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Review and study on the valorisation of cigarette butts

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Sommario del riassunto

Introduzione

I mozziconi di sigaretta sono uno dei rifiuti solidi più inquinanti. Si stima che ogni anno la produzione media di sigarette sia di circa 5,7 trilioni e ogni giorno una quantità colossale di mozziconi di sigarette viene gettata in natura. Questa è una vera piaga ambientale in termini di inquinamento del suolo e dell'acqua. Per questo, il presente studio si è concentrato sulla valorizzazione di mozziconi di sigaretta, prima facendo un'ampia ed approfondita ricerca bibliografica sugli studi fatti fino ad ora e poi mettendo in pratica una valorizzazione di mozziconi in carboni attivi.

Poiché i mozziconi di sigaretta sono uno dei più grandi rifiuti solidi del mondo, noi, come specie, abbiamo bisogno e urgenza di una valorizzazione. Bisogna notare che purtroppo molti mozziconi di sigaretta vengono gettati nell'ambiente, creando un problema diffuso. Infatti molti studi, come riporterò nelle pagine seguenti, hanno sottolineato la pericolosità di questi rifiuti, perché non solo sono molto tossici (presentando una vasta gamma di sostanze nocive), ma anche perché la loro decomposizione (da parte di batteri e funghi) richiede molto tempo, quindi si accumulano nell'ambiente. Questi pericolosi rifiuti possono causare danni considerevoli e sostanziali all'ambiente nel suo insieme.

Per risolvere questo enorme problema, dobbiamo trovare un modo intelligente per raccogliere e stoccare questi rifiuti e soprattutto trovare un modo sostenibile per riciclarli. Questo processo non solo porterà vantaggi economici, poiché saremo in grado di fare un nuovo prodotto da un rifiuto, ma ci aiuterà anche a pulire l'ambiente. I prodotti che si possono realizzare sono i più vari, infatti, possiamo avere produzioni ad alto valore aggiunto, ma che hanno bisogno di meno materiale di partenza e anche processi che possono utilizzare più mozziconi di sigaretta, pur producendo un output meno pregiato. La scelta tra i due non è vincolante, data la grande quantità di rifiuti presenti. Tra le opzioni di riciclo che sono state trovate in bibliografia ci sono la produzione di aerogel di acetato di cellulosa, che può servire come materiale per isolamento termico, materiali per assorbimento del suono, la fabbricazione di biocidi, materiale da aggregare in mattoni di argilla e calcestruzzo bituminoso, materiale di rinforzo per gomme, materia prima per produzione di polpa di cellulosa (per produrre carta), l'uso come carrier di biofilm, la produzione di carboni attivi e supporto per catalizzatori.

Tutte queste proposizioni di valorizzazione e riciclo sono state analizzate e riassunte, così da fornire al lettore una prima e preliminare lista delle più importanti e promettenti idee portate avanti a livello sperimentale (e non solo). Inoltre, è stata anche portata avanti una ricerca sulle aziende che già ad oggi stanno riciclando i mozziconi di sigaretta in nuovi prodotti o materiali: una recensione di queste aziende e della loro attività è stata fatta. Dalle varie analisi riportate, le industrie analizzate hanno la possibilità di essere punti centrali e pietre angolari nel riciclo di mozziconi di sigaretta, dato che hanno una struttura di raccolta, stoccaggio e manifattura e una organizzazione aziendale già ad oggi.

Per quanto riguarda la fase di laboratorio, più aspetti sono stati ispezionati. A partire dai risultati ottenuti dagli studi bibliografici, abbiamo analizzato i diversi percorsi di valorizzazione in carbone attivo per trovare quelli che volevamo eseguire durante le nostre prove di laboratorio: la pirolisi per ottenere carboni attivi è fatta esclusivamente sui filtri, fatti in acetato di cellulosa. I filtri sono stati pirolizzati in una fornace a 600, 700 e 800 °C, con diversi tempi di permanenza, compresi tra 5 minuti e 2 ore. Dalle analisi svolte in seguito, su tutte l'analisi BET per valutare la superficie specifica, è stato dimostrato a tutti gli effetti che dai filtri di mozziconi di sigaretta si possono produrre carboni attivi, con una superficie specifica media di circa 500 m^2/g e valori massimi di 700 m^2/g.

In seguito, è stata fatta una fase ottimizzazione, operando dei pre e post trattamenti. Queste operazioni sono state svolte basandoci sempre su articoli citati in bibliografia. All'inizio, lo studio si è concentrato sull'attivazione dei filtri con immersione in NaOH (idrossido di sodio) e KOH (idrossido di potassio) e seguente trattamento termico. Dalle analisi SEM e BET è chiaro che questo pretrattamento non abbia funzionato e la spiegazione che il presente studio da è che la presenza di cristalli di sodio (o potassio, se l'attivazione è stata fatta con KOH) abbia impedito la formazione di carboni attivi. Infatti, il sodio fondendo a una temperatura più bassa di quella di degradazione delle fibre di acetato di cellulosa, agisce come un rivestimento ed impedisce la reazione di pirolisi tra le fibre. Con i carboni prodotti in questo modo, le superfici specifiche ottenute sono dunque più basse di quelle ottenute da filtri non trattati e nell'intorno di 50 m^2/g. Successivamente sono stati analizzati il prelavaggio dei filtri di mozziconi di sigarette con etanolo e l'estrazione con CO_2 supercritica. Se per quest'ultimo non è stato possibile avere dei risultati per mancanza di tempo, mentre per il lavaggio ad etanolo è stato verificato un abbassamento delle prestazioni. Invece per quanto riguarda i post trattamenti, è stata notato un aumento dell'area specifica (come d'altronde verificato dalle referenze di letteratura), ma i dati ottenuti sono troppo pochi per offrire certezze.

Nel presente studio verrà inoltre riportata l'analisi più completa possibile dei carboni attivi prodotti nella campagna sperimentale, con confronti tra loro e con i risultati trovati nei riferimenti. Per poter fornire elementi utili ai futuri studi sulla ricerca di valorizzazione dei mozziconi di sigaretta in carboni attivi è stato sviluppato un primo studio sulla cinetica di pirolisi, per fornire una prima stima (e sicuramente imprecisa) di source terms per la modellizzazione alla scala di reattori piloti. Oltre al metodo BET per valutare l'area superficiale specifica (che è stato anche il parametro principale del successo degli esperimenti), tra le analisi ci sono l'adsorbimento di coloranti (Rhodamine B e blu di metilene), le analisi SEM sulle le materie prime e i carboni e l'analisi FTIR.

Infine, è utile ricordare che questo studio è un progetto preliminare, un proto-progetto potremmo dire. Mentre la ricerca bibliografica è stata fatta su lavori svolti da altri e già controllati e certificati, i risultati sperimentali ottenuti nel presente studio sono ancora alla ricerca di conferme e possono dare solamente una prima indicazione della via da seguire per la valorizzazione in carboni attivi. Mancano sicuramente un'analisi sulla variabilità della materia prima e soprattutto la ripetibilità degli esperimenti. Anche se per ogni esperimento è stato dato un protocollo, così da assicurare una possibilità di ripetere l'esperimento ad un altro soggetto, per massimizzare il numero di temperature, tempi di permanenza e trattamenti, i test sono stati svolti una volta sola. Questo non legittima il nostro lavoro, è vero, ma deve essere visto in un'ottica di introduzione allo studio di questo argomento (la letteratura tecnico-scientifica su questo soggetto è globalmente abbastanza modesta), richiedendo dunque una prima fase di pianificazione: con questo studio speriamo di sopperire al bisogno di test preliminari per identificare tendenze.

Contesto

Per iniziare ad analizzare il problema, mostriamo qui alcune statistiche sul consumo di sigarette e sull'inquinamento da mozziconi. Questi dati sono illustrati grazie alle informazioni e agli strumenti forniti dal Tobacco Altlas [18], una risorsa online, creata in collaborazione tra l'American Cancer Society e Vital Strategies, che delinea la natura e la portata dell'epidemia di tabacco e indica la strada per soluzioni chiare e provate. Da questa fonte abbiamo osservato che in Italia sono fumate circa 1493 sigarette per persona all'anno. Considerando che questo numero è la stima del consumo di sigarette legalmente vendute a macchina e rollate in proprio e considerando la popolazione di età ≥ 15 anni, possiamo affermare che, in media, ogni adulto fuma circa 4 sigarette al giorno. Per un confronto questo numero è più basso in Francia (1090), leggermente inferiore negli Stati Uniti d'America (1017) e quasi il doppio in Cina (2043).

La produzione di prodotti a base di tabacco, con le sigarette in testa, è immensa. Molteplici fonti riportano che ogni anno la produzione media di sigarette è di circa 5,7 trilioni (5.700.000.000.000), ma dobbiamo segnalare che dopo molti anni il numero di sigarette fumate nel mondo sta finalmente diminuendo. Inoltre, come riporta Tobacco Altas [18], il processo di fabbricazione dei prodotti del tabacco genera un'enorme quantità di rifiuti: l'ultima stima rigorosa, fatta nel 1995, riportava che l'industria del tabacco produce più di 2,5 milioni di tonnellate di rifiuti di fabbricazione e la maggior parte di questi rifiuti contiene sostanze chimiche pericolose (per esempio la nicotina).

Il mozzicone di sigaretta è fatto di 4 componenti: carta, cenere, tabacco (e additivi) e il filtro. Secondo Poppendieck et al. (2016) [20], un mozzicone (detto anche CB, cigarette butt) può essere definito come la sigaretta che rimane alla conclusione della fase di combustione dopo aver fumato. In genere è circa il 30% della lunghezza originale della sigaretta. La carta può impiegare circa 5 mesi per biodegradarsi nell'ambiente. Inoltre, come detto prima, abbiamo additivi incorporati nella miscela di tabacco: queste sostanze sono usate come umettanti (sostanze igroscopiche usate per mantenere le cose umide, impedendo o ritardando l'essiccazione del tabacco e in una sigaretta possiamo trovare glicerolo e glicole propilenico) o additivi di sapore. Infine e più importante, abbiamo il filtro. Questa parte del mozzicone, come affermano Kurmus e Mohajerani (2020) [11], è fatta principalmente di acetato di cellulosa: questo aumenta l'efficacia di filtraggio, ma limita il suo potenziale di biodegradazione. Siccome questa molecola ha un alto grado di sostituzione dell'acetato, la cellulosa nel mozzicone non può accedere ai microrganismi dell'ambiente per la decomposizione biologica e quindi questo prodotto è solo fotodegradabile. Inoltre, il tasso di decomposizione delle sigarette convenzionali è ostacolato dall'elevata compattazione delle fibre e dall'aggiunta di plastificanti. Questo è il motivo per cui ci vuole molto tempo perché i CB si degradino.

Questa immagine al SEM di un filtro di mozzicone di sigaretta mostra chiaramente la sezione a Y delle fibre di acetato di cellulosa:

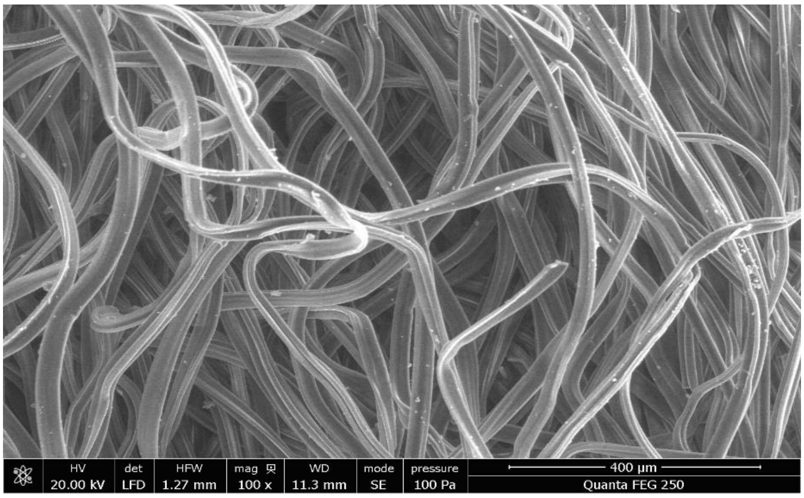

Figura [3], SEM di un filtro di un mozzicone di sigaretta, elaborazione dell'autore.

Purtroppo, molti fumatori hanno la cattiva abitudine di gettare i loro mozziconi di sigaretta per terra, ignorando il grande danno ambientale che questo può causare. Per studiare le fasi di degradazione dei CB e per comprendere meglio la dinamica di questi processi, Bonanomi et al. (2020) [13] hanno impostato un esperimento di 5 anni, sperimentando diverse condizioni ambientali. Alcuni campioni sono stati incubati in condizioni controllate e con diversi tipi di suolo (per esempio cambiando le proprietà fisico-chimiche del suolo) e in assenza di suolo. Hanno così verificato che i mozziconi sono più tossici subito dopo il fumo, e successivamente gli effetti inibitori diminuiscono durante la decomposizione. Tuttavia, hanno anche rivelato un secondo picco di tossicità in una fase intermedia (nella fase da 2 a 5 anni), che suggerisce un pericolo a lungo termine posto dai CB gettati nell'ambiente. Durante questo studio a lungo termine hanno anche scoperto che la perdita di massa dei mozziconi ha una tendenza di degradazione a tre stadi. Durante i primi 30 giorni ha luogo una rapida perdita di massa di circa il 20%, in associazione con la rapida degradazione dello strato esterno cartaceo. Poi, nei due anni successivi, il processo di decomposizione è rallentato, raggiungendo una perdita di massa complessiva di ~35%. Dopo 5 anni, le CB incubate in condizioni di laboratorio hanno mostrato un'elevata perdita di massa in tutti i tipi di suolo, raggiungendo circa l'80%.

Un altro fattore importante sono i contenuti dei mozziconi di sigaretta. Il fumo è una seria minaccia per gli esseri umani. Per ogni sigaretta fumata, un fumatore riceve circa 1,4-2,2 mg di composti pericolosi. Nel 2012 la Food and Drug Administration (FDA) degli Stati Uniti ha prodotto un elenco preliminare di 93 costituenti nocivi e potenzialmente nocivi nei prodotti del tabacco e nel fumo di tabacco che sono collegati a gravi effetti sulla salute: cancro, malattie cardiovascolari, effetti respiratori, problemi riproduttivi e dipendenza. Durante le fasi di coltivazione del tabacco e di produzione delle sigarette, vengono utilizzate molte sostanze chimiche e i residui di queste sostanze si possono trovare nei mozziconi di sigaretta. Tra questi, possiamo trovare erbicidi, pesticidi, insetticidi, rodenticidi e fungicidi. Inoltre, più di 4000 sostanze chimiche possono essere introdotte nell'ambiente o trattenute dai mozziconi di sigaretta durante il fumo. Da queste sostanze deriva un'enorme minaccia, dato che tra di loro abbiamo più di 50 composti che sono noti cancerogeni per l'uomo. Alcune delle sostanze chimiche che sono state trovate sono: ossidi di azoto, benzene, acetaldeide, formaldeide, fenolo, argon, idrocarburi policiclici aromatici, ammoniaca, monossido di carbonio, piridine e acetone. È vero che alcuni composti sono troppo volatili per essere trattenuti nel filtro e altri vengono trattenuti ma è molto improbabile che vengano rilasciati dai mozziconi di sigaretta perché non sono abbastanza volatili, ma il filtro trattiene la nicotina, etilfenolo e molti altri composti. Tutte queste sostanze chimiche rappresentano un pericolo per gli ecosistemi. Slaughter et al. [16] hanno studiato il ruolo della nicotina e dell'etilfenolo nell'ecotossicità. L'etilfenolo è usato come agente aromatizzante del tabacco ed è presente nel fumo di sigaretta: è stato dimostrato che questa sostanza chimica è tossica per gli organismi acquatici. Come sottolineano Araújo e Costa (2019) [15], gli effetti tossici della nicotina sui pesci sono stati studiati per più di 50 anni. Un articolo del 1970 (Konar, Nicotine as a Fish Poison [22]) ha mostrato che la soluzione diluita di nicotina testata sui pesci è associata a vari sintomi come avvelenamento acuto, paralisi delle branchie, convulsioni e infine morte.

Quindi la pericolosità ambientale di questi rifiuti è enorme. Citando da Kurmus e Mohajerani (2020) [11], che riassumono perfettamente il problema, "quando i mozziconi sono disseminati nell'ambiente, quantità significative di sostanze chimiche tossiche vengono lisciviate e potenzialmente accumulate in canali d'acqua, strade, strisce naturali e sentieri, ponendo così una seria minaccia agli organismi locali e alle specie acquatiche." Tutti gli studi visionati suggeriscono che più a lungo i CB rimangono nell'ambiente, peggiore è l'inquinamento causato. Secondo Araújo e Costa (2019) [15], un solo mozzicone di sigaretta può contaminare oltre 1000 L di acqua: si tratta quindi di una minaccia rilevante per la qualità delle acque urbane, compresi i serbatoi di approvvigionamento. Come osservano Bonanomi et al. (2020) [13], i mozziconi di sigaretta minacciano notevolmente anche la sicurezza degli organismi biologici che vivono in quegli ecosistemi. Molti autori, dopo aver raccolto un'enorme quantità di dati, hanno riferito che i mozziconi di sigaretta disseminati costituiscono una minaccia tossica per una grande quantità di animali come lumache, crostacei, insetti e piante. Inoltre, le sostanze chimiche presenti nei CB possono anche interferire con il comportamento degli uccelli e dei pesci più grandi.

Ricerca bibliografica sulla valorizzazione dei mozziconi di sigaretta

Ad oggi, i due metodi di smaltimento per la raccolta dei mozziconi di sigaretta sono la messa in discarica e l'incenerimento, ma entrambi i metodi sono costosi e hanno alti rischi di esposizione a fumi inquinanti pericolosi, che possono essere estremamente pericolosi per l'ambiente e la salute umana. Questi metodi convenzionali di raccolta e smaltimento non sono né sostenibili né economicamente fattibili né sicuri dal punto di vista ambientale.

Dalla mia ricerca bibliografica ho trovato che attualmente esistono diverse possibilità di riciclaggio dei mozziconi di sigaretta. Questi percorsi di valorizzazione vanno da applicazioni con prodotti finali di alto valore a quelle con zero o basso valore aggiunto, che hanno l'unico obiettivo di liberarsi di questi rifiuti. Le opzioni che in questo momento sono considerate come le scelte migliori sono le applicazioni di produzione di energia, l'adsorbimento chimico e la creazione di nanomateriali, ma molti altri percorsi di valorizzazione sono possibili e possono essere implementati. Un esempio è l'incorporazione dei CB nella costruzione civile, che è molto interessante se consideriamo il numero significativo di mozziconi che potrebbero essere utilizzati.

Sono stati pubblicati molti nuovi articoli sul riciclaggio dei mozziconi e molti risultati incoraggianti, anche se la letteratura sull'argomento è comunque abbastanza scarsa. Sono stati studiati diversi metodi e tra questi abbiamo il riciclaggio dei mozziconi di sigaretta in mattoni di argilla cotti e cemento asfaltato, come carboni attivi, come materiale fonoassorbente, isolante termico e molti altri. Lo scopo di questo studio è quello di identificare le migliori soluzioni e tecnologie per il riciclaggio dei CB, confrontando i risultati e facendo attenzione all'applicabilità ai contesti reali. L'obiettivo è ridurre la presenza di questi materiali pericolosi nell'ambiente e sponsorizzare la fabbricazione di un prodotto a partire da un rifiuto, seguendo i principi dell'economia circolare e dello sviluppo sostenibile.

Soluzioni per la valorizzazione

Nelle pagine seguenti sono riportate le più importanti soluzioni di riciclaggio trovate e una loro descrizione. Per maggiori informazioni si faccia riferimento al testo in inglese.

Una prima via di valorizzazione è quella di incorporare i mozziconi di sigaretta in **mattoni di argilla**. Questi sono fatti con argilla e sabbia, legati insieme ad alte temperature, fornendo così un materiale da costruzione incredibilmente forte. Lo studio di Mohajerani et al. (2016) [23] riporta che l'incorporazione di materiali di scarto nei mattoni di argilla cotta è già stata studiata per altri tipi di rifiuti. Questa potrebbe essere una buona idea poiché un gran numero di mozziconi potrebbe essere smaltito con queste tecniche. Gli autori hanno scoperto che c'è una diminuzione della resistenza alla compressione tra il contenuto di CB allo 0% e il contenuto di mozziconi al 10%, hanno allora proposto un'incorporazione dell'1% di CB in peso nel processo di fabbricazione dei mattoni di argilla cotti, che non dovrebbe cambiare le proprietà meccaniche del prodotto finale. Inoltre, mescolando i mozziconi nei mattoni di argilla, con un contenuto del 2,5% di mozziconi c'è un risparmio del 30% di energia di cottura.

Lo stesso concetto si applica all'incorporare mozziconi in **calcestruzzo d'asfalto**, un materiale composito comunemente usato per il rivestimento delle strade. Consiste di aggregato minerale legato insieme, legante bituminoso e riempitivo. L'applicazione di CB o di altri materiali di scarto nella produzione di miscele di asfalto può risolvere un importante problema ambientale, poiché non solo potrebbe ridurre la domanda di aggregati naturali, ma anche smaltire un rifiuto e possibilmente migliorare le prestazioni del calcestruzzo d'asfalto.

Un'altra via è quella del **rinforzo in gomma naturale**. La gomma naturale è altamente resiliente, ma non ha risultati eccezionali in aspetti come il modulo e la durezza. Queste caratteristiche possono tuttavia essere migliorate formando un composito con rinforzi. Lai et al. [9], nel loro lavoro del 2015 hanno riferito che le fibre di acetato di cellulosa del filtro possono aiutare a migliorare le proprietà meccaniche della gomma perché rimangono stabili fino a 300 °C, una temperatura adatta alla maggior parte delle applicazioni che richiedono la gomma. Gli autori hanno scoperto che l'aggiunta del 4% in peso di acetato di cellulosa al materiale è l'optimum per essere vantaggioso nel migliorare le proprietà reologiche e meccaniche. La resistenza alla trazione, la resistenza allo strappo e la coppia massima sono state migliorate, ma saranno necessarie ulteriori ricerche in questo campo per trovare maggiori informazioni sulla tossicità di questo prodotto.

Nel loro articolo del 2017, d'Heni Teixeira et al. [25] hanno fatto una ricerca sullo sviluppo di un processo per riciclare mozziconi di sigaretta in **pasta di cellulosa**, un prodotto fibroso lignocellulosico fabbricato estraendo chimicamente o meccanicamente le fibre di cellulosa dal legno e che è la principale materia prima utilizzata nell'industria della carta. L'idea principale dietro la produzione di pasta di cellulosa dai CB è di separare tutto il contenuto di cellulosa nel mozzicone con un'idrolisi dell'acetato di cellulosa dal filtro in presenza di NaOH.

Una buona via di riciclo è quella di produrre un **materiale idrofobo-oleofilo**, come studiato da Liu et al. [10] nel 2020. I gruppi idrofili sui mozziconi di sigaretta sono "consumati" attraverso legami idrogeno con l'aggiunta di polidopamina idrofila (PDA). Nel frattempo, le parti idrofobiche sono esposte, così sono stati ottenuti materiali idrofobici-oleofili. Questi materiali hanno prestazioni eccellenti nel rimuovere l'olio e separarlo dall'acqua: l'efficienza è stata riportata come superiore al 99,77%. Inoltre, questi materiali hanno dimostrato di essere durevoli in condizioni difficili e riescono a rimanere stabili anche dopo il più cicli.

Un'applicazione interessante è stata proposta da Dieng et al. (2013) [28], per produrre un **biocida**. In questo articolo hanno voluto verificare l'influenza dei mozziconi di sigaretta su Aedes aegypti, un vettore della Dengue (una malattia detta anche influenza tropicale e trasmessa dalla puntura di una zanzara Aedes portatrice di un virus della dengue). Come già detto prima, nei mozziconi di sigaretta ci sono prodotti chimici noti per avere proprietà di insetticida ed erbicida. Utilizzando soluzioni di percolato ottenute immergendo i CB in acqua distillata e variandone il contenuto, gli autori hanno studiato i tassi di mortalità di A. aegypti in diversi stadi di evoluzione delle larve. Dai risultati è emerso che, nel complesso, i mozziconi di sigaretta hanno mostrato attività insetticide contro le larve di zanzara. Tuttavia, si deve anche considerare che ci sono problemi derivanti da questo approccio. Quando contaminiamo un habitat con CB, come abbiamo già detto, è l'intero ecosistema che soffre e il danno può essere portato anche agli esseri umani. Tuttavia, lo studio propone anche un'altra idea interessante: si potrebbero produrre anche posacenere che possano fungere da trappole letali per A. aegypti.

Sono stati fatti studi sul riciclaggio dei mozziconi come **materiale fonoassorbente**. I campioni sono stati preparati mettendo manualmente (senza usare alcun tipo di legante) un certo numero di mozziconi di sigaretta nel tubo di impedenza, lo strumento usato per fare tutte le misure. Gómez Escobar et al. (2017) [2] hanno ottenuto valori di assorbimento abbastanza alti per tutti i campioni, indicando che questo metodo può essere utilizzato per fare materiali fonoassorbenti. Usando i CB come materiale assorbente, grazie alla natura porosa di questo rifiuto, è stato trovato un alto coefficiente di assorbimento di <0,90 dalle medie frequenze (>2000 Hz). I risultati hanno mostrato che le prestazioni acustiche di questi nuovi materiali sono simili a quelle di altri materiali fonoassorbenti commerciali. Come sempre con questo tipo di rifiuti, è anche fondamentale notare che i mozziconi di sigaretta contengono sostanze chimiche tossiche, e, quindi, richiederanno eventualmente qualche pretrattamento.

Sabzali et al. [29] nel loro 2011 hanno pubblicato uno studio volto a sviluppare un nuovo, efficiente e poco costoso **vettore di biofilm** con l'uso di filtri di sigarette. Questo studio ha scoperto che i filtri dei CB possono essere utilizzati come un mezzo efficace e per la rimozione di fosfato e materia organica dalle acque reflue.

Un'altra via di valorizzazione è la fabbricazione di **aerogel di acetato di cellulosa** (CA) fatto dai filtri di mozziconi di sigaretta. L'aerogel di CA è stato fabbricato con un metodo economico di liofilizzazione usando l'alcool polivinilico (PVA in breve) come reticolante. Gli aerogel di CA prodotti da Chau et al. (2020) [6] hanno mostrato una densità estremamente bassa (tra 0,003 kg/m^3 e 0,5 kg/m^3), un'alta porosità (tra 80% e 99,8%), una grande superficie specifica (tra 100 m^2/g e 1600 m^2/g) e una bassa conduttività termica (tra 0,034 e 0,039 W/(m*K)). Quindi, da questi risultati sperimentali possiamo vedere che l'aerogel CA è un materiale promettente per usi futuri nell'isolamento termico. Gli aerogel di CA hanno quindi una conduttività termica nella gamma degli altri materiali tradizionali utilizzati per l'isolamento termico e potrebbero essere utilizzati in situazioni industriali e di vita reale. Ad esempio, la lana di vetro ha una conducibilità termica tra 0,031 e 0,040 W/(m*K) e va notato che molti dei comuni materiali utilizzati per l'isolamento termico sono per lo più prodotti da risorse non rinnovabili e quindi hanno un impatto sull'ambiente.

La valorizzazione che è stata analizzata più a fondo e che è poi stata sviluppata nella fase sperimentale è la produzione di **carboni attivi**. Il carbone attivo è un materiale costituito essenzialmente da materiale carbonioso con una struttura porosa, che ha generalmente un'elevata superficie specifica, che gli conferisce un'alta capacità di adsorbimento. Di conseguenza, la produzione industriale di carboni attivi viene utilizzata per varie applicazioni come la cattura di inquinanti in fase gassosa o acquosa, processi di separazione dei gas e così via.

Nel 2002, Polarz et al. [30] hanno fabbricato carboni attivi dall'acetato di cellulosa presente nei filtri dei mozziconi di sigaretta. Il prodotto è stato ottenuto con un trattamento termico in condizioni inerti: le temperature di carbonizzazione sono state impostate a 800 °C e il tempo di mantenimento della carbonizzazione è stato regolato a 2 ore, quindi il processo è conveniente e non richiede ampi metodi preparatori. Il risultato principale è stato quello di dimostrare che biomolecole complesse come l'acetato di cellulosa possono essere una possibile fonte di carboni porosi e che questi prodotti hanno buone proprietà. Il carbonio attivo realizzato presentava posizioni ben definite su diverse scale di lunghezza che vanno dal micrometro al nanometro. Uno schema del processo è il seguente:

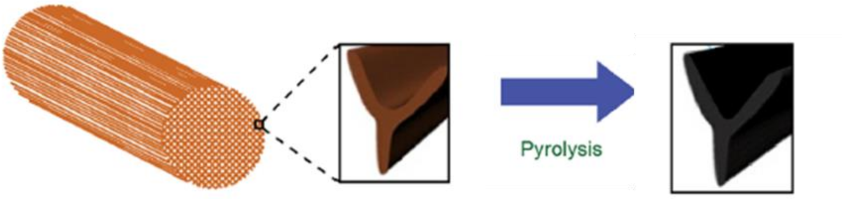

Figura [13], filtri CB pirolisi, modificata da [11].

Dopo il trattamento termico, come riporta questo schema, il filtro di acetato di cellulosa, grazie a una trasformazione morfologica, diventa un materiale nero simile al carbonio e l'area superficiale specifica era di 262 m^2/g (ottenuta con una caratterizzazione BET).

Koochaki et al. [5] nella loro pubblicazione del 2019, hanno realizzato carboni attivi partendo dai filtri di mozziconi con impregnazione con diverse soluzioni di idrossido di sodio. I filtri sono stati impregnati in soluzioni di NaOH con i seguenti rapporti (in peso): 12, 24 e 48% w/w. Successivamente il prodotto ottenuto è stato carbonizzato in fornace elettrica, in atmosfera inerte (introducendo azoto) a 400 °C per 2 ore. In un primo momento Koochaki et al. (2019) [5] hanno eseguito un'analisi elementare e hanno mostrato che la percentuale di carbonio è dell'81,73% e la percentuale di ossigeno presente del 18,27%. Pertanto, l'esistenza di ossigeno nei campioni potrebbe essere causata dall'esistenza di gruppi funzionali ossigenati sulla superficie delle fibre. L'area superficiale specifica media ottenuta è tra 900 e 1100 m^2/g, maggiori rispetto a quelle dei carboni attivati fisicamente. Questo è probabilmente spiegato dal fatto che l'NaOH "gonfia" le fibre di acetato di cellulosa e così rimuove l'acqua dal materiale grezzo originale e in questo modo la temperatura di carbonizzazione si riduce. Quindi, come risultato, temperature più basse significano minori formazioni di catrame nei pori durante il processo e portano a dimensioni dei pori più piccole. Tuttavia, nell'analisi sperimentale che è stata fatta, questi risultati non sono stati raggiunti (probabilmente anche per le modifiche fatte al protocollo).

Hamzah e Umar (2017) [4] hanno studiato la possibilità di fabbricare carbone attivo dai mozziconi di sigaretta con un'attivazione chimica utilizzando idrossido di potassio (KOH) e un trattamento con microonde. Il metodo di riscaldamento a microonde è stato applicato per preparare i carboni attivi poiché, come riporta lo studio, riscalda i materiali in modo rapido e uniforme. Inoltre, il microonde è un metodo ad alta efficienza energetica rispetto ai metodi convenzionali e potrebbe essere utile per migliorare la qualità dei prodotti finali. Con questa tecnica, i risultati hanno mostrato che i carboni attivi realizzati hanno una superficie specifica massima di 328,13 m^2/g con un diametro dei pori di 3,04 nm.

Blankenship e Mokaya (2017) [7] hanno studiato la carbonizzazione idrotermale di filtri di sigarette di mozziconi fumati e non fumati. La carbonizzazione idrotermale di una biomassa ricca di carbonio, in presenza di acqua, produce un materiale solido che viene definito hydrochar. La carbonizzazione idrotermale è un processo abbastanza nuovo e offre molti vantaggi rispetto agli altri. Poiché di solito ha bisogno di temperature più basse (tra 150 e 350 °C) e pressioni intorno ai 2 MPa e non genera rifiuti chimici pericolosi o sottoprodotti (come fa la pirolisi), è considerato a risparmio energetico ed ecologico. Inoltre, è fatta usando acqua, che agisce come solvente e catalizzatore; inoltre non c'è bisogno di un'atmosfera inerte. Poi c'è il processo di attivazione dell'hydrochar: è usato KOH, in un rapporto KOH/hydrochar di 4. Successivamente, la miscela KOH/ hydrochar è posta in un forno e riscaldata in atmosfera inerte a 600, 700 o 800 °C. Una volta attivati, gli hydrochar generano carboni porosi ricchi di ossigeno che hanno una superficie apparente estremamente elevata, con la maggior parte della superficie proveniente dai micropori (fino al 90%). Le aree specifiche ottenute vanno da 2393 m^2/g (per gli hydrochar trattati a 800 °C) a 4310 m^2/g (per gli hydrochar trattati a 600 °C). Gli autori dichiarano che non sono a conoscenza di alcun rapporto su aree superficiali più alte di quelle ottenute per i carboni attivi. Attribuiscono questa alta area superficiale apparente a una miscela ottimale di KOH, gli additivi metallici nell'hydrochar di partenza e una temperatura di attivazione ideale. Tuttavia, questi risultati sono davvero impressionanti.

Blankenship e Mokaya (2017) [7], viste le buone proprietà dei nuovi materiali e dato che lo storage di idrogeno nei carboni porosi è favorito dalla presenza di un'alta superficie proveniente dai micropori, hanno condotto esperimenti di laboratorio sui campioni. Le condizioni di stoccaggio per i test sono -196 °C e pressione variabile tra 0 e 40 bar. I valori più alti ottenuti portano a un assorbimento totale di idrogeno del 10,4 wt% e 11,2 wt% a 30 e 40 bar per i carboni prodotti trattando gli hydrochar a 600 °C. Inoltre, a 30 bar, la capacità di assorbimento dell'idrogeno supera già i valori normali dei MOFs (metal organic frameworks), che sono ad oggi materiali di alto interesse per lo stoccaggio di idrogeno. Oltre alla loro impressionante capacità di accumulo, i carboni prodotti da questo studio offrono anche una grande serie di vantaggi: facilità di lavorazione, alta stabilità chimica e meccanica e basso costo, oltre agli aspetti di valorizzazione e protezione ambientale associati all'uso di mozziconi di sigarette come materiali di partenza.

Da tutti questi studi è possibile dimostrare la fattibilità di produrre carboni attivi a partire da mozziconi di sigaretta e a partire da alcuni di questi, si sono poi sviluppate le analisi svolte in laboratorio e riportate in questo studio.

Per ultimo e in derivazione dagli studi presentati sulla valorizzazione in carboni attivi, Veerabagu et al. [1] nel loro studio 2021 hanno analizzato la possibilità di produrre un nuovo **catalizzatore a base di carbonio poroso** derivato da mozziconi di sigaretta per una reazione di cross-coupling Suzuki-Miyaura altamente efficiente.

Imprese del settore

Infine, è stata portata avanti una ricerca sulle aziende che si occupano di raccolta, stoccaggio e riciclaggio di mozziconi di sigaretta. Nella nostra ricerca abbiamo trovato industrie più e meno sviluppate che avevano un business plan più e meno dettagliato, ma in generale è possibile dire che tutte queste imprese, stanno facendo qualcosa per affrontare un problema e questo è notevole ed ammirabile. Alcune imprese che realizzano processi di recupero esistono a livello internazionale - la più riuscita è quella di Poiato Recicla in Brasile, che recupera mozziconi di sigaretta sotto forma di pasta di cellulosa, utilizzata poi nell'industria della carta. In seguito, TerraCycle è attiva in diversi paesi (USA, Canada, Australia e Regno Unito) e recupera l'acetato di cellulosa sotto forma di granuli di plastica. A livello europeo ci sono le francesi Mégo! e EcoMégot che propongono, a stadi più o meno avanzati, il recupero dei mozziconi. Nei prossimi paragrafi verranno brevemente descritte le attività di alcune di queste aziende.

TerraCycle è un'azienda americana fondata nel 2001. È un'azienda di riciclaggio innovativa che è diventata leader mondiale nella valorizzazione di rifiuti tipicamente difficili da riciclare. Come riporta l'azienda sul suo sito, nel 2012 ha fatto il lancio del primo programma di riciclaggio al mondo per i mozziconi di sigaretta. Il processo di TerraCycle per il riciclaggio dei mozziconi di sigaretta implica che i mozziconi vengono sottoposti a una serie di processi per rimuovere il tabacco residuo e la carta, entrambi i quali possono essere compostati dopo averli separati dall'acetato di cellulosa. Il materiale filtrante di acetato di cellulosa rimanente viene lavato per decontaminarlo. Da lì, il materiale viene trasformato in un formato di plastica rigida, che poi trasformano in polvere. Questo materiale in polvere può essere utilizzato per applicazioni commerciali come pavimento per esterni in composito o piccoli prodotti come posacenere.

MéGo! è un'azienda francese con sede in Bretagna che ha sviluppato il suo processo di riciclaggio dei mozziconi e ha ampliato il campo dei prodotti fatti con mozziconi di sigaretta riciclati. Questa azienda è molto presente sulla rete e sui social network, quindi è stato molto facile trovare informazioni su di essa. Come riportano nel loro sito [34], hanno ora un processo di riciclaggio prototipale e hanno in programma di creare un impianto industriale nella Francia orientale entro il 2021. La sua crescita si riflette comunque nel numero crescente di partnership e franchising (in particolare nelle città di Rennes, Poitiers, Parigi, Nantes, Grenoble e Caen) e si sta estendendo oltre i confini francesi. L'obiettivo di questo servizio nazionale è quello di raccogliere i mozziconi di sigaretta e poi riciclarli, istituendo un sistema di raccolta dinamico per i CB. Questa offerta permette alle città di inquinare meno e di comunicare il loro impegno a favore dell'ambiente. MéGO! fornisce una soluzione completa BtoB (business to business) per aziende, associazioni e autorità locali. Nei loro progetti di valorizzazione installano arredi urbani (posacenere e contenitori) e assicurano la raccolta, il riciclaggio, il follow-up statistico e l'impronta di carbonio di tutte le operazioni. L'obiettivo è quello di creare un approccio ecologico per ridurre l'impatto di carbonio delle persone e sensibilizzare i cittadini. Il processo implementato da Mé-Go! mira a produrre fogli di plastica, ottenuti dalla termocompressione di filtri di mozziconi di sigarette schiacciati e lavati. Questi fogli possono essere utilizzati per produrre una varietà di oggetti, dalle cover per cellulari all'arredo urbano (come i contenitori utilizzati poi per raccogliere altri mozziconi), dai pallet ai gettoni per i carrelli della spesa.

L'impresa brasiliana **Poiato Recicla** raccoglie e ricicla mozziconi producendo polpa di cellulosa da utilizzare nella produzione di quaderni. Il processo sembra essere ben avviato, avendo coinvolto ricercatori dell'Università di Brasilia, ed è oggetto di pubblicazioni (per esempio d'Heni Teixeira, citato in [25]). A partire dal 2018, il sito riferisce che in sei città dell'interno dello stato di San Paolo riciclano un totale di 575.000 mozziconi di sigarette ogni mese e vengono trasformati in cellulosa. Il lavoro viene fatto utilizzando circa mille scatole di raccolta, il che corrisponde a 230 kg di CB al mese. Il processo per produrre polpa di cellulosa genera due flussi di materiale: pasta di cellulosa, utilizzata pura o in miscela a seconda della qualità di carta desiderata e un "dark liquor" che concentra gli inquinanti dei mozziconi di sigaretta e che deve essere separato. Il surnatante ottenuto dopo il trattamento del dark liquor sarebbe interamente recuperato in un altro processo (ma non è specificato quale) e la società referisce che con le periodiche analisi il prodotto sarebbero conformi alle normative brasiliane, garantendo così la non contaminazione della pasta di cellulosa prodotta (non sono però menzionati gli inquinanti monitorati).

Fase sperimentale

Dopo aver descritto molti possibili percorsi di valorizzazione, con la consulenza del Professor Saleh, abbiamo deciso di metterne qualcuna in pratica. Purtroppo, poiché il tempo non era dalla nostra parte, le uniche valorizzazioni che sono state effettuate sono quelle per fare i carboni attivi. Lo scopo di questo studio è infatti quello di essere una ricerca preliminare per far seguire altri studi nel campo della valorizzazione dei mozziconi di sigaretta e risolvere questo enorme problema. Come già detto, i carboni attivi sono la via di valorizzazione più semplice e, per i nostri mezzi, anche la più fattibile.

Metodologia

La fornace utilizzata è una Vecstar MRF 2: la temperatura massima che può raggiungere è di 1250 °C. Il forno è stato installato in una cappa, per assicurare che qualsiasi fumo che potesse essere rilasciato, fosse aspirato. Poiché nella fornace non c'era un tubo per l'introduzione di azoto, nella camera di riscaldamento era impossibile eseguire una vera pirolisi. Di conseguenza, l'aria sarebbe stata sempre presente nella camera. Per risolvere questo problema, i crogioli sono stati coperti con il loro coperchio: in questo modo l'aria era presente nel crogiolo ma veniva rapidamente consumata e poi, se il processo di pirolisi si fosse svolto nel modo giusto, non sarebbe dovuta entrare ulteriore aria nel crogiolo. Questo processo è causato dal fatto che, durante la pirolisi, si liberano gas, aumentando la pressione nel crogiolo (coperto dal coperchio). Di conseguenza, grazie alla differenza di pressione, l'aria presente nella camera di riscaldamento non può entrare nel crogiolo, impedendo così la combustione o l'ossidazione. I gas liberati dal processo di pirolisi fuoriescono dal crogiolo ed è proprio questo il processo che evita all'aria di entrare nel crogiolo, poiché l'aria viene "spinta via" dal gas in entrata. In realtà, dopo un certo punto il processo di pirolisi arriva alla fine e quindi l'aria può entrare nel crogiolo, provocando il processo di ossigenazione e degradazione. Ecco perché, nei nostri esperimenti, è stato davvero importante capire quando fosse il momento ottimale per estrarre i crogioli: se era troppo presto, la pirolisi non era ancora finita, se era troppo tardi l'ossigenazione era già iniziata e rimaneva solo cenere.

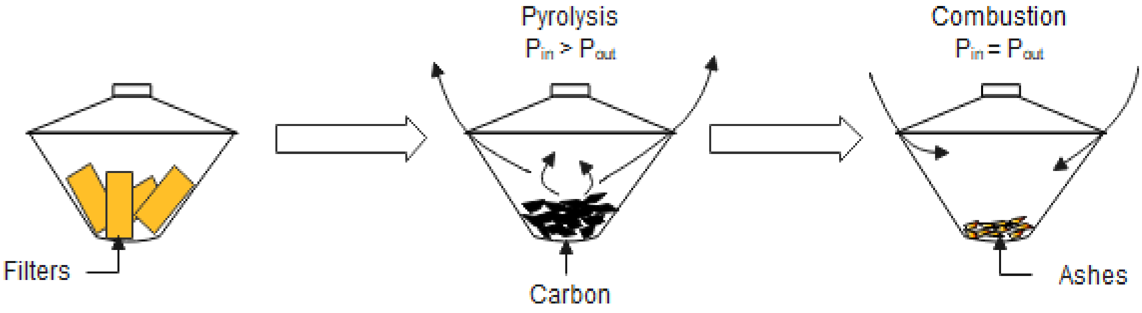

Figura [32], Simulazione del processo che avviene nel forno, elaborazione dell'autore.

Questo dà l'opportunità di parlare delle incertezze: i risultati che seguono arrivano tutti con incertezze, poiché le operazioni sono state effettuate in modo non controllato. Innanzitutto, la pirolisi non è una vera pirolisi, ma una "simil-pirolisi" che dopo un certo tempo diventa una vera ossigenazione (abbiamo giudicato che non è una vera combustione, poiché non ci sono fiamme, ma il campione comunque si consuma). Poi, il crogiolo con il coperchio è stato anche una fonte di inaffidabilità: il coperchio non era molto stabile, quindi a volte cadeva o oscillava e rendeva possibile l'ingresso di aria. Infine, c'è il fattore della temperatura: anche se la temperatura target che veniva indicata dall'apparecchiatura fosse stata quella reale (cosa comunque non veritiera), c'erano altri problemi. Quando si apre il forno, la temperatura diminuisce e poi ci vogliono un paio di minuti per tornare al punto iniziale. Dopo questa spiegazione di ciò che dovrebbe accadere nel forno, è importante sottolineare che questo è solo uno studio preliminare alla valorizzazione dei mozziconi di sigaretta come carboni attivi e che una piena comprensione dei processi richiederebbe un lavoro sperimentale più ampio. Inoltre, va detto che con l'attrezzatura che abbiamo usato non abbiamo potuto controllare le condizioni all'interno del forno: di conseguenza i risultati di questo lavoro devono essere considerati solo come lo spunto per un nuovo e più approfondito studio su questo argomento e non come certezze.

Il protocollo che abbiamo cercato di seguire è quello per la pirolisi dei filtri di Polarz et al. (2002), che prevede di mettere i filtri nel forno direttamente a 800 °C per 2 ore (tempo di mantenimento della carbonizzazione) con una velocità di riscaldamento controllata a 5 °C/min. Sfortunatamente, non è stato possibile per il presente studio seguire questo protocollo, poiché dopo un po' di tempo arrivava l'ossigenazione e la degradazione del campione, quindi è stato adottato un approccio simile. Infatti, quando i filtri sono stati messi direttamente nel forno a 800 °C con un tempo di mantenimento di due ore, il risultato non è stato altro che cenere. Si è così deciso di testare le seguenti temperature: 400, 600, 700 e 800 °C. La temperatura obiettivo di 400 °C è stata scelta per seguire il protocollo di Koochaki et al. (2019) [5]. Inoltre, bisogna dire che dai test preliminari si è visto che la carbonizzazione per 600, 700 e 800 °C avveniva con tempi di mantenimento molto bassi (già dopo soli 5 minuti c'è una materia nera e carboniosa nel crogiolo). D'altra parte è apparso chiaro che per 400 °C sono necessari tempi di mantenimento maggiori. Di conseguenza, i tempi di mantenimento per queste temperature più alte erano diversi: da 5 a 45 minuti e poi 60, 75, 90 e 120 minuti. Al contrario per 400 °C i tempi erano: 30, 60, 90, 120, 150, 180 minuti.

