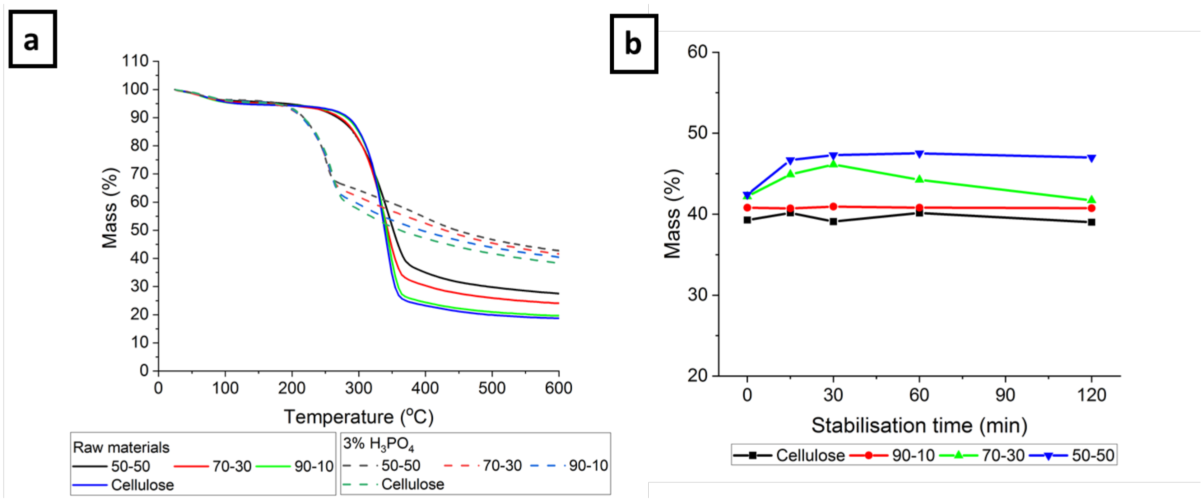

Figure 6: Influence of lignin content on the catalytic ability of H_3PO_4: a) normal TGA b) with simulated stabilisation program in air at 200 °C.

As discussed in the previous section, H_3PO_4 treatment may have a different impact level on cellulose and lignin. There are still some lignin monomers released during the TGA measure while cellulose pyrolysis products were almost eliminated. Therefore, further study on the influence of H_3PO_4 on lignin was conducted by samples with different lignin content (90-10, 70-30, 50-50) and pure cellulose fibres. The TGA results are shown in Figure 6a. Without H_3PO_4 treatment, the char yield increases with the increase of lignin content which was previously shown here as well as previous findings in the field [11,25]. With H_3PO_4 treatment, the char yield is significantly higher for all samples. However, the impact of lignin content on char yield reduces, suggesting a higher impact caused by the H_3PO_4 treatment on cellulose rather than on lignin. The difference in the chemical structure of cellulose and lignin leads to this phenomenon. Cellulose consists of D-glucose units which are easier to dehydrate than phenol units in lignin. Consequently, the impact of H_3PO_4 treatment on cellulose is greater than on lignin.

Further investigation was conducted by stabilising H_3PO_4 treated samples with different time before measuring char yield. The stabilisation temperature was reduced from 280°C to 200°C as the degradation temperature decreases and the results are shown in Figure 6b. Stabilisation has little impact on the char yield of the treated samples of cellulose and 90-10 eliminating the need for stabilisation, but for higher lignin content samples (70-30 and 50-50), stabilisation exhibited a modest increase in char yield, further emphasizing the importance of stabilisation, particularly for lignin.

Conclusion:

In this paper, several different key parameters of stabilisation (atmosphere, cellulose-lignin composition and accelerating catalysts) have been studied by utilizing TGA to simulate stabilisation. The impact of oxygen in stabilisation has been investigated by using two different stabilisation atmospheres: an oxygen-free atmosphere (nitrogen) and an oxygen containing atmosphere (air). It was found that oxygen plays a significant role in increasing the rate of stabilisation and char yield. This was particularly the case for lignin for which the oxidation of the phenol units was promoted, increasing the crosslinking within the precursor. Using flame retardants as a catalyst for stabilisation was shown to be another approach to boost char yield. Several flame retardants were evaluated, but H_3PO_4 was shown to have the best performance with a 100% increase in char yield and reduced stabilisation temperature by 30%. Stabilisation could be avoided when using H_3PO_4 for the high cellulose content fibres (cellulose and 90-10) but showed an effect for the higher-lignin content fibres. In this work, several parameters have been studied as a strategy to increase char yield, without considering the impact upon the morphology and physical properties. Two other effects of these strategies have been to increase the fibre diameter[20] and reduce the char deposit on the fibre surface. The larger fibre diameter would be expected to increase tensile and compressive strength for individual filaments, while the char deposit and other fibre defects[20] are reduced because of the reduced gas emission. TGA has proven to be a simple and effective tool to study the stabilisation of lignin cellulose composite fibre as well as optimizing the stabilisation conditions.

Conflicts of interest:

There are no conflicts to declare.

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Chemically accelerated stabilisation of a cellulose-lignin precursor as a route to high yield carbon fibre production

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