Un altro passo importante della campagna sperimentale è stato quello di trovare un pre o post trattamento che permettesse di aumentare la superficie specifica. Mentre alcuni studi non avevano alcun trattamento, altri ne avevano uno o più.

Il primo pretrattamento che è stato provato è stata l’immersione dei filtri in soluzioni di NaOH, seguendo la guida dello studio di Koochaki et al. (2019) [5]. Tuttavia, dato che in laboratorio non c'era la possibilità di effettuare correttamente la pirolisi è stato necessario scrivere un nuovo protocollo. Inoltre, lo studio a cui ci siamo ispirati ha utilizzato soluzioni acquose di NaOH con un rapporto di in peso NaOH/acqua del 48%, il che significa che la concentrazione della soluzione era quasi 13 M. Di conseguenza, è stata utilizzata una soluzione di idrossido di sodio con una concentrazione di 0,5 M per immergere i filtri per 24 ore. La stessa cosa è stata fatta per l’immersione dei filtri in KOH.

Come sarà riportato dai risultati nella sezione seguente, il pretrattamento con NaOH non è andato come previsto: invece di aumentare la superficie specifica (che era il nostro obiettivo primario), l'ha diminuita e a volte azzerata. Per questo, sulla scia del lavoro di Yusop et al. (2021) [43], sono stati proposti dei post trattamenti, ovvero dei trattamenti sui filtri già pirolizzati. Su questi carboni è stata fatta un’immersione in una soluzione 0,5M di KOH o NaOH per 24 ore in un rapporto di circa 1:1. In seguito, questi campioni sono stati trattati termicamente a 600 °C per 5 minuti. Purtroppo, solo i carboni che non sono stati trattati termicamente di nuovo sono stati passati al BET (il che significa che sono solo stati immersi in NaOH o KOH per 24 ore), quindi i risultati non possono essere confermati.

Un altro pretrattamento studiato è il lavaggio dei filtri di mozziconi di sigaretta con etanolo. Questo passo viene fatto per estrarre molti inquinanti dal filtro della sigaretta, che, come è stato studiato nella parte bibliografica, rimangono intrappolati nel filtro durante il processo di fumo. Prendendo ispirazione dal protocollo di Hamzah and Umar (2017) [4], abbiamo immerso i filtri in etanolo per 2,4,8 e 24 ore, rimosso e poi fatto seccare i filtri. L’etanolo è stato recuperato per poter effettuare una cromatografia, che però poi non è stato possibile effettuare. Comunque poi, nello studio dei carboni attivi tutti i campioni trattati con etanolo sono stati studiati insieme.

Un'alternativa a questo metodo sembra essere l'estrazione con fluido supercritico (SFE) con CO_2 supercritica. L'anidride carbonica è un solvente chimicamente neutro e il processo ha il vantaggio che non ha bisogno di una fase di separazione dopo l'estrazione, perché la CO_2 diventa un gas e il residuo liquido è facilmente recuperabile. Solamente un test è stato realizzato, per mancanza di tempo e per dare un’idea del risultato (ricordo sempre che questo è un proto-progetto e che questo argomento non è stato ampiamente studiato e all'UTC questa ricerca è iniziata con me, quindi non ho avuto molti riferimenti da seguire). Le condizioni del separatore sono state selezionate a 50 bar e 30 °C e il flusso di massa di anidride carbonica è stato impostato a 1,2 kg/h. Il test è durato un'ora e il recupero dell'estratto è stato eseguito ogni 10 minuti. Meno di 1 mL di estratto è stato recuperato dai 20 mozziconi usati. Abbiamo notato che i mozziconi erano più puliti di prima e soprattutto non avevano il caratteristico odore pungente. Purtroppo non abbiamo avuto il tempo di eseguire i test di trattamento termico sui campioni trattati con CO_2 e quindi non possiamo dire quale sia la superficie specifica (ma abbiamo ipotizzato che dovrebbe essere simile a quelli trattati con etanolo).

Poi c'è la possibilità di un trattamento a microonde. Seguendo l'articolo di Hamzah et al. (2017) [4] abbiamo eseguito i nostri test. Gli autori dello studio che abbiamo seguito riportano che il metodo di riscaldamento a microonde è stato applicato per preparare i carboni attivi perché riscalda rapidamente e uniformemente. Inoltre, è un metodo ad alta efficienza energetica rispetto ai metodi convenzionali e potrebbe migliorare la qualità dei prodotti finali. Il microonde usato è un Anton Paar's Microwave Synthesis Reactor Monowave 300. Nel nostro riferimento, i filtri delle sigarette, immersi in una soluzione 0,5M di KOH, sono stati attivati in un reattore tubolare di vetro con una potenza di 630 W e un tempo di irradiazione di 20 minuti. Nel nostro studio abbiamo deciso di lavorare basandoci sulla temperatura invece che sulla potenza. Abbiamo scelto di mettere i campioni nel microonde e attivarli per 20 minuti a 120 °C e con un'agitazione con una barra magnetica a 1000 rpm. Dato che poi dall'analisi SEM abbiamo visto che questo pretrattamento non dava buoni risultati abbiamo provato un post-trattamento. Seguendo il lavoro di Yusop et al. (2021) [43], abbiamo impregnato in KOH i carboni (quindi la materia prima è già stata trattata termicamente) e poi trattato i campioni in microonde a 120 °C per 20 minuti.

Risultati

Nei prossimi paragrafi verranno discussi i risultati ottenuti. Per la metodologia delle analisi si faccia riferimento allo studio in inglese.

La **TGA** (analisi termogravimetrica) è stata svolta per meglio comprendere le proprietà dei filtri dei mozziconi. I nostri risultati verificano quelli trovati in letteratura. La rappresentazione grafica è in Figura [48]. Come negli studi bibliografici che sono stati riportati, il comportamento termico dei filtri dei mozziconi di sigaretta si divide in tre fasi. Il primo è a circa 105 °C, dove si perde tutta la massa data dall'acqua, ma è una perdita di massa abbastanza piccola. La perdita di massa maggiore (di circa il 65%) si osserva a partire da 280 °C fino a circa 340 °C, che è legata alla decomposizione dei componenti emicellulari delle materie prime. Quindi la disidratazione e la rimozione dell'acido acetico causano una perdita di massa di circa il 70%, un valore che è in buon accordo con la quantità relativa attesa di H_2O e acido acetico da rimuovere dal campione. Poi c'è una terza perdita di massa a circa 500 °C, molto probabilmente dovuta alla reazione di cracking dei legami C-C: è infatti piccola e lenta. Pertanto, il rendimento del carbonio può essere stimato al 13-18%, che è in buon accordo con i valori corrispondenti riportati in letteratura.

Inoltre sono stati anche analizzati alla TGA i filtri pretrattati con NaOH (Figura [49]). È da segnalare che questi sono stati utilizzati erano ancora umidi, quindi l'analisi potrebbe essere un po' falsata. Facendo un confronto tra le due curve (Figura [50]) il picco di perdita in massa è diverso: la curva NaOH ha un picco a temperatura più bassa, il che significa che il processo di degradazione è più veloce e inizia prima; ma d'altra parte, il processo richiede più tempo per arrivare a regime. La stessa perdita di massa avviene in un periodo di tempo più lungo e inizia a temperature più basse, dando una curva meno netta. Molto probabilmente questo è dato dall'introduzione di gruppi funzionali ossigenati che facilitano la degradazione della materia prima. Infine, è importante dire che questi risultati, tuttavia, hanno bisogno di più conferme e il processo ha bisogno di più ricerca.

Dopo le prove di carbonizzazione, per capire meglio il processo, abbiamo cercato di identificare la **cinetica della reazione**, anche se sappiamo che è abbastanza impossibile ottenere stima di una cinetica reale. Tuttavia, sono stati fatti dei grafici per vedere l'evoluzione della massa nel tempo. L'analisi è stata fatta pesando il campione prima del trattamento termico (ed etichettando questa massa iniziale come m_0) e pesandolo dopo il trattamento termico (ed etichettandolo m_f). Facendo m_f/m_0 abbiamo così calcolato la frazione di massa rimanente. La Figura [54] ci mostra che la perdita di massa è molto rapida, il che significa che la pirolisi è stata quasi istantanea. Ogni punto rappresenta una prova diversa, ed è da notare che in questo studio, a causa della mancanza di tempo, non c'è stata una ripetibilità, poiché non è stato eseguito più di un test. Il processo è un decadimento di massa, quindi può essere facilmente rappresentato come una funzione esponenziale. Dopo 5 minuti massa residua per le tre temperature è circa il 13% e dopo questo valore inizia a diminuire ulteriormente. Ci sono alcuni punti che risentono delle incertezze e si vedono i relativi picchi e avvallamenti. Comunque, per i campioni di 20 minuti e 30 minuti abbiamo notato una buona quantità di carbonio e un po' di ceneri, il che significa che molto probabilmente la pirolisi a quei tempi di permanenza è finita e l'ossigenazione è iniziata: l'ossigeno inizia a reagire con il carbone ad alta temperatura e lo degrada. Le ceneri sono di un colore bianco/grigio e quando i campioni iniziano a degradarsi (ad esempio per i campioni estratti dal forno dopo 30 minuti) è possibile vedere che sulla superficie dei carboni ci sono delle parti grigie, ma, date le molte incertezze, capire esattamente a che momento finisca la pirolisi e dove inizia l'ossigenazione è quasi impossibile. Inoltre si nota che, come prevedibile, a temperature più alte la degradazione è più veloce.

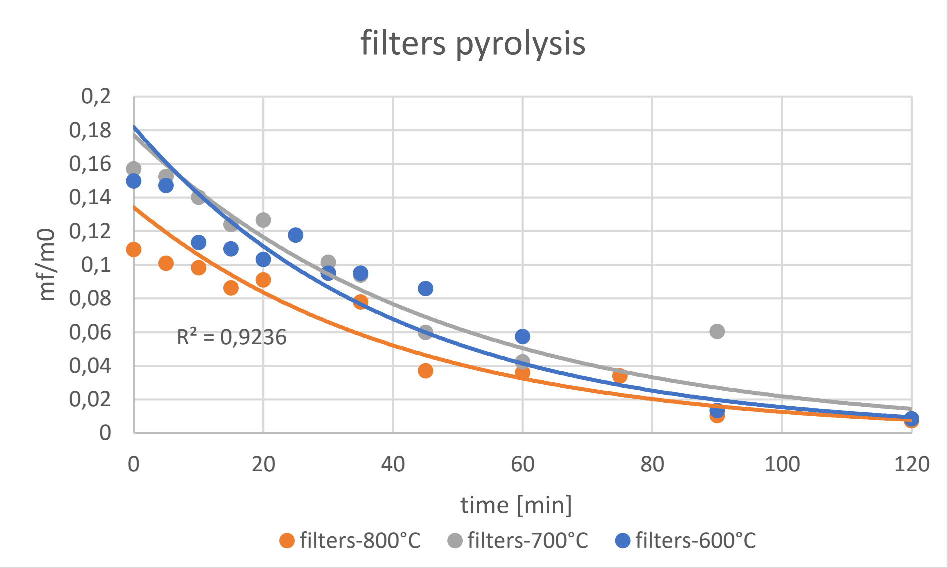

Figura [54], Evoluzione del residuo di massa con l'hold time a 800, 700 e 600°C per i filtri, elaborazione dell'autore.

Questo significa che la reazione di pirolisi (se avviene) è abbastanza veloce e la maggior parte di essa avviene nei primi 30 minuti e poi inizia l'ossigenazione. Allora si è deciso di analizzare solo i primi cinque minuti: I punti scelti sono stati quelli da 10 a 60 secondi con un intervallo di 10 secondi e poi ogni 30 secondi. Questo procedimento è stato fatto solo per 600 °C. Dal grafico in Figura [56], possiamo vedere che l'andamento è come una legge di Arrhenius: la perdita di massa è concentrata nei primi 3 minuti e poi abbiamo quasi un plateau. Tuttavia, dal grafico mostrato prima (Figura [54]) è chiaro che l'andamento è esponenziale. Quindi, la spiegazione è che molto probabilmente fino a 30 minuti c'è una pirolisi e poi inizia l'ossigenazione. Per visualizzare meglio questo, possiamo unire i punti da 0 a 5 minuti e gli altri punti a 600 °C. Inoltre per facilitare la lettura i punti sono stati uniti, ma questo è un errore. Non ha alcun significato matematico, perché non abbiamo una statistica dei risultati e perché non è il frutto di una prova sola ma di più test uniti, ma è stato fatto solo per rendere il grafico più leggibile.

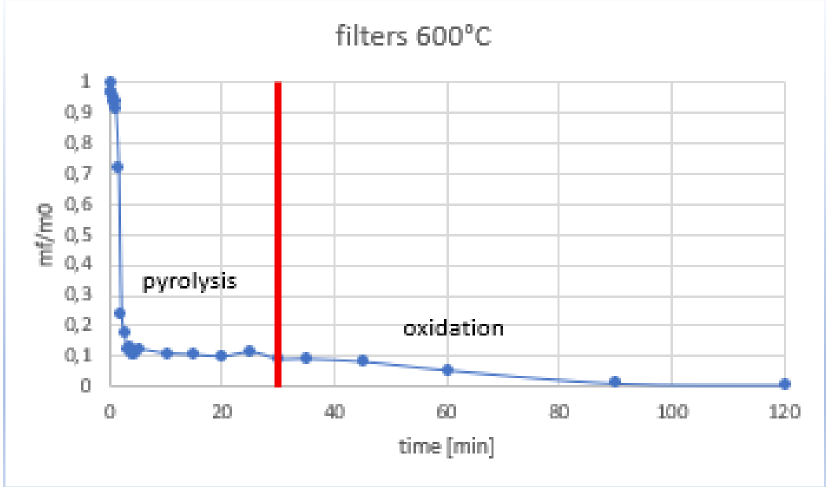

Figura [57], Evoluzione del residuo di massa con l'hold time a 600 °C per i filtri CBs 0-120 minuti, elaborazione dell'autore.

Da questo grafico appare più evidente che ci sono due fasi diverse nel processo, anche se non c'è una ripetibilità e ci sono sicuramente errori e che non c'è una distribuzione statistica. La prima parte, che abbiamo ipotizzato andando fino a 30 minuti, è la fase di pirolisi, dove si consuma la maggior parte della massa e dove si formano i pori. Successivamente, inizia la fase di ossigenazione: man mano che l'aria entra nel crogiolo la massa rimanente inizia a bruciare, con un andamento esponenziale.

Con l'aiuto del professor Elias Daouk, ho cercato di capire meglio la legge cinetica della pirolisi e capire se effettivamente la legge di Arrhenius può essere usata per rappresentare la decomposizione termica dei solidi. Abbiamo anche cercato di stimare i parametri (A, E_a e n dell'equazione (4.6)). Innanzitutto, bisogna sottolineare che nei filtri c'è anche circa il 10% di acqua, che deve essere presa in considerazione, e che la produzione di carbonio è circa il 13% della massa originale. Per trovare le incognite, il professor Daouk ha risolto un sistema di 5 equazioni differenziali, dove ha impostato l'equazione della temperatura, la velocità di degradazione dei filtri, la velocità di degradazione dell'acqua, la velocità di formazione del carbone e il bilancio di materia della reazione. Il sistema di equazioni differenziali è stato risolto con un codice MATLAB. Dalla Figura [59], troviamo che il comportamento della perdita di massa è ben modellato dalla legge di Arrhenius e questo buon adattamento è dato anche dal fatto che abbiamo introdotto la frazione di acqua nelle equazioni. Il grafico mostra che la perdita di massa data dai dati estratti dal test di laboratorio (i punti blu), sono molto ben rappresentate dalla curva del modello, la curva verde. Poi possiamo vedere i componenti: i filtri (curva rossa) diminuiscono a partire da 0,9 che è il valore che abbiamo impostato all'inizio considerando un 10% di acqua. Dunque una legge di tipo Arrhenius può similare la pirolisi dei filtri di mozziconi di sigaretta.

Per concludere questa parte, possiamo dire che dai grafici presentati abbiamo evidenziato che c'è un consumo molto veloce del campione, che in tre minuti perde quasi tutta la sua massa. Nella figura [66], possiamo vedere l'evoluzione già riportata della massa rimasta a 800 °C nel tempo, confrontata con il risultato dato dalla TGA (la linea rossa). Possiamo vedere che la TGA, che ha raggiunto la temperatura di 1000 °C, ha una massa residua di circa il 14%. Tuttavia, il grafico che abbiamo riportato a 800°C, già a 5 minuti mostra una massa residua che è inferiore al 14% e se andiamo avanti nel tempo, vediamo solo che c'è una diminuzione di questo valore. Questo significa che quello che otteniamo nel nostro crogiolo e nei nostri grafici, non è solo il risultato della degradazione termica (altrimenti avremmo un risultato leggermente inferiore a quello della TGA, che arriva a 1000 °C) ma anche di una reazione chimica. La reazione è una reazione di ossidazione: inizialmente possiamo descriverla come una vera e propria combustione (infatti in alcuni campioni abbiamo visto delle fiamme nel crogiolo), ma dopo la fase di pirolisi, una volta formatosi il carbone, abbiamo una fase di reazione tra il carbone e l'ossigeno, che consuma e degrada il nostro prodotto, portandoci ad avere solo cenere dopo un tempo abbastanza lungo.

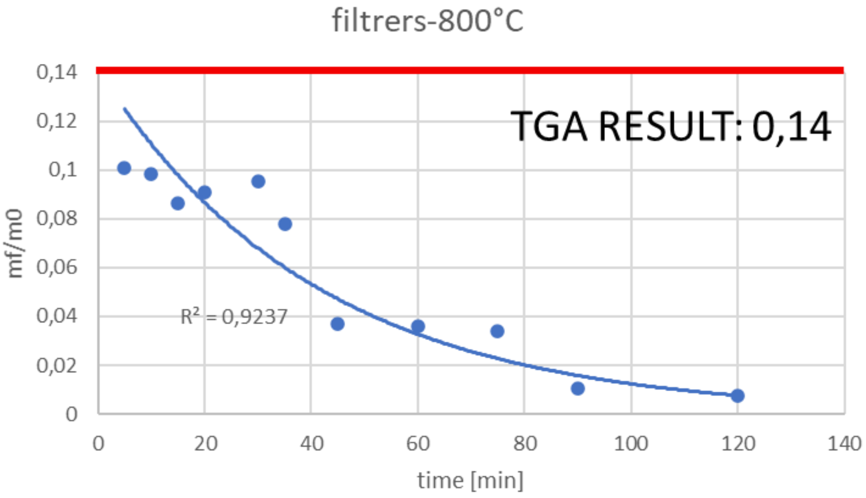

Figura [66], Evoluzione del residuo di massa con hold time a 800°C rispetto al risultato TGA, elaborazione dell'autore.

In seguito, lo studio di una stima della cinetica è stato fatto anche per i filtri NaOH. Non è stato esteso ai filtri KOH ed etanolo perché, dato che il numero di prove che è stato fatto era molto più piccolo, i risultati non davano veramente un'idea di come fosse il processo (bisogna ricordare che mentre sui filtri NaOH è stato fatto uno studio più approfondito, per confrontarlo con i filtri normali, sui filtri KOH ed etanolo è stato testato solo un piccolo numero di tempi di permanenza, dove pensavamo potessero essere i risultati più interessanti). Il grafico in Figura [60] ci mostra che i filtri trattati con NaOH hanno una curva più bassa, il che significa che sono più consumati dal trattamento termico. Quindi, molto probabilmente, questo è causato dal pretrattamento con NaOH: l'idrossido di sodio aiuta nella creazione di gruppi funzionali ossigenati sulla superficie delle fibre del filtro e questo effetto aumenta di conseguenza la cinetica della reazione.

L'analisi **FTIR** (Fourier Transform Infrared Spectroscopy) è stata fatta sui carboni e sui filtri per identificare le bande e i gruppi funzionali presenti e quindi determinare la composizione e la struttura molecolare dei materiali. Da questa abbiamo visto che tutti i filtri (gli spettri sono mostrati in Figura [67]) presentano il picco a 1072 cm^{-1} che corrisponde al gruppo $O–C=O–CH_3$ ed è tipico dei legami di acetato di cellulosa. Inoltre è molto interessante notare che presentano leggeri picchi nella regione da 1650 a 1500 cm^{-1} che sono caratteristiche dei legami aromatici C=C. I filtri hanno anche un debole picco di assorbimento a 873 cm^{-1}, che è attribuito alla vibrazione di flessione del legame C-H nell'alto grado di sostituzione dell'anello aromatico. La scoperta più interessante è che ci sono i legami aromatici C=C, poiché molto probabilmente questo deriva dall'attività attiva dei fumatori, come riportato nella parte bibliografica.

Invece i filtri pretrattati con NaOH hanno uno spettro che, oltre a queste caratteristiche in comune con gli altri, ha anche altri picchi. Sono da sottolineare la banda dei C-OH a circa 3430 e a circa 3700 cm^{-1}, il picco C=O a 1710 cm^{-1} e la vibrazione C–O a 1380 cm^{-1}. Da questi risultati possiamo affermare che i filtri NaOH contengono alcoli, esteri, chetoni, aromatici e acidi carbossilici. Questo ci porta a dire che, come sospettato, l'immersione con NaOH porta alla creazione di gruppi funzionali ossigenati, che facilitano la degradazione.

Per quanto riguarda la FTIR dei carboni, i risultati sono ripostati in Figura [69]. Per quanto riguarda il campione prodotto dai filtri non trattati, questo ha uno spettro difficile da analizzare perché quasi piatto. Comunque si vedono bande assegnate a gruppi C–H e un'ampia banda tra 1000 e 1300 cm^{-1} che si trova di solito con carboni ossidati ed è stata assegnata allo stiramento C–O in acidi, alcoli, fenoli, eteri ed esteri. Per gli altri campioni analizzati (da filtri pretrattati con KOH, etanolo o NaOH), gli spettri sono più o meno gli stessi, ma i picchi per il campione KOH sono molto più intensi. Troviamo un picco C=O a 1710 cm^{-1}, la banda 3584-3700 cm^{-1} che rappresenta l'O–H negli alcool. Per il KOH ci sono anche bande nella regione da 1650 a 1500 cm^{-1} erano caratteristiche dei legami aromatici C=C e un'ampia banda tra 3000 e 3500 cm-1 che può essere anche associata all'O–H.

In seguito, l'**adsorbimento di blu di metilene** e quello della Rhodamine B sono stati eseguiti solo come proof of concept. Una proof of concept è una dimostrazione di fattibilità, e lo scopo finale è quello di mostrare la fattibilità di un processo o di un'innovazione, nel nostro caso il fatto che i carboni attivi realizzati possano effettivamente adsorbire il blu di metilene, il che significa che hanno una buona superficie specifica. Pertanto, è stato fatto solo su un singolo carbone, per capire la fattibilità, F800C5min. Poi, altri campioni sono stati passati sulla BET, per stimare l'area superficiale in modo più accurato. Qui riportiamo la Figura [81], che rappresenta il test di adsorbimento di Rhodamine B.

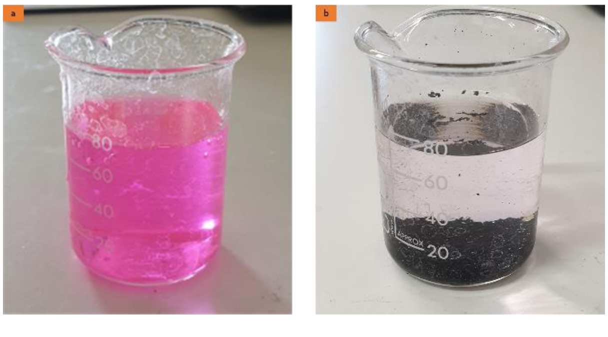

Figura [81], test di adsorbimento della Rodamina B, elaborazione dell'autore.

Da qui è chiaro che il carbone decolora completamente la soluzione. La foto della soluzione rosa è stata fatta alla fine di un pomeriggio e la foto della soluzione decolorata è stata fatta la mattina seguente. È stato quindi possibile dire che in circa 12 ore (ma forse anche meno) la soluzione si sia completamente decolorata. Questo significa che il carbone prodotto ha un potenziale di decolorazione del colorante rosa, il che significa che ha una certa capacità di adsorbimento e di conseguenza che possa dare buoni risultati nel test di adsorbimento BET.

Di seguito sono riportati i risultati della **SEM.** Nella Figura [70], ci sono le immagini SEM dei filtri normali (a) e dei filtri pretrattati con NaOH (b). Si vede chiaramente che le fibre di acetato di cellulosa, come previsto, hanno una forma a "Y" e le immagini corrispondono alle immagini dei nostri riferimenti. Le fibre di NaOH, invece, pur presentando più o meno la stessa forma, hanno dei granelli bianco sopra. Quindi è stato fatto uno zoom che è riportato in figura [73] (a) e (b), qui riportata. Da questa immagine è chiaro che ci sono dei cristalli sulla superficie. Dall'EDX, è stato constatato che i cristalli mostrati sono cristalli di sodio. Dalle analisi è risultato che nei filtri si possono trovare altre sostanze come alluminio, calcio, titanio e silicio, accanto agli elementi più presenti: carbonio e ossigeno, che infatti sono i costituenti dell'acetato di cellulosa, il materiale principale che fa i filtri delle sigarette.

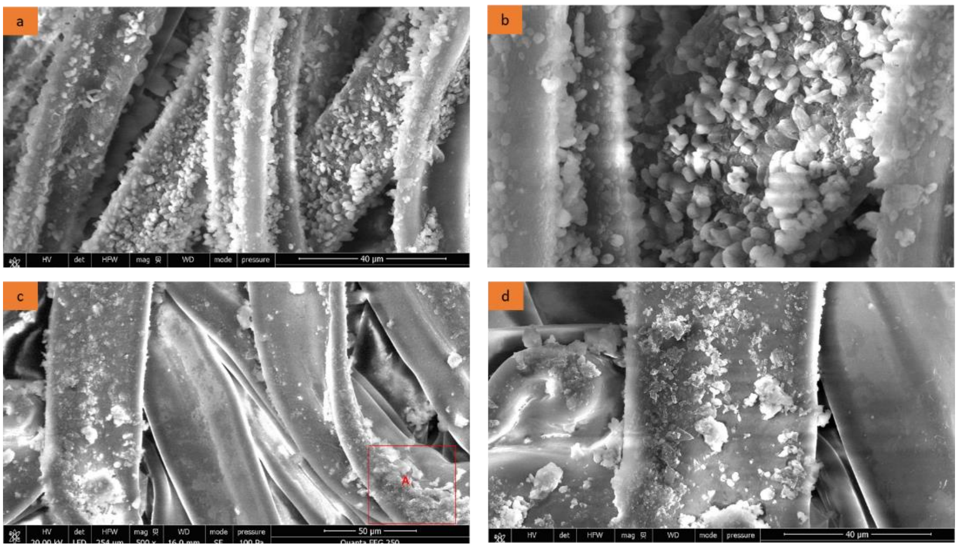

Figura [73], SEM di filtri pretrattati con NaOH (a, b) e filtri laminati (c, d), elaborazione dell'autore.

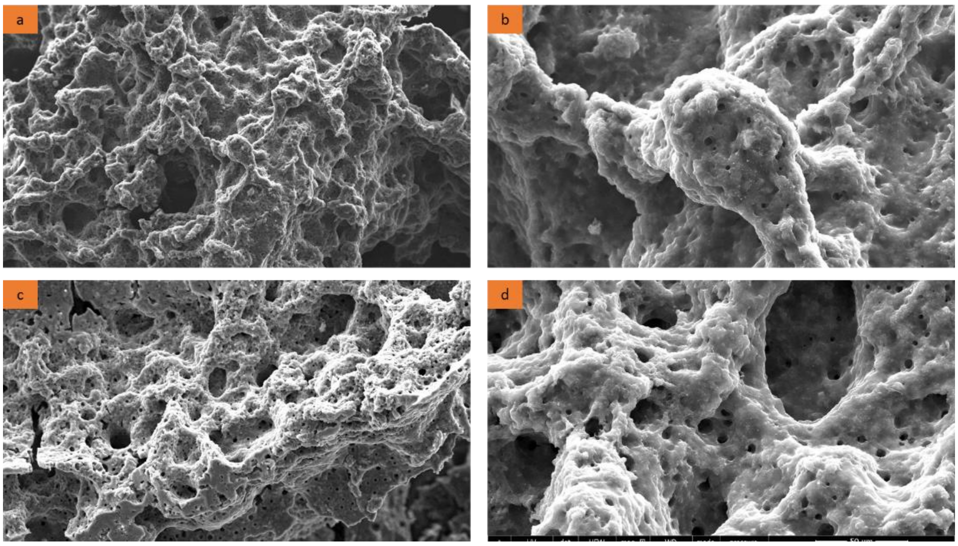

Figura [75], SEM di F800C5min (a, b) e F800C20min (c, d), elaborazione dell'autore.

Poi sono state fatte le analisi sui carboni. Se F800C20min e F800C5min hanno mostrato una morfologia davvero buona con molti pori (in particolare, dalla qui mostrata figura [75] (b) e (d) è chiaro che a 20min ci sono più pori che a 5min), i carboni NaOH non hanno avuto affatto un bel risultato. Sembra che le fibre non si siano carbonizzate e che molte di esse siano ancora intatte (quindi questo spiega perché i campioni NaOH hanno mantenuto la loro forma originale dopo essere stati trattati termicamente). Il confronto tra le due serie di campioni è abbastanza facile e anche nel caso della differenza tra F800C20min e F800C5min, è evidente che il 20 minuti ha presentato un maggior numero di pori e anche pori più piccoli. Come vediamo quindi dalla SEM dei filtri non trattati, un cambiamento nella morfologia è chiaro. Lo sviluppo di una struttura gerarchica dei pori durante il processo di carbonizzazione è molto probabilmente una conseguenza della modifica dell'acetato. Il carbone attivo prodotto ha generalmente una grande superficie specifica e una porosità che va dal micrometro al nanometro e questo è anche dimostrato dalla BET.

Inoltre dall'analisi SEM è dimostrato che il campione trattato con etanolo ha una superficie porosa, mentre quello pretrattato al microonde no, quindi abbiamo evitato di svolgere le analisi BET per questo. Infine, per concludere, dall'analisi al SEM otteniamo un grande risultato: possiamo dire che un pretrattamento dei filtri per immersione in una soluzione liquida di NaOH non funziona come trattamento attivante. La nostra ipotesi è che, quando inizia la pirolisi ci sono delle reazioni tra le fibre, che grazie alle loro proprietà di superficie le fanno reagire. Invece, quando abbiamo il trattamento con NaOH, succede qualcos'altro. Abbiamo già visto che ci sono i granuli di sodio depositati sulla superficie e la nostra ipotesi, da confermare, è che il sodio, che fonde a 97 °C ed evapora a 882 °C, fonde sulle fibre a una temperatura che non ha ancora permesso alle fibre di degradarsi. Questo crea un rivestimento di sodio, che rimane liquido, sulle fibre e quindi impedisce alle fibre di reagire tra loro, mantenendo una struttura fibrosa e ostacolando la formazione di pori. Questo è il motivo per cui, dopo la pirolisi (come riportato in figura [80]), ci sono ancora i granuli di sodio.

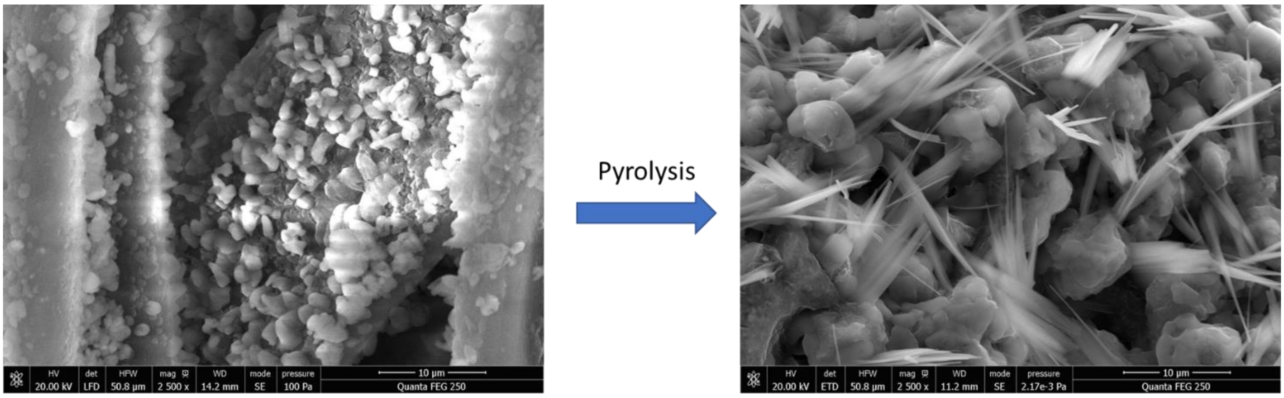

Figura [80], SEM di filtri NaOH prima e dopo la pirolisi, elaborazione dell'autore.

Infine è stata fatta un'analisi **BET** per valutare le superfici specifiche di qualcuno dei campioni preparati. BET sta per Brunauer-Emmett-Teller e come già detto è un metodo molto usato per misurare la superficie specifica di materiali adsorbenti.

Dalla Figura [87] vediamo l'insieme di tutte le superfici specifiche valutate. Si può già vedere l'enorme differenza che c'è tra i filtri non trattati o quelli post-trattati con etanolo e quelli pretrattati con NaOH o KOH. Per il KOH6005min, l'area era così piccola che l'apparecchiatura di misura ha avuto problemi nel valutare la superficie e ha poi dato un valore finale di 5 m^2/g. Questo conferma l'ipotesi data dopo i test al SEM: i granuli di sodio (o potassio nel caso dei filtri pretrattati con KOH) fondono ed impediscono la reazione tra le fibre per dare una superficie porosa. Nonostante questi risultati non ottimali, che però hanno permesso di scartare un pretrattamento, il grande risultato è che ci sono alcuni carboni che hanno buone aree specifiche, confermando che è possibile trasformare i mozziconi di sigaretta in buoni carboni attivi. I risultati dei test BET ci mostrano che c'è una buona performance in media dei filtri non trattati. I migliori sono a 800 °C con i campioni tenuti per 20 e 30 minuti (dove si è stimato che la pirolisi inizi a terminare), con superfici specifiche di circa 600 m^2/g (F800C30min e F800C20min hanno una superficie specifica sono di circa 650 e 600 m^2/g, rispettivamente.), che sono già buone cifre. La media dei carboni ottenuti dai filtri non trattati è intorno a 500 m^2/g. I mozziconi trattati con una rampa di temperatura da temperatura ambiente a 800 °C, producono un carbone che ha una superficie specifica di 720 m^2/g, la più grande realizzata.

Un altro risultato è che la superficie data dai micropori è sempre intorno ai due terzi, che è un ottimo risultato. La Figura [89] ha mostrato che la colonna arancione, che rappresenta l'area di micropori, è sempre circa due terzi della colonna blu, la superficie totale. Questo è un ottimo risultato perché significa che c'è una ripetibilità e che il comportamento è mostrato da tutti i campioni, indipendentemente dal pre o post trattamento (sempre tranne che per i carboni NaOH e KOH). I valori massimi delle percentuali di micropori sono dati da F700C20min (71,6%) e F800C20min (70,3%), ma quasi tutti gli altri si attestano ben oltre il 60%.

Abbiamo anche voluto vedere l'influenza della temperatura e del tempo. Possiamo ben vedere che la temperatura che rende meglio è 800 °C. Questo effetto è chiaramente visibile nella serie a 20 minuti ed è indicato e sottolineato dalla freccia nella Figura [90]: a 800 °C abbiamo una superficie specifica molto maggiore che a 700 e 600 °C. Tuttavia, i campioni a 5 minuti riportano un risultato diverso, in quanto le due superfici analizzate sono quasi uguali o quella a 600 °C è un po' migliore. Quindi, ancora una volta affermiamo che tutti questi risultati hanno bisogno di conferme e che sono solo un primo tentativo di dare indicazioni per gli studi successivi. D'altra parte, possiamo anche analizzare l'effetto del tempo. Dalla Figura [90] appare chiaro che 30 minuti sia la tempistica migliore: questo è probabilmente causato dal fatto che (come è riportato in figura [57]), il processo di pirolisi termina a circa 30 minuti di tempo e questo significa che fino a questo punto si formano ancora pori e dopo questo tempo, inizia il processo di ossigenazione, degradando la materia e distruggendo i pori. Questa tendenza è qui riportata e chiara per la serie 800 °C: il carbonio realizzato con un tempo di mantenimento di 5 minuti ha un'area superficiale specifica ben più bassa di quelli a 20 e 30 minuti.

Inoltre questi risultati ci mostrano che i pretrattamenti fatti sui filtri non funzionano. In particolare l'immersione dei filtri in NaOH o KOH ha dato pessimi risultati. Le aree sono tutte sotto i 100 m^2/g tranne quella trattata termicamente con una rampa. Di conseguenza, questa è una seconda conferma di quanto affermato nelle pagine precedenti: il campione trattato con una rampa, anche per i campioni di NaOH che di solito hanno un'area molto più piccola, ha avuto un rendimento migliore. Dunque, nei lavori futuri, questa informazione deve essere presa in considerazione e sviluppata, per ottenere conferme. Anche il pretrattamento con etanolo mostra dei risultati inferiori rispetto ai filtri non trattati (con una media di 350 m^2/g), quindi un lavaggio con etanolo si è dimostrato inutile e non necessario. Ma questa idea è da rivedere se si guarda il problema dal punto di vista del gas di pirolisi: se certe sostanze che potrebbero finire nel gas di pirolisi fossero rimosse dal lavaggio con etanolo, forse la leggera riduzione della superficie specifica del carbone attivo prodotto sarebbe un buon compromesso per evitare una successiva purificazione del gas. Tuttavia, da questo studio possiamo vedere e provare solo che i filtri lavati con etanolo danno una minore superficie specifica.

Abbiamo visto che invece c'è la possibilità di migliorare le performance con un post trattamento. Il grafico in Figura [92] mostra che quando immergiamo il carbone prodotto da un primo trattamento termico in KOH, abbiamo una diminuzione della superficie specifica: questo è molto probabilmente causato dal fatto che ci sono alcuni cristalli di potassio che si depositano sulla superficie impedendo l'accesso ai pori e riducendo così l'area specifica. Tuttavia, quando trattiamo questo campione in un microonde abbiamo un aumento della superficie specifica: anche se l'area totale è più piccola di quella originale (ma non così più piccola), l'area dei micropori è aumentata (anche se non molto). Questo fenomeno potrebbe essere causato dal fatto che il KOH introduce la creazione di alcuni gruppi funzionali ossigenati sulla superficie, che con il riscaldamento aiutano a formare più pori (e micropori in particolare). Tuttavia, questa è solo un'ipotesi e questa idea dovrebbe essere verificata. Comunque, in studi futuri, questo percorso di post-trattamento dei carboni, con immersione in KOH o NaOH e poi un secondo trattamento termico, dovrebbe e potrebbe essere sviluppato e migliorato. Infatti, sempre da Figura [92], possiamo vedere che il post trattamento con immersione in NaOH e successivo secondo trattamento termico, ha decisamente migliorato le prestazioni del carbone pretrattato con etanolo. Se quindi mettiamo un carbone in idrossido di sodio e poi riscaldiamo a 600 °C per 10 minuti, l'area specifica può aumentare. Ancora una volta c'è una conferma: un post-trattamento chimico e termico potrebbe essere una buona idea. Quindi possiamo affermare che un post trattamento chimico con successivo trattamento termico migliora decisamente alcuni risultati (ed è anche dimostrato da diversi studi in letteratura), ma purtroppo non siamo stati in grado di fare tutte le analisi necessarie per confermare questi effetti.

Conclusione

Per concludere, abbiamo presentato qui alcune statistiche sul consumo di sigarette e sull'inquinamento da mozziconi. Questi non sono biodegradabili e contengono oltre 7000 componenti tossici. Quando i mozziconi di sigaretta vengono gettati nell'ambiente, quantità significative di sostanze tossiche vengono rilasciate e potenzialmente accumulate, costituendo una grave minaccia. Per risolvere questo enorme problema, dobbiamo trovare un modo intelligente per raccogliere e stoccare questi rifiuti e, soprattutto, trovare un modo sostenibile per riciclarli. Nella prima parte del presente studio, sono state riportate delle valorizzazioni e molte soluzioni sono state ritenute davvero interessanti. Soluzioni come la miscelazione in mattoni di argilla cotta o in calcestruzzo d'asfalto potrebbero essere di valore dato che potrebbero utilizzare grandi quantità di mozziconi. D'altra parte, ci sono anche soluzioni più tecnologiche, come l'uso come vettore di biofilm o un aerogel di acetato di cellulosa per produrre un isolante termico.

Il mio lavoro sperimentale si è focalizzato alla valorizzazione in carboni attivi. Lo scopo di questo studio era quindi una ricerca preliminare per altri studi futuri nel campo della valorizzazione dei mozziconi. I carboni attivi sono il modo più semplice e, per i nostri mezzi, anche il più fattibile di recupero. I risultati dei test BET ci mostrano che c'è un buon rendimento in media dei filtri non trattati. I migliori risultati sono a 800 °C con i campioni tenuti per 20 e 30 minuti (punto dove si stima che la pirolisi sia terminata), con superfici specifiche di 600 m^2/g, che sono già buone cifre. La media dei carboni ottenuti da filtri non trattati era di circa 500 m^2/g. Il carbone trattato con una rampa di temperatura da temperatura ambiente a 800 °C ha una superficie specifica di 720 m^2/g, il migliore risultato ottenuto. Inoltre, la superficie data dai micropori è sempre intorno ai due terzi, che è un ottimo risultato. In secondo luogo, questi test ci mostrano che i pretrattamenti fatti sui filtri non funzionano. In particolare l'immersione dei filtri in NaOH o KOH ha dato pessimi risultati. Anche il trattamento con etanolo mostra risultati inferiori rispetto ai filtri non trattati (con una media di 350 m^2/g). Abbiamo visto che c'è la possibilità di migliorare con dei post-trattamenti, ma purtroppo non abbiamo potuto fare tutte le analisi necessarie per confermare questi effetti.

Anche se ci sono risultati da confermare, possiamo dire con certezza che immergere i filtri in NaOH o KOH non funziona come attivazione chimica, come pensavamo. Come abbiamo visto dal SEM dei filtri non trattati, è evidente un cambiamento nella morfologia: lo sviluppo di una struttura gerarchica dei pori durante il processo di carbonizzazione è molto probabilmente una conseguenza della modifica dell'acetato. Il carbone attivo prodotto ha in generale un'alta superficie specifica e una porosità che va dal micrometro al nanometro. Al contrario, i filtri pretrattati con NaOH hanno aree specifiche basse. Dal SEM vediamo che i filtri hanno cristalli di sodio depositati sulle fibre: dopo il trattamento termico ci sono alcune fibre che sono intatte e altre che sono state parzialmente trasformate, ma ci sono ancora i cristalli di sodio e alcuni di essi sembrano essere fusi insieme. Poiché questi elementi si trovavano sulla superficie dei filtri, la nostra ipotesi, da confermare, è che il sodio, che fonde a 97 °C ed evapora a 882 °C, si fonda sulle fibre a una temperatura che non ha ancora permesso alle fibre di degradarsi. Questo crea un rivestimento di sodio, che rimane liquido, sulle fibre e quindi impedisce alle fibre di reagire tra loro, mantenendo una struttura fibrosa e ostacolando la formazione di pori.

Dobbiamo anche pensare a un modo integrato di procedere (schema in Figura [94]). La pirolisi può essere effettuata sui mozziconi, ma sarebbe intelligente sfruttare anche i gas di pirolisi e dopo aver usato i carboni attivi effettuare un secondo trattamento termico, per produrre calore o fare cogenerazione. Le ceneri verrebbero messe in discarica, ma in quantità molto minore rispetto ai materiali utilizzati nel processo e soprattutto sono inerti. Quindi, possiamo ora trarre le conclusioni finali. Lo studio che è stato realizzato è solo l'inizio di un progetto più ampio. Tutti questi risultati sono preliminari e devono essere confermati, ma possono essere sviluppati ulteriormente e aprire la strada a studi futuri. I punti su cui dovremo concentrarci saranno la ripetibilità dei test (ricordiamo che abbiamo effettuato un solo test per campione, per testare il maggior numero possibile di temperature e tempi di residenza) e la variabilità della materia prima.

Con questo studio abbiamo voluto dare al lettore un'ispirazione, passando in rassegna e riportando diverse opportunità e modalità di valorizzazione, ottenute esplorando la bibliografia e cercando di riprodurre una di queste valorizzazioni, spiegando che un riciclaggio di mozziconi di sigarette in un nuovo prodotto è possibile, fattibile ed auspicabile.

Summary

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1. Introduction

In this work I will present my bibliographical researches and the tests in laboratory that I did, in search of technical solution and promising valorisation to the problem of cigarette butts. To conduct my bibliographical research, I used the databases "Scopus", "Web of science" and "PubChem". The laboratory tests were conducted in the Centre de Recherche of the Université de Technologie de Compiègne (UTC).

As cigarette butts are one of the biggest solid waste in the world, we, as a species, need and urgent way for valorisation. We must remark that unfortunately many cigarette butts are discarded in the environment, creating a widespread problem. As the cigarette butts end up in both terrestrial and aquatic environments, they are a great threat to the well-being of these environments. Many studies, as I will report in the following pages, remarked the danger of cigarette butts, because not only they are very toxic (presenting a wide range of harmful substances), but their decomposition (by bacteria and fungi) takes a long time, so they accumulate in the environment. This dangerous waste can cause considerable and substantial damage to the environment as a whole.

To resolve this enormous problem, we must find an intelligent way to collect and stock this waste and most importantly find a sustainable way to recycle it. This process not only will bring economic advantages, as we will be able to make a product from a waste, but it will also help us clean the environment. Another important step, that I will approach in the last part of my research, is to raise awareness among smokers (starting from the students of UTC) to make them understand the danger of cigarette butts and the necessity to get to a smart way of valorisation. The products we try to manufacture are the most varied. In fact, we can have productions with high added value, but which need less starting material and also processes which can use more cigarette butts, though producing a less valuable output. The choice between the two is not binding, given the large amount of waste present.

To start the research, it has been important to find the most important keywords linked to cigarette butts. The initial keywords that are used were "cigarette butt" and "cigarette filter", to find the most publications as possible. As suggested by the article by Kurmus and Mohajerani (2020) [11], after the initial findings these keywords, were coupled with the so called "secondary keywords", as "valorisation", "recycling" and "toxicity". From the found articles, all the ones that were analysing the social or economic aspects of cigarette butts were relegated to the background, since this project focuses on the technical solution to the cigarette butts' problem. In the end about 20 articles were considered as fundamentals to start the research. To give the idea of the amount of research that scientists all over the world are doing about this thematic, I've done a brief Excel table that reports the number of articles related to "cigarette butts" or "cigarette filter" in two of the major scientific database: Scopus and Web of Science.

Table [1], Summary of literature searches., author's elaboration.

Database	Keywords	n° of papers	Search date
Scopus	"cigarette butts" or "cigarette filter"	1,121 documents	10/02/2021
Web of science	"cigarette butts" or "cigarette filter"	543 documents	10/02/2021

At first, we had to comprehend how the tobacco industry works and what we can find in cigarette butts. Then, starting from the results obtained by the bibliographical studies, we proceeded to analyse the different valorisation paths to find the ones we wanted to perform during our laboratory tests. Then there will be described the making of active carbons in a furnace and the pre-treatments that were done to obtain better performances. At first, the study focused on the activation part: activating with NaOH (Sodium hydroxide), KOH (Potassium hydroxide). Furthermore, it will be described the washing process with ethanol and the extraction with supercritical CO_2. Moreover, there will be reported the analysis on the active carbons that have been produced in the experimental campaign, with comparisons between them and with the results found in the references. Between the analysis there are the adsorption with methylene blue, SEM analysis results for the raw materials and the carbons, the BET method to evaluate the specific surface area (that was also the main parameter of the success of the experiments) and the FTIR analysis.

2. Context

2.1 Tobacco:

To start to analyse the problem, we here show some statistics of cigarette consumption and cigarette butts' pollution. This has been done thanks to the information and tools provided form the Tobacco Altlas [18], an online resource, created in partnership between the American Cancer Society and Vital Strategies, that outlines the nature and scale of the tobacco epidemic and points the way to clear and proven solutions. From this source we observed that in France were smoked 1,090 cigarettes smoked per person per year. Considering that this number is the estimates are of legally sold machine-made and roll-your-own cigarette consumption and consider the population age ≥ 15, we can affirm that, on average every adult smokes around 3 cigarettes per day. For a comparison this number is higher in Italy (1,493), slightly lower in the United States of America (1,017) and almost the double in China (2,043).

Furthermore, as the Tobacco Altas [18] reports, the tobacco product manufacturing process generates an enormous amount of waste: the last rigorous estimate, made in 1995, reported that the tobacco industry produces more than 2.5 million tonnes of manufacturing waste and the majority of this waste contains dangerous chemicals (for example nicotine). The production of products made for tobacco, with cigarettes on top of them, is immense. Multiple sources report that every year the average production of cigarette is about 5.7 trillion (5,700,000,000,000), but we have to report that after many years the number of cigarettes smoked worldwide is finally decreasing. Another interesting fact, also stated in the same report is that many of the tobacco industry's largest markets are highly populous countries across Asia, and the fastest growth is largely in Africa and the Eastern Mediterranean.

The tobacco industry is highly polluting: not only smoking presents health issues, but also the environmental impact of the industry is taken into account. Unfortunately, this aspect, even if it's fundamental to fully understand the difficulty, is usually overlooked when addressing the problem. Zafeiridou et al. (2018) [14] in 2018 evaluated the global footprint of the tobacco industry, using a cradle-to-grave approach. With this viewpoint they evaluated the energy and matter needs across the entire supply chain, process and waste treatment of the production. In their study the considered the different steps of the fabrication chain: cultivation of the tobacco plant, curing, primary processing, manufacturing, distribution, use and final disposal. Each step needs resources and energy and produces a certain amount of waste. To report a few examples, cultivation needs agrochemicals, land and water (among others) to grow the plants, and produces solid waste and emissions (to air, water and soil). Furthermore, in the manufacturing step, we have transport and packaging. As the supply chain goes on, more resources and energy are needed, and more waste and emissions are produced. Finally, we have the use and disposal, making the last contribution to the already enormous quantity of waste produced all along the process.

As a result of this very extensive and in-depth study, Zafeiridou et al. (2018) [14] reported that in 2014 the energy input for the whole supply chain are more than 62 million GJ (more or less the power produced by 2 nuclear reactors) and the total land need is over 4 million hectares (more or less the area of Switzerland).

Moreover, the manufacturing process has an output of almost 6 trillion cigarette (which will later become more waste) and 25 Mt of solid waste. Additionally, 84 Mt of CO_2 equivalent were estimated to be emitted into air; this value is reported to be around 0.2% of the global total CO_2 equivalent emissions. Zafeiridou et al. (2018) [14] also studied the tobacco industry contribution to ecotoxicity of our planet and found that 490 000 tonnes 1,4-dichlorobenzene equivalents were produced. This numbers were reported and calculated by doing Life Cycle Analysis with SimaPro 8 software and the ReCiPe Midpoint methodology, using data from a range of different sources, including industry and market research reports and peer reviewed studies.

From this study we can come to two important conclusions. Firstly, in the process of cigarette making, the factor most impacting on environment is energy use, since it accounts in more than half of all the impact categories. Furthermore, with this data we can know how polluting is a single cigarette and we can compare the habit of smoking to other highly polluting productions, like the meat and sugar industry.

Zafeiridou et al. (2018) [14] report that one single smoked cigarette has a climate change impact of 14 g of CO_2 equivalent emissions, a fossil fuel equivalent of 3.5 g of oil and a water footprint of 3.7 L. Therefore, if we compare the annual environmental footprint of an average smoker (7.3 kg tobacco per year) to an average consumption of red meat (14.4 kg meat) and sugar (24.3 kg sugar), we can see that the impact of cigarettes is far greater than the one of those other typical consumer commodities. With their research Zafeiridou et al. (2018) [14] estimated that the water depletion caused by smoking is 5 times more than the one caused by the other 2 industries and contributes 4 times more to climate change then the consuming of sugar does.

2.2 Definition of Cigarette Butt:

Before defining what a cigarette butt is, we have to define what a cigarette is. As the Cambridge dictionary definition says: “a cigarette is a small paper tube filled with cut pieces of tobacco that people smoke”. Obviously, we need a definition that is much more scientific than this one.

The following image, inspired by an illustration in the article by Kurmus and Mohajerani (2020) [11], easily defines the fundamentals and basic parts of a cigarette, that will be better described later.

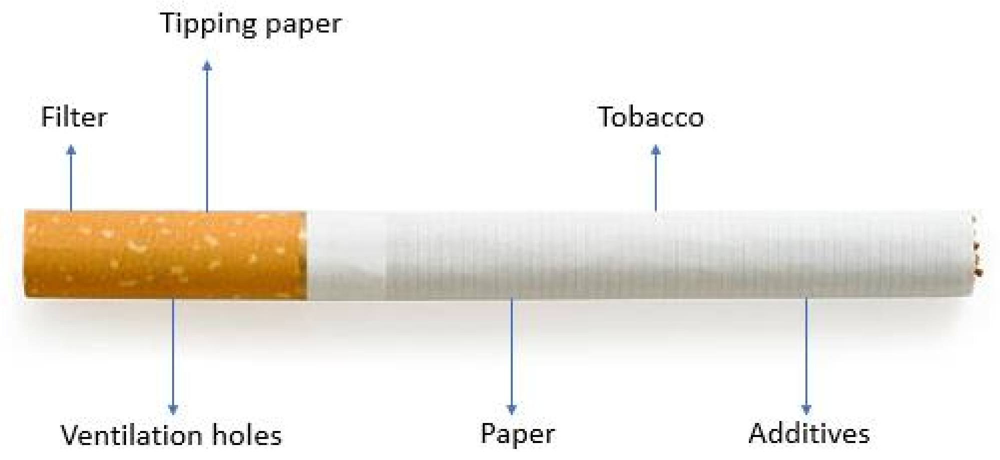


Figure [1], Scheme of a cigarette, modified from [11].

Before defining what a cigarette butt is, we have to give the definition of what a cigarette is. As the Cambridge dictionary definition says: “a cigarette is a small paper tube filled with cut pieces of tobacco that people smoke”. Obviously, we need a definition that is much more scientific than this one.

As well defined by Kurmus and Mohajerani [11] in their 2020 paper, an industrial cigarette is made by various parts:

- A filter, made by cellulose acetate thin fibres, designed to increases filtering efficiency, stopping a portion of the smoke form being inhaled. About 97% of cigarettes contain filters. This element was added to cigarettes in the ‘50s after the understanding that smoking caused serious health problems like lung cancer. The acetate cellulose fibres have a diameter of ~20 μm and they are treated with titanium dioxide (to reduce the lustre of the fibres). Then they are packed in 15 000 fibres units, with the use of glycerol triacetate as a binding agent, creating thus a filter
- Tipping paper, the paper part that is wrapped around the filter and that keeps the filter connected to the rest of the cigarette. This paper, that surrounds the filter contains chemicals like sodium acetate, to maintain the burning process while the cigarette is being smoked, and glues to hold the paper together
- Ventilation holes, on the tipping paper, that when unblocked, help to dilute the inhaled smoke with fresh air
- Cigarette paper, that holds the tobacco in place and that has various chemical added to control the burning time of the cigarette (as it can’t burn too fast)

- Tobacco, the most important ingredient, to which are added many different chemicals to enhance the flavour or make smoking more pleasing and satisfying
- Additives, chemicals put on tobacco leaves in the processing phase.

Now that we have defined the main components of a cigarette, we can analyse what remains of the cigarette after smoking it, the cigarette butt. Cigarette butts is made of 4 components: paper, ash, tobacco (and additives) and the filter. According to Poppendieck et al. (2016) [20], a CB can be defined as "the cigarette remaining at the conclusion of the smouldering phase following smoking. The conclusion of the smouldering phase is defined as when the entire cigarette butt reaches the ambient temperature of the environment in which it is located. The CB includes any remaining paper (wrapping paper, tipping paper, and plug wrap paper)". It is typically about 30% of the cigarette's original length.

The paper can take about 5 months to biodegrade in the environment. Moreover, as said before, we have additives incorporated in the tobacco mixture: these substances are used as humectants (hygroscopic substances used to keep things moist, preventing or delaying the drying of tobacco and in a cigarette we can find glycerol and propylene glycol) or flavour additives.

Finally and most importantly, we have the filter. This part of the cigarette butt, as Kurmus and Mohajerani (2020) [11] state, is made mostly of cellulose acetate. Since this molecule has a high degree of acetate substitution, the cellulose in the littered CB cannot access the microorganisms in the environment for biological decomposition. That is the reason why it takes a lot of time for the CBs to degrade.

A great graphical representation of the components of a CB has been made by Poppendieck et al. (2016) [20]:

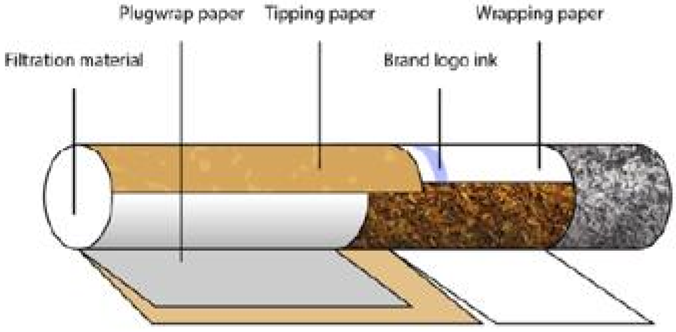


Figure [2], Graphical representation of a cigarette butt, modified from [20].

In the following image is showed a scanning electron microscope (also known as SEM) image of a CB:

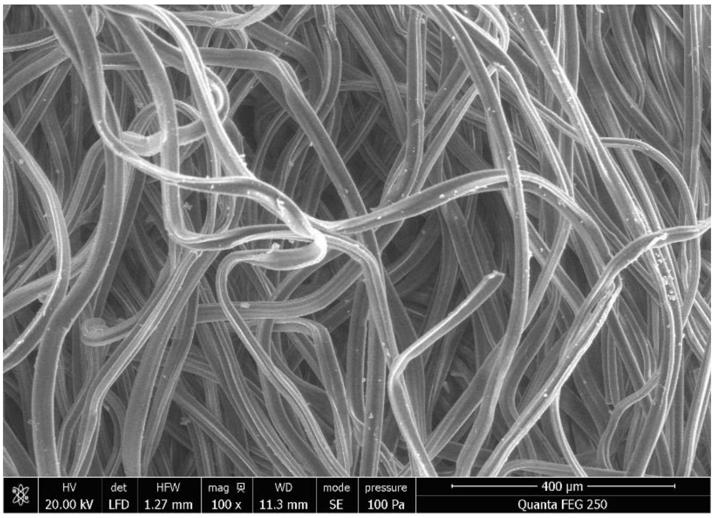


Figure [3], SEM of a cigarette butt, author's elaboration.

This SEM image of a cigarette butt clearly shows the Y-shaped cross-section of acetate cellulose fibres. The same thing is shown in many other studies, like the one from the 2020 study by Koochaki et al. [5].

2.3 Fate of Cigarette Butts:

Unfortunately, many smokers have the bad habit of throwing their cigarette butts on the ground, disregarding the great environmental damage this can cause. This happens more in the city centre, where more people are passing to do their shopping and can have the habit of smoking while they are waiting, as Roder Green et al. (2014) reported. As they discard their cigarette waste, they damage the environment for a long time, but some studies (like Smith and Novotny, 2011 [21]) showed that this behaviour is not perceived as polluting as other littering forms, as plastic bottles. Even if some smokers feel that littering is bad, they continue to do it as they don't see an alternative.

Littering is one of the major causes of pollution. The accumulation of cigarette butts on costal environment, as Araújo and Costa (2019) [15] report, is caused by many factors, but human influence is the essential and determinant one. Even if the CBs found on beaches isn't always linked to smoking specifically on those beaches, many other pollution ways, from a various distance rage, are pollable. For example, we have the transportation form nearby roads or from the drains of building that can be close or not to the costal environment.

In the following figure, inspired by an illustration in the article by Araújo and Costa (2019) [15], represents the ways of pollution and the impacts that CBs littering has on beaches. Not only we have a visual pollution, as the CB are accumulated on the sand clouding the beach, environmental pollution and damage to the biota, but this phenomenon causes also social and economic problems. The CBs need to be removed, se there is a cleaning cost, and if beaches are dirty, there will be a decrease in tourism.

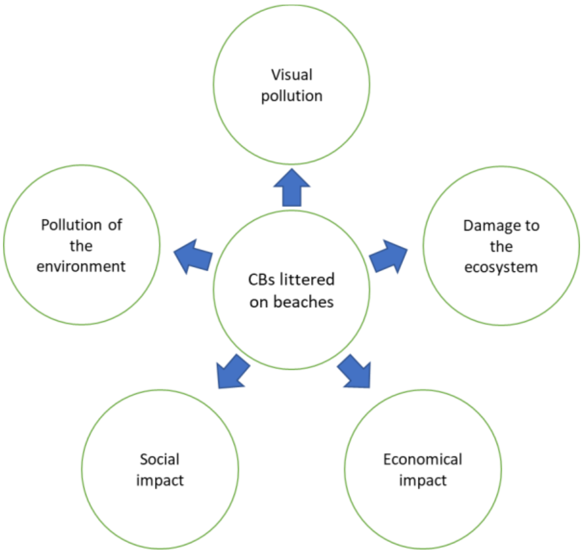


Figure [4], Scheme of beach pollution, modified from [15].

Therefore, a major problem linked to this waste is that institution don't have a control of where it accumulates, as it is usually freely dispersed in various environments. Nevertheless, another important factor that we have to consider, after littering, is that CBs are not biodegradable and contain over 7000 toxic components, as Marinello et al. (2020) [12], between the others, cite.

The fact that CBs are almost not biodegradable or have a really slow decomposition rate is one of the most significant causes of accumulation in the environment. Most CBs, as already said, have a filter and this is the big problem. Filters are made of plasticized cellulose acetate, compressed and wrapped in an outer paper layer; as Bonanomi et al. (2020) [13] and Araújo and Costa (2019) [15] (among the others) state cellulose acetate is really different form cellulose, because of its plasticisation. Cellulose is biodegradable by, any organisms using the cellulase enzyme. Cellulose acetate, due to modifications of cellulose, has a large degree of acetate substitution (more or less 2.45): this increases the filtering efficacy, but limits its biodegrading potential. The chemical process makes cellulose acetate inaccessible to microbial decomposition and thus this product is only photodegradable. Moreover, the decomposition rate of conventional cigarettes is hindered by the high fibre compaction and addition of plasticizers.

Additionally, CBs have a low nitrogen content (having a carbon to nitrogen ratio of about 200) and this further limit the possibility of microbial decomposition. This is also why after the rapid deterioration of the external paper wrapping, the degradation proceeds very slowly, independent of environmental conditions. In fact, as Bonanomi et al. (2020) [13] say, the role of nitrogen availability in plant-based litter decomposition has been remarked as one of the most important factors together with temperature and soil moisture. If we have a low nitrogen content, the organic substrate is difficult to biodegrade, as we reach a state of nitrogen starvation.

Furthermore, to study the degradation stages of CBs and to better understand the dynamics of these processes, Bonanomi et al. (2020) [13] set up a 5 years experiment, experimenting different environmental conditions. Some samples were incubated in a controlled and field conditions with different kinds of soil types (for example changing the physical-chemical proprieties of the soil) and in the absence of soil. At first, they wanted to verify the findings of previous studies that assessed that CBs are most toxic immediately after smoking, and subsequently the inhibitory effects decrease during decomposition. They verified these findings, but they also revealed a second toxicity peak at an intermediate stage (in the phase from two to five years), that suggests a long-term hazard posed by CBs discarded in the environment.

During this long-term study they also found that mass loss of CBs had a three-stage degradation trend. During the first 30 days a rapid mass loss of about 20% took place, in association with the fast degradation of the outer cellulose layer. Then, over the next two years, the decomposition process slowed down, reaching an overall mass loss of ~35%. After five years CBs incubated under laboratory conditions showed high mass loss in both soil types, reaching about 80% when incubated with soil, a percentage that was significantly higher than samples incubated without soil (52%).

From all their test's results Bonanomi et al. (2020) [13] arrived to the conclusion that nitrogen promotes cigarette butts decomposition only when cellulose acetylation falls below a threshold of substitution degree. In this way the microorganisms can efficiently use nitrogen and convert CBs fibers into organic material.

2.4 Toxicity of Cigarette Butts:

Smoking is a serious threat to humans. For every cigarette smoked, a smoker receives around 1.4–2.2 mg of dangerous compounds. As Marinello et al. (2020) [12] report, in 2012 the U.S. Food and Drug Administration (FDA) produced a preliminary list of 93 harmful and potentially harmful constituents (called HPHCs) in tobacco products and tobacco smoke that are linked to the five most serious health effects of tobacco use: cancer, cardiovascular disease, respiratory effects, reproductive problems, and addiction.

The list is reported in the Annex [1] and as we can see between these chemicals, we have the most various substances: from ethylene oxide and hydrazine to benzene and nickel, from styrene and uranium-235 to acrolein and arsenic.

As Slaughter et al. (2011) [16] said, during the phases of growing tobacco and manufacturing cigarettes many chemical products are used and, consequently, the residues of these products may be found in cigarettes prepared for consumption. Between these we can hence find various substances like herbicides, pesticides, insecticides, rodenticides and fungicides. Moreover, more than 4000 chemicals can also be introduced to the environment by cigarette particulate matter (tar) and smoke, that comes from actively smoking. From these substances comes an enormous threat, since between them we have more 50 compounds that are known cancerogenic to humans. Some of the chemicals that were found are: nitrogen oxides, benzene, acetaldehyde, formaldehyde phenol, argon, polycyclic aromatic hydrocarbons, ammonia, carbon monoxide, pyridines and acetone.

It has to be considered that tobacco contains a lot of additives too. As a matter of fact, major American cigarette companies in 1994 introduced approximately 600 additives in their manufacturing process (Slaughter et al. (2011) [16]). These chemicals are usually used to make cigarettes (and other tobacco products) more attractive to consumers. To give a couple of examples, humectants (like glycerol, diethylene glycol and propylene glycol, all possibly carcinogenic to humans) and sugars make smoke easier and milder to inhale, moreover humectants prolong shelf life, menthol and eugenol effectively numb the throat and ammonia may enhance the delivery of nicotine.

The following image, inspired by an illustration in the article by Marinello et al. (2020) [12], easily defines the fundamentals toxic compounds of a cigarette, that will be better described later.

Figure [5], Scheme of a cigarette, modified from [12].

This image shows some of the chemicals that are present in a cigarette and in the ash. Clearly, not all the chemicals that are in the cigarette and that are produced in the combustion process remain in the CB. There is a number of substances that is retained in the cigarette butt and then will emit into the air. Obviously, on the other side, some compounds are too volatile to get retained in the filter, while others are retained but subsequently are very unlikely to be emitted from cigarette butts because they are not volatile enough.

Accordingly, it has to be highlighted that smoked cigarette butts show a greater toxicity than unsmoked CBs because, as it has already been said, the filter retains nicotine and many other compounds produced during tobacco combustion such as ammonia, benzene, acetaldehyde, hydrogen cyanide, formaldehyde, pyridines, and phenols.

As already shown, cigarette smoke is a complex mixture (40 000 to 100 000 compounds, as Poppendieck et al. (2016) [20] state), so the chemicals present in CBs are a gigantic amount. To give an example of the variety of chemicals present in CBs and their concentration, quoting from Poppendieck et al. (2016) [20], we can say that:

- Cadmium, manganese, copper, manganese and zinc were detected in cigarette butts at concentrations up to 104 µg/g of cigarette butt
- Mercury and arsenic concentrations in cigarette filters have been measured up to 0.051 mg/kg of cigarette butt and to 0.651 mg/kg of cigarette butt, respectively
- Zinc and iron have been discovered in the cigarette tobacco, filter and ash

- Maleic hydrazide (1,2-dihydro-3,6-pyridazinedione), a plant growth regulator that inhibits the growth of suckers (secondary stems from the base) on tobacco plants, is often present in cigarettes with concentrations up to 100 μg/g cigarette
- Rutin, a kind of phenolic compound, was found in cigarette filters at a mass of 0.3 μg/filter

All these chemicals represent a danger on the ecosystems. Slaughter et al. [16] studied the roles of nicotine and ethylphenol in ecotoxicity. Nicotine, being an antiherbivore chemical naturally produced in the tobacco plant, is a commonly used insecticide. Ethylphenol is used as a tobacco flavouring agent and is present in cigarette smoke: it has been demonstrated that this chemical is toxic for aquatic organisms.

As Araújo and Costa (2019) [15] remark, the toxic effects of nicotine on fishes have been investigated for more than 50 years. A 1970 article (Konar, Nicotine as a Fish Poison [22]) showed that diluted nicotine solution tested on fish are associated with various symptoms like acute poisoning, palsy of gills, convulsion and finally death.

Moreover, as we approach the problem of leaching, we need to understand the concept behind the filter. A filter is used to reduce the amount of smoke, tar and fine particles inhaled (produced by the combustion process) while smoking and to keep tobacco flakes off the smoker's mouth. The main function of the filter s to capture and retain many toxic substances, but we need to think that when cigarette butts are littered, those dangerous chemicals can leach out of the cigarette filter.

Quoting from Kurmus and Mohajerani (2020) [11], that perfectly resumed the problem, "when CBs are littered into the environment, significant amounts of toxic chemicals are leached and potentially accumulated in water channels, streets, nature strips, and footpaths, thereby posing a serious threat to local organisms and aquatic species." All things considered, studies suggest that the longer CB stay in the environment, worse is the pollution caused. According to Araújo and Costa (2019) [15], one single cigarette butt can contaminate over 1000 L of water. Therefor this is a relevant threat to the quality of urban waters, including supply reservoirs.

To study the danger of cigarette butt leachate to freshwater and marine ecosystems, Slaughter et al. [16] (2011) conducted an extensive research to identify the possible danger to marine and freshwater environments. There is not only the risk of ingestion but, in addition, chemicals present in cigarettes can also be harmful to aquatic organisms. Furthermore, aside to the harm caused to the environment, CBs pollution generally damages the ecosystem as a whole. As Bonanomi et al. (2020) [13] remark, cigarette butts are also considerably menacing the safety of the biological organisms that live in those ecosystems. Many authors, after collecting a huge amount of data, reported that littered cigarette butts pose a toxic threat to a great amount of animals like polychaete, snails, mussel, insects, and plants. Furthermore, the chemicals present in CBs can also interfere with fish bird behaviour.

Slaughter et al. (2011) [16] made tests to identity the LC50 (lethal concentration 50, the concentration that kills 50% of a sample population) of cigarette butt leachate on two different fished: the fathead minnow (that lives in freshwater) and the topsmelt (that lives in a marine habitat). Both species are usually used as a laboratory animal in ecotoxicology to assess the action of certain water pollutants. The LC50 for leachate from smoked CBs was 0.97 CB/l the freshwater fathead minnow and 1.1 CB/l for the marine topsmelt. Moreover, cigarette filters exhibited a lower toxicity, showing a LC50 of 4.3 CBs/l for the freshwater fish. Finally, for unsmoked cigarette filters, the LC50 values that were found by this study were 13.5 CBs/l and 5.1 CBs/l. Hence, form these experimental results, it is evident that the toxicity of smoked filters is greater than the one for unsmoked filters. The explanation, as it has been already said, is that during the smoking process many harmful chemicals get trapped in the filter and consequently, after the leaching process, end up in the water.

Finally, Bonanomi et al. (2020) [13], during their 5 years study, researched the levels of ecotoxicity in time. They remarked that the toxic effect of nicotine starts to decline after 30 days of decomposition: as a matter of fact, nicotine disappeared completely after 30 days (in presence of soil). Unfortunately, other substances are not degraded, highlighting a second toxicity peak and showing that CBs are a hazard to the environment not only in the brief period but also long-term.

To resume, the tobacco in the cigarette contains an enormous number of potentially harmful compounds, and when CB are littered in the environment, these substances, including trace metals, nicotine and various other compounds, are liberated. It is evident that the filter retains many of the compounds present in tobacco and many compounds that are produced while smoking, so if we litter the CBs their filters can harm the environment. The filters can act as the vector for the toxic and dangerous chemicals (we need to remember that many of those are already considered as carcinogens to aquatic habitats), and consequently cause pollution of the ecosystem. Furthermore, CBs can be ingested by animals thus releasing these substances within the animal's body and addition to damaging the environment, cigarette butt's pollution is also associated with serious economic and social problems.

2.5 Danger in current situation:

As of today, the two disposal methods for CBs collecting are landfilling and incineration but, both methods are costly and have high risks of exposure to hazardous polluting fumes, that can be extremely dangerous to the environment and human health. As Kurmus and Mohajerani (2020) [11] and Marinello et al. (2020) [12] described, these conventional collecting and disposal methods are neither sustainable nor economically feasible nor environmentally safe.

As already said, heavy metals are one of the most common pollutant in CBs, moreover it has been already mentioned that although cigarette filters are designed to trap the pollutants coming from cigarettes, these substances are gradually leached into the environment. Torkashvand et al. [19] in their 2021 study on landfill leachate, studied a pilot landfill and the effect of CBs on this system. They analysed the concentration of some heavy metals like cadmium chromium and nickel in the landfill's leachate. The study found out that mixing 1.3% (in weight) of freshly smoked CBs in the pilot landfill leads to increased 3.72% of total heavy metals concentrations; furthermore, this addition leads to an increased 10.52% health risk values from the leachate of the landfill pilot. Furthermore, the study showed that the rate of heavy metals leakage from CB is not equal: lead and strontium have a higher leaching ratio than other metals like aluminium and titanium.

From the following graph, elaborated by Torkashvand et al. (2021) [19], we can see the hazard quotient (HQ) values and ecological risk values for the pilot landfill leachate with different mixing percentages (with CBs % as S1<S2<S3). Landfill leachate without CB (LL) showed significantly lower values than the leachate contaminated by CBs, and the more the CBs were present the higher these indexes were.

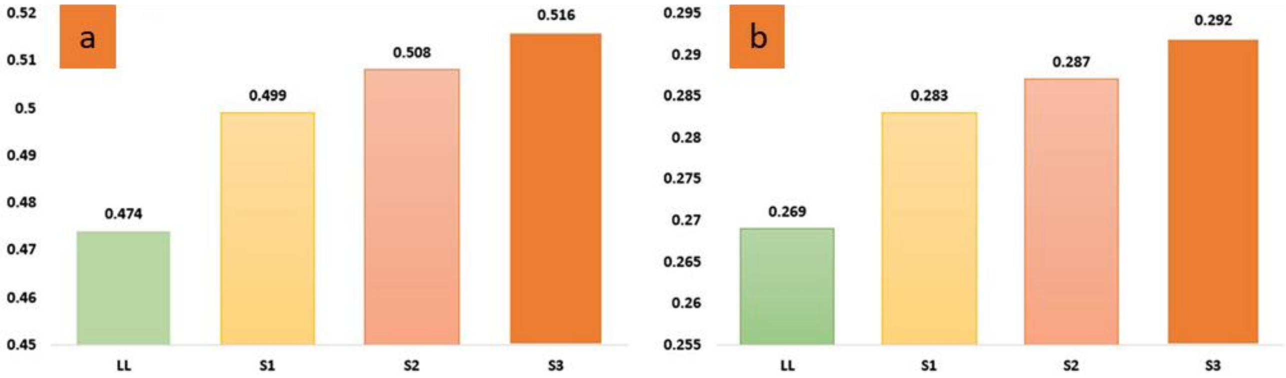


Figure [6], HQ(a) and ecological risk values with different CBs %, modified from [19].

All things considered, the conclusion is that CBs should not be disposed in landfills or incinerators, due to the highly possible health risk, therefore it is necessary find other ways to manage this waste. As the CBs numbers are enormous, it is essential to find effective management solutions for this waste.

3. Bibliographical research on valorisation of CBs

From my bibliographical research I found that currently there are many different possibilities for recycling cigarette butts. This valorisation pathways go from applications with high-value end products to ones with zero or low added-value, that have the only objective of getting rid of this waste. As Kurmus and Mohajerani (2020) [11] remarked in their review, the options that right now are considered as the best choices are applications of energy production, chemical adsorption and creations of nanomaterials, but many other valorisation pathways are possible and can be implemented. An example is incorporation of CBs in civil construction, that is very interesting if we consider the significant number of CBs that could be used.

A lot of new papers have been publicized on recycling CBs and many encouraging results. Numerous methods have been studied and between them we have recycling of cigarette butts in fired clay bricks and asphalt concrete, as active carbons, as a sound absorbing material, a thermic insulator and many more. The aim of this study is to identify the best solutions and technologies for recycling CBs, comparing the results and paying attention to applicability to real contexts. The aim is to reduce the presence of these dangerous materials in the environment and to sponsor the manufacturing of a product from a waste, following the principles of circular economy and sustainable development.

The following image, inspired by an illustration in the article by Marinello et al. (2020) [12], easily defines the distribution of the industries that could possibly implement CBs as a feedstock. This graph has been made after a review of many articles that reported how different valorisation could be implemented on an industrial scale and could possibly do a scale up, after a pilot experiment. The uses have been listed in different industries to better comprehend in which direction the valorisation possibilities are leading to.

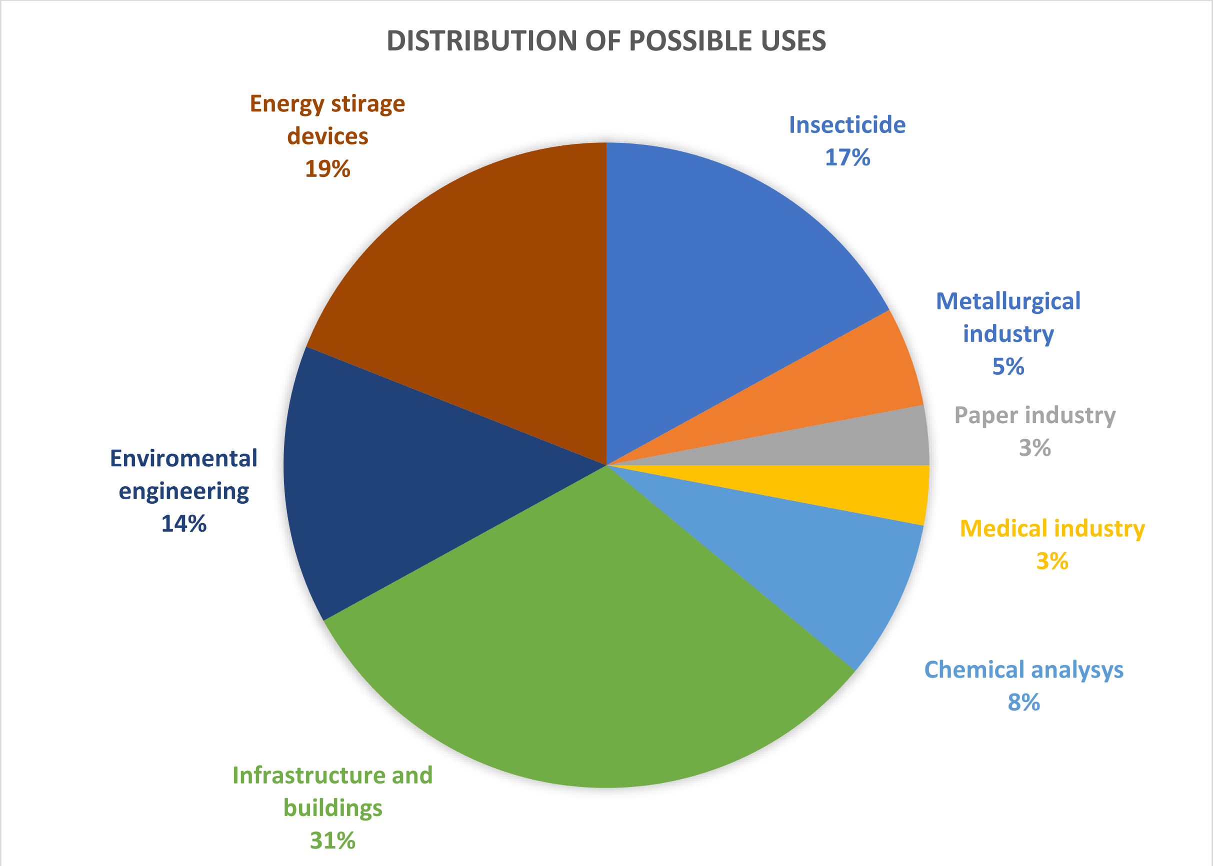


Figure [7], Distribution of possible CBs uses, modified from [12].

In the following pages are reported the found recycling solutions and their description.

3.1 Mixing in fired clay bricks:

Fired clay bricks are made with clay and sand, bound together under high temperatures, thus providing an amazingly strong construction material. As Kurmus and Mohajerani (2020) [11] report, the incorporation of waste materials in fired clay bricks has been investigated, since there is a great number of CBs that could be disposed with these techniques. Many studies were made to investigate CBs recycling in fired clay bricks and among them there is the 2016 paper by Mohajerani et al. [23].

This research did a series of laboratory experiments, preparing clay bricks with a percentage of cigarette butts in the mixture: the bricks had a 2.5%, 5%, 7.5%, and 10% CB content w/w. To measure the results, the mechanical and physical properties of the samples were tested and then were compared to control bricks with 0% CB content. Mohajerani et al. (2016) [23] found that there is a decrease in compressive strength between the 0% CB content (25.65 MPa) to the 10% CB content (3 MPa). This is the reason why this study proposes an incorporation of 1% CBs in weight in the manufacturing process of fired clay bricks.

Furthermore, the laboratory tests suggest that by incorporating a 2.5% CB content in the clay bricks, there is a firing energy saving of 30.8%, and a 58.4% energy saving with an incorporation of a 5% CB content. An increase in CB content also resulted in a reduction of thermal conductivity and this was caused by an increase in porosity.

Hence, this is a feasible and possible valorisation pathway, but it surely needs further research.

3.2 Mixing with asphalt concrete:

Asphalt concrete is a composite material commonly used to surface roads. It consists of mineral aggregate bound together, bituminous binder and filler. The application of CBs or other waste materials in producing asphalt mixtures may solve a major environmental problem, since not only it could reduce the demand for natural aggregates, but it will also dispose of a waste and possibly improve the performance of asphalt concrete.

In a recent study by Mohajerani et al. (2017) [24] the application of CBs in asphalt concrete has been investigated. At first the experimental team dried the cigarette butts in an oven to eliminate any trapped moisture and the CBs were encapsulated with hot bitumen and paraffine wax. Asphalt mixes with 10 kg/m^3 and 15 kg/m^3 cigarette butts content showed acceptable bulk density, good percentage of air voids and resilient properties.

Figure [8] and [9], Fired clay bricks (left) and Asphalt concrete (right), modified from [11].

3.3 Reinforcement in natural rubber:

Natural rubber is highly resilient, but it doesn't have outstanding results in aspects like modulus and hardness. These characteristics can however be improved by forming a composite with reinforcement. Lai et al. [9], in their 2015 paper studied the incorporation of CBs to reinforce natural rubber. They reported that cellulose acetate fibres from the filter can help improving the mechanical properties of the rubber because they remain stable up to 300°C, a temperature suitable for most applications that require rubber.

After extracting and drying the cellulose acetate (CA) from CBs, the CA is added into the rubber with 2,4,6 and 6% in weight. To perform the process, activators, like zinc oxide and stearic acid, and crosslinking agent were also added. The authors found that the addition of 4% in weight of CA to the material is the optimum to be beneficial in improving rheological and mechanical properties. Tensile strength, tear strength and maximum torque were improved.

Finally, il will be need to further research in this field to find more information about the toxicity of this product.

3.4 Production of cellulose pulp:

In their 2017 paper, d'Heni Teixeira et al. [25] researched about the development of a process for recycling cigarette butts into cellulose pulp. Pulp, as Kurmus and Mohajerani (2020) [11] report, is a lignocellulosic fibrous product manufactured by chemically or mechanically extracting cellulose fibres from wood. By mixing with water and other chemical, pulp is the major raw material used in the paper industry. The main idea behind the production on pulp from CBs is to separate all the cellulose content in the CB with a hydrolyzation of the cellulose acetate from the filter in the presence of strong alkali. As the following figure reports (Figure [10]), the project is separated in three steps: mixing, the reaction and the separation of the by-product.

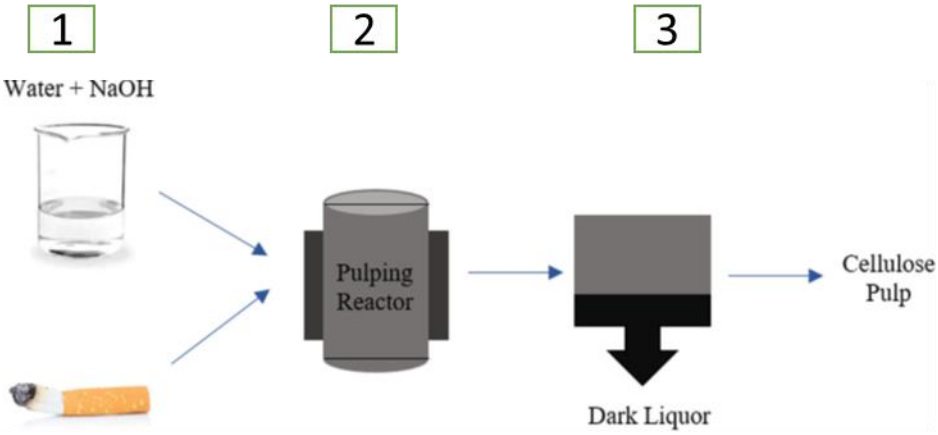


Figure [10], Cellulose pulp production scheme, modified from [11].

The process is based on hydrolyzing the CBs for 3 hours in the presence of NaOH. The experimental results confirmed that the cellulose pulp produced could be actually used in the paper industry.

During the process the cellulose pulp is produced, but unfortunately there is also a by-product, a dark and viscous liquor. This product contains very high resistant organic content, including toxic compounds, however there is not yet a sustainable method to clarify the effluent. In this way constant production of a side stream will be produced and therefore, as there isn't a real utility for this liquor, to put this solution into act a practical solution is essential.

3.5 Utilization as corrosion inhibitor:

Numerous researches have been conducted to determine the corrosion inhibitive efficiency of nicotine. Zhang et al. [26] in 2011 revealed that there is an increase in inhibition efficiency for N80 steel in HCl of 95.3% by adding CuCl and 9% CB water extract to the material. Furthermore, other laboratory results confirm that the copper added water extract from cigarette butts improved the N80 steel surface with a protective coat. Even if the results are promising, the paper requires further research. As Kurmus and Mohajerani (2020) [11] report, it is necessary to further analyse the possibility of toxic leaching during the lifetime of the modified material.

3.6 Production of superhydrophobic sorbent:

Liu et al. [10] in 2020 published a paper where they studied the valorisation of discarded cigarette butts to make a hydrophobic-oleophilic material. Traditionally hydrophobic-oleophilic surfaces are manufactured with low surface energy materials, that are hazardous to ecosystem and human society and moreover some of them have really complex production systems that need massive amounts of energy. This is the reason why it is necessary to study solution to produce easy-to-make, low-cost and eco-friendly materials.

For this study the hydrophilic groups on cigarette butts were 'consumed' through hydrogen bonds by adding hydrophilic polydopamine (PDA). In the meantime, the hydrophobic parts were exposed out, so hydrophobic-oleophilic butt-regenerated materials (HOBRMs) were obtained. These materials had excellent performances in removing oil and separating it from water: the efficiency is reported to be higher than 99.77%. Furthermore, these materials proved to be durable under harsh conditions and managed to stay stable even after cycling.

Ifelebuegu et al. (2018) [27], after the ultrasonic cleansing of the cigarette butts' filters and surface-modify them by chemical vapour deposition using methyltrichlorosilane, produced a superhydrophobic and oleophilic sorbent for application in oil/water separation and spill clean-up. These products can be used for the clean-up of water/oil spills as the processed cellulose acetate fibres show a good wetting behaviour towards kerosene and water, enhancing the separation. Moreover, the filters absorbed oil 16 to 26 times their weight.

This innovative and green approach for manufacturing hydrophobic- oleophilic materials may solve two of the biggest environmental problems: CBs disposal and oily wastewater treatment.

3.7 Biocide:

An interesting application has been proposed by Dieng et al. (2013) [28]. In this article they aimed at verifying the influence of cigarette butts in Aedes aegypti, a vector of dengue. Dengue or 'tropical flu' is a disease transmitted by the bite of an Aedes mosquito carrying one of the four dengue viruses. According to the WHO, in 2018, 3.9 billion people in 138 countries are at risk of dengue infection. Each year, there are an estimated 390 million infections worldwide, including 96 million people who are ill, half a million who are hospitalised (severe dengue), and 20,000 deaths, a very high proportion of whom are children.

Many strategies have been developed to control vectors in dengue epidemic areas with insecticides. As already said before, in cigarette butts there are chemical products known to have pesticidal, fungicidal, insecticidal, and herbicidal properties. Therefore, the study Dieng et al. (2013) [28] was carried out to examine the developmental alterations of Aedes aegypti in the presence of CB waste

Using leachate solutions obtained by soaking the CBs in distilled water and varying contents of smoked CBs the authors studied the mortality rates of A. aegypti in different stages of larvae evolution. From the results it was clear that overall, cigarette butts showed insecticidal activities against mosquito larvae. Furthermore, younger larvae were found to be more sensitive to the presence of toxic elements. As of their experiments, the authors found that in great presence of CBs, mortality was high not only in early phases of development, but even for the late developmental stages. These results suggest that mosquito larvae are vulnerable to cigarette butts' presence in their habitats.

However, it must also be considered that there as issues coming from this approach. When we contaminate a habitat with CBs, as we already said, it's the whole ecosystem that suffers and harm can be brought also to humans. Nevertheless, the study also proposes another interesting idea: if CBs have a vector control effect, also ashtrays that can act as lethal A. aegypti traps could be manufactured.

So, CB waste can be used as a vector control strategy since it causes alterative effect on adult life traits of Aedes aegypti. This is the reason why cigarette new pathways to produce novel insecticide products from this waste are open.

3.8 Electric material:

Moroz et al. [17] in their 2021 review for possible CBs recycling solutions reported that in the field of electric applications, CBs demonstrate interesting possibilities. To give an example, good conductive material can be obtained by a simple heat treatment process. In addition, the article reports that CBs can be considered as potential filler material for a PVC cement resin composite, a substance with adhesive properties used to "weld" pieces of plastic together

3.9 Sound absorbing material:

Two studies were made about the recycling of CBs as a sound absorbing material: Gómez Escobar et al. [2], in 2017 and Gómez Escobar et al. [3], in 2019.

Cigarette butts obtained from different sources and come from different brands were used. As of these differences the CBs had different lengths and diameters, as it could most probably happen in a real-life recycling situation. In both studies the CBs were separated visually by similarity and samples were prepared with butts of the same group: there are doubts about this step on an industrial level. The samples were prepared by manually placing (without using any sort of binder) a certain number of cigarette butts in the impedance tube, the instrument used to do all the measurements.

Furthermore, various samples were prepared, differing in the number of cigarette butts in the samples: this ranged from 10 to 14. Clearly, when the number of CBs was increased the sample was compacted the sample. In the figure below (Figure [11]) we can see it well this compression of the cigarette butts:

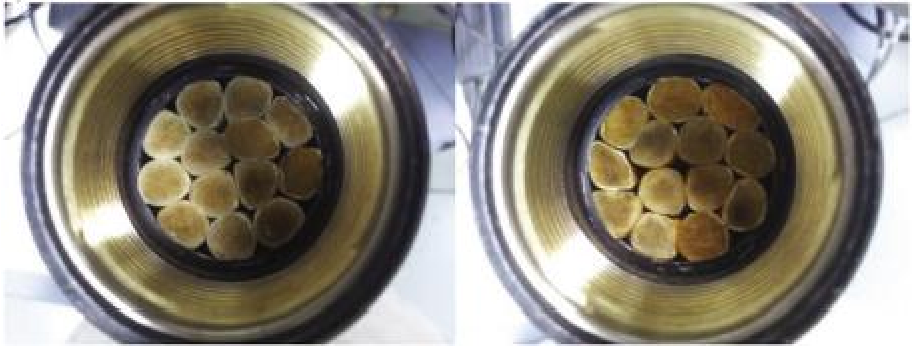


Figure [11], Sound absorbing material, modified from [2].

Gómez Escobar et al. (2017) [2] obtained quite high absorption values for all the samples is quite high, indicating that this method can be used for making sound absorbing materials. Using CBs as an absorbing material, thanks to the porous nature of this waste, a high absorption coefficient of <0.90 from mid-frequencies (>2000 Hz) was found.

When the number of CBs in the samples was increased a slight displacement in the maximum absorption coefficient was observed through lower frequencies, as well as a decrease in the value of this absorption. The authors say that this can be explained because as the porosity of the sample decreases there is an increase of the flow resistivity, which is one of the most important properties of a porous sound absorber. Gómez Escobar in the following paper, Gómez Escobar et al (2019) [3], also remarked that as the geometry of the samples is also a very important factor. As the sound absorption relies on the porosity of the sample, we have to consider that there is a double porosity: the own porosity of CBs and the porosity given by geometry, resulting from the air gaps between cigarette butts. Moreover, according to this study, the sound absorption efficiency also depends on other variables like the presence of burnt regions, the removal of the paper that wrapped the filter and the length of the butts used for sample preparation.

As always with this kind of waste, it is also fundamental to remark that CBs contain toxic chemicals, and, therefore, will possibly require some pre-treatment. Furthermore, the samples made in this study used intact CBs, and, most importantly, the obtained absorption coefficients are valid only for perpendicular incidence. This is the biggest limitations, as for a real-life situation it is necessary to know the random incidence absorption coefficient, but as these were preliminary studies to evaluate the feasibility of this valorisation pathway, this parameter was not considered.

All things considered, the results showed that the acoustical performances of these new materials are similar to the ones of some others commercial sound absorbing materials, and sometimes the CB material demonstrated better performance, indicating indicates that they could be used as possible alternatives. In the future this kind of materials coming from cigarette butts could be used and compete with commercially available acoustical products, helping to solve two major problems at once: noise and environmental pollution.

3.10 Use as biofilm carrier:

Biofilm reactors are mostly used to remove the nitrogen species and organic carbon in wastewater treatment with a biological process. Sabzali et al. [29] in their 2011 published a study aimed to develop a new, efficient, and inexpensive biofilm carrier with the use of cigarette filters. This study found that CBs' filter rods (wasted filter in tobacco factories) can be used as effective and a feasible media for the removal of phosphate and organic matter from wastewater.

Good organic carbon removal percentages, average ammonia removal and removal efficiency of total phosphorus were achieved. However, as Kurmus and Mohajerani (2020) [11] remark in their review, the study lacks of an adequate in-depth analysis to further investigate the problem of a leachate and a life cycle assessment (LCA).

3.11 Cellulose acetate aerogels:

Chau et al. (2020) [6] researched on the fabrication and applications of cellulose acetate (CA) aerogels made from cigarette butts. The CA aerogel was fabricated with a cost-effective freeze-drying method using polyvinyl alcohol (PVA for short) as a cross-linker. The cellulose acetate fibres were obtained from waste of cigarette butts' filters.

The preparation that Chau et al. (2020) [6] reported is quite easy and replicable. At first, the raw CA fibres were blended to reduce the length of the fibres below 5 mm. Then these shortened fibres were dispersed with polyvinyl alcohol with a concentration that varied from 1% in weight to 3% in weight. The mixture that was obtained was subsequently homogenized in a probe sonicator for 20 minutes and further treated at 80°C in an oven for 3 h. With these steps it was possible to create gel with stable three-dimensional network. Ultimately the gel was frozen in a refrigerator at 4°C for 24 h and after all it was a freeze-dried to obtain the CA aerogel.

The resulting aerogel made by Chau et al. (2020) [6] is reported in Figure [12]. It is also possible to see the original CA fibres, which were recovered from the CBs' filters.

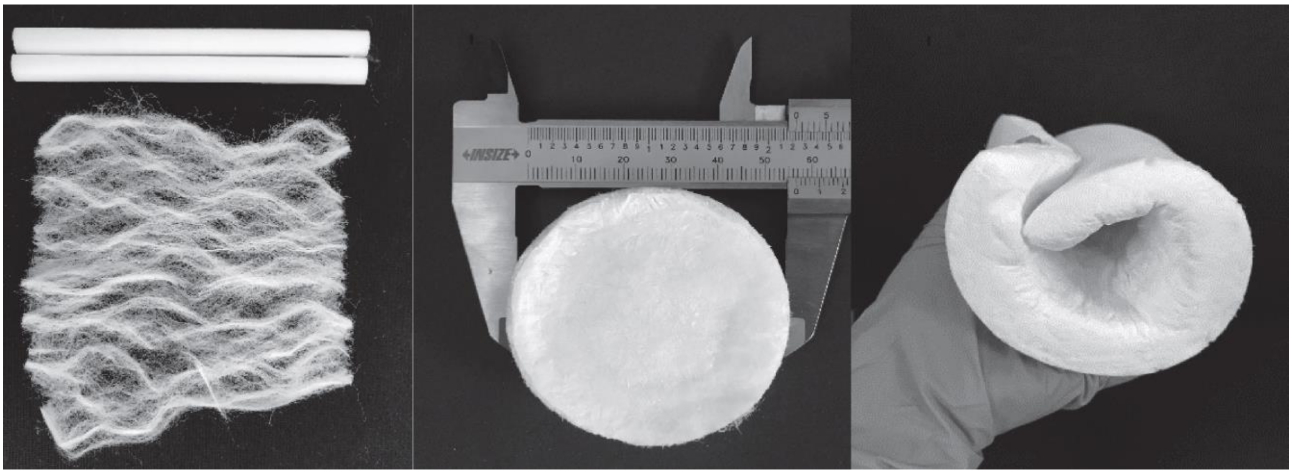


Figure [12], CA fibres and cellulose acetate aerogel, modified from [6].

The CA aerogels that were produced showed an extremely low density (between 0.003 kg/m^3 and 0.5 kg/m^3), a high porosity (between 80.00% and 99.80%), large specific surface area (between 100 m^2/g and 1600 m^2/g) and a low thermal conductivity (between 0.034 W/(m*K) and 0.039 W/(m*K)). Hence, from these experimental results we can see that the CA aerogel is a promising material for future uses in thermal insulation. The paper found out that the pore size was in the range 1.35-2.81 nm, so the pores were both mesoporous and microporous.

By changing concentration of cellulose acetate fibres and polyvinyl alcohol the authors investigated the effects of variable concentrations on the morphology of the aerogels. For the changings in CA concentration it has been remarked that a higher CA concentration resulted in a narrower size of the pores. The porosity changed from 97.52% to 96.39%. In addition, when more cellulose acetate fibres were added and their concentration increased, it was reported a mass increment and a following increase of the density of the aerogel, that passed from 0.022 g/cm^3 to 0.046 g/cm^3. Moreover, an increase in cellulose acetate fibres made the controlling of the aerogel shape easier: the CA fibres help preventing the shrinkage of aerogels during the freeze-drying process, hence helping to maintain a highly porous structure of CA aerogels. These are the reason why it is really important to pay attention to the concentrations of CA fibres and PVA, as depending on theme the properties of CA aerogels can change.

As far as the aerogel's mechanical properties Chau et al. (2020) [6] reported that the product exhibited a low range of Young modulus (between 3.19 and 27.41 kPa) and that the cellulose acetate aerogel was flexible enough to easily roll up. Furthermore, increasing concentration of fibres enhanced the Young's modulus because the addition of fibres reinforced the gel structure during the freeze-drying process.

The most interesting proprieties of this material are the thermal ones. The main application of this product probably is thermal insulation. To be used as a thermically insulating product, CA aerogels need to have good thermal stability and a low thermal conductivity.

To verify the thermal profile of the CA aerogel a thermogravimetric analysis (TGA) was conducted and the results exhibited that CA aerogels had a remarkable thermal stability, up to 300°C. This value is similar to the one seen for other cellulose aerogels.

In addition, the study reported that the material has an actually low thermal conductivity: the highest thermal conductivity reported by the authors is 0.039 W/(m*K), achieved with a 3% of fibres concentration. On the other hand, the lowest thermal conductivity was 0.034 W/(m*K) and it was performed at 1% of fibres concentration. This trend shows that when the fibre concentration increased, the thermal conductivity of CA aerogels increased as well.

To be used for industrial and real-life situations, the CA aerogels need to have a thermal conductivity in the range of the other traditional materials used for thermal insulation. The most used materials nowadays are:

- glass wool, that has a thermal conductivity between 0.031 and 0.040 W/(m*K)
- mineral wool that has a thermal conductivity between 0.031 and 0.040 W/(m*K)
- expanded polystyrene that has a thermal conductivity between 0.033 and 0.040 W/(m*K)
- foamed glass that has a thermal conductivity between 0.037 and 0.048 W/(m*K)).

It should be noted that many of these common materials used for thermal insulation are mostly produced from non-renewable resources and so have an impact on the environment, while the cellulose acetate aerogel comes from a waste and in this way it has a great advantage.

Following this step, Chau et al. (2020) [6] investigated the possibility of oil absorption ability for their CA aerogels. This material, at first, is hydrophilic, because there are hydroxyl groups in the CA structure and PVA. To make the aerogels hydrophobic and thus to find uses in oil treatment, the cellulose acetate aerogels were coated with methyltrimethoxysilane, MTMS for short. This chemical was used for CA modification because of it has a low cost and a simple procedure for coating. After being coated with MTMS, the aerogels became more hydrophobic.

As a result, even if the main use could be the production of CA aerogel for thermal insulation, also an application for the oil spill treatment.

3.12 Activated carbons:

This section will be the most important of the bibliographical part, as many articles were found on this subject. Activated carbon is a material essentially made up of carbonaceous material with a porous structure, which has undergone a special preparation and which, as a result, has a high degree of ability to fix and retain certain molecules brought into contact with it. An activated carbon generally has a high specific surface area, which gives it a high adsorption capacity. As a consequence, the industrial production of activated carbons is used for various applications such as the capture of pollutants in the gaseous or aqueous phase, gas separation processes, and so forth.

However, the fabrication of active carbons (AC) involves expensive and toxic chemicals and also sophisticated techniques. As Koochaki et al. (2019) [5] remark in their paper, activated carbons are generally obtained via two methods: a physical method and a chemical method.

In the physical method, the raw carbonaceous material is pyrolyzed until an initial carbonic base is formed and then, the obtained product is activated by exposing it to an activating gas with high temperatures. This activator factor could be steam or dioxide carbon or oxygen or a mixture of these. The gas reacts with a part of carbon in the material and thanks to the hight temperature can remove it in the form of CO_2. In this way, after removing a part of the original carbon present in the raw material the remaining carbonaceous product will have a porous structure.

On the other had there is a chemical method. Here the initial material, before being pyrolyzed, is mixed with alkaline metals like potassium hydroxide (KOH), sodium hydroxide (NaOH) or some acids like sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). Here, the activator removes the water from the structure of the raw material, lowering the required temperature of carbonization and preventing the formation of tar. This process leads to the formation of the porous structure.

For activated carbons production staring from cigarette butts as a feedstock, numerous studies have been conducted. Between them, there are different approaches and results and in the following part I will expose them and describe the works presented in the retained papers. The studies will be classified with the techniques used and the finals materials obtained. Consequently, I will also elaborate on the differences in these techniques and on the variety of the obtained results.

3.12.1 Pyrolysis:

In 2002, Polarz et al. [30] manufactured active carbons from the cellulose acetate present in cigarette butts' filters. The researchers found that with a process based on a simple one-step procedure porous carbons could be easily prepared. The main result was to show that complex biomolecules like cellulose acetate can be a possible source of porous carbons and these products had good proprieties.

This study is a milestone in the study for the valorisation of CBs and most importantly for active carbon production from biomolecules. The precursors that were choses were the filters of smoked and unsmoked cigarettes; the product was obtained with a thermic treatment under inert conditions. Carbonization temperatures were set at 800 °C and carbonization hold time was adjusted to 2 h, thus the process was cost-effective and didn't require extensive preparative methods. The active carbon that was made exhibited well-defined positions on different length scales ranging from the micrometre to the nanometre.

The following scheme is an image from the review by Kurmus and Mohajerani (2020) [11] and perfectly resumes the process:

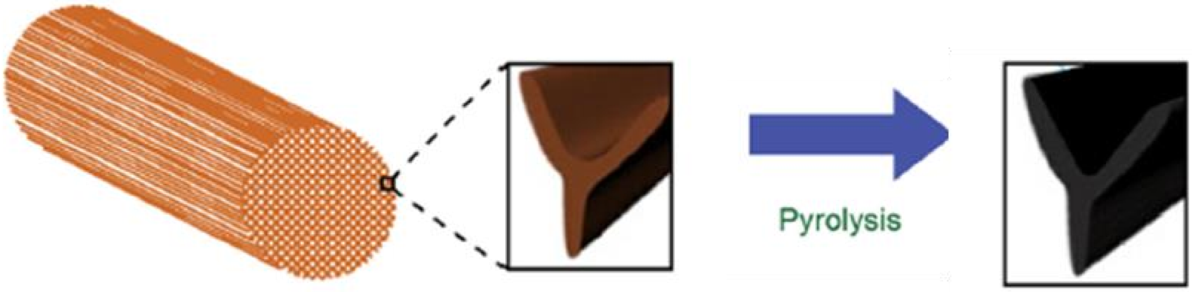


Figure [13], CBs' filters pyrolysis, modified from [11].

After heat treatment, as this scheme reports, the cellulose acetate filter, thanks to a morphological transformation, becomes a black carbon-like material. The pyrolyzed material is described as brittle and less dense than the original cigarette butt's filter. Furthermore, the carbon structure derived from the pyrolysis treatment of cellulose acetate is notably different from the original morphology since the new carbon exhibits a hierarchical structure of different length scales. The range is from 100 nm up to the micrometer domain; moreover, the obtained material has a well-defined mesoporosity, showing an average pore diameter of 4-5 nm.

In the study the authors also compared the results with pure cellulose as a carbon precursor, where there is not a change in the microstructure after heat treatment, therefore saying that the development of a hierarchical pore structure during the carbonization process is most probably consequence of the acetate modification.

To compare with the other solution the data that are needed are the specific surface area and the porosity. Polarz et al. (2002) [30] with their experimental studies found that for their activated caron the specific surface area was 262 m^2/g (obtained with a BET characterisation, the Brunauer–Emmett–Teller theory, which will be explained later) and the porosity was 0.21 cm^3/g. The study revealed that with this data the manufactured material could be used for applications in the gas purification field.

3.12.2 Pre-Swelling with NaOH:

Koochaki et al. [5] in their 2019 publication, made activated carbons starting from CBs' filters and by impregnation with different percentages of NaOH solutions. The study was aimed to compare the activated carbons obtained with a pre-swelling with NaOH and an activated carbon prepared only by physical activation (thus pyrolysis, the method reported before).

The filters were impregnated in NaOH solutions with the following ratios (in weight): 12, 24, and 48% w/w. To remove the excess of NaOH, the filters were compressed. Afterwards the obtained product was carbonized through conventional method in an electrical furnace, in an inert atmosphere (made by introducing nitrogen) at 400 °C for 2 h with a 5 °C/min heating rate.

At first Koochaki et al. (2019) [5] performed an elemental analysis and showed the percentage of carbon is 81.73% and the percentage of oxygen present 18.27%. Therefore, the existence of oxygen in the samples could be caused by the existence of oxygen-activated groups at the carbon surface. Subsequently, the swelling rate was analysed. As we can see from Figure [14], modified from Koochaki et al. (2019) [5], the amount of swelling increases with the increasing of NaOH concentration. The cellulose acetate in the raw filters (a) are less swelled than the filters that swelled with NaOH solution at percentages of 12 (b), 24 (c), and 48% w/w (d).

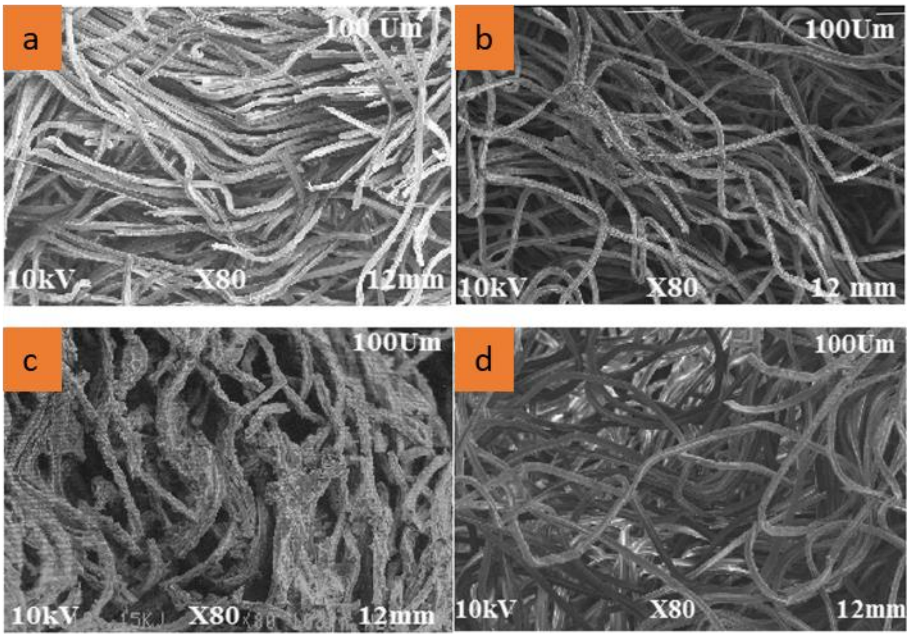


Figure [14], SEM of the pre-carbonisation cellulose acetate fibres with different NaOH ratios, modified from [5].

Then, after the carbonisation process and the formation of activated carbons, the sizes of their pores were observed, always using the scanning electron microscopy (SEM). From the following figure (Figure [15]), it is possible to see the surface of the activated carbon with 12% NaOH (a), 24% NaOH (b), 48% NaOH (c) and the physically activated carbon (d). The figure also exhibits the different morphologies of the obtained ACs from the filters that swelled. The images show that all the obtained activated carbons have porous structure: there is a pore development in parts a, b, and c.

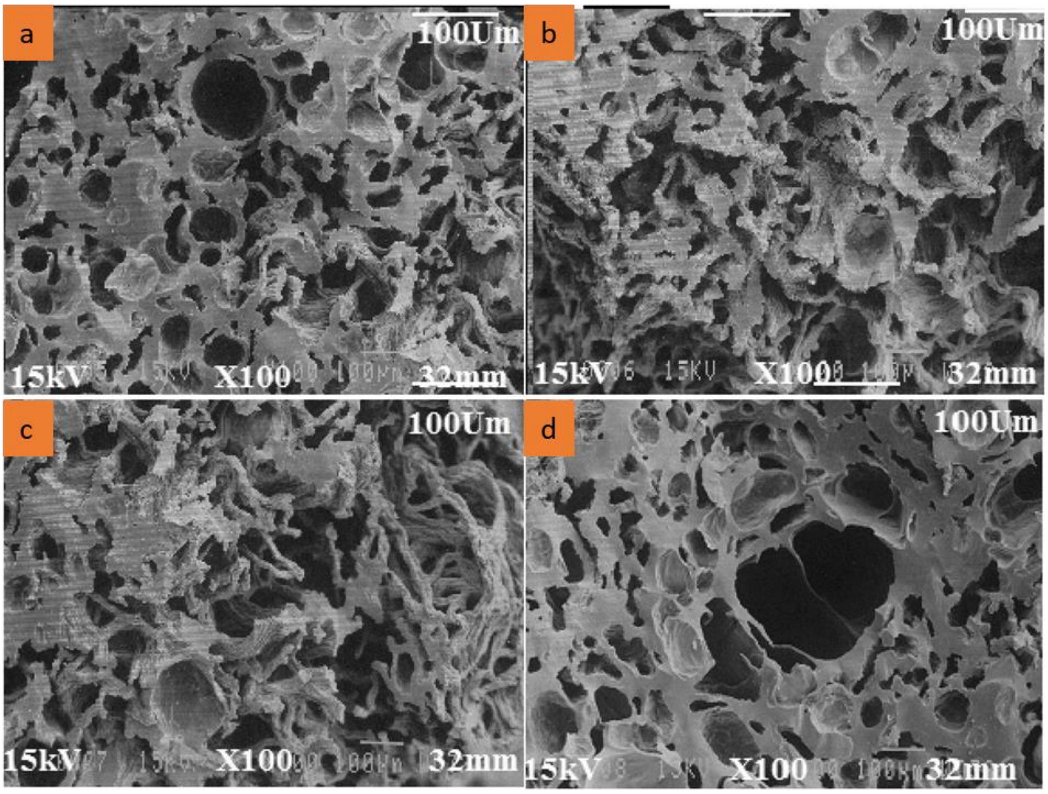


Figure [15], SEM of the activated carbons, modified from [5].

The physical activated carbon has macropores and mesopores, while all the activated carbons that had a NaOH pre-treatment, even if they had different swelling agent concentrations, showed meso and micropores. Therefore, as they have smaller pores, the absorption rates are facilitated.

Here is reported the table (Table [2]) that was made from the results by Koochaki et al. (2019) [5] where the authors compare the specific surfaces that they found in their extensive experiments. To make the comparison with the other studies that I will report in the following sections I will only retain the results of the activated carbon made by pyrolysis and the chemically activated carbon with the highest specific surface (the one with a NaOH ration of 1:3). As we can see the physical activated carbon samples have specific surface area of 570.75 m^2/g, and a diameter of 2.651 nm; on the other hand the samples that got swollen with 48% of NaOH have surface area of 1083.33 m^2/g and a diameter of and 2.203 nm.

Table [2], Activated carbons made by Koochaki et al. (2019) [5] comparison table., modified from [5].

sample code	specific surface [m^2/g]	pore size [nm]	pore volume [cm^3/g]
Ph.OAC	570,75	2,651	0,373
Ch.OAC.12%	953,56	2,28	0,594
Ch.OAC.24%	1001,4	2,254	0,621
Ch.OAC.48%	1083,33	20203	0,654

The average specific surface area was calculated with a BET analysis and we can see that the activated carbons that were pre-treated with NaOH showed an increased surface area when compared to the physically activated ones. Furthermore, as we already said, the pore size decreases when the amount of swelling agent increases (which is intuitive as the specific surface areas increase when pore diameters decrease). This is probably explained by the fact that swelling agents remove water from the raw original material and in this way the carbonisation temperature is reduced. Therefore, as a result, lower temperatures mean lower formations of tar into the pores during the process and leading to smaller pore size.

Hence, with these findings, it is possible to affirm that the activated carbon produced by NaOH impregnation is a very good precursor in comparison with that produced via physical activation method and thus has clearly better results.

3.12.3 Microwave-induced KOH activation:

Hamzah and Umar (2017) [4] studied the possibility of fabricating activated carbon from cigarette butt waste by a chemical activation using potassium hydroxide (KOH) and a microwave input power Hamzah and Umar (2017) [4] remark that these active carbons are especially suited for being an alternative for oil-water separation, methylene blue adsorption, and super capacitors.

Microwave heating method has been applied to prepare active carbons since, as the study reports, it heats the materials rapidly and uniformly. Furthermore, microwaving is an energy-efficient method compared to conventional methods and could be helpful in improving the quality of final products.

As a feedstock cigarette butts' filters, and unwrapped from the cigarette paper, were used. This methodology required a longer pre-treatment phase: before being processed the filters were washed with water and then washed again with 96% ethanol. Afterwards, they were placed into a vacuum oven for 3 hours at 230˚C for a first heat treatment. Finally, the samples were crushed into a powder size of about 100 µm. and activated with a KOH solution. Only after all these pre-treatments the activation step was performed. This was carried out in a tubular glass reactor with a microwave input power of 630 W at 2.45 GHz frequency and irradiation time for 20 minutes.

The samples were activated with different ratios of KOH, to later analyse the effects of the activating compound. CF-1 had a 1:1 ratio to CB's filter mass and CF-3 has a 3:1 ratio to CB's filter mass.

To define the results of this procedure, Hamzah and Umar (2017) [4] executed nitrogen adsorption-desorption isotherms measurement by using the BET method. With this technique, the results showed that the activated carbons that had been made with a microwave-induced KOH activation had a maximum specific surface area of 328.13 m^2/g with pore diameter of 3.04 nm. This result was achieved with a ratio of KOH to carbon of 1:3 in weight. Nevertheless CF-1, the filter that was treated with the least KOH, showed a specific surface area of 303.49 m^2/g. Subsequently, as for the dimensions of the pores, all samples of the active carbon showed both meso pores and micropores, with the diameter of about 50 µm.

Hamzah and Umar (2017) [4], to better understand the absorption abilities of the product that they fabricated, conducted an adsorption experiment of methylene blue (also known as MB), a very used blue dye. The following graph (Figure [16]) shows the different results for the active carbon prepared with different KOH impregnation. All the samples had good results and CF-3 showed relatively high MB adsorption capacity of 88.77 mg/g.

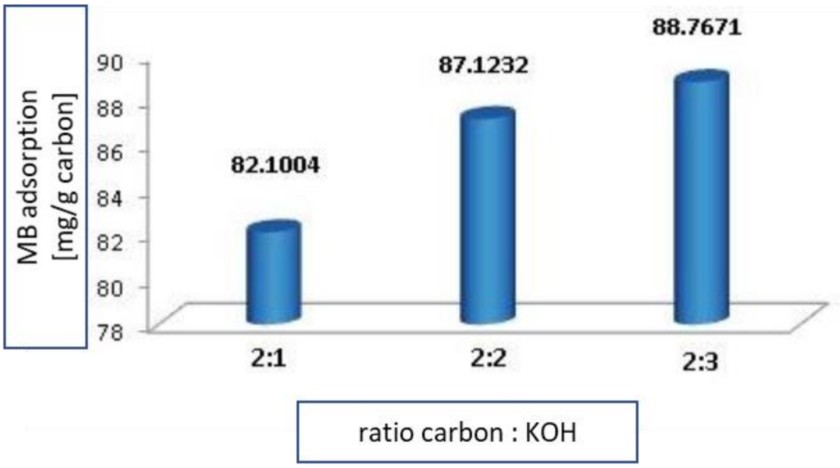


Figure [16], MB adsorption capacity for different sample, from [4].

3.12.4 Hydrothermal carbonisation and activation

Blankenship and Mokaya (2017) [7] studied the hydrothermal carbonisation of cigarette filters of smoked and unsmoked cigarette butts. The hydrothermal carbonization of a biomass rich in carbon, in the presence of water, produces a solid material that is referred to as hydrochar. When activated the hydrochars generate oxygen-rich porous carbons that have extremely high apparent surface area (up to 4300 m^2/g), with most of the surface area coming from micropores (up to 90%).

Hydrothermal carbonization is a fairly new process and gives many advantages if compared to the others. As it usually needs lower temperatures (between 150 and 350 °C) and pressures around 2 MPa and it does not generate hazardous chemical waste or by-products (as pyrolysis does), it is considered energy-saving and eco-friendly. Furthermore, is made using water, which acts as a solvent and catalyst; moreover there is no need for an inert atmosphere.

After having removed the wrapping paper from the filter, the filters obtained from cigarette butts were hydrothermally carbonised by heating a mixture of the filters and water in a stainless steel autoclave to 250 °C, holding at 250 °C for 2 h and then cooling to room temperature. The ratio of filter to water was 1 g filter to 10 mL water. The obtained product, the hydrochar, is a carbonaceous matter. Then there was the activation process: for the activation KOH was used, in a KOH/hydrochar ratio of 4. Subsequently, the KOH/hydrochar mixture, in alumina boats, was placed in a furnace and heated in an inert atmosphere to 600, 700 or 800 °C.

The activated carbons had different denomination. At first, the hydrochars obtained from the hydrothermal carbonization process, were denoted as FF-hydrochar (fresh filters) or SF-hydrochar (smoked filters). Then, after the activating phase, the activated carbons were designated as FF-4T (group F, fresh filters) or SF-4T (group S, smoked filters) where 4 is the KOH/hydrochar ratio that was used and T is the activation temperature (600, 700 or 800 °C).

At first in their analysis, Blankenship and Mokaya (2017) [7] studied the elemental composition and nature of carbon. Interestingly, they found that the fresh FF-hydrochar has a higher oxygen content (32.2% in weight) compared to 24.8% in weight for smoked SF-hydrochar. Moreover, these products were oxygen-rich and showed a variety of oxygen functional groups such as COOH, C–OH and O–C=O. Furthermore, SF-hydrochar contains some nitrogen while the FF-hydrochar was free of it. This is probably explained by the fact that in the filters, during smoking, nicotine gets trapped, while in the fresh unsmoked cigarettes this doesn't happen.

The porosity of the activated carbons was probed by nitrogen sorption analysis. The surface area, pore volume and pore size results are reported here:

Table [3], Characteristics of the porous carbons produced from Blankenship and Mokaya (2017), modified from [7].

sample code	specific surface [m2/g] (a)	pore size [Å]	pore volume [cm3/g] (b)
FF-4600	1970 (1512)	6	0,86 (0,59)
FF-4700	2803 (1901)	6,8	1,23 (0,73)
FF-4800	4113 (2075)	6,8	1,87 (0,79)
SF-4600	4310 (3897)	6,4	2,09 (1,71)
SF-4700	2512 (2019)	6,8	1,20 (0,91)
SF-4800	2393 (1810)	6	1,09 (0,70)

The values in the parenthesis refer to: micropore surface area (a) and micropore volume (b). For the comparison with the other methods, only the highest results were picked: the results showed by the samples FF-4600 and SF-4600.

As we can see from Table [3], the values for the smoked samples (SF series) show an anomalous trend with respect to the effect of activation temperature. Generally, when the activation temperature increases, the porosity generated, as measured by the amount of nitrogen adsorbed, increases as well; here is the opposite, as porosity decreases going from 600 to 800 °C. Also, for the SF series, the highest surface area is at 600 °C and then it decreases for samples activated at a higher temperature. As Blankenship and Mokaya (2017) [7] remark, the anomalous trend is explained by the presence of significant amounts of metal additives in the hydrochar derived from CBs. The metal additives like K, Ca, Na and Mg can themselves act as activating agent in addition to the added KOH.

Furthermore, these materials not only are super porous and have ultra-high surface area (the apparent surface area is highest at 4310 m^2/g for sample SF-4600, but also the other samples reported really high values), but we must consider that pore volume comes almost entirely (more 90% in many of the cases) from micropores. For example, SF-4600 despite the very high apparent surface area, it still exhibits an extremely high micropore surface area of 3867 m^2/g, which is 90% of the total surface area. Not all the samples show this amazing result (the proportion of micropore surface area is 77% for FF-4600, and 68% for FF-4700 and 51% for FF-4800), but it is still a great result.

The authors, viewed the good proprieties of the new materials and as hydrogen storage in porous carbons is really favoured by the presence of high surface area coming from micropores, conducted laboratory experiments on the samples. As of the hydrogen storing materials, currently there are two main groups, that have two different strategies. The first one is storing hydrogen via chemisorption and it includes materials such as metal hydrides; the second one is physisorption and requires highly porous materials with a high surface area such as carbons, metal organic frameworks (called MOFs) and covalent organic frameworks (called COFs).

The storing conditions for the tests are -196 °C and pressure variable between 0 and 40 bar and were chosen because cryo-storage under these conditions is considered viable for low pressure vehicular hydrogen storage. The results that Blankenship and Mokaya (2017) [7] obtained showed that at 20 bar, excess hydrogen uptake has a value of 6.4 wt% for the sample FF-4700 and of 7.0 wt% for FF-4800 (fresh filters at 800 °C) and is higher than most previously reported porous carbons. Furthermore, the corresponding total uptake at 20 bar for FF-4800 is 8.2 wt%; as the authors reports, this value is higher than the best reported hydrogen uptake values under such conditions (-196 °C and 20 bar): 7.03 wt% and 7.3 wt% obtained respectively for polypyrrrole-derived activated and compactivated carbons.

The higher obtained values for the FF series rise to a total hydrogen uptake of 10.4 wt% and 11.2 wt% at 30 and 40 bar. Moreover, at 30 bar, the hydrogen uptake capacity of SF-4600 already outperforms the normal values for the MOFs. In addition to their impressive storage capacity, the present carbons also offer a great series of advantages: easy processing, high chemical and mechanical stability and low cost, in addition to the valorisation and environmental protection aspects associated with using cigarette butts as starting materials.

In the following table (Table [4]), from Blankenship and Mokaya (2017) [7], all their hydrogen uptake results are reported:

Table [4], Hydrogen uptake (wt%) of the porous carbons produced from Blankenship and Mokaya (2017), modified from [7].

sample code	1 bar	20 bar	30 bar	40 bar
FF-4600	2	5,2 (4,6)	5,6 (4,8)	5,9 (4,9)
FF-4700	3,2	7,2 (6,4)	7,8 (6,6)	8,3 (6,7)
FF-4800	3	8,2 (7,0)	9,1 (7,2)	9,7 (7,3)
SF-4600	4	9,4 (8,1)	10,4 (8,3)	11,2 (8,4)
SF-4700	2,7	6,8 (6,0)	7,4 (6,2)	7,8 (6,3)
SF-4800	3	6,6 (5,9)	7,2 (6,1)	7,6 (6,2)

Since they exhibit the combined effects of high microporosity, high surface area and an oxygen-rich nature, these materials could help in the search for new hydrogen storing solutions, which will show improved properties, will be easier and cheaper to prepare, and that will be environmentally sustainable.

Among others, also Lima et al. (2018) [8], investigated this product. In their 2018 interesting study the authors investigated the synthesis of hydrochars from CBs with a low-temperature hydrothermal carbonization, without using inert gas. The study reports that is already know the application of hydrochars as adsorbents in the removal of metals, drugs, dyes and herbicides from aqueous solutions, but there hasn't been a huge development because hydrochars have generally low porosity and specific area (so usually a lower adsorption ability). As the other study that was reported, also Lima et al. (2018) [8] have submitted hydrochars to an activation process to increase its adsorptive capacity.

Differently from Blankenship and Mokaya (2017) [7], in this study the authors performed a low temperature hydrothermal carbonization: the CBs samples were treated with water at a temperature of 463 K (189,85 °C) for 48 or 72 h. In addition, the chemical activation was made using sodium hydroxide (NaOH). The samples' names were HCB48 and HCB72 (for the hydrochars, with the name varying in function of the carbonisation time) and HCB48-ATV and HCB72-ATV (for their respective NaOH activated versions).

As usual, the specific area was calculated from the Brunauer–Emmett–Teller (BET) isotherm using N_2 adsorption data. This analysis gave fairly disappointing results: the BET specific areas of HCB48-ATV and HCB72-ATV were 2.30 and 3.74 m^2/g, respectively. These outcomes are not only far from the findings by Blankenship and Mokaya (2017) [7], but also less than normal surface area for active carbons (which typically have surface areas greater than 600 m^2/g). It was clear that the activating process using NaOH and low temperature did not lead to pore formation, neither to a significant increase in specific area.

To better understand these findings a scanning electron microscopy (SEM) was made. The resulting images are reported in the following figure, Figure [17]:

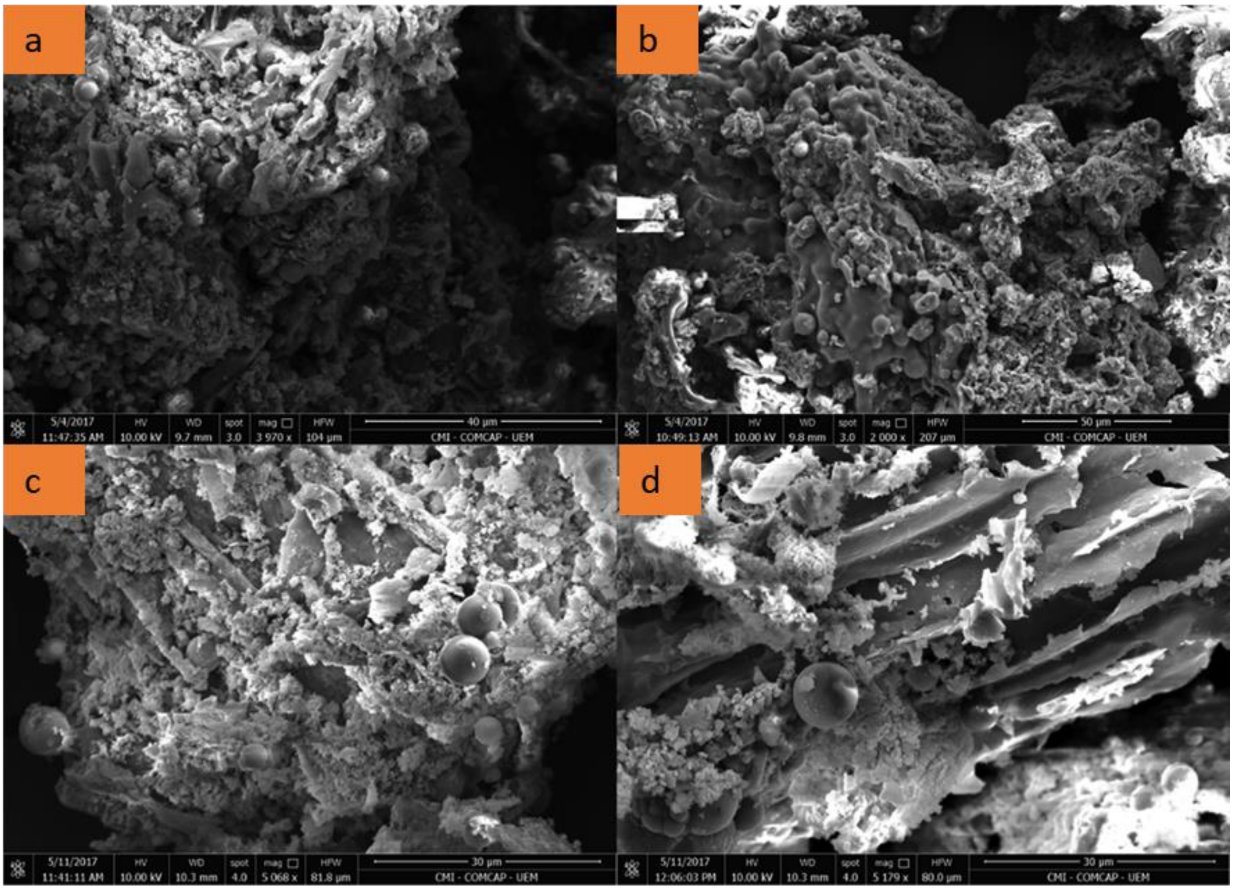


Figure [17], SEM of HCB48 (a), HCB72 (b), HCB48-ATV (c) and HCB72-ATV (d), modified from [8].

These scanning electron micrographs were obtained to evaluate the morphologies of the prepared materials before and after activation. As it is possible to see, the HCB48 and HCB72 materials (shown in Figure [17] (a) and (b)) exhibited irregular surfaces without pores. Many spherical particles were observed on the surfaces of all samples, both the hydrochars and the active carbons. Lima et al. (2018) [8] remark that the origin of these microspheres could be associated with “decomposition, condensation, dehydration, or polymerization and aromatization of cellulosic components during the hydrothermal carbonization”.

To better analyse the results, a chemical characterization of the surface was done. In this way it would’ve been easier to understand the chemical transformations that occurred during the conversion of cellulose acetate to carbonaceous products in the hydrothermal carbonization. A spectroscopic characterisation was carried on: the FTIR spectra of HCB48, HCB72, HCB48-ATV and HCB72-ATV were analysed.

The study found that all the profiles that were observed in all the samples were similar and bands were observed at about 3700 cm^{-1}, which represents the hydroxyl groups (-OH); the highest intensity reported was in HCB48 and HCB72. This excess in OH^- ions could be useful for adsorption in a basic environment. Moreover, as the authors report, “the band at 1790 cm^{-1} corresponded to the stretching of CO bonds associated with esters, acetone aldehydes, and carboxylic groups and exhibited lower intensity in the HCB48-ATV and HCB72-ATV samples”. Finally, the band observed at 1072 cm^{-1} is the one that corresponds to $O\text{-}CO\text{-}CH_3$ that is typical in cellulose acetate bonds and exhibited a higher intensity in HCB48-ATV and HCB72-ATV.

To conclude, from Figure [17] and the FTIR analysis it is clear that the activation with NaOH at low temperatures did not result in pore formation and it plainly indicates that this process of activation provided changes only to the surface groups of the activated hydrochars.

As a consequence, Lima et al. (2018) [8] report that event if hydrochars don’t have great specific areas, they contain a greater number of functional groups on their surface and so for the adsorption of cationic dyes they can be superior adsorbents. This is the reason why adsorption assays of methylene blue solution (MB) with varying concentrations were carried on. As the solution pH is an important factor affecting the adsorption this factor was changed in the range of 3.0 to 11.0.

The chemically activated materials (the ATV series) exhibited greater ability for adsorption with increasing adsorption rated at higher pH values. The authors report that “at high pH, the large quantity of OH^- ions increased the negative potential of the adsorbent surfaces, providing greater removal of positively charged MB. Electrostatic interactions possibly were the main drivers for the adsorption process”. The highest removal efficiency of MB for the non-activated samples was observed at pH 11.0 with maximum removed amounts of 184.68 and 209.64 mg/g by HCB48 and HCB72, respectively. This is already a great adsorption capacity, nevertheless the amounts adsorbed by the activated samples were almost three times higher than those by the non-activated ones. The sample HCB48-ATV showed an adsorbed amount of 561.73 mg/g while the sample HCB72-ATV of 548.72 mg/g.

Hence, the two reported studies both showed different but amazing results. Blankenship and Mokaya (2017) [7] in their publishing found a material with amazing proprieties. They state that they are “unaware of any reports of higher surface area (above 4300 m^2/g) for activated carbons. We attribute this high apparent surface area to an optimal mix of KOH, the metal additives in the SF-hydrochar and an ideal activation temperature”. Nevertheless, these results are really impressing. On the other hand, Lima et al. (2018) [8] didn’t achieve the same results, but the materials that they manufactured showed a great capacity for adsorption in a basic environment, owing to excess OH^- ions that enhanced the negative potential of the adsorbent surfaces, resulting in great removal of MB.

As already anticipated, to better understand the result and to compare the different active carbons that have been made, a table has been done, where the specific surface area, the porosity and the pore size were reported (when available from the studies).

From the following table, Table [5], it is possible to make the comparisons between the carbons made in the different studies. Furthermore, as the comparative table might be less easy to follow a graphical representation of the results obtained with the different techniques has been made.

Table [5], active carbon from references comparative table, author's elaboration

sample name	specific surface area [m^2/g]	porosity [cm^3 /g]	pore size [nm]
Polarz et al. [30] - pyrolysis	262	0,21	3
Koochaki et al. [5] - pyrolysis	570,75	0,373	2,651
Koochaki et al. [5] - NaOH pre-swelling	1083,33	0,654	2,203
Hamzah and Umar [4] - microwave-induced KOH activation	328,13	/	3,04
Blankenship and Mokaya [7] - Hydrothermal carbonisation and KOH activation - SF4600	4310	2,09	2,1
Blankenship and Mokaya [7] - Hydrothermal carbonisation and KOH activation - FF4800	4113	1,87	2,1
Lima et al. [8] - Hydrothermal carbonisation and NaOH activation - HCB72-ATV	3,74	/	no pores

Moreover, also a graph for comparing and better visualising the differences in specific areas has been elaborated:

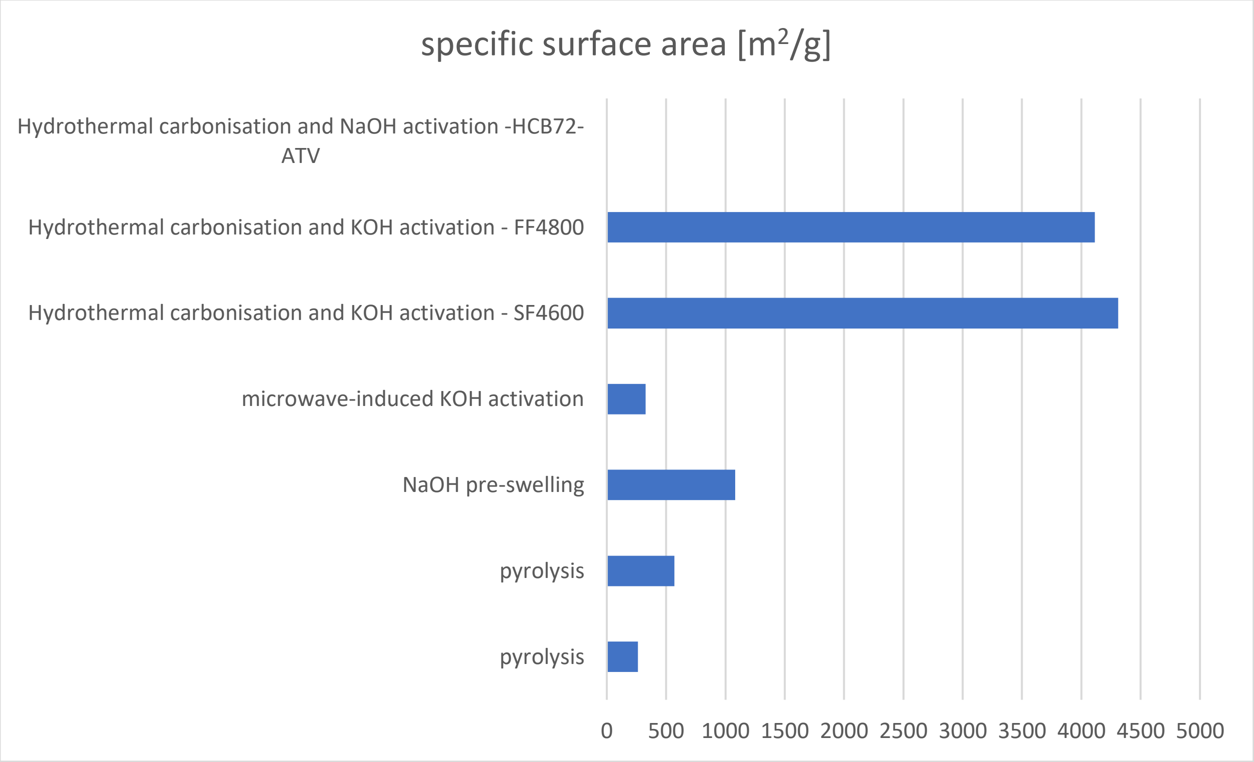


Figure [18], Comparative graph for specific surface, author's elaboration.

From this graph it appears more clear than ever that the results reported by Blankenship and Mokaya (2017) [7] are really an exception and should really be investigated and remade with care, as they could in actual fact be an optimal solution for an imminent future and a sustainable alternative in the active carbon manufacturing, as it is important to remember that these materials all come from the cigarette butts' waste, that in the current situation is still considered as a waste and not a possible raw material.

3.13 Carbon-based catalyst:

Veerabagu et al. [1] in their 2021 study analysed the possibility of the production of a novel cigarette butts-derived porous carbon-based catalyst for highly efficient Suzuki-Miyaura cross-coupling reaction.

As the authors report, "Suzuki-Miyaura cross-coupling is a key reaction in organic synthesis for C–C bond formation. Synthesis of biaryl compounds via coupling aryl halides with aryl boronic acids in the presence of palladium catalyst are widely used in many areas, including medicine, cosmetics, engineering materials and so on".

The process to make the catalysts needs a series of pre-treatments. First of all, there is the need of producing the carbonaceous base. To do this at first the wrapping paper and tobacco were removed and, in order to remove the cigarette smoke, cigarette filters were treated by washing with ethanol. Then the samples, derived from cigarette butts, were heated under argon gas to 800 °C for two hours. In addition, the resulting materials were dispersed in water under ultrasonication and then Na_2PdCl_4 was added. The resulting catalyst was called Pd@CCB and palladium-dispersed material coming from CBs (CCB). A similar procedure was followed to prepare a catalyst coming directly from cigarette butts, called Pd@CB. Cigarette butts were used as support and then Na_2PdCl_4 was added.

Veerabagu et al. (2021) [1] report that the Brunauer-Emmet-Teller (BET) surface area was calculated. For the carbonaceous base, CCB, the specific surface area was 1247 m^2/g (a good results considering that it had only been washed with ethanol and was subject to pyrolysis) and a pore volume CCB was 0.55 cm^3/g. As observed by the authors, after the impregnation of Pd nanoparticles, the surface area and pore volume of Pd@CCB reduced to 886.07 m^2/g and 0.52 cm^3/g. This result demonstrated that the palladium Pd nanoparticles were scattered on the surfaces of CCB and partially occupied some of the pores of CCB. This are the reasons why Veerabagu et al. (2021) [1] remark that the high surface area of Pd@CCB could expose more active sites in Suzuki-Miyaura cross-coupling reaction and therefore it would lead to high activity.

The surface morphology of Pd@CB, CCB and Pd@CCB was investigated by field emission scanning electron microscopy (FE-SEM). We can see the results in the following figure (Figure [19]). From these images it is confirmed that the long continuous triangular fibres, typical of the cellulose acetate (the starting material), were converted into irregular particles of carbon. Furthermore, after loading the Pd nanoparticles, Pd@CCB showed similar morphology to that of carbon derived from cigarette filters.

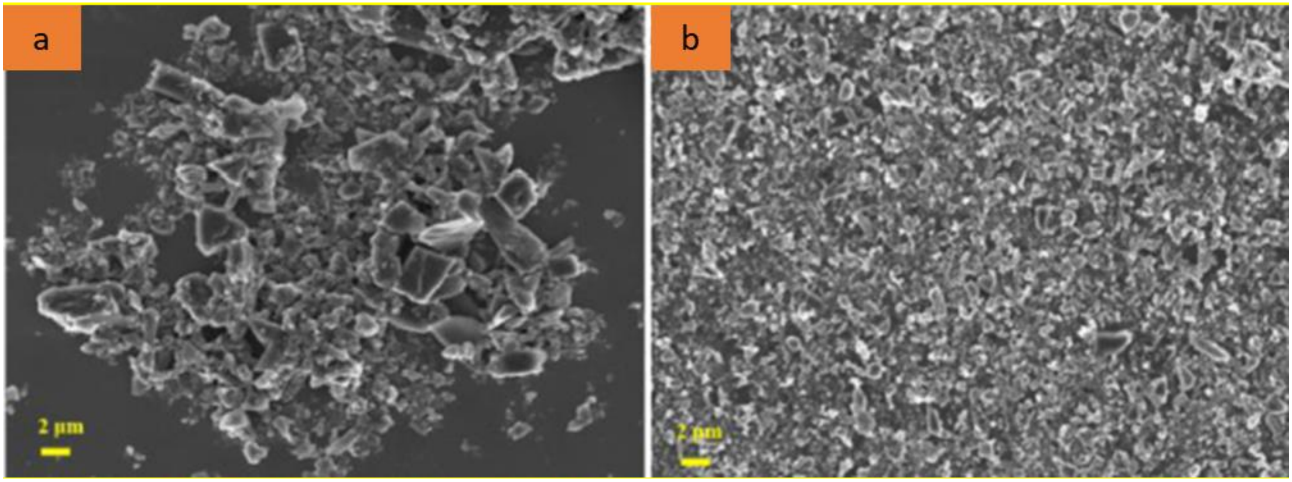


Figure [19], FE-SEM images of CCB (g) and Pd@CCB (h), modified from [1].

From the scanning transmission electron microscopy (called S/TEM), reported in Figure [20], the study investigated the morphology of CCB and Pd@CCB catalyst. As we would think and as also the other studies on active carbons from CBs have reported, the CCB support had various micropores after the thermal modification of the CB. In addition, the Pd@CCB catalyst showed a well-ordered distribution of palladium nanoparticles with nearly spherical morphology on the surface of their support. The originally triangular fibres shown in the CBs, were thermally modified to high-surface and microporous carbon, and this process favoured a good interaction between Pd nanoparticles and the support. This is the reason why the aggregating of Pd nanoparticles has been prevented. It has to be reported that, for reasons of space, Figure [20] has been cut and modified by the author, but by any means the original meaning of the image has not been changes.

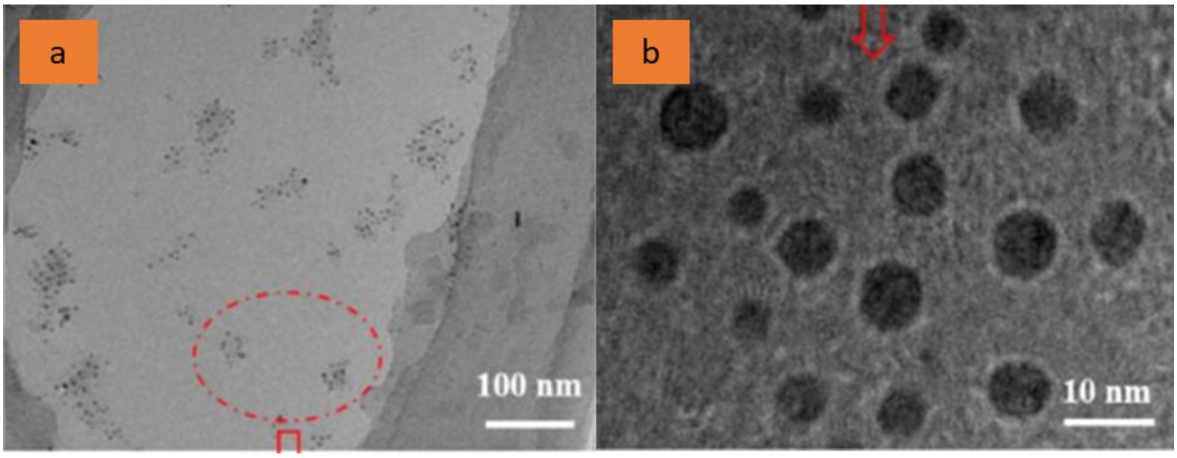


Figure [20], S/TEM images of Pd@CCB catalysts at two levels of magnification, modified from [1].

Additionally, the authors reported the EDS mapping that they performed and this confirmed that the Pd@CCB is composed of C and Pd elements, and the uniform Pd nanoparticles, as we can see in Figure [21] are well dispersed throughout the carbon support.

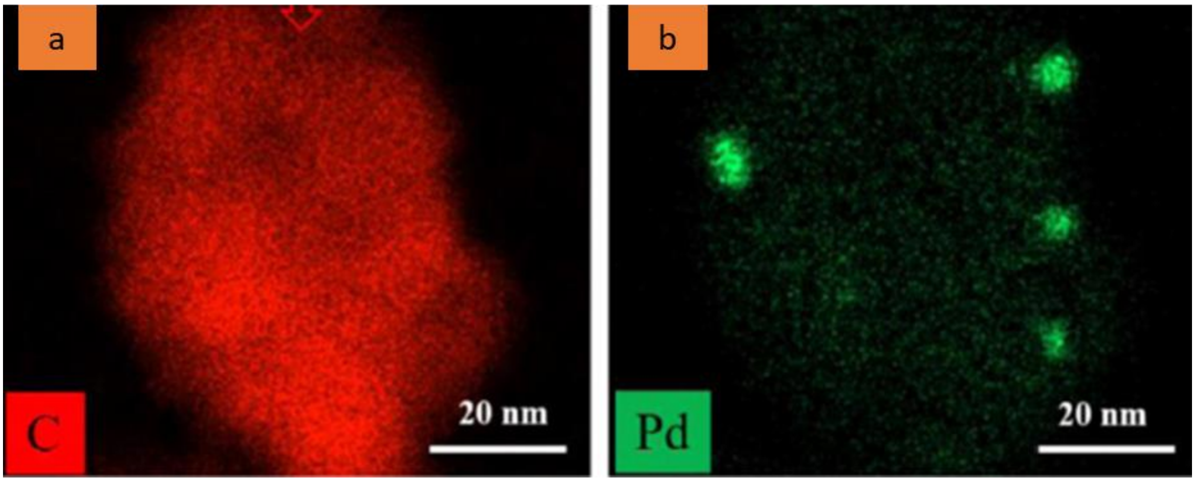


Figure [21], EDS mapping of Pd@CCB catalysts, modified from [1].

From all these results it is obvious to say that the palladium particles were dispersed as small crystallites over their carbonaceous support; moreover the fact of having a material that was derived from CBs (namely CCB) and not using directly CBs as a carbon-base, resulted to be advantageous. From the chemical characterisation of the catalyst, revealed by powder X-ray diffraction (XRD) patterns, it was clear to see that the obtained porous carbons contained a large number of oxygen-containing functional groups, in particular groups as COOH, C–OH and C=O. Veerabagu et al. (2021) [1] state that "These groups can serve as bridges or coordinating sites to capture and anchor Pd ions, followed by in situ Pd nanoparticles formation after the introduction of reductant, which leads to robust fixation and high dispersion of nanoparticles. It makes cigarette butts-derived carbon an ideal host for robustly accommodating ultrasmall nanoparticles".

So, after having seen that the cigarette butt-derived carbon was really porous and had a great surface area, which effectively improved the dispersion of Pd nanoparticles, Veerabagu et al. (2021) [1] effectively tested the ability as a catalyst of their material. Heterogeneous catalysts, like Pd@C, show several advantages to the purpose: easy separation from the reaction, minimal product contamination and possibility of reuse.

The authors investigated the catalytic performance of Pd@CCB and Pd@CB for Suzuki-Miyaura cross-coupling reaction between a series of substituted aryl halides and 1-naphthyl or phenylboronic acids. The two products showed several differences.

At first Veerabagu et al. (2021) [1] used bromobenzene and 1-naphthylboronic acid as the model substrates to optimize the reaction conditions. Even if for the Pd@CB catalyst the reaction yield was of 84%, a great quantity of palladium was needed. This is the reason why the Pd@CCB was developed. As a result, the desired product was obtained in the yield of 82% when this new catalyst was used; the authors think that this is due to the fact that the new product had a higher surface area and better dispersion of Pd nanoparticles and most importantly it didn't show serious agglomerations.

Moreover, also the solvents and the bases are an important factor. By choosing a water and ethanol mixture as a solvent (and it is important to remember that it is a green solvent) and KOH as a base, the amazing yield of 96% was obtained. The following figure and table (Figure [22] and Table [6]), extracted from [1], perfectly resumes all the results that were achieved.

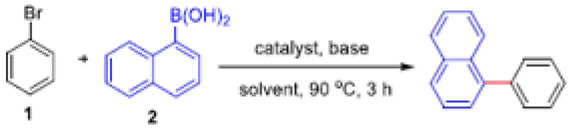


Figure [22], Reaction catalysed with Pd@CB or Pd@CCB catalyst, modified from [1].

Table [6], Optimization of the reaction conditions, modified from [1].

entry	catalyst	Pd loading (wt%)	base	solvent	yeild (%)
1	Pd@CB	3,50%	BuOK	EtOH:H_2O (1:1)	84
3	Pd@CCB	1,50%	BuOK	EtOH:H_2O (1:1)	82
4	Pd@CCB	1,50%	BuOK	H2O	45
5	Pd@CCB	1,50%	BuOK	EtOH	75
6	Pd@CCB	1,50%	BuOK	EtOH:H_2O (2:1)	94
7	Pd@CCB	1,50%	K_2CO_3	EtOH:H_2O (2:1)	65
8	Pd@CCB	1,50%	KOH	EtOH:H_2O (2:1)	96
9	Pd@CCB	1,50%	KOH	EtOH:H_2O (2:1)	71

Resuming the final results, the developed catalyst had a yield up to 98% and a metal loading of 1.5 wt%, which is quite low. Furthermore, it can be easily separated from the reaction mixtures and the paper states that it can maintain a high activity even after seven cycles. Overall, it is possible to say that the catalyst proposed by Veerabagu et al. (2021) [1] is a promising low-cost solution for future use in C-C coupling.

To conclude, transforming cigarette butts into carbon materials for catalysts is a promising strategy for developing porous support for anchoring nanoparticles, since the base material has a good specific surface area and remarks the presence of many micropores. The greatest advantages of this methodology, compared with other porous carbon materials, are the availability and the extensive sources (as CBs are the feedstock) and low cost are also its outstanding advantages. Furthermore, these techniques will also allow us to move away from coal-based precursors to biomass or waste-derived starting materials for carbon synthesis.

3.14 Cellulose nano-crystals:

In a recent research, Abu-Danso et al. (2019) [32] investigated the use of CBs for the removal of diclofenac (a product that belongs to the class of non-steroidal anti-inflammatory drugs and is widely distributed in the world pharmacopoeia under various names and also marketed under the name Voltaren) from water.

Cellulose nanofibers (CNFs) were first extracted from CBs with a process that cleaved the acetyl group by alkali treatment and etched with phosphate ions (HPO) from phosphoric acid to obtain the variably charged HPO-CNFs. Then sulfuric acid was used under high temperatures to cleave phenol moieties from CNFs to obtain cellulose nano-crystals (CNCs). The SEM images revealed the exfoliated fibre strands of CNFs after extraction procedure. The experiments revealed a maximum removal capacity of 107.9 mg/g of diclofenac and this founding suggests that celluloses extracted from cigarette butts can potentially be used as an absorbent for the removal of diclofenac from water. Furthermore, Langmuir model fitted well to the adsorption data.

3.15 Enterprises in the field:

In this following chapter, some international projects will be presented. The researched industries are business that collect, treat and recycle cigarette butts; in our research we found more and less developed industries that had more and less detailed business plan, but in overview it is possible to say that all of these enterprises, are doing something to deal with a problem and this is still remarkable.

As we already remarked, many investigations are carried out in the research world, for valorisations in various fields. However, in most cases, the fate of the pollutants has not yet been studied, as the studies focus primarily on the expected characteristics of the products resulting from recycling, thus making the process to go from an idea presented in a scientific article to a real-life business project harder and harder.

Some enterprises that perform recovery processes exist internationally - the most successful of these is run by Poiato Recicla in Brazil, which recovers cigarette butts in the form of cellulose pulp, used in the paper industry. Moreover, TerraCycle is active in several countries (USA, Canada, Australia and the UK) and recovers cellulose acetate in the form of plastic granules. In France, only Mégo! and EcoMégot offer, at more or less advanced stages, material recovery of butts. The former has a prototype unit for recycling butts into plastic sheets that can be used for various purposes (mainly street furniture). The issue of pollution control and the fate of pollutants during the process seems to have been addressed, but no experimental data was obtained. The second, at this stage, is still exploring several material recovery options.

In the following part some examples of recycling business will be reported and described. All the information that has been recovered on them was completely found on their official sites, which are obviously always quoted and stated in the references. A study and comparing the different solutions performed by different companies all around the world, but with a focus on France, was done by Leymarie et al. [36] in their 2019 study of recycling methods for cigarette cigarette butts, a report produced for the French Ministry of Ecological and Solidarity Transition.

3.15.1 TerraCycle

TerraCycle is an American company founded in 2001. It is an innovative recycling company that has become a global leader in recycling typically hard-to-recycle waste. TerraCycle offers free recycling programmes funded by brands, manufacturers, and retailers around the world to help people collect and recycle your hard-to-recycle waste. To date, over 202 million people are collecting and recycling in 21 countries and have collected billions of pieces of waste, raising over 44 million dollars for charities around the world.

As reported in their site [37] “TerraCycle avoids waste-to-energy and never uses it as an end-of-life solution for anything that we guarantee to be recycled. TerraCycle only utilises waste-to-energy in select cases, such as when a material is required to be handled this way due to legal restrictions (i.e. hazardous medical waste originating from hospitals)”.

It is based in Great Britain and collects cigarette butts from France and Europe (for example they do the CBs recycling at the Davos forum). However, it claims that the flows collected are still insufficient to go beyond the "recycling test" stage. The literature search on their website [36] also revealed that this company recycles cigarette butts in Canada (collection activities identified in Montreal, Vancouver and Belleville), as well as in the United States (partnership with the Port of San Diego, in particular) and in Australia, with the city of Melbourne.

As the company reports on their site, in 2012 they did the launch of the world's first recycling programme for cigarette butts. TerraCycle's process for recycling cigarette butts implies that the butts are put through a series of processes to remove the residual tobacco and paper, both of which can be composted after separating them from the cellulose acetate. The remaining cellulose acetate filter material is washed to decontaminate it. From there, the material is transformed into a rigid plastic format, which we then process into a powder. This powdered material can be used for commercial applications such as composite decking or smaller promotional products such as ashtrays.

Additional information provided from their site, indicates that the water used for decontamination is used in a closed circuit, and that the powder obtained from the filters represents, depending on the product, 10 to 60% of the mass. However, Leymarie et al. (2019) [36] in their report state that several indications gathered suggest that TerraCycle does not have its own processing facilities and occasionally calls on subcontractors to manage the flows of butts that have been previously massaged at consolidation facilities.

To conclude, as Koochaki et al. (2019) [5] remark, recently this company "collected cigarette filters from nine countries including Australia, Canada, Spain, Hungary, and America and separated the cellulose acetate in the filters and then used them in numerous industrial productions like pallet". The acknowledgement by a such innovative article is a really nice sign that the path taken by TerraCycle is a good one and can be imitated in other places in the world.

3.15.2 MéGo!

MéGo! is a French company based in Bretagne that has developed its CBs recycling process and expanded the field of products made from recycled cigarette butts. This company is very present on the net and social networks, thus was very easy to find information about it. As they report in their site [34] it now has a prototypical recycling process and has plans to set up an industrial facility in eastern France by 2021. Its growth is nevertheless reflected in the increasing number of partnerships and franchises (notably in the cities of Rennes, Castres, Poitiers, Paris, Nantes, Grenoble and Caen), but are now extending beyond the French borders. The aim of this national service is to collect cigarette butts and then recycle them, by setting up a dynamic collection system for CBs. This offer allows cities to get less polluted and to communicate on their commitment in favour of the environment. MéGO! provides a complete BtoB (business to business) solution for companies, associations and local authorities.

In their valorisation projects they install street furniture (ashtrays, containers) and ensure the collection, recycling, statistical follow-up and carbon footprint of all the operations. The aim is to set up environmental-loving approach to reduce peoples' carbon impact and raise awareness among citizens.

The process implemented by Mé-Go! aims to produce plastic sheets, obtained by thermocompressing filters of crushed and washed cigarette butts. These sheets can be used to produce a variety of objects, ranging from mobile phone holders to street furniture, pallets and shopping trolley tokens. The sit-stand bench, reported in Figure [23]) is currently the product on which MéGo! is focusing its development efforts.

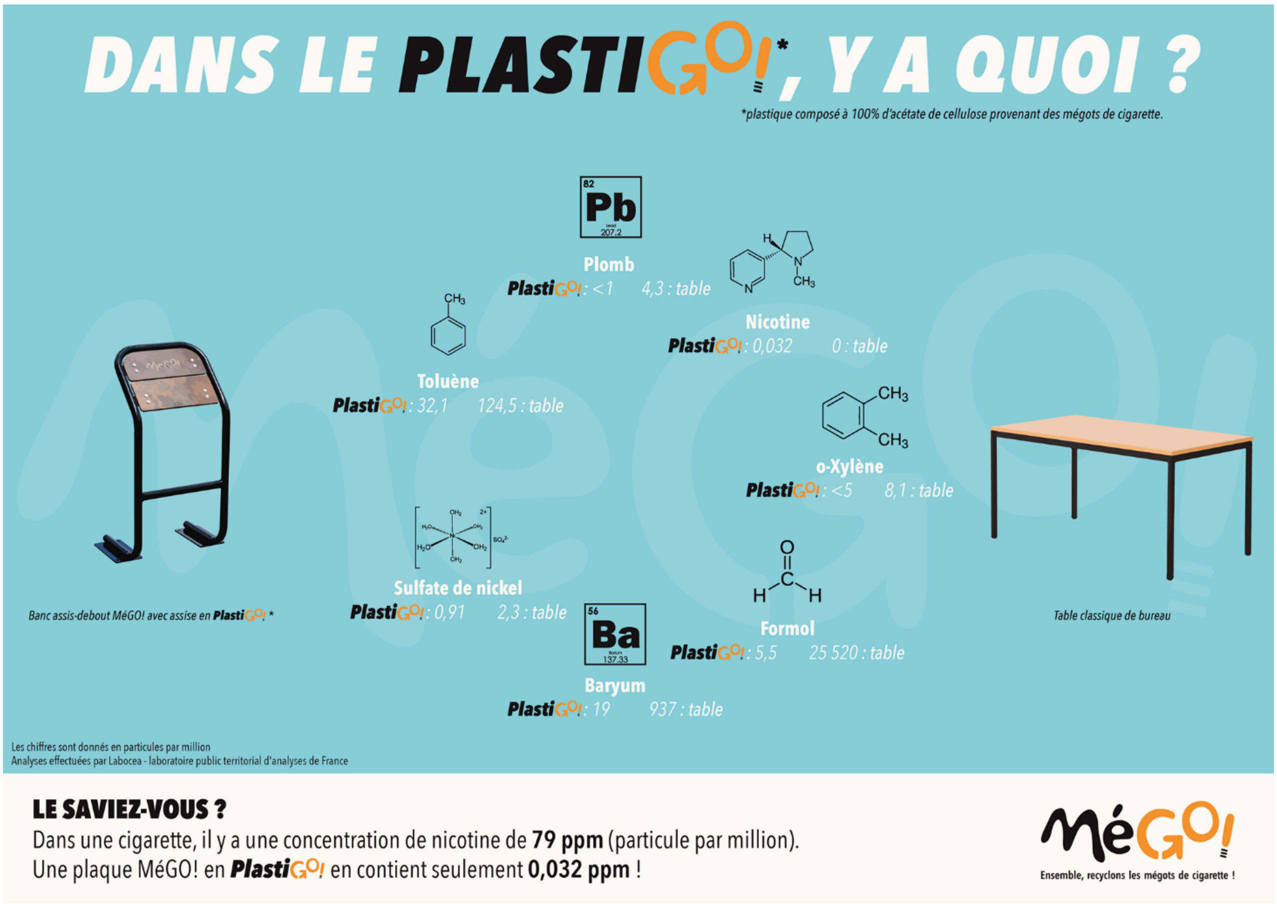
Figure [23], sit-stand bench, advertisement from [34].

As Leymarie et al. (2019) [36] reported, to perform the process, the CBs are first sorted manually to remove undesirable elements, and then the ash, paper and tobacco fraction is separated from the filters by a sieving and grinding stage. The filters are washed with water before being dried and crushed again for the compression stage. MéGo! reports that the proportions of the different outflows observed are: unwanted (7%), ash, paper and tobacco (15%), process sludge (8%) and recycled product (70%).

In this process, the extraction of the hazardous substances contained in the butts would be ensured by the water washing stage with an adjuvant (natural active principle not communicated, as it is confidential), carried out in a closed circuit, with several successive baths. The combined action of the water and the adjuvant would thus enable polar and apolar pollutants to be treated. The pollutants would thus be concentrated in the sludge obtained by treating this water, ensuring the removal of almost all (from 90 to 100% as the company reports) of the pollutants from the butts.

In the following figure, Figure [24] is reported an advertisement by MéGo! where the company shows the composition of their plastic. Their approach is really focused on the environmental advantages that a valorisation of CBs can give, even if it's not a highly technological one (they make furniture out of recycled CBs).

Finally, concerning the economic cost of this recovery, a cost of 10 € / kg of cigarette butts is realised. However, as Leymarie et al. (2019) [36] remark, this figure should be treated with caution, as it is not specified whether it takes into account transport or only the recycling operation.



DANS LE PLASTIGO!*, Y A QUOI ?

*plastique composé à 100% d'acétate de cellulose provenant des mégots de cigarette.

Plomb
PlastiGO! : <1 4,3 : table

Nicotine
PlastiGO! : 0,032 0 : table

Toluène
PlastiGO! : 32,1 124,5 : table

o-Xylène
PlastiGO! : <5 8,1 : table

Sulfate de nickel
PlastiGO! : 0,91 2,3 : table

Formol
PlastiGO! : 5,5 25 520 : table

Baryum
PlastiGO! : 19 937 : table

Banc assis-debout MéGO! avec assise en PlastiGO! *

Table classique de bureau

Les chiffres sont donnés en particules par million
Analyses effectuées par Labocea - laboratoire public territorial d'analyses de France

LE SAVIEZ-VOUS ?
Dans une cigarette, il y a une concentration de nicotine de **79 ppm** (particule par million).
Une plaque MéGO! en **PlastiGO!** en contient seulement **0,032 ppm** !

MéGO!
Ensemble, recyclons les mégots de cigarette !

Figure [24], MéGo! advertisement, from [34].

To resume MéGO's process for dealing with cigarette butts there are five steps:

- Collecting and storing the butts: as Leymarie et al. (2019) [36] report MéGo! sets up ashtrays at their customers' premises and empty them at least once every three months. The butts are stored in airtight containers before being processed.

- Sorting: the batches are sorted manually at the MéGO site to eliminate other waste (cigarette packets, aluminium, matches, etc.). As the company reported to Leymarie et al. (2019) [36], "this is a tedious step, difficult to mechanise because we don't know how to automatically differentiate between a cigarette butt and other waste. "
- The cleaning of the butt: this is the biggest challenge, because it has to be cleaned in a closed circuit. The butts are immersed in rainwater baths, without energy or detergents, to remove nicotine and tar. At the end, all that remains is the filter, which, as already said is made of cellulose acetate and is a harmless polymer. Moreover, regarding the water, they clean it up to reuse it and not harm the environment.
- Drying and fine grinding of the filters.
- Thermo-compression: the crushed filters are compressed and heated to a high temperature, and they emerge as rigid plastic plates. As Leymarie et al. (2019) [36] remark, this plastic cannot yet be considered a raw material, for regulatory reasons, but it retains its waste status. This does not prevent it from being used to make objects.

3.15.3 ECOMEGOT

As reported on their site [38] the EcoMégot project was initiated by Erwin Faure, who is passionate about social entrepreneurship and the environment. Erwin was surprised to see the considerable environmental impact of cigarette butts: while working on the subject, he noticed that no viable depollution and recycling solution existed. It didn't take long for him to put his business training and network to good use in an initiative that would address this issue.

As of 2019, EcoMégot has collected approximately 7 million units of butts, or 1.5 tonnes. EcoMégot's investigations are deployed in parallel on several management channels. Leymarie et al. (2019) [36] state that the preparation of solid substitute fuel (SSF) is the most secure outlet to date. To produce this product they use partner sites, all of which are located in France, to promote the local economy and thus reduce their carbon impact. They process and package the cigarette butts into fuel briquettes: these briquettes are burned at over 1450°C in an environment equipped with high-performance filters, so the butts do not release any toxins into the atmosphere and leave no residue. In addition, one of the peculiarities of ECOMEGOT is that they do not use water or solvents to clean up the cigarette butt.

Thanks to the cellulose acetate in the butt filter, ECOMEGOT is able to extract it and mix it with other recycled plastics to create a new recyclable plastic polymer. As regards to this material recovery, a first preparation stage consists in the separation of filters from undesirable materials and the paper, tobacco and ash fraction. For the filters thus cleaned, they perform the production of fibres from cellulose threads; in this process, some of the pollutants from the cigarette butts are extracted without going through an aqueous extraction phase. The final production consists of making plastic granules, after crushing, compacting and formulating the cigarette butt filters, as seen in Figure [25].

Figure [25], ECOMEGOT's products, advertisement from [38].

3.15.4 POIATO RECICLA

This Brazilian enterprise collects and recycles cigarette butts in Brazil, producing cellulose pulp for use in the production of notebooks. The process appears to be well underway, having involved researchers from the University of Brasilia, and is the subject of publications (for example d'Heni Teixeira, that we altrady quoted in [25]).

As we can see from their site [45], they say that every cigarette butt is recycle to paper. As of 2018, the site reports that in six cities in the interior of São Paulo they recycle a total of 575,000 cigarette butts every month and are turned into cellulose. The work is done by using around one thousand collecting boxes, which corresponds to 230 kilograms of CBs per month. Poiato Recicla says that the collection bins are now present, besides Votorantim, the city where they started, in other big Brazilian cities like Campinas, Ilhabela, Boituva, Laranjal Paulista and Sorocaba. In this one, he also highlights that the material is collected in response to private initiatives, but that the bins already arrive in the streets also due to governmental actions. After being collected, the material is sent to the recycling plant, installed in Votorantim, where the cigarette butts are processed and become cellulose mass, which is donated to institutions and schools, which with this material perform a work of social inclusion and income generation.

The proposed valorisation is exactly the valorisation that we found in the article from d'Heni Teixeira et al. (2017) [25]. The process, developed to recover butts in the form of cellulose pulp for the paper industry, generates two material flows: cellulose pulp, used pure or in a mixture depending on the desired paper quality and a "dark liquor" concentrating the pollutants from cigarette butts. The process applied at their facility, has so far resulted in the recovery of approximately 40 million cigarette butts (approximately 8 tonnes).

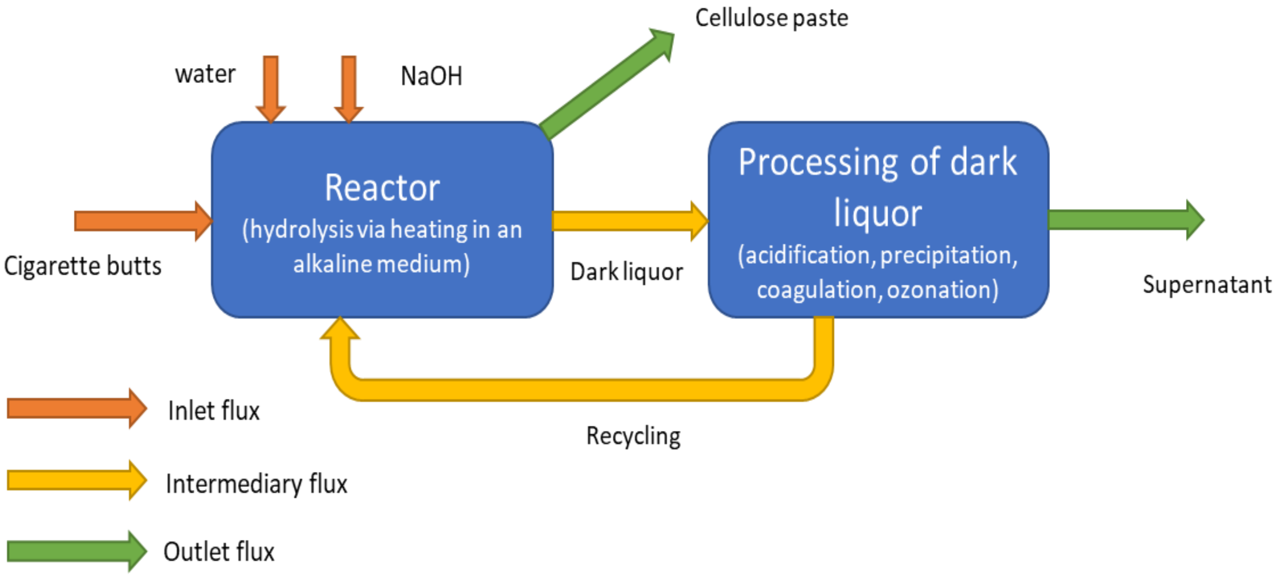


Figure [26], Diagram of the recovery process used by Poiato Recicla, modified from [36].

The authors, as we already said before, were interested in the possible management of this liquor and carried out work aimed at concentrating the pollutants it contained in a solid phase, and reusing the effluent in a closed loop in the process, thus generating no liquid waste. Although this publication presents the most advanced thinking on the environmental performance of cigarette butt recycling, it does not provide a mass balance of pollutants and does not present any chemical analysis results on the cellulosic pulp stream.

Leymarie et al. (2019) [36] report that, after an email exchange avec the company, they had some information about their recycling processes. This was because the information obtained elsewhere sheds more operational light, but remains rather limited, as the company Poiato Recicla preferred not to answer some of the questions asked. Nevertheless, in direct exchanges with Poiato Recicla, Leymarie et al. (2019) [36] found that the supernatant obtained after treatment of the dark liquor would be entirely recovered in another process (but did not specify which one) and moreover, after having periodically carried out analyses at different stages of the process, the results would comply with Brazilian regulations, thus guaranteeing the non-contamination of the cellulose pulp produced (the pollutants monitored were not mentioned, however).

4. Experimental phase:

After describing many possible valorisation pathways, with the advice of Mr. Saleh, we decided to put the valorisation on a graph, to better visualise them. This figure (Figure [27]) shows the CB in the middle and all the possible valorisations on the external circle. In the middle circle, between the valorisation and the CB, we have the "pathway" of the valorisation process: the catalyst or the first stage are shown in the first step to the valorisation, and then the process or the second stage are in the second circle. In this way we managed to exclude the valorisation pathways that we felt that weren't feasible during our laboratory experiences.

After a meeting with Mr Saleh and Mr Bals we decided to focus on the active carbons. This decision was made considering the fact that, from the bibliographical research, many different ways of producing active carbons from cigarette butts were found, offering in this way the possibility to make a comparison between the various samples manufactured. We had to exclude the asphalt concrete, the cellulose pulp, the corrosion inhibitors and the cellulose nano-crystals due to technical difficulties. Also the acoustic insulation was left aside, as the acoustic tests were considered more difficult to make in the Centre de Recherche, and due to the lack of bibliographical material that was found (only one research team considered and studied this valorisation option).

As these decisions were made, we also adjourned our graph, highlighting in green the paths certainly viable, in yellow those to be tried and in red those left aside:

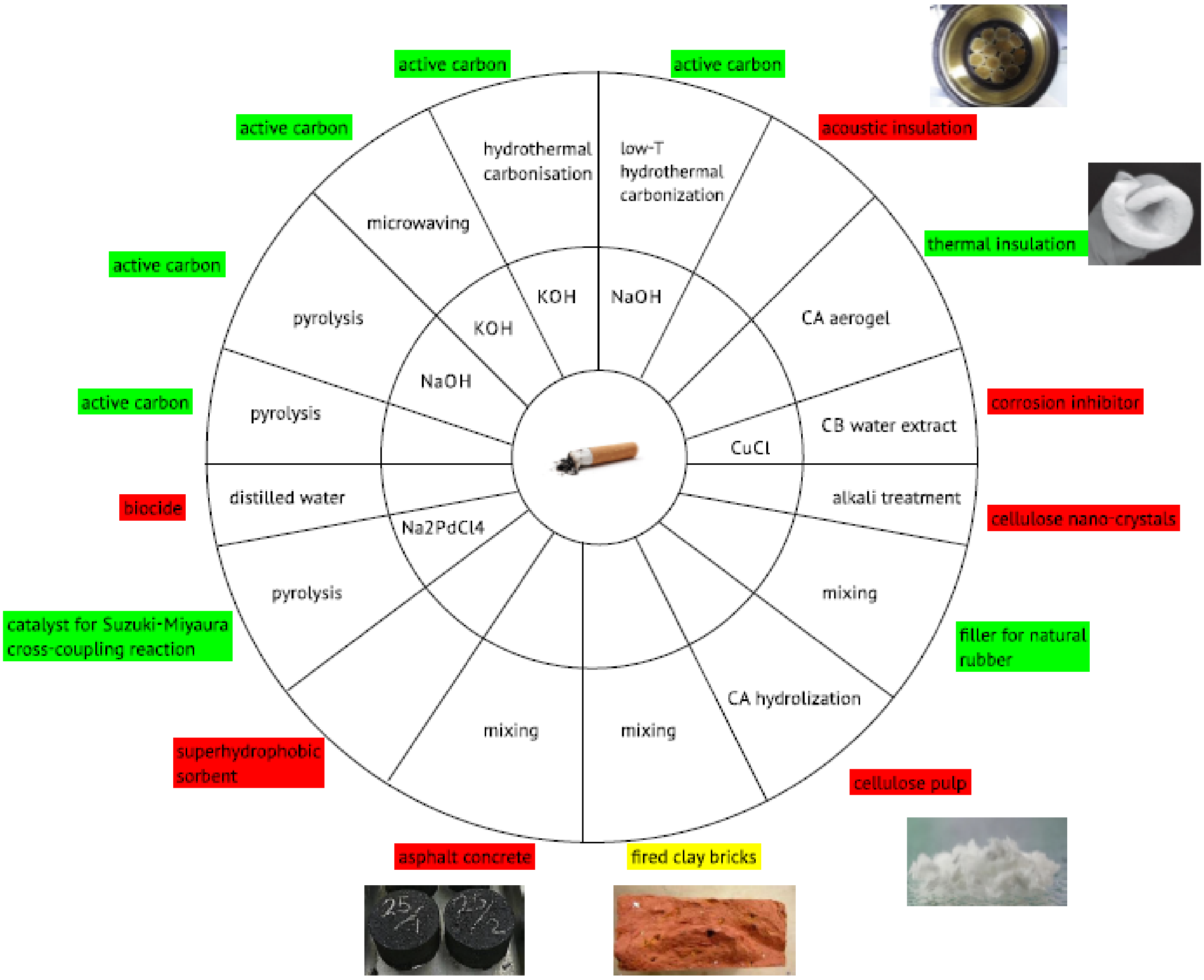


Figure [27], Valorisation pathways, author's elaboration.

Unfortunately, as the time was not on our side, the only valorisations that were performed are the ones to make active carbons. The aim of this study was thus to be a preliminary research to have more studies follow suit in the field of the valorisation of CBs. As already said, the active carbons are the easiest valorisation way and, for our means, also the most feasible.

At first, an electrical furnace was used. With this equipment there were performed tests of carbonisation and pyrolysis. Then the study was more focused on the pre-treatments and the activating substances that could be used to enhance the performances of active carbons and their specifical surface. The selected treatments were washing with ethanol, immersion in NaOH and KOH, supercritical CO_2 extraction and activation with microwaves. Unfortunately, due to the lack of time caused by the Covid 19 restrictions, these two last options couldn't be appropriately thoroughly deepened.

As far as the chemical-physical analysis that were made, thanks to the equipment present in the UTC's Centre de Recherche, it has been possible to perform a thermal gravimetric analysis (TGA) of the filters; performances analysis on the active carbons that were made (adsorption–desorption experiments and BET method used to measure the specific surface areas) and a scanning electron microscope of the original filters and the results. A FTIR test was made on the raw materials and on the obtained carbons.

In the following pages there will be firstly reported and described the tests performed of the electrical furnace, furthermore the pre-treatments that have been carried on will be outlined and then all the analysis that were subsequently made will be delineated. The methodology of the laboratory tests and analysis will be reported first and then the results will be later described.

4.1 Methodology:

In the following pages there will be described the methods and procedures applied in the phase of studying our subject. The protocols are also detailed for every valorisation path and a description of how the test were done and what was the chronological vision that this study had is also reported. For the analysis of the results, there will be detailed all the analysis techniques with all the equipment that was used.

4.1.1 Pyrolysis in electrical furnace:

The essays with the electrical furnace were the first essays that were made. The very first thing that we did was to separate the samples in 3 groups:

- The cigarette butts as they were
- The filters with still their paper on
- The unwrapped filters

The separation of the filters from the ash, the remaining tobacco and the paper was done by hand. Obviously, in an industrial context this cannot be done in this way, thus in the following of this research, a further analysis of this problem will be made. The different samples of filter were photographed and reported in the following image:

Figure [28], Different samples of raw material, author's elaboration.

The heating chamber that was used is a Vecstar MRF 2: the maximum temperature that can reach is 1250 °C. All the information that was gathered about this particular equipment was found on the site of Vecstar [33]. This furnace is a chamber furnace with simple operation and robust construction. The door opens vertically to ensure the hot plug is away from the operator at all times and the door safety switch turns off the power to the elements whenever the door is opened. This kind of equipment, as their site says, is typically used in general laboratory research and light industrial. The machine's dimensions (in mm) are 455x375x575 and its net weight is 57 kg. A picture of the furnace is reported in the next figure:

Figure [29], Vecstar MRF 2, modified from [33].

The furnace was installed in a fume hood, to assure that any fume that could be released, would be sucked up from the hood; this choice, as the hood did not leave much space to operate on the furnace, was one of the factors of uncertainty of the analysis that we will better describe later.

The positioning and layout were the ones reported in the following figure (Figure [30]), made with the software "Wondershare EdrawMax":

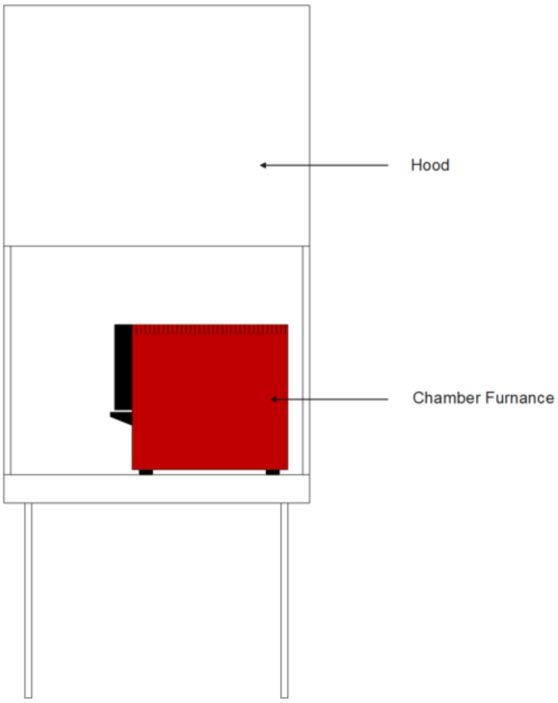


Figure [30], Positioning of the Vecstar MRF 2 in the laboratory, author's elaboration.

This disposition, although not optimal for the heating operations, was considered to be the best one from a safety point of view. The furnace was positioned with the opening all inside the hood, so that even if there was some smoke that came from the oven, the ventilation system could manage to capture it. When operating the hood was closed, while, clearly, to take the samples out of the oven it was necessary to open the hood. Then, to let the samples in the melting pot cool down, the hood was closed again. The melting pots were placed on a panel made from an isolating material, so that we could prevent heat shock and a quick breaking of the melting pots.

The first tests that were made were done only to prove the feasibility of these valorisation with this machine. Unfortunately, as the furnace didn't have a hole for the introduction of nitrogen, we couldn't operate in an inter atmosphere. As the goal was to perform a pyrolysis, this was the first obstacle that was in front of us.

Therefore, at first, only a carbonisation was performed. The samples were placed in some melting pot, made for high temperatures. The first essay was performed with the entire CBs, the filters still with the paper and the filters alone. It is to remark that manually unwrapping and removing the remaining tobacco is not only a long process, as one has to make pressure on the CB and make sure to all remove, but it is also very unpleasant, since the CB have a really bad smell. In addition, we have to consider that on an industrial scale an unwrapping phase could be expensive and energy-intensive. These are two of the reasons why in the following studies it would be important to try not to unwrap the CBs and find a valorisation optimum that could also avoid the preliminary unwrapping phase, but unfortunately, due to a lack of time, this could not be done in this present study.

The beforementioned samples were thermically treated at 800°C, starting from ambient temperature. It is noteworthy to mention that the electrical furnace was of difficult programming, as it was a new machinery in the UTC's Centre de Recherche, as a result at first it wasn't possible to control the heating ramps. The samples were heated from about 20°C to 800°C in more or less 1 hour and 35 minutes, making it ~ 8°C for minute.

The staring samples and the results that were obtained are reported in the following figure:

Figure [31], Before (left) and after (right) carbonisation at 800°C, author's elaboration.

As we can see, the samples are completely burned. This was the expected result: not surprisingly, all that remains are the ashes. Even if in the melting pot, after being removed from the furnace and after cooling at room temperature for 20 minutes (when the photo on the right was taken) the samples look quite solid, during the removing phase they resulted to be really fragile and volatile. To calibrate the machine and to start to understand the procedure, other tests were performed. The filters, the filters with paper and cigarette butts were tested directly at 800°C with a hold time of two hours: the resulting material was always ashes.

It is noteworthy to say that with the equipment that it was installed, it has been very important the aspect of safety. The person that carried out the experiments, when opening the furnace, had to be very careful when handling the melting pots: these were extremely hot and of an orange-looking colour and from the furnace it came a great deal of heat; for preventing and accident the user always had to used heat-protective gloves, protective glasses and a face mask.

Afterwards, after understanding how the furnace worked, we had to address the pyrolysis problem. As in the furnace there wasn't a tube for the introduction of nitrogen, in the heating chamber was impossible to perform a real pyrolysis. As a consequence, air would've been always present in the chamber. To solve this problem, the melting pots were covered with their cover: in this way the air was present in the melting pot but was quickly consumed and then, if the pyrolysis process was carried out in the wright way, no additional air should've entered into the melting pot. This process was caused by the fact that, when carrying on the pyrolysis, gases are liberated, increasing the pressure into the melting pot (covered by the cover). As a consequence, on the difference of pressure, the air that was present into the heating chamber couldn't enter into the melting pot, thus preventing the combustion. The gases liberated from the pyrolysis process leak from the melting pot, escaping from it: this is precisely the process that avoids air to get into the melting pot in the first time, as air is "pushed away" from the incoming gas.

However, it has to be considered that the "simil-pyrolysis" that we carry on is not always done in the most perfect was. Indeed, after a certain point the pyrolysis process gets to an end and therefore air can enter the melting pot, causing the oxygenation and degradation process. This is why, in our experiments, it has been really important to understand when was the optimum time to get the melting pots out: if it was too soon, the pyrolysis was not yet over, if it was too late the oxygenation already started and we had only ashes left.

To better understand this concept, a graphical representation is shown in the figure below. It represents the entire process with a visual approach, trying to easy the concept:

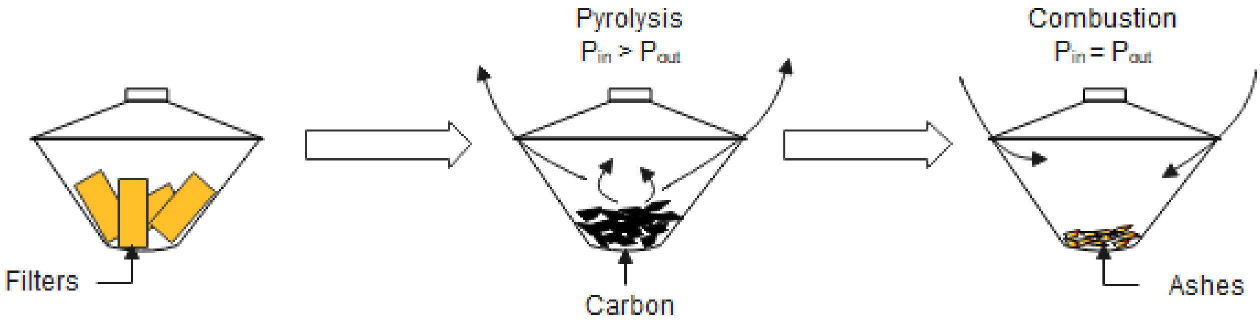


Figure [32], Simulation of the process that happens in the furnace, author's elaboration.

After this explanation of what should happen in the furnace, it is important to remark another time that this is only a preliminary study to the valorisation of cigarette butts as active carbons and that a full understanding of the processes would require a more extensive experimental work. In addition, it has to be said that with the equipment that we used we could not control the conditions inside the furnace (because the temperature changes a bit, going up and down, and because there is no way to make the chamber inert): as a result the results of this work must only be considered as the staring for a new and enhanced study on this matter.

This process gives the opportunity to talk about the uncertainties: the following results are all coming with uncertainties, as the operations were carried out in almost an amatorial way. First and foremost, the pyrolysis is not a real pyrolysis (no inert atmosphere), but a "simil-pyrolysis" that sometimes (especially at higher times) became a proper oxygenation (we judged that it is not a real combustion, as there are no flames, but we consume and degrade the sample). Then, the melting pot with the lid was also a source of unreliability: the lid was not very stable on it, thus sometimes falling of oscillating and making possible for air to get inside. This happened when putting the melting pot inside the furnace (as the floor of the furnace had a rough surface and facilitated the oscillation of the lid with each movement) but also when the pot was recovered from the furnace, as sometimes the grip slipped. Another factor that did not help the reliability of the process was the position in the furnace, but we decided to ignore it. Finally, there is the factor of temperature: even if the target temperature that was indicated by the equipment was the real one there were other problems linked to it. When opening the oven, the temperature decreased and then took a couple of minutes to get back to the original point. To try to standardise all the samples, it was decided to start measuring the time with a chronometer only when the temperature came back to the target temperature. However, some samples took more time than other to get back to it, making the real time of the heating process a bit offset.

The protocols that we tried to follow are the ones for pyrolysis of CBs' filters by Polarz et al. (2002) [30] and Koochaki et al. (2019) [5]. The first study performed their tests tube oven (Heraeus Thermicon P) equipped with a quartz tube and flooded it with nitrogen prior to slow heating (1 °C/min) to the final temperature, that was set to be 800 °C, maintaining this temperature for 7 h under a continuous gas flow. The second study that made our reference, put filters in the furnace directly at 800°C for 2h (carbonization hold time) with a heating rate that was controlled at 5 °C/min. Then, after carbonization, the resulting activated carbons were washed with 0.1 M HCl to dissolve ash.

Unfortunately, it was not possible for the present study to do a real pyrolysis since after some time the oxygenation and degradation of the sample comes along, therefore a similar approach was taken, but obviously not the same. Before writing the protocol for this study, a trial test was performed. The filters were put directly in the furnace at 800 °C for a carbonisation process with a hold time of two hours. The result was nothing but ashes. Nevertheless, more times and temperatures were tested. The decision was to test the following temperatures: 400, 600, 700 and 800 °C. The 400 °C target temperature was chosen because Koochaki et al. (2019) [5], as it will be reported in the following section about pre-treatments, put the NaOH pre-treated filters in a furnace at 400 °C, so it was thought to be possibly interesting to try out this method. Furthermore, from the TGA test, which will be described later, it was evident that at 400 °C the mass loss process is almost concluded. The other temperatures were chosen from the TGA: after 600 °C no reactions are seen, so in the long run (meaning after a considerable amount of time) all the samples treated at 600, 700 and 800 °C should have the same result.

In addition, it has to be said that from preliminary tests it was seen that carbonisation for 600, 700 and 800 °C happened at really low hold time (already at 5 minutes there is a carbon like matter in the melting pot). On the other side it appeared clear that for 400 °C greater hold times were necessary. Consequently, the hold time for these higher temperatures were different: from 5 to 45 minutes and then 60, 75, 90 and 120 minutes. On the contrary for 400 °C the times were: 30, 60, 90, 120, 150, 180 minutes. It is also important to remark again that, when performing the thermal test, after having put the filters inside the furnace, we waited until the temperature came back to the target temperature; it was also weighted a sample that was put in the furnace and the took out when the target temperature was recovered. These samples were called at the time zero and the graphs that were then made start from these.

As a result, the protocol was the following:

1. Separate the filters of CBs from the remaining material
2. Weight the starting sample
3. Start the furnace and get to the desired temperature
4. Put the filter material into the melting pot and then into the furnace (Vecstar MRF 2) directly at the target temperature
5. Wait to the temperature to get back to the target temperature
6. Hold the sample at this temperature for the wanted hold time
7. Take out the melting pot and leave it cool down on a plate made with an insulating material
8. Weight the final sample

Having said all this, many tests have been performed. In the following there will be reported the results: in the results part, the obtained carbons will be shown and all the analysis that have been made, between which there is an estimate of the kinetics, that however, due to the numerous uncertainties, has to be seen only as a first attempt to understand the process. Since we do not have a reproducibility, as it will be later explained, the curves are oscillating, but this was only a study to understand and obtain a procedure of working with this new raw material. I have once again to stress that this subject has not been widely studies and that at UTC this research has started with me, so there were not many references to look at.

4.1.2 Pre-treatments:

Another important step of the experimental campaign was to find a correct pre-treatment for the cigarette butts. While some studies didn't have any pre-treatment, others had one or more. For example, we have to consider that some valorisation pathways didn't require to unwrap the cigarette butts form the cigarette paper, while others did.

In this following section we will analyse different pre-treatments. At first, following the different publications that have been studied in the bibliographical part, the study focused on the activation part; the activating step was studied by pre-treating the cigarette filters with NaOH (Sodium hydroxide) and KOH (Potassium hydroxide). Furthermore, it will be described the use of ethanol to "clean" the filters from the pollutants that are trapped in it. Then, the same concept has been applied to the extraction with supercritical CO_2 but in this case the extract was much more concentrated. The results of all these pre-treatments are reported in the following pages. The protocols and methods were adjusted during the experiments and laboratory time, but all the methods will be explained in a chronological order, along with the reasons that lead us to a change.

4.1.2.1 NaOH activation

A pre-treatment that has been described as very useful and important for the valorisation of cigarette butts to prepare active carbons is Sodium hydroxide, NaOH. Sodium hydroxide, also called caustic soda, is a white, solid, inorganic and ionic compound consisting of sodium cations Na^+ and hydroxide anions OH^-. In addition, it is a highly caustic base and alkali. This pre-treatment was the first one that was tested and the one that we were able to perform the most: this is the reason why the graphs to describe the trend of the mass loss are more detailed and analysed and why we made much more comparisons with the untreated filters.

To verify the work of Koochaki et al. (2019) [5], we followed their lead and experimented with this chemical pre-treatment. As already portraited in the first part of this review, Koochaki et al. (2019) [5] were not the only ones that performed tests and laboratory experiments with NaOH as an activating agent, nevertheless their work is the most extensive one and it focalised principally on the effect of sodium hydroxide in the chemical activation of active carbons. By following the study, in the tests that were performed, CBs' filters were impregnated with different percentages of NaOH solutions, and then pyrolyzed, however in our tests there were some modifications.

Firstly, it is necessary to show the protocol written by Koochaki et al. (2019) [5], which we used as a foundation to write our own protocol. The protocol is the following:

1. Unwrap and remove filters from the cigarette paper
2. Place in an oven at 80 °C for 12 h
3. Immerse 15 g of the filters in different NaOH solutions (12, 24, and 48% w/w ratio)
4. Stir solution for 2 h with a mechanical stirrer, take filters out of the solution and compress the excess NaOH out of the filters
5. Place samples in an electrical furnace. Introduce nitrogen gas into the furnace at a rate of 100 cm^3/mm for 45 min to provide an inert atmosphere
6. Carbonization operation at 400 °C for 2 h at 5 °C/min heating rate
7. For full pyrolysis of the samples, introduce nitrogen gas at the same rate for several hours until the furnace temperature reaches the room temperature and then, take the samples out of the furnace
8. After carbonization wash activated carbons with 0.1 M HCl to dissolve ash
9. Use hot water to wash the activated carbons
10. Dry and sieve

This protocol, for the purpose of our study was really effective. Nevertheless, as in the laboratory there wasn't the possibility to fully study the pyrolysis process (it is to remember that the furnace did not have an entry for nitrogen gas to inert it), it was not feasible. This is the reason why it was necessary to write a new protocol. Furthermore, Koochaki et al. (2019) [5] used NaOH solutions with a 48% w/w ratio, meaning that the concentration of the solution was almost 13 M, and Professor Saleh judged it too dangerous to perform. From the Material Safety Data Sheet for sodium hydroxide [40] it is possible to remark that this compound at these concentrations may be corrosive to metals, causes severe skin burns and eye damage and may cause respiratory irritation.

As a result, a sodium hydroxide solution with a concentration of 0.5 M was used.

Furthermore, as the concentrations that we used were different than the ones on the original protocol, we made some further adjustments in our own protocol. The final result is the following task list:

1. Unwrap and remove filters from the cigarette paper
2. Dry the filters for 24 hours at 105°C in an oven
3. Immerse 10 g of the filters in a NaOH solution (0.5 M)
4. Stir solution for 2 h with a magnetic agitator
5. Let the solution sink in for 24 h
6. Take filters out of the solution and compress the excess NaOH out of the filters by using a weight
7. Place samples in a furnace
8. Carbonization operation

The carbonisation operation will be better defined later; as far as the chemical activation, we can say that the cigarette butts' filters, after the treatment have increased in size and look more "porous". Furthermore, even if they were compressed to remove all the excess sodium hydroxide, they were obviously heavier than the original ones. This situation was a problem in our goal to standardise our samples to carbonise. To bypass this obstacle the solution was to always use the same number of filters that were used in the experiments without pre-treatment, to assure a way to compare the final results.

Moreover, as already reported in the first part of this study, Koochaki et al. [5] remark a change in the morphology of the filters. Therefore, a SEM test was done and the results will be reported later. A TGA analysis was also conducted, to see if there were any differences with the "normal" untreated filters, but the results were not much different. In any case, the results and the descriptions of those will be reported later.

Then the carbonisation process was tested. As it was done for the carbonisation process without any pre-treatments, at first many ways were testes. Our preceding schedule followed more or less the valorisation path proposed by Koochaki et al. (2019) [5] that heated the pre-treated filters to 400°C for 2 hours. Differently from this scheme, the chosen process was to thermally treat the NaOH activated filters (from now on they will be called NaOH filters, for short) at the same temperature that the physically activated ones were prepared. This means that at first, we placed the pre-treated filters in our furnace at 800°C. As well as it was done for the non-pre-treated filters, a graph that represents the trend and progress of the carbon residue on the hold time, was realised and it's shown and analysed in the following part.

Similarly to the first carbonisation process, also for the NaOH filters it was performed a test to provide the 0 hold time. This, again, means that the NaOH filters were place in the furnace opened at 800°C and when the furnace was closed the temperature was noted. Furthermore, it was timed the period of time that it took to get back to 800°C and then the chronometer was set, to measure the wanted hold time. Finally, it has to be remarked that this process was done to "standardise" the samples, as when opening the oven and then closing it we were not always at the same temperature. Obviously, since this phenomenon lead to a longer or shorter waiting time to get back to 800°C, this selected "zero time" was different, but it helped us keep the samples uniformed.

As there will be reported from the results in the following section, the NaOH pre-treatment did not go as planned: instead of increasing the specific surface (that was our primary objective), it decreased it and sometimes it zeroed it. This was most probably caused by the presence of sodium crystals on the surface of the treated fibres, but it will be further analysed later. As a result, another idea that came to mind to increases the surface area was to try a washing with NaOH of the carbons obtained after the pyrolysis. This could be seen as a post-treatment of the carbons. A procedure like this one was proposed by Yusop et al. (2021) [43]

(even if later they used a microwave treating). However, it was decided to try this procedure. The protocol is the following:

1. Carbonisation phase without any pre-treatment (at different temperatures and times)
2. Immersion in a 0,5M solution of NaOH for 24 hours in a ratio of about 1:1
3. Sieve the carbons
4. Dry the carbons in an oven at 105 °C
5. Thermally treat the sample at 600 °C for 5 minutes in the furnace

The procedure was quite simple: after passing in the Micromeritics 3Flex (to record its specific surface, as it will be described later), as the carbons were recovered and placed in a beaker with NaOH for 24 hours. We realised that the mass ratio of the carbon and the NaOH could be important, but as this project was a starting point for future research, for NaOH pre-treating this point was not studied. In our research we did not look at this factor, but we can estimate that the samples that were made had a mass ratio of about 1:1 (NaOH to carbon). Unfortunately, only the carbons that were not thermally treated again were passed at the BET (meaning that they only were immerged in NaOH for 24 hours), so the results cannot be confirmed.

4.1.2.2 KOH activation

A pre-treatment that has been described as very useful and important for the valorisation of cigarette butts to prepare active carbons is potassium hydroxide. Chemical activation with potassium hydroxide (KOH), is almost the same as activation with NaOH. For this second process, the protocol on which the experimental campaign was based was the one by Hamzah et al. (2017) [4]:

1. Unwrap filters from the cigarette paper and wash with hot water
2. Wash filters with ethanol for 3 times
3. Dry in open air for 72 hours
4. Place into a vacuum oven for 3 hours at 230˚C for heat treatment
5. Crush filters into a powder size of about 100 μm
6. Active the CF powder with potassium hydroxide (KOH) solution at ratio carbon-to-alkali from 1, 2 and 3
7. Activation step: tubular glass reactor with a microwave input power of 630 W at 2.45 GHz frequency and irradiation time for 20 minutes
8. Wash samples with hot distilled water (85˚C) until the pH of the filtrating solutions was neutral (pH = 7.0)
9. Dry samples in a vacuum oven at 100˚C for 60 hours to eliminate moisture

As it is possible to see, the concentration of the KOH solution was not indicated. As a result, the chosen value was to the as the sodium hydroxide (0,5 M), to have the chance to compare the two activations. Moreover, the protocol that was here reported, does also require a microwave pre-treatment: we will analyse this processing further in the study. In addition, this protocol implements also the ethanol washing pre-treatment that will be described later.

To prepare the KOH at a concentration of 0,5 M, a protocol, similar to the one for NaOH, was written:

1. Weigh 5.6g of solid KOH using a cup and a precision balance, not forgetting to make the TARE
2. Dilute the solid KOH in a beaker by alternately adding demineralised water and solid
3. Transfer the dissolved KOH into a 200mL precision flask using a funnel, taking care to rinse the cup, beaker and funnel with demineralised water
4. Fill the flask to ¾ full
5. Cover and homogenise
6. Fill the flask with the meniscus tangent to the gauge line
7. Cover and homogenise

Since measuring exactly 5.601g it is nearly an impossible task, we had a bit of incertitude: it is crucial to consider the uncertainty of our equipment. Therefore it appeared important to calculate the uncertainty of the concentration, ΔC, by the following formula:

$$\Delta C = \left(\frac{\Delta m}{m} + \frac{\Delta V}{V}\right) * C \tag{4.1}$$

And remembering that:

$$C = \frac{m}{V * M} \tag{4.2}$$

With:

- m= weighted mass
- Δm= mass uncertainty
- V= volume of water
- ΔV= volume uncertainty
- C= concentration
- M= molar mass

To give an example, in one of our tests the values were:

$\Delta m = 0{,}0001g$
$m = 5.6095g$
$V = 0{,}2L$;
$\Delta V = 0.00015L$;
$M = 56{,}1056\ g/mol$;
$C = 0{,}4999\ mol/L$,

As a result, the value of the uncertainty on our concentration, ΔC, was 0.000384 mol/L.

After having produced the potassium hydroxide for the activation step, a protocol of our own had to be written. Since the final goal of this second chemical activation was to determinate if it is better the activation with KOH or NaOH, the procedure that was carried on was almost the same as for the NaOH:

1. Unwrap and remove filters from the cigarette paper
2. Dry the filters for 24 hours at 105°C in an oven
3. Immerse 10 g of the filters in a KOH solution (0.5 M)
4. Stir solution for 2 h with a magnetic agitator
5. Let the solution sink in for 24 h
6. Take filters out of the solution and compress the excess KOH out of the filters by using a weight
7. Place samples in a furnace
8. Carbonization operation

It needs to be remarked that the filters were put in a beaker and immersed into the aqueous solution, therefore the is not a determined volume of liquid that has been used in our tests. Furthermore, the samples were stirred with a magnetic agitator and then, after having retrieved the magnetic tool, left for 24 hours.

Unfortunately, the KOH activation could not be deeply studied and tested as the NaOH activation, due to a time limitation imposed by the Covid-19 laboratory rules. Nevertheless, we were able to test the heat treatment at 400, 600, 700 and 800°C. For the highest temperatures, we chose to focus on the lower time regions (from 5 to 20 minutes), where the pyrolysis came to an end in our "pyrolysis-like" experiments. The results are all reported in the following part: as the KOH pre-treatment was our second one and as time was not in our side, for KOH we could not do a SEM of the treated filters, nor a TGA.

As for the pre-treatment with NaOH, also the KOH pre-treatment did not have good results in improving the specific surface area, if anything it was even worse (there are some samples, as it will be better detailer later, that had a specific surface area of 5 m^2/g). However, another strategy was used, in vision of the obtained results: the KOH washing after the carbonisation. Like Yusop et al. (2021) [43] reported, when carbonising, the volatile substances leave the raw material, leaving a vacant space, therefore creating a pore network was formed. Furthermore, using KOH to wash and immerse the results, there is a chemical activation: metallic potassium ions, K^+ travel deep into the pores and increase their number. The protocol was really simple, as for the NaOH activation:

1. Carbonisation phase without any pre-treatment (at different temperatures and times)
2. Immersion in a 0,5M solution of KOH for 24 hours in a ratio of about 1:1
3. Sieve the carbons
4. Dry the carbons in an oven at 105 °C
5. Thermally treat the sample at 600 °C for 5 minutes in the furnace

For the KOH activation, it was also tried an activation with a mass ratio of 3:1. At first the mass ration between KOH and carbon was not considered but then it was estimated to be around 1:1. As a result the 3:1 was tried and analysed, but only to verify the BET specifical surface area, our main objective. The results are reported in the next chapter. Unfortunately, only the carbons that were not thermally treated again were passed at the BET (meaning that they only were immerged in KOH for 24 hours), so the results cannot be confirmed.

4.1.2.3 Ethanol washing:

The most common pre-treatment put in place (even if, since there is not a standardisation of the experimental method, it has been done in various and different ways), is washing the cigarette butts with ethanol. This step is done to extract many pollutants form the cigarette filter, that, as it has been investigated in the bibliographical part, get trapped in the filter during the smoking process. We need to remember that, as it has been explained in the first part, numerous compounds rest trapped into the filter and between them there are: ammonia, benzene, acetaldehyde, hydrogen cyanide, formaldehyde, pyridines, and phenols. The result is that the smoked cigarette looks darker than the unsmoked one. It is clearly visible when we look at the before and after pictures of the filter in the smoking process. The filters are white before smoking, but, even if in the complete CBs it is partially covered by the wrapping paper and the tipping paper, the filters are usually of a brownish colour, indicating that they have trapped different substances (nicotine, for example).

On the other hand, when we wash or immerge filters in ethanol, we extract many of the pollutants, therefore the filters obviously appear whiter than the smoked ones:

Figure [33], Filters before and after the ethanol pre-treatment, author's picture.

As this is a pretty easy treatment and could possibly give us some advantages in obtaining better specific surfaces on activated carbons and more experimental information on the compounds present into the CBs' filters, the ethanol treatment was performed.

The protocol that has been proposed by Hamzah and Umar (2017) [4], is made of few easy steps for the ethanol washing pre-treatment. The protocol consists in:

1. Unwrap the filters from the cigarette paper
2. Wash the filters with hot water
3. Washed again with 96% ethanol for three times
4. Dry in open air for 72 hours

Unfortunately, this protocol seemed to be time consuming and product consuming, as it is necessary to wash also with water and then 3 times with ethanol. This is the reason why, in this campaign we also tried our own protocols, by using a Buchner funnel and by immerging the filters and cigarette butts in ethanol, with different hold times. This second approach seemed more feasible on an industrial scale and, more importantly, makes us save energy and time. The energy saving is really important in this study, as it is founded on sustainability principles and on the values of circular economy. This is the reason why also other choices will be justified in the name of those principles.

The protocols that were studied are reported in the following paragraphs. After having produced the samples, the two different sets (the immersion one and the Buchner funnel one) were tested for our pyrolysis experiments, but only in the time ranges going from 5 to 30 minutes, because the time to analyse everything was not enough. However, in these time ranges there were the optimums in carbon production for the other samples (as it will be better explained later), so it was not seen as a great difference to not tests the conditions at higher time ranges. The only kickback of this approach is that the kinetic of the reaction in the oven could not be fully detailed.

At first, we will talk about the immersion in ethanol. The protocol that was followed is this:

1. Place in a 500 mL beaker
2. Pour in ethanol until all butts are immersed
3. Leave for 2h, 8h or 24h
4. Use a funnel to filter the butts
5. Remove the butts which will be used to carry out pyrolysis tests
6. Recover the ethanol

As we can see from the protocol, we chose to immerse for 2, 8 and 24 hours. The choice of 2 hours was made following the article by Koochaki et al. (2019) [5], while 8 hours was chose since this timing made possible to immerse the filters, let the immersed for the set time and retrieve them before the laboratory closed. In addition, 24 hours was chosen to increase the exchange time and see the results. The visual results of the residual ethanol were the following:

Figure [34], Ethanol residue after the ethanol pre-treatment, author's picture.

Unfortunately, from the pictures (Figure [34]) is not very clear but in person it was quite clear to distinguish the three colours, with the 24 hours ethanol residue that was visibly darker than the other ones.

Then we proceeded to test with the Buchner funnel. A representation of this tool is showed here below in Figure [35]:

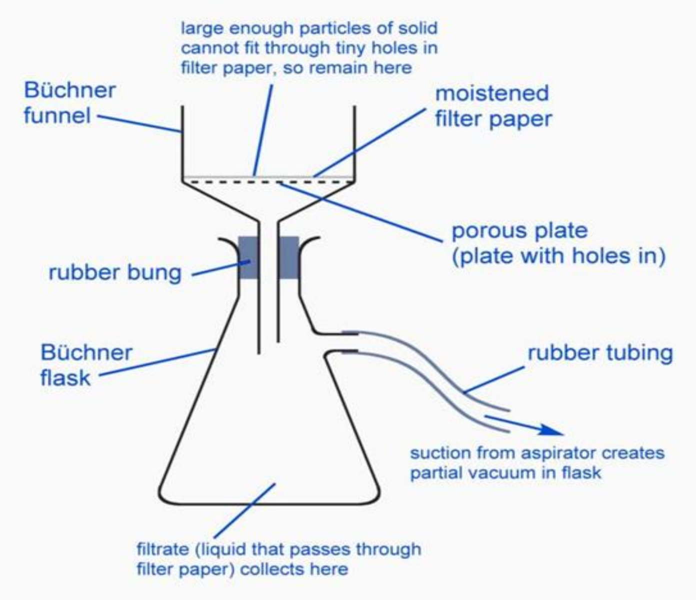


Figure [35], Buchner funnel representation, from [41].

For this pre-treatment we have to remark a few things. The ethanol volume was divided in three parts and the rinsing process was done in three times, every time using one third of the fresh solvent. This process was done to optimise the equilibrium curve; for the same principle we decided not to use all the ethanol at once and the recycle it, as there was the possibility that the CBs had a concentration of polluting substances lower than the ethanol. If this was the case, there would be a mass transfer in the opposite sense than the one that we want: from the ethanol to the CBs. Moreover, the aspiration to suck the ethanol down was made with a vacuum pump.

Therefore, the protocol that was written is the following:

1. Prepare the set-up and put the CBs in place
2. Moisten the filter with ethanol to ensure a good seal
3. Press the cigarette butts on the paper filter
4. Rinse the filter with ethanol in 3 times
5. Wait for the ethanol to be sucked out and gently move the filters with a spatula
6. Remove the washed butts which will be used to carry out pyrolysis tests
7. Recover the ethanol

To get a visual comparison, we also make an immersion test that lasted one week. The recovered ethanol is shown in the following figure (Figure [36]), in order to show the colour differences that there were with the 24h-immersion and the Buchner funnel:

Figure [36], Ethanol residue after the ethanol pre-treatment, author's picture.

The picture this time is closer to the reality. The one-week ethanol (on the left) was really dark and much darker than the 24 hours one (in the middle). On the other side, the Buchner funnel ethanol (on the right) was clearly brighter: this was also caused by the fact that the volume of ethanol used in the Buchner funnel was almost three times more than the one usually used for the immersion tests.

Then, the two sets of pre-treated filters were tested for the carbonisation process. As we didn’t remark any differences between them and that the kinetics that were extracted were really similar, only one curve will be shown. In addition, as the time to perform laboratory tests was not much, we decided to focus on the time regions where we found the other optimums, meaning from 5 to 20 minutes.

As the BET results were not extremely satisfactory, another idea that came to us was to try a washing of the carbons obtained after the pyrolysis. This could be seen as a post-treatment of the carbons. The basic idea is that in out carbons it can happen that some pores are still obstructed by certain particles such as tars. By washing with a polar solvent such as ethanol, we could get rid of these particles and thus increase, although most probably by a small fraction, the specific surface area. However, it was decided to try this procedure:

1. Carbonisation phase without any pre-treatment (at different temperatures and times)
2. Immersion in ethanol for 48 hours
3. Sieve the carbons
4. Dry the carbons in an oven at 105 °C

The procedure was quite simple: after passing in the Micromeritics 3Flex (to record its specific surface, as it will be described later), the 800°C-20 min was recovered and placed in a beaker with ethanol for 48 hours. Due to the short time this research has taken, it has not been possible to make other attempts on other times or other carbons, but in any case, being a proto-project, this may help future studies on the subject to have more indications. No attention was payed to the ratio between carbon and ethanol. Afterwards, this post-treated carbon, which had already been analysed, was returned to the analysis laboratory and passed through the Micromeritics 3Flex after being degassed, as described in the protocol. The results of the BET analysis are reported in the next chapter.

4.1.2.4 CO_2 extraction:

An alternative to this method appears to be the supercritical fluid extraction (SFE) with supercritical CO_2. Extraction of compounds from natural sources is the most widely studied application of supercritical fluids with several hundreds of published scientific papers. Carbon dioxide is a chemically neutral solvent and the process has the advantage that doesn’t need a separation step after the extraction, because the CO_2 becomes a gas and the liquid residue is easily recovered. Furthermore, this new extraction technique, when compared to the traditional extraction techniques, is a flexible process and allows the elimination of polluting organic solvents and of the expensive post-processing of the extracts for solvent elimination, even if for us this will not be the case. Therefore, the extraction with supercritical CO_2 is a technique that is getting more and more success.

Carbon dioxide is the most popular SFE solvent because it is safe, readily available and has a low cost. As Mohamed and Mansoori [31] report in their 2002 review of this technology (The Use of Supercritical Fluid Extraction Technology in Food Processing), CO_2 use has been rapidly developing. This is caused by various factors, usually linked to the food industry (thus it is not strictly linked to the present study, but it is interesting to know to better understand the technology itself). As they report, between the factors that helped the increase in the use of these machines there is “the increasing public awareness of the health, environment and safety hazards associated with the use of organic solvents in food processing and the possible solvent contamination of the final products”. Moreover, it is important to remark that the cost of organic solvents is getting higher and the environmental regulations are getting more and more stringent; furthermore, the medical and food industries has a need for ultra-pure and high added value products. All these factors showed that it is necessary to develop new and clean technologies for the processing of food products. In this respect, supercritical fluid extraction with carbon dioxide can be of great help and lead to the development of new approaches: CO_2 has shown that it can provide as an excellent alternative to the use of chemical solvents; in time it has shown more and more that it can be easily used for extractions.

To perform the first test experiment, that was carried out only to see the feasibility of the process, an extraction with supercritical CO_2 was done. Since there was any similar application in the literature, we could not have a reference, hence we chose the temperature and pressure almost in a random way. As already said, carbon dioxide is supercritical over the temperature and pressure of 31°C and 75 bar. The initial option was to do the test in the conditions of 50°C and 100 bar, but as suggested by the technical expert, we finally performed it at 200 bar, to enhance the extraction of the polluting compounds. The conditions of the separator were selected to be 50 bar and 30°C, as in these conditions the CO_2 is a gas.

The P&ID of the machine is reported in the following figure (Figure [37]):

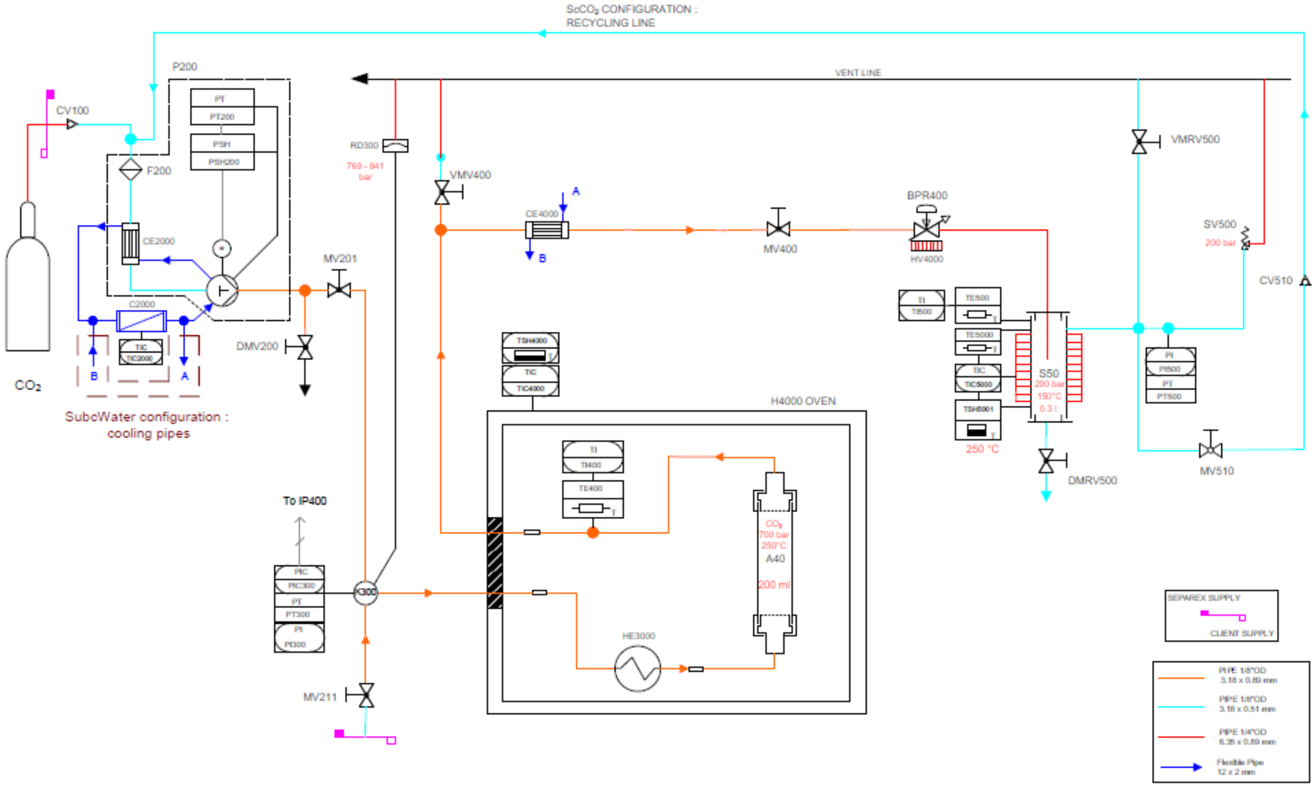


Figure [37] P&ID of the Supercritical Fluid Equipment, modified from [35].

As we can clearly see from the graph, CO_2 starts from a bottle. In the drawing, blue indicates the liquid state, red the gaseous state and orange the supercritical state. When the equipment is up and running at full capacity, operation is quite straightforward. The carbon dioxide leaves the cylinder and is in a liquid state (we must remember that it is at about 50 bar). From here it passes into a heat exchanger to increase the temperature. It then arrives at the pump, where it is compressed to the desired pressure (200 bar for our experiment) and passes into the supercritical state. It then arrives in the autoclave, where the samples on which to perform the extraction are placed. CO_2, thanks to its properties as a solvent, manages to solubilise certain substances and after the extractor and a temperature stabilisation phase, it passes through a valve. This valve, adjusted with a knob (by checking the pressure on the main screen of the machine), lowers the pressure to the desired value (50 bar for us, as we cannot go too low because we will have to re-compress the CO_2 later). Thus, in the separator, the extracted substances are in the liquid state and the carbon dioxide is in the gaseous state. By virtue of this it comes out of the top and thanks to the opening of a valve, is almost entirely recycled (of course we always have a small part of purging, which is compensated for by the addition of fresh CO_2 from the bottle). Thanks to the recirculation the process continues until the end of the experiment.

As a result of our previous choices, the extractor was set for 60°C and 200 bar, in the hope of having some extract. In the first test it was chosen to use the intact cigarette butts. This choice was motivated by two reasons:

the first is that the cigarette butts contain more compounds than the filters, so the possibility of obtaining a reasonable extract (even when using low quantities of raw material) is greater; furthermore, the filters need to be unwrapped before, making this less feasible and practical on an industrial scale.

To perform the essay, about 20 CBs where used, which weight about 4.5 g. The mass flow of carbon dioxide was set to be 10 g/min (or 1.2 kg/h). At first, the machine was turned on, to set the temperatures of the extractor and the separator. This process took about 30 minutes, as the temperatures needed to stabilise to the selected values. Then, the carbon dioxide, that came in liquid state, was put into the circuit and after about 10 minutes, the pump was started. After having opened the valves and set the process in motion, it has been recommended to wait about 30 minutes to stabilise the CO_2 into the circuit and to make the operative conditions, namely temperature and pressure, as steady as possible. It is relevant to note that the pressure increased more slowly before the supercritical phase than after.

The test lasted for one hour and the retrieval of the extract was performed every 10 minutes. At first only small drops came out of the extract tube, then, as the extraction proceeded, larger and larger drops managed to come out. Towards the end it was noticed that the amount of extract was less and less, leading to the conclusion that the chosen extraction time (1 hour) was correct. The results of the extraction are reported in the following figure (Figure [38]):

Figure [38], Extraction sample in the end (left) and after the first retrieval (right), author's elaboration.

We noticed that the filters were cleaner than before and most of all they didn't smell. It has to be remarked that the CB usually have a strong and pungent smell: after the extraction, the extract had this smell, and it was event stronger. Also during the retrieving phase, it was evident to smell, as there are surely some compounds that are still in the volatile phase that came out of the extraction tube in a gaseous state, as a fraction of the carbon dioxide.

The next step, before optimising the conditions, it would be important to verify what was into the extract. For this purpose, chromatography analyse should be performed, but due to technical problems it has not been possible. The chromatography is important to do before repeating the tests: indeed, the pipe, after the first extraction, was very dirty and a lot of impurities remained in the pipes: it was necessary to dismantle everything and wash with ethanol to be able to clean in a good way. It appeared evident that we needed to re-optimise the expansion conditions to avoid molecules remaining in the pipe, but to do so it was crucial to understand what was in the extract.

Unfortunately, as the time was not much we did not have the time to perform our heat treatment tests on the CO_2-treated samples and therefore we cannot say whether or not the specific surface is more or less than the others (possibly it should be similar to the ethanol-treated ones) or what is the "shape" that a kinetic graph of this pre-treatment and how it may look like.

Overall, it is possible to say that CO_2 extraction of cigarette butts could be a possible pre-treatment; surely if the main objective is to retrieve many polluting components, it could be an important step to further analyse.

On the other hand, talking about carbonisation, there is not enough information to give an opinion, but further studies should be done on the subject.

4.1.2.5 Microwave pre-treatment

It has already been mentioned that there is a possibility of microwave pre-treatment. By following the article by Hamzah et al. (2017) [4] we performed our own tests. The authors of the study that we followed report that microwave heating method has been applied to prepare active carbons because it rapidly and uniformly heats. In addition, it is an energy-efficient method compared to conventional methods and could improve the quality of final products. As Yusop et al. [43] report in their 2021 study, the activation process that uses a conventional furnace has some disadvantages "such as high energy consumption and long activation time". These are some of the reasons why researchers are now keener in using microwave heating techniques as an alternative to the furnace step in the activation process. Yusop et al. (2021) [43] remark that microwave energy "induces the dipole rotation in the atomic scale of the material at the rate of over a million times per minute", therefore the resulting frictional force between atoms and molecules within the material creates heat that is distributed rapidly throughout the material.

The microwave that was used was the Anton Paar's Microwave Synthesis Reactor Monowave 300. As reported on the manufacturer's site [42], this machine, introduced in 2009, the Monowave 300 is an instrument that has been optimized with respect to easy handling and low maintenance in addition to impressive performance and utmost monitoring precision. The operation limits of this machine are 300 °C and 30 bar. The maximum possible deliverable power is 850 W. It has a standard borosilicate glass vials and a SiC vessel, which provides ultra-fast heating even for microwave transparent reaction mixtures. Furthermore, the Monowave 300 has 4 different reaction vials and volumes between 0.5 mL and 20 mL. The vials are sealed leak-proof with a PEEK snap cap and a PTFE-coated silicone septum and when using it, cap and septum can close any reaction vial just with the click of a thumb. In case of remaining post reaction overpressure the vials are automatically depressurized during the opening process of the cavity cover. Finally, for the temperature measurement it has an infrared sensor.

Figure [39], Anton Paar's Microwave Synthesis Reactor Monowave 300, modified from [42].

This object is different from a usual microwave. In a big and classical kitchen microwave, there is a magnetron, a high-power vacuum tube that generates microwaves using the interaction of a stream of electrons with a magnetic field. The microwaves hit on the mirrors that help the microwaves go all over the cavity, but this unfortunately does not heat in equal ways all the cavity: there are surely parts of the cavity that are less hot than others. This is the reason why usually conventional kitchen microwaves turn. On the other hand, the Monowave 300 laboratory microwave works in a different way: firstly, it does not turn, but for an agitating purpose there is a magnet bar that we have in our reactor. The tube reactor does not move, but there is a cavity that makes the microwave power the same in all the environment, so that there is any dissipation. Therefore, when we use the kitchen microwave at 900 W to heat water, we need a minute or more, since the power is dissipated; on the laboratory microwave, the water gets to 100°C much faster, as there is little or no dissipation.

For a temperature measurement in the microwave machine, as already said, there is an infrared sensor. The sensor refers the temperature and therefore the microwave adapts the power to the temperature. To seal the tube reactor we use the septum and the cap and it is the same, no matter the size of the tube. The septum is important because the pressure sensor is upon it, so if we do not seal in the correct way, we might have a problem. It is also important to have a stirrer bar, because with the agitating of the environment, a better estimate of the temperature will be made, most of all in a heterogeneous environment as the KOH-cigarette butts one.

It is important to say that microwaves are more than twice reactive when the environment is polar and ionic: these are the two systems that absolutely increase the microwave absorption and thus increase the heat flow. So, because of these phenomena, when we have distilled water in the tube reactor, we managed to heat it to 100°C in more or less one minute, while when we did it with tap water, the heating was much faster (about 35 seconds), because ions, present in tap water, allow a faster temperature increase. This is the reason why, in our own environment, where we have CBs and KOH, the heating will be faster.

In our reference, the cigarette filters were activated in a tubular glass reactor with a microwave input power of 630 W at 2.45 GHz frequency and irradiation time for 20 minutes. In our study we decided to work based on the temperature instead that on the power. This is given by the fact that when we work based on power, we need the best estimate of the temperature and need to be very precise, because if we go to 200-300 W the temperature increases really fast. Again, this machine heats ultra-rapidly and the power is not dissipated, on the contrary of the kitchen microwave: when we increase rapidly the temperature, the pressure will increase a lot as well. As a result, in our first attempt we chose to work at 120°C. Moreover, when the test is finished, to cool the reactor tube down, some compressed air is sent to the cavity. The temperature decreases and the cavity opens only when the temperature has descended to a selected target value (55°C for us).

Therefore, the protocol was defined:

1. Unwrap and remove filters from the cigarette paper
2. Dry the filters for 24 hours at 105°C in an oven
3. Immerse 10 g of the filters in a KOH solution (0.5 M)
4. Stir solution for 2 h with a magnetic agitator
5. Let the solution sink in for 24 h
6. Take filters out of the solution and compress the excess KOH out of the filters by using a weight
7. Place the samples in the microwave and activate for 20 minutes at 120°C and with an agitation with a magnetic bar at 1000 rpm

The graphs of the temperature, made by the microwave are reported in the following figure (Figure [40]):

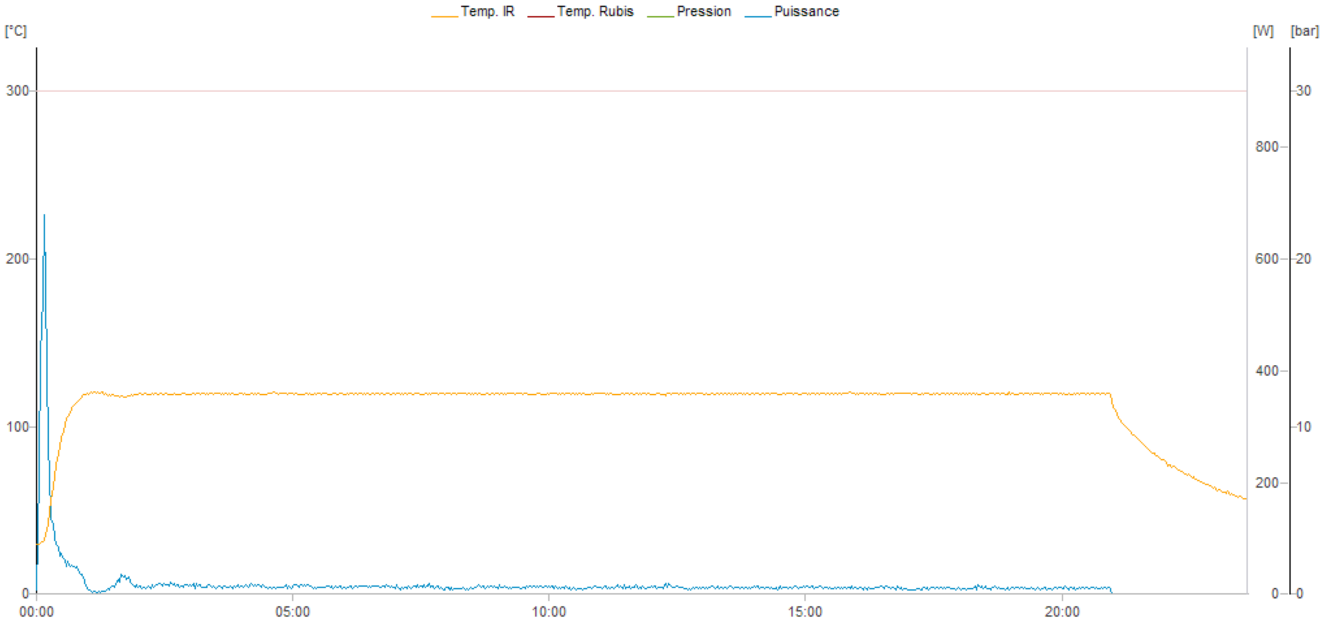


Figure [40], Profiles of temperature, power and pressure in microwave treatment, author's elaboration.

As already said the microwave adapts the power to the temperature. Since we want a ramp of temperature, the power will increase really fast to get to the wanted temperature as fast as it can. It can happen that the target temperature is overpassed, even if the machine always tries not to, but if it does the power abruptly decreases. Nevertheless, as we see from the graph, there is a sudden peak of power, but then it decreases, while the temperature reaches its final target. To stabilise and maintain the wanted temperature, a certain power (between 5 and 15 W) is always kept in.

It is important to remark that sometimes the procedure did not work as expected and the pressure augmented abruptly, so the test was terminated. The following image (Figure [41]) reports a failed attempt that was done:

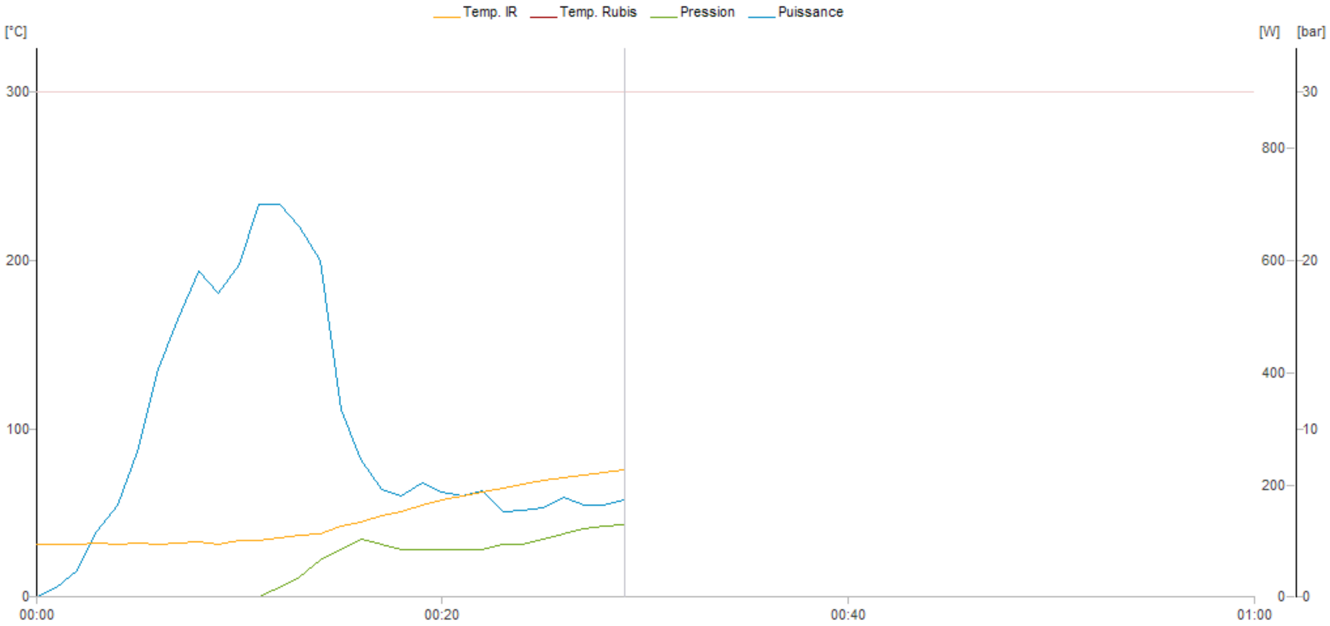


Figure [41], Profiles of temperature, power and pressure in failed microwave treatment, author's elaboration.

As we can see from the above image, the pressure increases to 5 bars in a matter of seconds, so the tests were manually abruptly ended. The tests stop themselves when the pressure reaches 30 bar, but as there is the risk to break the reactor, it is always better to stop them before 10 bar and before they start to run away.

It was then decided to try another temperature set. As discussed, we decided to not go over 140°C, because there could be some problems related to pressure increase. All these questions, duly pondered, raise doubts as to whether the perception of difficulties should undergo modifications regardless of the preferred directions towards a temperature progress. As we can see from the above image, up to 2-3 bar the pressure is controllable, when it is higher than this value there could be some problems in the tube: the pressure increases really fast. When we have water at 160 °C, it is in the vapour phase and temperature is quite easily measured; in our system we have some solids (the cigarette butts), so the infrared temperature sensor can take some time to adjust and the power could be too high, increasing the pressure and failing the test.

In addition to the microwaving pre-treatment, then it was necessary to do a carbonisation phase. The temperatures chosen were the same as for KOH activated filters: 400, 600, 700 and 800 °C. The hold time for the higher temperatures were between 5 and 20 minutes. Before the treatments the samples were dried in an oven at 105°C for two hours. The results of the SEM analysis that was done on these carbons are reported in the next chapter. From those it was clear to see that no pores were produced, so a new approach was taken.

Another way of doing a chemical activation, as reported by Yusop et al. (2021) [43], is done by impregnating a char (so the raw material has already been thermally treated) with chemical activating agents like KOH, phosphoric acid or zinc chloride and then once again at moderate temperature before being heated once again at moderate temperature. This would be more of a physicochemical activation combines both physical and chemical activation, where the physical heating treatment is done at a moderately high temperature. In their research, Yusop et al. (2021) [43] looked on the possibility of manufacturing acacia wood-based activated carbon (called AWAC for short) with a physicochemical activation process that consists of potassium hydroxide treatment, followed by carbon dioxide gasification under microwave heating. Even if this is not strictly related to cigarette butts, we thought that might be useful and an innovative technique to try.

In their process, they heated the raw material at 550°C for 1 h with N_2 gas purging through a furnace at the rate of 150 cm^3/min and then the resulted char was then impregnated with KOH at various impregnation ratio (between 0 and 2,5 g/g). The KOH was added as solid (the impregnation ratio is the ratio between the weight of solid KOH and the weight of char) and then 250 mL of deionized water was added to dissolve the KOH pellet. Afterwards, the impregnated sample was left in an oven for 24 h at 110 °C for chemical activation and dehydration process to occur. This first thermal step is introduced to further remove the moisture: during this step many reactions take place and between them there are reactions of depolymerization, dehydration, and condensation. As these reactions occur the authors describe and remark a higher carbon yields with less tar formations. Moreover, as the study reports, "the depolymerization of cellulose, hemicellulose, and lignin which catalysed by KOH has led to decrease in mechanical resistance, has subsequently causes swelling of the particle". Furthermore, the condensation reaction may induce the formation of small pores, which is actually the desired result for the active carbons.

After all these pre-treatment stages, the sample are heated in a microwave oven at different radiation power (between 144 and 736 W, but we need to consider that we work with temperature, so for us this data will not be very useful) and different radiation time (from 2.60 to 9.40 minutes). The obtained sample that are retrieved from microwave oven are washed with hot deionized water and 0.1 M HCl solution and then kept in oven for 24 h at 110 °C to dry.

Yusop et al. (2021) [43] found some really interesting results: the BET surface for the char that was first made was 425,41 m^2/g, which is similar to the one that it was found in our research at 600 °C. This rising is due by the removal of moisture content and light volatile matter compound from the raw material (acacia wood): when these substances leave the raw matter, there are some vacant spaces and therefore a pore network is created. Then, as already said, with the chemical activation, the metallic potassium ions (K^+) travel deep into these pores network and have the effect of increasing them. Afterwards, with the microwave treatment, the char was heated and more of the heavy volatile matter had been removed. All these processes resulted in an increment of BET surface area, that in the end was of 1045,56 m^2/g and the average pore diameter for the completed activated carbon is 2,78 nm, which lies in the mesopores region.

After having read and studied this research, it was decided to imitate and mimic it; indeed we could not reply it because we did not have the equipment. Firstly, we could not heat under nitrogen gas, but we used the covered melting pot trick to simulate the pyrolysis. But, on the other hand, this other approach to a microwave pre-treatment could have been really interesting for the present study. As a result, after a couple pf attempt, the protocol that we followed is the following:

1. Unwrap and remove filters from the cigarette paper
2. Dry the filters for 24 hours at 105°C in an oven
3. Place the samples in the furnace at 800°C for 5 and 20 minutes
4. Immerse the resulted carbons in a KOH solution (0.5 M) with a 1:1 ratio
5. Stir solution for 2 h with a magnetic agitator
6. Let the solution sink in for 24 h
7. Place the samples in the microwave and activate for 20 minutes at 120°C and with an agitation with a magnetic bar at 1000 rpm

The results look like carbons, so we analysed them to know the BET surface and see the presence of micropores. The results of the BET analysis are reported in the next chapter and will be confronted with the untreated carbons and with the carbons immersed in the KOH without microwaving.

4.1.3 Analysis methods

In the following pages, there will be reported the methods that were implemented to do the analysis on the raw materials and on the active carbons that have been produced in the experimental campaign, with comparisons between them and with the results found in the references. Between the analysis there are the thermogravimetric analysis (TGA) analysis, the comparisons between Scanning Electron Microscopy (SEM) results for both starting materials and the carbons, the Fourier-transform infrared spectroscopy (FTIR) analysis of the raw materials and the produces carbons, a methylene blue adsorption experiment with one produced carbon to prove the real absorption capacity and the Brunauer–Emmett–Teller (BET) theory, to calculate the specific areas of the carbons (that was also the main parameter of the success of the experiments).

The description of the method will be presented at first, given both from information received from the various technicians that helped in this project, but also from a references research. There will be described not only the methodology of the analysis, but also the bibliographical references that influenced some particular choices during the laboratory experience. Furthermore, the pictures of the used equipment will be shown.

Before introducing this part, it is important to say how the samples were made. The first part comes from the raw material (F for untreated filters, NaOH for NaOH pre-treated filters, KOH for KOH pre-treated filters, Eth for ethanol pre-treated filters and microwave for microwaved filters), then the temperature (for example 800C if the treatment was done at 800 °C), then the hold time and finally the post-treatment, which is always introduced by a "+" (for example "+ KOH" means that the carbon was immersed in KOH, after carbonisation).

Thermogravimetric analysis (TGA):

At the beginning, to understand the behaviour of the raw material, a thermogravimetric analysis (TGA) analysis was performed on cigarette butts' filters. As the raw material that was chosen to be used were the filters, it was valued as unnecessary to do a TGA also on the entire CBs. The TGA is a technique that combines heat treatment with weight measurement: it is used to monitor the loss of mass of a sample during heat treatment in a controlled atmosphere. We chose to perform out tests under a nitrogen atmosphere, to try to better understand the pyrolysis mechanism on our raw material.

The equipment that was used was the Setaram SETSYS-1750 CS Evol and the software used to analyse the results was Calisto. The used melting pot was a AI203, with a volume capacity of 100 µL. A picture, made by the author, of the machine is in the following figure (Figure [42]):

Figure [42], Setaram SETSYS-1750 CS for TGA, author's elaboration.

This is a machine that can go up to 2400 °C. This system has a most sensitive balance, designed specifically for thermogravimetry, for unparalleled sensitivity and long-term stability.

At first, to decide the protocol, it was necessary to look at the bibliographical research to have some information about the path of the mass loss. After having found many information we decided to analyse it and the following analysis has been found. Polarz et al. (2002) [30] describe that for the filters the transformation to carbon via dehydration starts at a temperature of 280 °C and is completed at a temperature of 360 °C. As the authors state "the dehydration and removal of acetic acid causes a mass loss of about 65%, a value that is in good agreement with the expected relative amount of H2O and acetic acid to be removed from the sample". Then, going up to 600 °C, the study finds a further mass loss of 20% and remark that it is possibly due to an incomplete degree of carbonization (C_xH_y species). Finally, the carbon yield of CBs' filters is around 10-15% when subject to a pyrolysis treatment. This behaviour is confirmed by the study by Koochaki et al. (2019) [5]: a weight loss is observed at 280 °C and is due to exit of free water connecting the surface of raw material; then the authors report that there is an intensive weight loss from 280 °C to 370 °C which is related to the decomposition of hemi cellular components of raw materials and finally a third step, where there is a slow mass loss by increasing the temperature to 800 °C, due to the cracking reaction of C–C bonds and it is very low and slow. Hamzah et al. (2017) [4], in a similar way, have found that the highest mass loss trend was observed starting at 260 °C and completed 350 °C, afterwards at higher temperatures, the sample mass decreased slightly up to 600 °C.

Starting from this information, we then proceeded to make our own TGA experiments. Before doing the experiment, it was necessary to blend and scramble the filters: indeed the filters have a really low density, therefore, as the melting pot for the TGA is really small (volume capacity of 100 µL), to have a considerable mass, it was important to blend the raw material. Furthermore, the blended filters were introduced in the machine and a first cycle was done (from the lowest to the highest target temperature and then back to ambient temperature), then a second identical cycle was performed: so when the results of the second are subtracted to the results of the first, the real behaviour of the product is given; in this way all the uncertainties linked to the equipment and others (as the uncertainty given by remaining of precedent materials in the melting pot, that sometimes can happen).

The protocol was then decided to be the following (same for the sample and for the blank):

1. A purge phase to go to a stage of high vacuum (20 °C for 3300 seconds and with a flow of nitrogen of 200 mL/min)
2. A stabilisation phase under a flow of nitrogen (20 °C for 600 seconds and with a flow of nitrogen of 100 mL/min)
3. The sequence for the samples (going up to 1000 °C and then back to 20 °C)
4. Another stabilisation phase under a flow of nitrogen (20 °C for 600 seconds and with a flow of nitrogen of 100 mL/min)
5. The sequence for the blank (going up to 1000 °C and then back to 20 °C)

The heating sequences, that were exactly the same were the following (in Table [7]):

Table [7], TGA heating sequence, author's elaboration.

number	type	T start (°C)	T end (°C)	time [s]	nitrogen flow [mL/min]
1	→	20	20	300	100
2	↑	20	105	1020	100
3	→	105	105	14400	100
4	↑	105	375	3240	100
5	→	375	375	14400	100
6	↑	375	1000	7500	100
7	→	1000	1000	1800	100
8	↓	1000	20	3920	100
9	→	20	20	1800	100

The chosen plateaux were at 105, 375 and 1000 °C. These values were justified from the references, but then another experiment was done with a plateau at 550 °C, due to the findings that were made (that will be explained later). The same thing was done for the other sample analysed, the NaOH pre-treated filters. The results and comparisons are all reported in the next chapter.

Fourier Transform Infrared Spectroscopy:

FTIR (Fourier Transform Infrared Spectroscopy) analysis was made both on the manufactured active carbons and on the original raw materials. FTIR is a technique used to obtain infrared absorption, transmittance and emission of a certain sample. As an FTIR spectrometer allows the simultaneous collection of spectral data over a wide spectrum, we chose to acquire a spectrum between 4000 and 600 cm^{-1}.

The purpose of any absorption spectroscopy, including FTIR, is to measure the amount of light absorbed by a sample as a function of wavelength and in this way, once verified all the spectra, identify the bands and the functional groups that are present and thus determine the material's molecular composition and structure. To perform our tests, the infra-red spectroscopy spectra was obtained using a Thermo Scientific Nicolet iS5 FTIR spectrometer. A picture of the equipment is reported in the following figure (Figure [43]):

Figure [43], Thermo Scientific Nicolet iS5 FTIR spectrometer for FTIR, author's elaboration.

As already mentioned, the FTIR tests were performed on the raw material and on the final result. At first, however we decided to focus on the obtained result. The chosen samples were:

- Filters, pyrolysed at 800°C for 30 minutes (F800C30min), also called simples
- Filters activated with NaOH, pyrolysed at 800°C for 10 minutes (NaOH800C10min), also called NaOH
- Filters activated with KOH, pyrolysed at 800°C for 10 minutes (KOH800C10min), also called KOH
- Filters activated with ethanol, pyrolysed at 800°C for 10 minutes (ethanol800C10min), also called ethanol

The first analysis was on the simple filters, then we analysed the others: in this report, in the following chapter, we will show all the pre-treated samples in comparison with the first set. This was the toughest sample to analyse because it was not a powder, neither easy to crush, since it was in pieces. Therefore, before coming to a good performance, we had to repeat the test several times.

Then the tests were done on the raw materials. The materials that were analysed are the following:

- Filters, simples as they are, called simple
- Filters from rolled cigarettes (we noticed that usually they have a darker colour), called rolled
- Filter treated with NaOH and then dried, called NaOH
- Filter treated with ethanol and then dried, called ethanol

The results and comparisons are all reported in the next chapter.

Scanning Electron Microscopy:

Scanning Electron Microscopy (SEM) is an electron microscopy technique capable of producing high resolution images of the surface of a sample using the principle of electron-matter interactions. The interaction between the electron probe and the sample generates low-energy secondary electrons which are accelerated towards a secondary electron detector which amplifies the signal. Each point of impact is associated with an electrical signal. The intensity of this electrical signal depends both on the nature of the sample at the impact point, which determines the secondary electron yield, and on the topography of the sample at the point. It is thus possible, by scanning the beam over the sample, to obtain a map of the scanned area.

The used equipment was a Quanta FEG 250. This equipment has a Schottky field effect gun (FEG) and is high vacuum (HV) mode can go to 10-4 Pa. The vacuum is required so that the electrons can circulate in the machine. Imaging was done in the high vacuum mode under an accelerating voltage of 20 kV, using secondary electrons. Furthermore it does an environmental field effect scanning electron microscope (ESEM FEG): this means that to do the analysis, it is not necessary to have a sample that conducts electricity (so in our case there is not the necessity to cover the sample with a metal, platinum usually, with a maximum thickness of 5 nm, so that electrons can move). A picture of this equipment is shown in the following figure (Figure [44]):

Figure [44], Quanta FEG 250 for SEM, author's elaboration.

The samples that were analysed are the following: a simple filter, a NaOH pre-treated filter, a filter from a rolled cigarette, an ethanol pre-treated filter, F800C5min, F800C20min, NaOH800C5min, Eth600C10min, F400C2h30, F800C5min+KOH and microwaveKOH800C5min. The sample holders are made of zinc or aluminium and with a carbon part, which has a glued face where it is possible to glue the samples. To not to lose the samples, they were numbered. This was really important in the analysis of active carbons, as they all look pretty much the same. Moreover, if the tweezers to take the sample was pressed too much on the carbon, due to its fragility, it broke into pieces. The samples were analysed at 1 mm, 400 µm, 50 µm and 10 µm, as it was advised from the references.

EDX analysis

Energy dispersive X-ray (EDX) spectrum is used to understand the chemical and physical analysis of the percentage of elements in the raw materials and in the activated carbon samples. This is an analytical technique used for the elemental analysis or chemical characterization of a sample.

This analysis was done on the same samples of the SEM, as it was done with the same equipment, the Quanta FEG 250.

Methylene blue adsorption

Methylene blue (MB for short, with chemical formula $C_{16}H_{18}ClN_3S$), or methylthioninium chloride (represented in Figure [45]), is a phenothiazine derivative that is widely used as a dye, mainly in laboratory applications. It is an odourless crystalline solid and is soluble in water. To compare the performances as an active carbon used in our society of the different samples that were prepared, it was chosen to carry on some laboratory tests on the active carbons that were fabricated during our study. The adsorption process is a spontaneous process accompanied by a decrease in free energy, and entropy also decreases because the degrees of freedom of the molecules decrease with this phenomenon. Therefore, the methylene blue adsorption tests will be a test to grade the performances of adsorption of our own carbons.

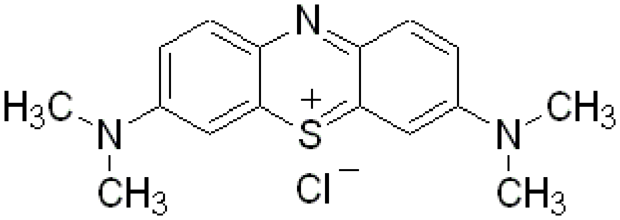


Figure [45], Structure of methylene blue, from [44].

The intrinsic characteristics of active carbons (high degree of porosity and specific area) make them an excellent adsorbent material and it is consequently used to separate different substances from aqueous or gaseous mixtures in order to remove them. In fact, its porous structure causes the particles of adsorbed substance penetrating the micropores to bind through van der Waals forces (this is consequently physical adsorption) to the inner surface of the activated carbon. This makes it necessary in numerous processes in the chemical industry such as filtration, purification, metal extraction and decolourisation.

In the present study, the adsorption mechanism is complicated by the energetically heterogeneous nature of the mixture: it is indeed formed by water, methylene blue and activated carbon and moreover it has to be considered that the active sites of the activated carbon have different sizes and thus the dye molecules are adsorbed differently.

The experiments that were carried on were based on the adsorption of methylene blue by activated carbon made during the study: the first solution, with a volume of 500 mL of water concentrated to 50 mg/L of methylene blue, then it was divided in 7 container of 20 mL each. Then these solutions were each mixed with 0,1 g of active carbon using a magnetic plate with a stirrer in order to speed up the adsorption process. Starting from a null time (the first test tube), the other six where marked as 15 and 30 minutes, 1, 2, 4 and 24 hours. Therefore, the active carbons were taken out at different times. When the time came, the wanted recipient was taken and the contained liquid-carbon mix was put in a beaker by a sieve, so that the carbon could be separated from the solution.

This test was used as a proof of concept, also called POC. A proof of concept is demonstration of feasibility, and the final purpose is to show the feasibility of a process or an innovation, in our case the fact that the made active carbons could actually adsorb the methylene blue, meaning that it had a good specific surface area. Therefore, it was done only on one single carbon, to understand the feasibility, F800C5min. Then, other samples were passed on the BET, to estimate the surface area in a more accurate way. Similarly, this process was done also for Rhodamine B, a pink dye. This experiment was done without measuring the conditions, only leaving the solution mixed with F800C5min all night long and see the results the next morning.

Brunauer–Emmett–Teller theory

BET stands for Brunauer–Emmett–Teller and is a theory used to explain the physical adsorption of gas molecules on a solid surface: it is thus very used to measure the specific surface area of adsorbing materials, the produced carbons in our case. The BET method was developed by Stephen Brunauer, Paul Hugh Emmett and Edward Teller - B.E.T. stands for their surnames, Brunauer, Emmett, Teller - and published in 1938 in an article entitled "Adsorption of Gases in Multimolecular Layers" in the Journal of the American Chemical Society [46]. The BET method was an extension to the Langmuir theory, that had been developed by Irving Langmuir in 1916. The major assumption of this theory was that adsorption takes place as a monolayer of adsorbed molecules on the surface of the adsorbent (furthermore other theories were developed, like in the case of physisorption of molecules with a weak interaction with the adsorbent, because it is necessary to take into account the formation of a multilayer of adsorbed molecules).

The experimental procedure was done using the Micromeritics 3Flex. This machine is a high-performance adsorption analyser and is able to determine the isotherms of adsorption and desorption and measure surface area, pore size, and pore volume of the chosen samples. To do the adsorption and desorption, an inert gas is used: usually (and also in this case), nitrogen. The nitrogen was taken from a nitrogen bottle and thank to a pump, pumped in the machine.

Figure [46], Micromeritics 3Flex, author's elaboration.

Before passing the samples in the Micromeritics 3Flex it was necessary degassing the carbons. This process was done with a Micromeritics Smart VacPrep, that has six degassing stations, and a choice of vacuum or gas flow preparation on each of the six stations. There are two pumps: a primary one and a secondary one. There is also a heating possibility, but as in the used machine it was broken, pre-heating was done in an oven. The equipment is shown in the following image, Figure [47]. It is possible to see the primary pump on the right side of the picture and a sample that was degassing in the first degassing station.

Figure [47], Micromeritics Smart VacPrep, author's elaboration.

Then, the analysis to evaluate the specific surface area is performed. It is done by adding in steps known amounts of nitrogen pressure (called p_0) to the sample container, so that different vapour pressures (p) are reached at the equilibrium of the system. During the procedure, a pressure sensor monitors the pressure variations due to the adsorption processes (the nitrogen gets pumped in the sample holder and if the sample is porous, it is adsorbed from the carbon, so the pression varies) and when the saturation pressure is reached this means that no more physical adsorption takes place. The pressure data collected are presented in the form of the BET isotherm, which relates the volume of adsorbed gas as a function of relative pressure (p/p_0). The results will be therefore presented in this way.

4.2 Results and discussion

In this section the obtained results will be discussed. First of all, the TGA results will be reported, to make the reader understand the mechanism of degradation that happens in the filtering material. Then, a first estimation of the kinetics of the reaction will be presented, along with the graphical representation of the obtained carbons, to show visually the result of the process. In the following the SEM and FTIR analysis results will be introduced and discussed. Finally, the proof of concept on methylene blue and Rhodamine B will be presented, and after all, the results of the BET analysis, to show the specific surface area of the obtained carbons. As this was the main parameter and the objective of our optimisation goal, from these BET results we will be able to demonstrate if the presented pre and post treatments have worked or not, giving fundamental indication to further and more in-depth studies and researches.

4.2.1 Thermogravimetric analysis

The TGA was performed as discussed in the methodology part. At first, the analysis for the filters without pre-treatments was done. In the following graph (Figure [48]) are represented the temperature evolution (red curve) and the mass loss evolution (in percentage, green curve) over time. Then, for the part were the mass loss was the biggest, the derivative was traced (black curve):

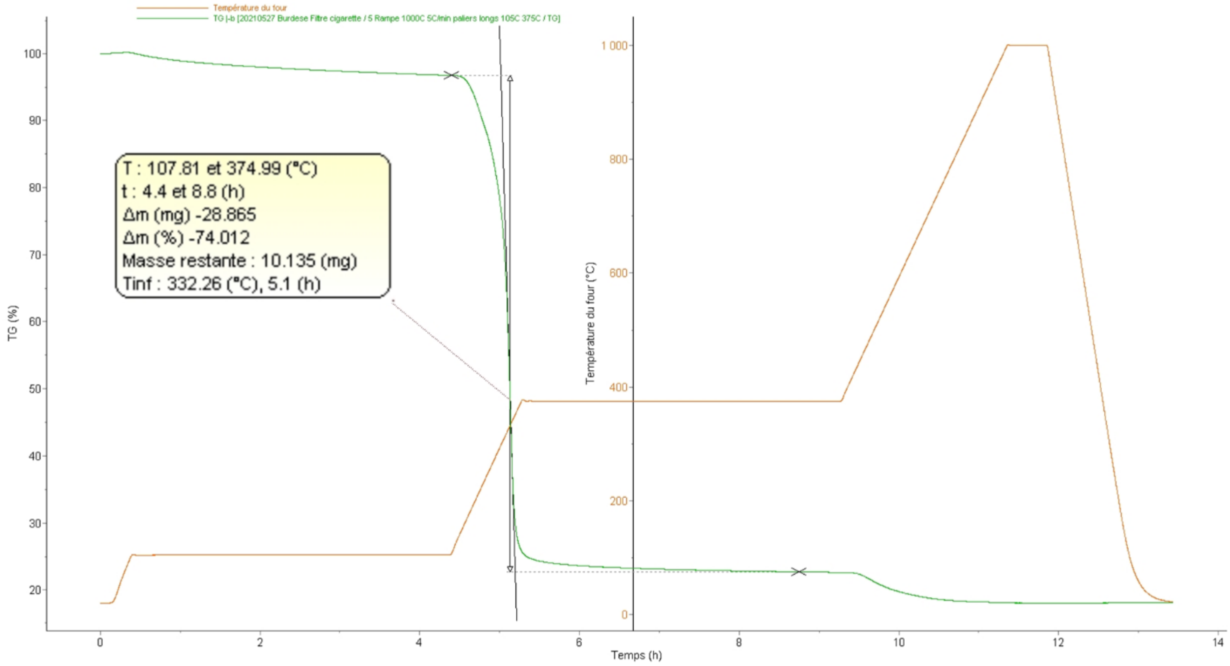


Figure [48], TGA of CBs' filters, author's elaboration.

As in the bibliographical studies that were reported, thermal behaviour of cigarette butts' filters is divided into three steps. The first one is at around 105 °C, where we lose all the mass given by water, but it is a fairly small mass loss. The biggest mass loss (of about 70%) is observed starting at 280 °C to around 340 °C (we here reported one particular analysis, but having done more than one a mass loss at ~340 °C on average was observed): this surely is caused to the decomposition of acetic acid; then there is a third mass loss at about 500 °C, most probably due to the cracking reaction of C–C bonds: it is indeed low and slow, as expected. Therefore, our results are in agreement with the results reported in our references.

Moreover, as we did for the normal and untreated filters, in the following image (Figure [49]) it is reported the TGA results for NaOH pre-treated filters. It is to report that the NaOH pre-treated filter that were used were still wet, therefore there are two main factors that have influenced the analysis. The first one and most immediate to understand is that there will be a bigger mass loss at around 100 °C, as there is more water to lose. In addition, during the purge phase there is a moment where the machine is in vacuum mode: therefore, as the pressure is lower than atmospheric pressure, there is some water and other compounds that already evaporate, as their boiling point lowers. From these conclusions we can say that the obtained results are not perfect but need to be understood and seen as a first attempt to approach the subject, giving only some critical information to do more and in-depth research.

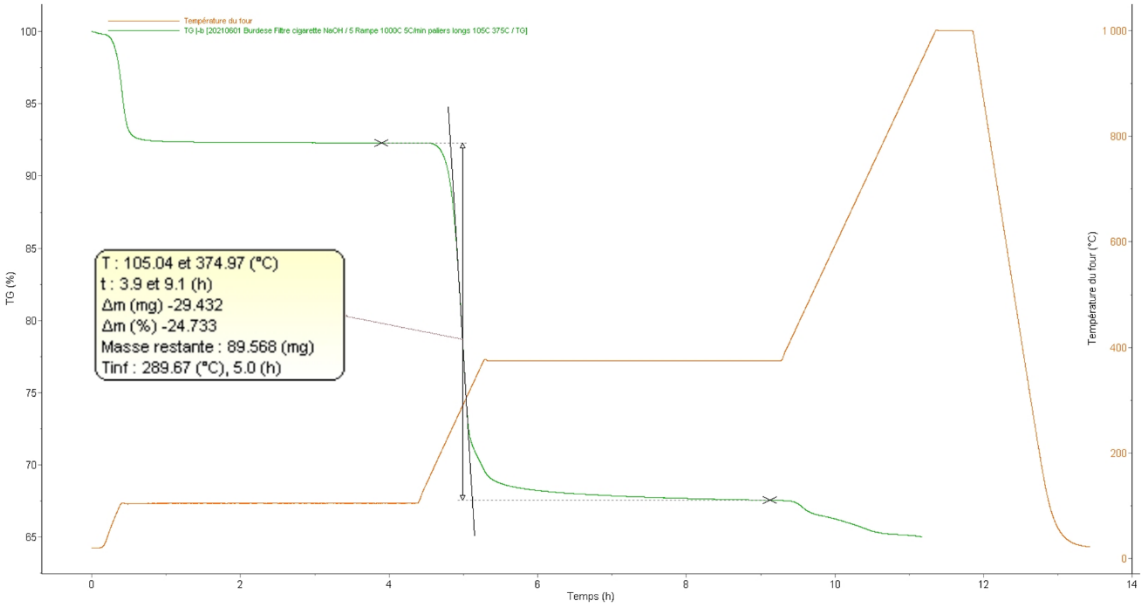


Figure [49], TGA of NaOH pre-treated filters, author's elaboration.

We can see that apart from the first part, the trending of the curve (the green curve represents the mass loss (in %)) is very similar to the precedent one. Also, the slopes are similar. In the profile, there is a first mass loss at 106 °C and is due to water: as already said the sample that was analysed was still wet, so it is clear that water will evaporate. Then there is the second mass loss at about 290 °C and finally a third one at 460 °C. The trending is the same, but the temperatures are lower: this is probably caused by the presence of oxygenated functional groups. Most probably, the sodium hydroxide helps in the creation of oxygenated functional groups on the surface of the fibres of the filter and this effect accordingly enhances the kinetic of the reaction.

It was possible to put the two curves on the same graph, to compare them (in Figure [50]). This time the mass loss (in %) was compared over the temperature and not over time.

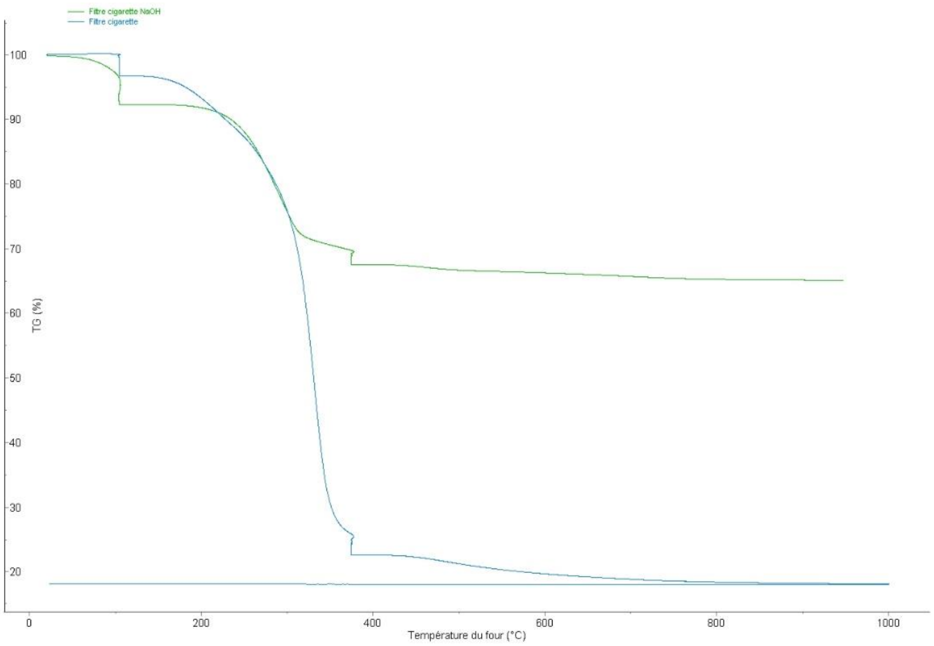


Figure [50], Comparison of TGA of filters (blue) and NaOH pre-treated filters (green), author's elaboration.

As already told, the analysis needs more study. The two curves have the same trending, but the NaOH one (green) is higher because of the mass loss during the purge phase. It is also possible to show the integral pf the derivative of the temperature (with the two curves on the same level), to better understand the process.

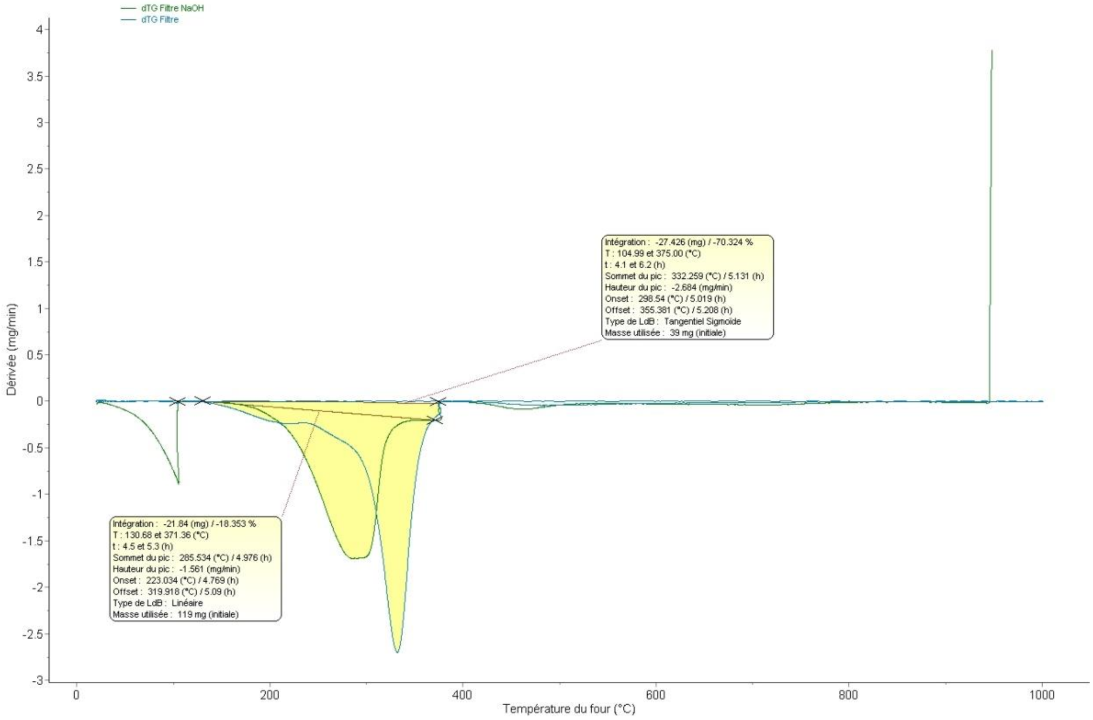


Figure [51], Comparison of TGA of filters (blue) and NaOH pre-treated filters (green), author's elaboration.

The peak is different: the NaOH curve has a peak at lower temperature, meaning that the degradation process is faster and starts before; but on the other hand, the process takes longer to get up to speed. The same loss in mass is incurred over a longer period of time and starts at lower temperatures, giving a less sharp curve. Furthermore, the peak of temperature at the fat left of the graph is an error of blank subtraction given by the breakdown of the machine, which is also the reason why a test on the dry NaOH sample was not done. Finally, it seems important to say that these results, however, need more confirmation and the process need more research.

4.2.2 Estimate of the kinetics:

After the carbonisation tests, to better understand the process, we tried to identify the kinetics of the reaction, even if we know that it was quite impossible to achieve the evaluation of a real kinetic. Nevertheless, graphs to see the evolution of mass over time were made. The analysis was made by weighting the sample before the heat treatment (and labelling this initial mass as m0) and the weight it after the heat treatment (and labelling it mf). By doing mf/m0 we actually managed to calculate the fraction of remaining mass, thereby making the result obtained independent of the initial mass. Therefore, the evolution of the mass residue with the hold time at a given temperature for CBs' filters was plotted. At first, the tests at 800 °C were performed. The obtained results of the mf/m0 are reported in the following graph (Figure [52]). These are experimental points, so this is the way they are represented in the following figure:

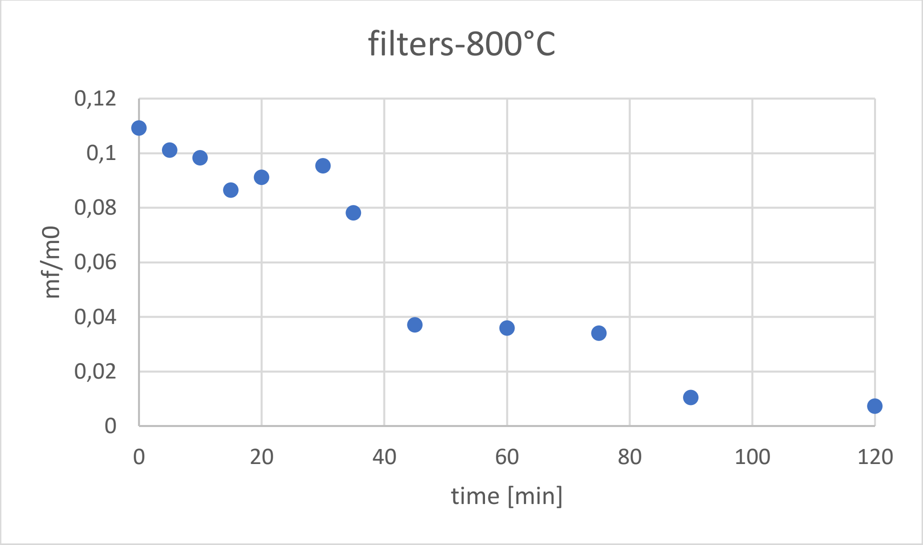


Figure [52], Evolution of the mass residue with the hold time at 800°C for CBs' filters, author's elaboration.

From the above graph it was not very clear the trending of these data, therefore it was thought to make a more understandable graph, by linking the points with a curve. This would have been an error; it does not have any mathematical significance, because we do not have a statistic of the results but joining the dots with a line makes no sense. Therefore it did make sense to try to plot a trend line: even if we did not have a theorical curve to reproduce (therefore the parameters of the eventual trending curve could not be compared to anything) this process seemed interesting.

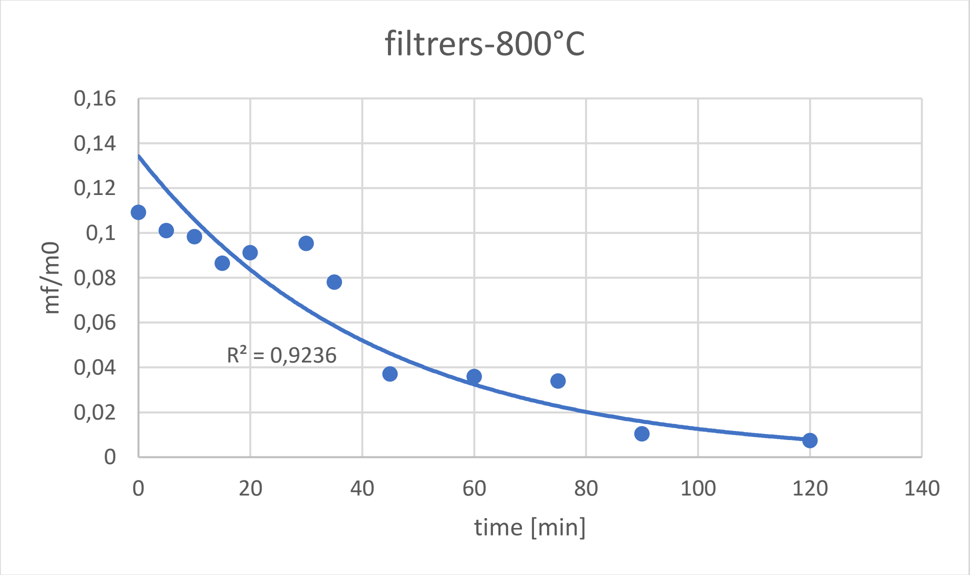


Figure [53], Evolution of the mass residue with the hold time at 800°C for CBs' filters, author's elaboration.

It is to remark that in this study, due to a lack of time, there has not been a repeatability, as no more than one test was performed. This choice is justified by the fact that this is a preliminary study and that at UTC the study in this subject has started with the present analysis. This research, that started with me, has the goal to understand in which direction the following studies should undergo and to start with a procedure and some data in the following investigations. This is a first screening, so the most temperatures and pre-treatments possible were tried out, and the trend curves were done to try to understand what can possibly happen, but do not have the goal of detailing it.

As a result, this graph (Figure [53]) allowed us to better see the trending, keeping in mind that it does not represent a real behaviour. In addition, it is again to remark that due to a lack of time, it was not possible to have more data to compare, therefore there are not any errors or a standard derivative of these points. Few words need to be spent on the shape of the trend line: even if a polynomial curve of third degree had a better fit of the points, it did not represent the physical behaviour of the process. The process is a mass decay therefore it can be easily represented as an exponential function. All considering this is the most appropriate way to describe what is happening and even if some points are out of the exponential trending (as it will be better explained later), the exponential behaviour appears quite logic: again, the exponential has a lower R^2 than a polynomial, hence a worse fit, but better represents, albeit with its limitations, the physical behaviour of the process

The graph shows us that the mass loss is very rapid, meaning that the pyrolysis was almost flash. At the zero hold time (that on average was between 2 and 3 minutes) there was a remaining mass of less than 12% and after this value it starts to further decrease. There are some points that are affected from uncertainties and we see relative peaks and troughs. Anyways, for the 20 minutes and 30 minutes samples (that will be showed later) we noticed a good amount of carbon and some ashes, meaning that most probably the pyrolysis had been finished and the oxygenation started: the oxygen starts reacting with the hot carbon and degrades it. The ashes are indeed of a white/grey colour and when the samples start to burn it is possible to see that on the surface of the carbons there are some grey parts, but understanding at what time the pyrolysis ends and where the oxygenation begins is quite impossible.

Then the tests were also performed for 600 °C and 700 °C. The graph that represent the trending of the fraction of remaining mass with the hold time for all the temperatures is in the figure below:

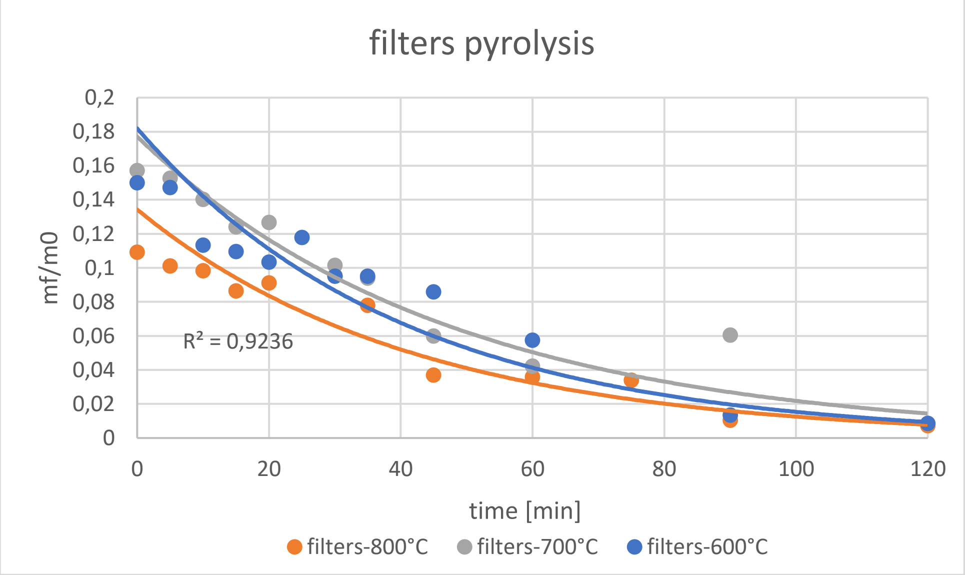


Figure [54], Evolution of the mass residue with the hold time at 800, 700 and 600°C for CBs' filters, author's elaboration.

As of the trend curves, the same thing happens for the other temperatures (600 and 700 °C). This is because these points are at already very large mass losses (more or less 90% of the mass is already lost after 5 minutes). The graph shows also the factor R^2 for the filters treated at 800 °C, which Excel gives us to understand the good quality of a fitting. Moreover, here is possible to state a couple of things; first of all, at 800 °C, as we would imagine, the mass loss is faster than for lower temperatures. In addition, there are points that show the great quantity of uncertainties in our system. There are sudden peaks (like the grey point at 90 minutes) that should not be there, but as a result of an experimental campaign, are there. Finally, it is possible to remark, as it was already prospected, that for higher hold times the three curves (reminding that they are experimental points that are joined with a curve only to facilitate the readability of the graphs) overlap, implying a certain similar behaviour between the three systems. This was also shown from the TGA, where at about 600 °C there were the last reactions that developed the last mass loss, then no further reaction was developed.

Afterwards, the samples were tested at 400°C. As the study by Koochaki et al. (2019) [5] proposed a hold time of two hours, we followed suite. Then other hold times were tested and the obtained graph (always reminding that the experimental points are only points and that there is not a repeatability) is the following:

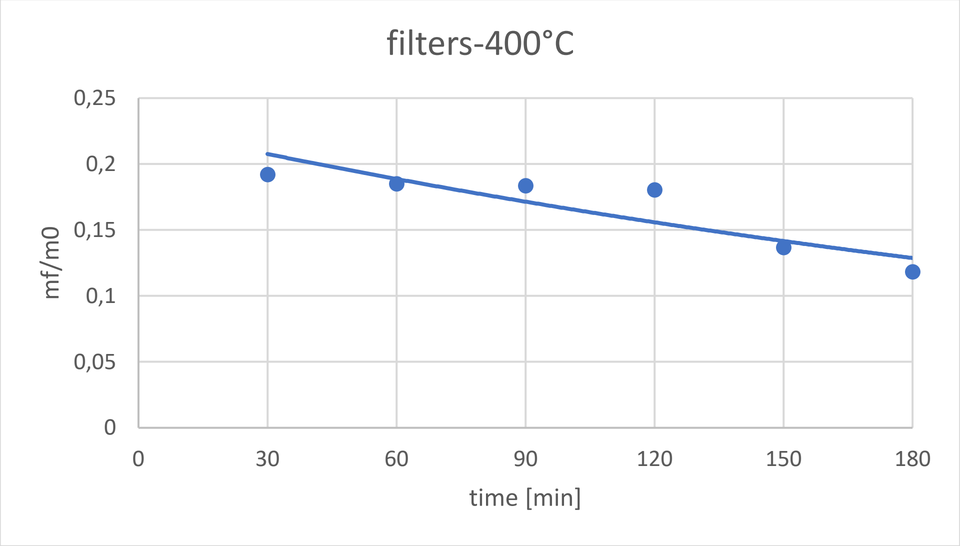


Figure [55], Evolution of the mass residue with the hold time at 400 °C for CBs' filters, author's elaboration.

Also in this case the trend curve is an exponential, but the trend looks much more linear; nevertheless, the mass loss after 30 minutes (the first point that was taken) was already about 80% and it decreases to about 90% after 3 hours. This means that the reaction of pyrolysis (if it happens) is quite fast and most of it is done in the first 30 minutes and then remains constant for the following times.

As of this result, that was noticed for all the temperatures, it was decided to analyse only the first five minutes. Therefore, by making other tests, we did a zoom in the 0 to 5 minutes zone.

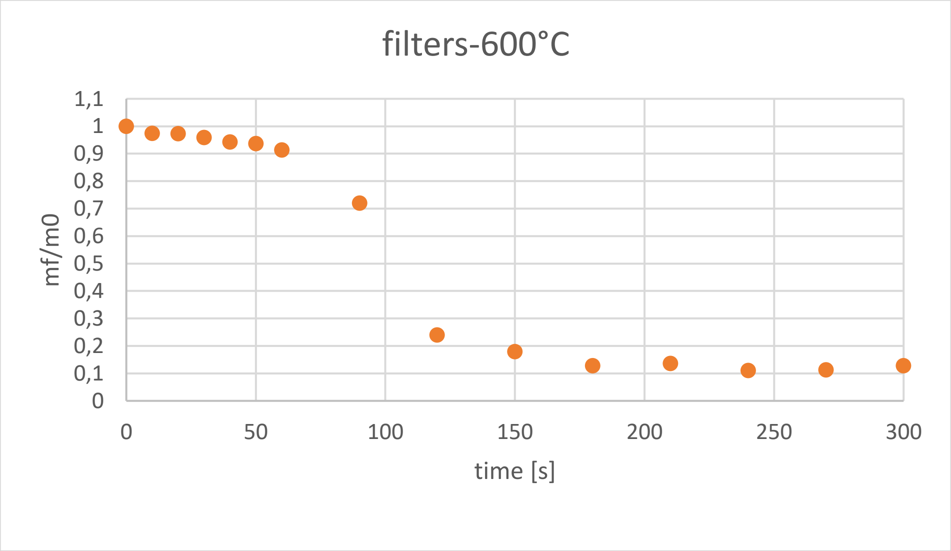


Figure [56], Evolution of the mass residue with the hold time at 600 °C for CBs' filters 0-5 minutes, author's elaboration.

The tests were done by simply weighting the sample, putting the melting pot inside the oven and take it out (without waiting for the "zero time"), so that the hold time was the real time that the sample spent in the oven. The chosen points where from 10 to 60 seconds with an interval of 10 seconds and then every 30 seconds.

From the above graph (Figure [56]), we can see that the trend is like an Arrhenius's law. The mass loss in concentrated in the first 3 minutes and then we have almost a plateau. But, from the graphs showed before (Figure [54]) it is clear that the trending is exponential. Therefore, the explication is that most probably up to 30 minutes there is a pyrolysis and then the oxygenation takes on. To better visualise this, we can join the points of the 0 to 5 minutes of the last experiment presented and the other points at 600 °C (keeping in mind that the points are not the real hold time, which is different of 2-3 minutes). In addition to facilitate the reading the points were joined, but this is an error. It does not have any mathematical significance, because we do not have a statistic of the results, but it was done to just make the graph more readable. This is shown in Figure [57]:

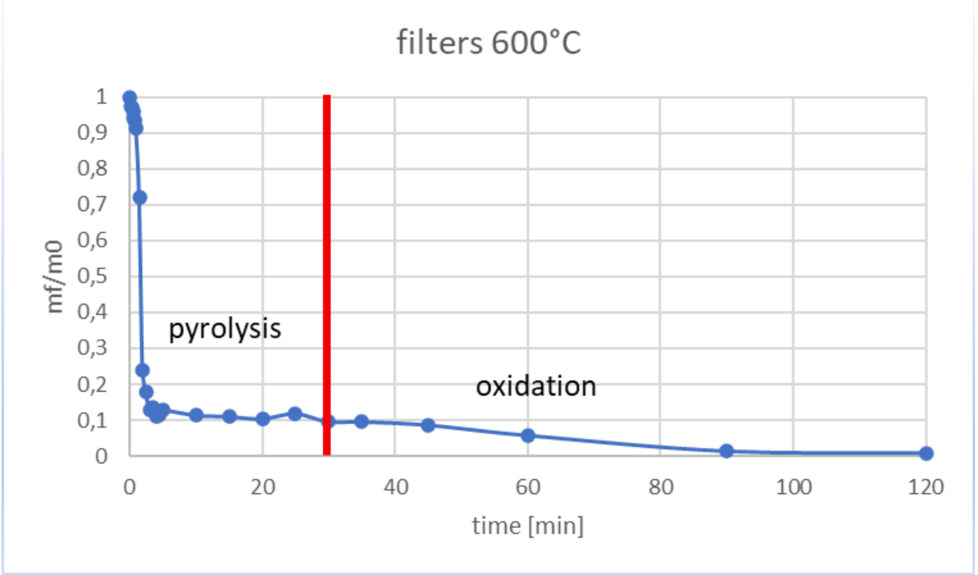


Figure [57], Evolution of the mass residue with the hold time at 600 °C for CBs' filters 0-120 minutes, author's elaboration.

From this graph it appears more evident that there are two different phases in the process, even if there is not a repeatability and there are surely errors and that there is not a statistical distribution. The first part, that we hypothesized going until 30 minutes, is the pyrolysis phase, where the majority of the mass is consumed and where the pores are formed. Subsequently, the oxygenation phase started: as air enters the melting pot the remaining mass starts to burn, with an exponential trend (as explained in the graphs before, like Figure [54]). Again, it is important to remark that these are hypothesis and that this study only hopes to do a first screening of the problem and therefore, as there is not a repeatability, should not be considered as sure: it will need further study and confirmation.

With the help of Professor Elias Daouk, I tried to better understand the kinetic law of the pyrolysis and to see if we could try to extract some parameters that could be useful in the following works. A very good amount of help, to better understand the topic, has come from the slides for wood pyrolysis of NF24 [47], a course done by Professor Daouk. Kinetics is the study of the rate of chemical reactions and in particular, the kinetics of the thermal decomposition of solids, is discussed here. This study only deals with the kinetics of solid degradation and does not take into account the heat transfer part of pyrolysis models. This kinetic law represents the rate of a chemical reaction. In thermal degradation, this law is composed of two parts, a law of variation of the rate and a conversion function. It has been shown in the literature that Arrhenius' law can be used to represent the thermal used to represent the thermal decomposition of solids. The following form form is used:

$$k(T) = A * \exp\left(-\frac{E_a}{RT}\right) \qquad (4.3)$$

With, k being the law of speed variation; A the pre exponential factor; Ea the activation energy; R the constant of perfect gases and T the temperature (in K). As the slides of professor Daouk [47] report, this model was originally developed in gas kinetics. The pre-exponential factor corresponds to the frequency of collision between molecules. The activation energy corresponds to the minimum energy required for the transition to take place. So, we have a model which says that the speed of reaction depends on a certain energy needed for the reaction to take place. Below this, the collision produces nothing, the collision is elastic, above it the energy to produce a new system, for example to create new molecules. It is also clear that the speed of chemical reactions depends strongly on temperature.

Now we have to define a function of conversion. The conversion function represents the behaviour of the mass, as a function of temperature and time temperature and time, during the reaction. The one that we chose in the following:

$$f(\alpha) = (1-\alpha)^n \tag{4.4}$$

This model is called the deceleration model where the reaction rate is maximum at the beginning and decreases gradually. α is the coefficient of conversion (or degree of conversion) and is denoted as:

$$\alpha = 1 - \frac{m(t)}{m0} \tag{4.5}$$

The coefficient n is presented as the order of the reaction and can be interpreted as a means of representing the influence of each mass on the overall model. This function is part of the kinetic law and it is determined experimentally. And here there is the first step: we used the data that I collected from the experimental campaign (the data shown in Figure [56]), that was from 0 to 3 minutes. Unfortunately, I could not do many points and my precision was limited, therefore a spline was done, to obtain more points for the kinetic model. The graph of the spline is the following (Figure [58]), with the circles that represent the experimental points obtained by this campaign. From these points we can know the f(α).

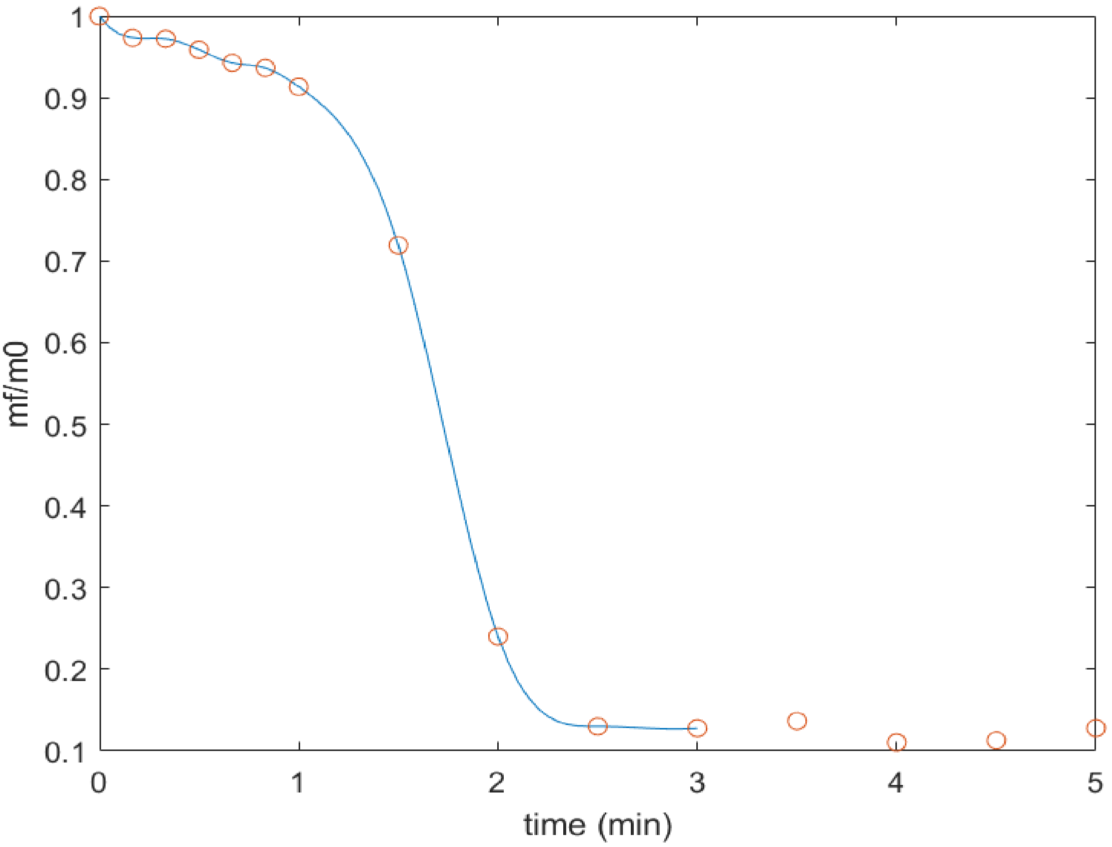


Figure [58], Spline of the mf/m0 graph, from 0 to 3 minutes, author's elaboration.

We now have the complete function of the kinetic law for the modelisation of the degradation of a solid:

$$\frac{d\alpha}{dt} = k(T) * f(\alpha) = A * \exp\left(-\frac{E_a}{RT}\right) * (1-\alpha)^n \tag{4.6}$$

This is a differential equation and we need to calculate the 3 kinetic parameters: A, E_a and n. These parameters and their numbers depend on the chosen reaction mechanism, therefore it needs to be better analysed.

A classical single reaction mass degradation (by putting cellulose acetate as the raw material) is denoted by the following diagram:

$$Cellulose\ acetate \rightarrow \nu\ Carbon + (1-\nu)\ Gas$$

With ν as the stochiometric mass coefficient. This transformation is modelled with an Arrhenius type law with three unknowns (A, E_a and n). Furthermore, it needs to be remarked that in the filters there is also about 10% of water, which needs to be taken into account, and also from the experiments (and from the TGA results that will be presented later) we saw that the carbon production is about 13% of the original mass.

To find these values, from [47], professor Daouk solved a system of 5 differential equations, where he set the equation of the temperature, the speed of degradation of the filters, the speed of degradation of water, the speed of formation of the carbon (which is the same one as the one for the filters but with negative sign, as when the filters are consumed, the carbon is formed) and the matter balance of the reaction:

$$\frac{dT}{dt} = \frac{h*A}{\rho*C_p} * (T_{oven} - T) \tag{4.7}$$

$$\frac{d\alpha_{filters}}{dt} = A_1 * \exp\left(-\frac{E_1}{RT}\right) * (1-\alpha_{filters})^{n1} \tag{4.8}$$

$$\frac{d\alpha_{carbon}}{dt} = -A_1 * \exp\left(-\frac{E_1}{RT}\right) * (1-\alpha_{filters})^{n1} \tag{4.9}$$

$$\frac{d\alpha_{water}}{dt} = A_2 * \exp\left(-\frac{E_2}{RT}\right) * (1-\alpha_{water})^{n2} \tag{4.10}$$

$$\frac{d\alpha}{dt} = 0{,}9 * \frac{d\alpha_{filters}}{dt} + 0{,}13 * \frac{d\alpha_{carbon}}{dt} + 0{,}1 * \frac{d\alpha_{water}}{dt} \tag{4.11}$$

Therefore, the system of equations has been defined. The valued that will be needed to be calculated are A_1 and A_2, E_1 and E_2, n_1 and n_2. The parameters are all already known and explained, but the ones for the temperature equation. Their meanings and values (that we estimated for the cigarette butt filters, therefore they might be different and our results might change) are the following:

- h=15 $\frac{W}{m^2K}$ it is the convection coefficient of cigarette filters
- A=$\frac{4}{0{,}003}\frac{1}{m}$ it is the specific length
- ρ=60 $\frac{m^3}{kg}$ it is the density of the filters
- C_p=1600 $\frac{J}{kgK}$ is the specific heat of the filters

The system of differential equation was solved with a MATLAB code, which I cannot report here, therefore in this paragraph I will try to explain it. The code initialises all the α at zero, because at the time 0 there is no mass loss or mass gain. Then, a first set of parameters "AEn" was defined: the chosen values were almost random. One important thing to remark is that the values were multiplied for some constants, to get values that between them were of a comparable order. Then the algorithm resolves the differential equation with the function "ode" and the residual (the difference between the experimental α and the modelled one) is the optimised with the least squared method.

Finally, we can comment the results. From the figure below, Figure [59], we find that the behaviour of the mass loss is well modelled by Arrhenius' law and this good fit is also given by the fact that we introduced the fraction of water in the equations. The graph shows that the mass loss given by the data extracted from the laboratory test (the blue dots), are very well represented from the model curve, the green curve. Then we can see the components: the filters (red curve) decrease starting from 0,9 which is the value that we set at the start by considering a 10% of water. Water and filters get all consumed and carbon is produced, reaching a maximum of 0,13 as stated in the settings. From the MATLAB code we also got the source terms, the six wanted results:

- $A_1 = 0{,}1*10^{11{,}76}$
- $A_2 = 1{,}04*5^3$
- $E_1 = 0{,}92*162$ kJ/mol
- $E_2 = 0{,}56*70$ kJ/mol
- $n_1 = 0{,}93$
- $n_2 = 0{,}8$

This therefore is a step to find the source terms at the particle scale, to allow the possibility of a modelling of a reactor on the pilot or industrial scale.

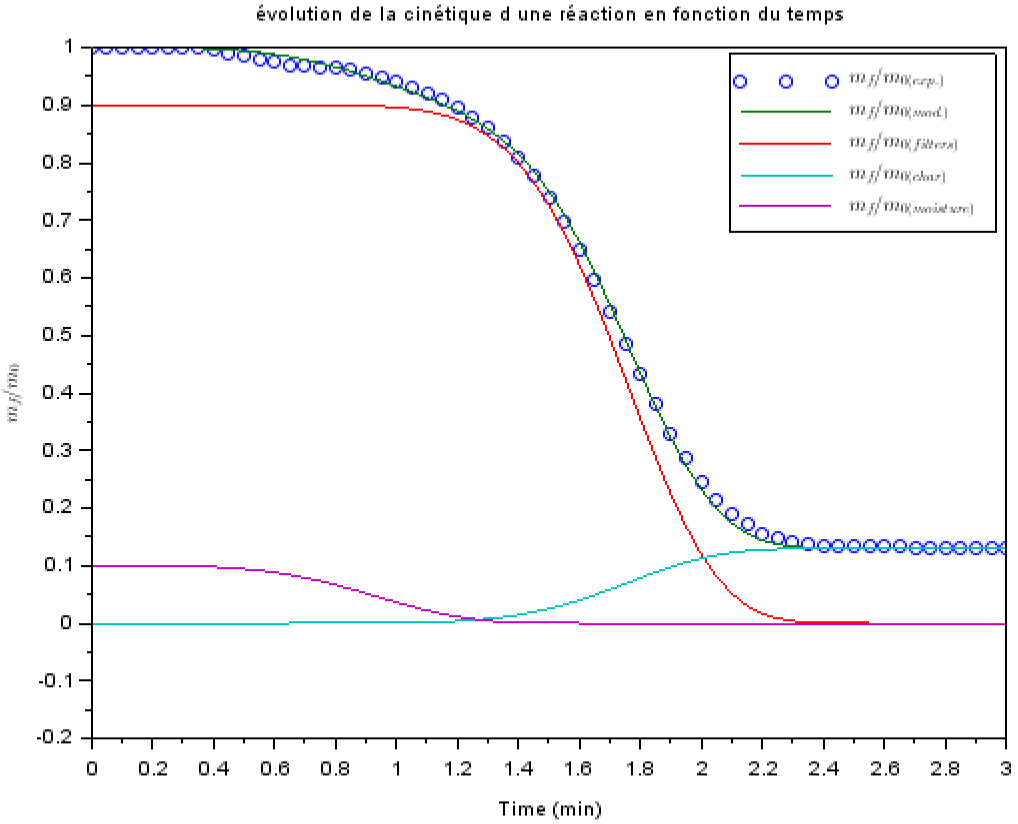


Figure [59], Evolution of the kinetics in time, author's elaboration.

Consequently, the study of an estimate for the kinetics was done also for the NaOH filters. It was not extended to the KOH and ethanol filters because, as the number of points that was done was much smaller, the results did not really give any idea of what the process looked like (it has to be remembered that while on the NaOH filters, a more in depth study was made, to compare it with the normal filters, on KOH and ethanol filters only a small number of hold times, where we thought that the most interesting results could have been, were tested).

As a result, in the following pages there will be represented the NaOH points compared with the "normal filters" at the different temperatures chose and then the NaOH filters compared between them, to give the reader an idea of what the profiles look like. Firstly, the graph that represents the evolution of the mass residue with the hold time at 800°C for NaOH filters is reported in the following figure, Figure [60]. As it was already remarked, our results are affected by much uncertainty, because it was not really possible to perform a pyrolysis and the opening of the oven changed the effective hold times. These are the reasons why the 20 minutes mf/m0 is lower than for 30,35,45 and 60 minutes. Nevertheless, the obtained curve was an acceptable one, also if compared with the results that we reported in Figure [57]: these points represent the final part of the mass decay and could be approximated as an exponential function. Before proceeding to the specific surface analysis part and compare it with the results obtained by Koochaki et al. (2019) [5] and the ones obtained without pre-treatment, it can be helpful to compare these obtained curves. Again, it is crucial to remember that these are experimental points and there is no repeatability for our results: therefore, the estimate of the kinetics is only to consider as a first approach to the problem. Moreover, we did not do further analysis to better understand the kinetic of our reaction because there was no time, due to Covid-19 restriction, and because the furnace that we used was not controllable and reliable. This consideration is valuable for all the other graphs reported in this section.

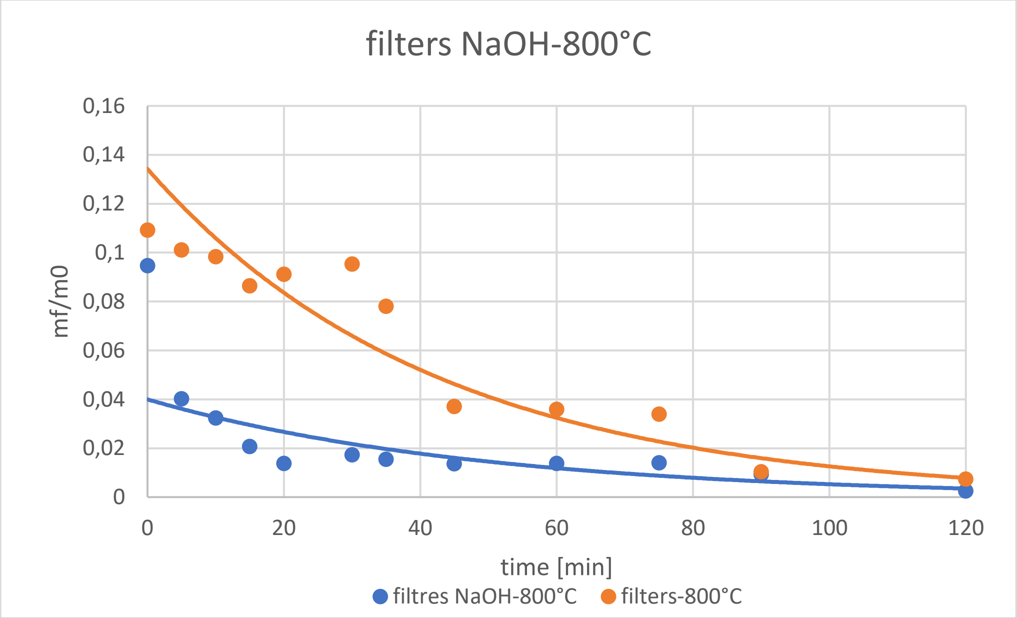


Figure [60], Comparison, at 800°C, between normal filters and NaOH filters, author's elaboration.

As it is evident to remark, even if most probably, as it was already said, there is a great deal of uncertainty in the curve that was made for the untreated filters, the NaOH-treated filters (blue line) are much more degraded then the normal filters (red line), mostly at lower hold time. It is possible to remark that the remaining mass, at 15 minutes hold, is about 9% for the normal filters and 2% for the NaOH filters. Once again, form this image we can see that the plateau between 45 and 75 minutes is present in both curves, and this could probably mean that between these hold times, there is no further degradation. Finally, the two sets of samples get to the same final point, where, as the air could get into the melting pot, we started to burn our raw mass and the final result was only ashes. Surely the greater mass loss is due to the bigger presence and quantitative of water into the NaOH filters. It is crucial to remember that 0,5M is a really small concentration, so there is a lot of water in our samples. A first attempt to remove water, however, was to compress the pre-treated filters, to make the excessive NaOH leave the raw matter. Nevertheless, the water is still present into the used samples, so it affects our graphs. As already remarked, the pyrolysis is almost instantaneous, so also the water at these temperatures evaporates immediately.

To better understand, on the other hand, what are the effects of water, we made another test. Before pre-treating the filters, we weighted them. Then we proceeded with the NaOH immersion as described in the protocol and finally we weighted them again. In this way we could see the percentage of water that we introduced. The result was that water makes about 40% of the pre-treated filter's mass. Similarly, to confirm this result, we placed the NaOH immersed filters into an oven at 100°C for one hour, then we weighted it. We left it for another hour and we weighted it again. Since the weights was not the same, we understood that some water had evaporated during the second hour. We did the same thing for a third hour and remarked that the weight change was minimal, so all water had evaporated. Nevertheless, even if the weight change was greater, we would've still stopped the experiment, as after three hours at 100°C the raw filter matter would start to degrade. From this analysis we managed to understand and confirm that the percentage of water is about 40% into the NaOH filters. This result, however, needs to be considered as our estimate, as there was a certain variety in our tests. With this new data, we managed to correct the curve and to take into account the effect of water, to see what the NaOH alone does. To do this we multiplied the obtained weights for the original NaOH filters mass for 0,6 (the filters made on average 60% of the weighted mass of the experiments done before). The obtained graph is the following:

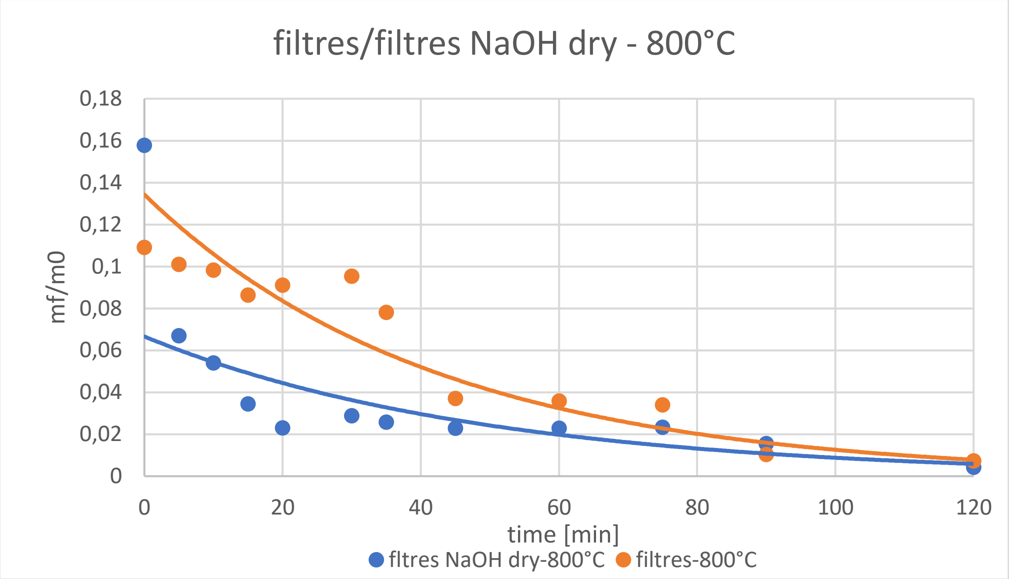


Figure [61], Comparison, at 800°C, between normal filters and NaOH filters, author's elaboration.

Another time the graph shows us that the filters treated with NaOH have a lower curve, meaning that they are more consumed by the heating treatment. Therefore, most probably, this is caused by the NaOH pre-treatment: the sodium hydroxide helps in the creation of oxygenated functional groups on the surface of the fibres of the filter and this effect accordingly enhances the kinetic of the reaction.

After these first experimentations, it was also decided to perform the tests at the other chosen temperatures and to get a constant comparison, there will also be represented the values for the 800°C. Then the other temperature that were experimented, as for the normal filters, were 600 and 700 °C.

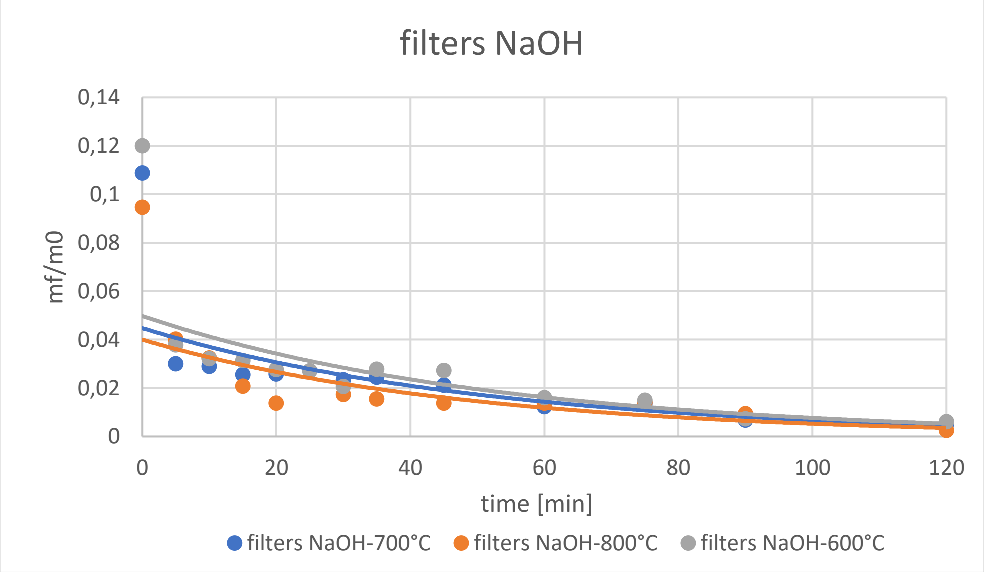


Figure [62], Comparison between NaOH filters at 600, 700 and 800°C, author's elaboration.

As it is possible too clearly see and obvious to imagine, the filters heated at 700°C (blue line) were subjected to a smaller mass loss than the ones at 800°C (red line). This is mainly caused by the temperature increase and it is well visible even if there are some uncertainties. Nevertheless, the results that were obtained for the 700°C series were quite optimised and did not have many oscillations. It was however remarked that there is a plateau between 15 and 45 minutes, then the curve decreases and gets stable as only the ashes remain. In addition, the NaOH filters heated at 600 °C (grey line) showed a plateau in the remaining mass, when considering the hold times between 15 and 45 minutes. Nevertheless, it is crucial to affirm that the mass loss is always already close to 95%, so there can be really small changes and the result is only relatively significant, since most of the mass is already pyrolysed anyway. In any case, the three curves are almost superposed.

Furthermore, we can plot the curves of the untreated filters and the NaOH filters to the difference between the two series of activated filters. Once again, the original filters have a smaller mass loss than the pre-treated ones:

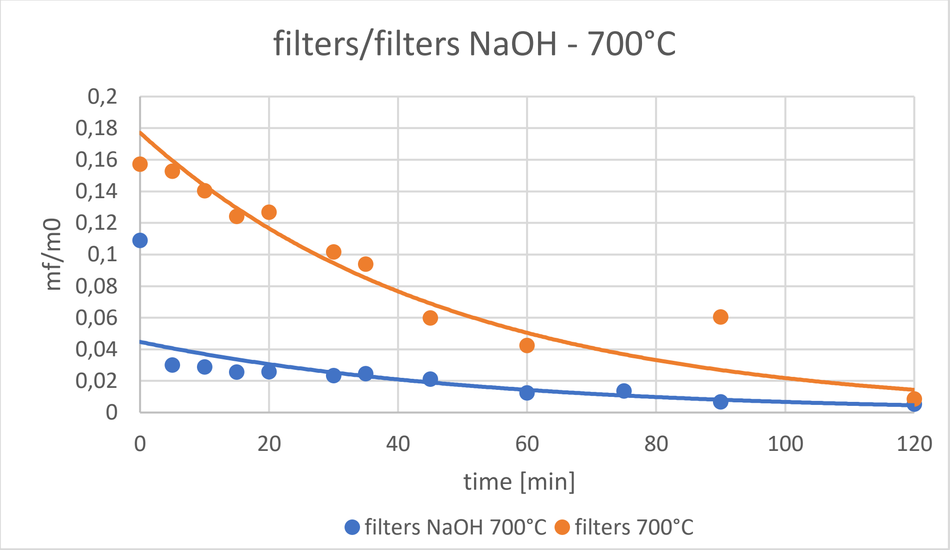


Figure [63], Comparison, at 700°C, between normal filters and NaOH filters, author's elaboration.

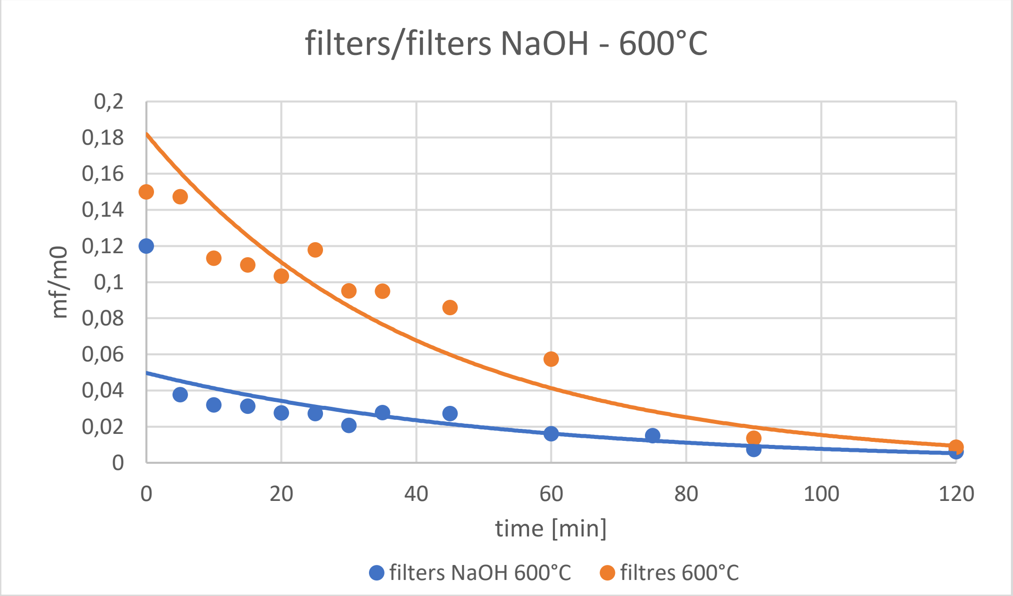


Figure [64], Comparison, at 600°C, between normal filters and NaOH filters, author's elaboration.

Once again, the original filters have a smaller mass loss than the pre-treated ones and it is probably caused by the NaOH, as it creates oxygenated functional groups on the surface of the fibres and therefore enhances the kinetic of the reaction.

Finally, we tested the thermal treatment at 400°C. This temperature is really far from 800°C and the reactions that occur at more than 600°C (but, keep in mind, starting from 550 °C as it will be more velar from the TGA), do not occur at 400°C, so the graph is completely different and it's not worth it to make a comparison between the two of them. In addition, the x-axis is totally different, as for the thermal treatment at 400°C the hold time were usually far more than one hour and the small ones (5,10 and 15 minutes) were not taken into account.

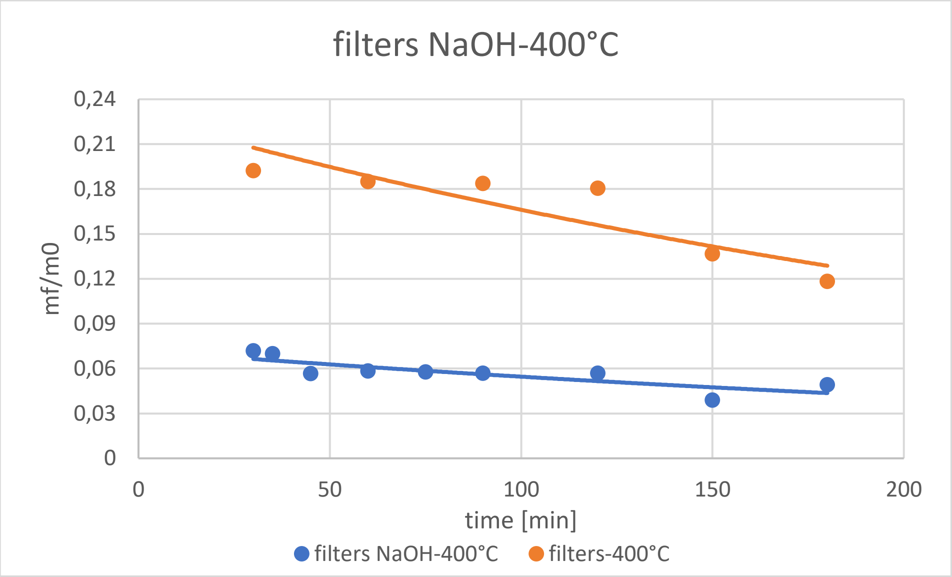


Figure [65], Evolution of the mass residue with the hold time at 400°C for NaOH filters, author's elaboration.

The oscillations are most probably caused by the always present uncertainty problems (simulated pyrolysis, opening of the oven that distorted the true hold time and also the position of the melting pot into the furnace). However, it is clearly visible that for the NaOH filters there is a plateau at 0,07 meaning that at 400°C we can get to about 93% of the total mass to be pyrolyzed. Furthermore, as these temperatures are quite low and not all the reactions that should occur to form active carbons are really taking place, there wasn't the certainty to really have a pyrolysis. Because all of this it was also supposed that the process that was carried on was a torrefaction: a general roasting process, which subjects a substance to a high temperature in order to dehydrate, oxidise and in some cases even partially carbonise it (widely used for the preparation of tobacco, coffee beans and tea). And there is the rub: there was the necessity to understand if the obtained products were active carbons or not and if they had a good specific surface or not. At this point the samples were taken to the BET laboratory in the UTC's Centre de Recherche to be analysed. The samples that were analyse were chosen by a visible presence of carbon and considering our results obtained in Figure [57]: if the sample presented ash it was discarded as already burnt and the same happened if it was possible to see that the pyrolysis process was not concluded yet (evident for all the 5 minutes samples).

To conclude this part, we can say that from the presented graphs we evidenced that there is a very fast consummation of the sample, that in three minutes loses almost all of his mass. In Figure [66], the figure below, we can see the already reported evolution of the remained mass at 800 °C in time, compared to the result given by the thermogravimetric analysis (the red line). We can see that the TGA (from Figure [49]), that reached the temperature of 1000 °C, has a remaining mass of about 14%. However, the graph that we reported at 800°C, already at 5 minutes shows a remaining mass that is lower than 14% and if we go on in time, we only see that there is a decrease in this value. This means that what we obtain in our melting pot and in our graphs, is not only the result of thermal degradation (otherwise we would have a slightly lower result than TGA, which reaches 1000 °C) but also of a chemical reaction. The reaction is an oxidation reaction: at first we can describe it as a real combustion (in fact in some samples we have seen flames in the crucible), but after the pyrolysis phase, once the coal has formed, we have a reaction phase between the coal and the oxygen, which consumes and degrades our product, leading us to have only ashes after a fairly long time.

The Figure [66], therefore is another evidence that in our experiments we did not perform a real pyrolysis even at the beginning and that after some time an oxidation reaction comes along.

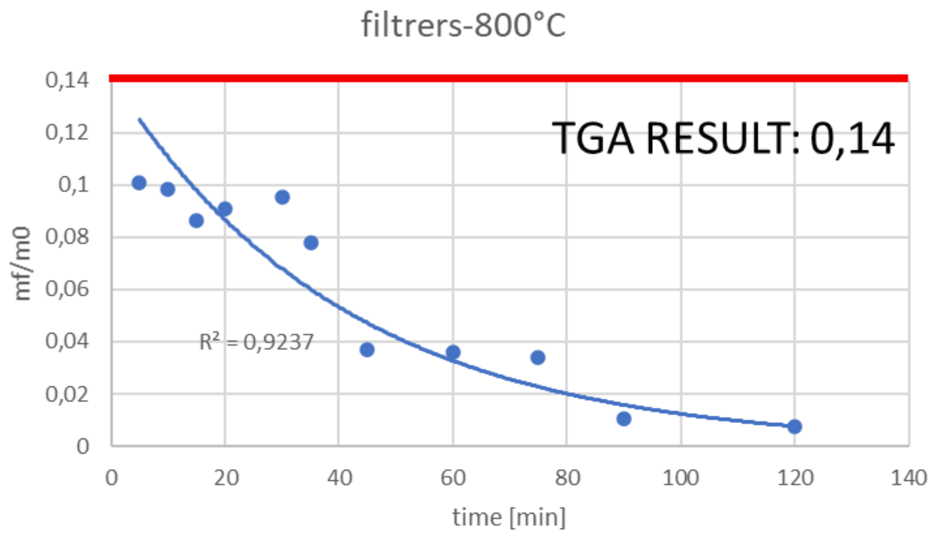


Figure [66], Evolution of the mass residue with the hold time at 800°C compared to TGA result, author's elaboration.

4.2.3 Fourier Transform Infrared Spectroscopy:

The FTIR was conducted as described in the section above. By following a logical thinking, as done also in the other parts of the discussion of the results, the raw material will be presented before the produced carbons.

First of all, it needs to be said that the untreated filters were classified as "simples" if industrial filters coming from industrial cigarettes and as "rolled" if filters coming from rolled cigarettes. This differentiation was done as the rolled filters appeared quite different from the industrial ones, so we wanted to attest is there were any differences between them in the infrared spectroscopy.

After analysing the data, the following graph (Figure [67]) was produced:

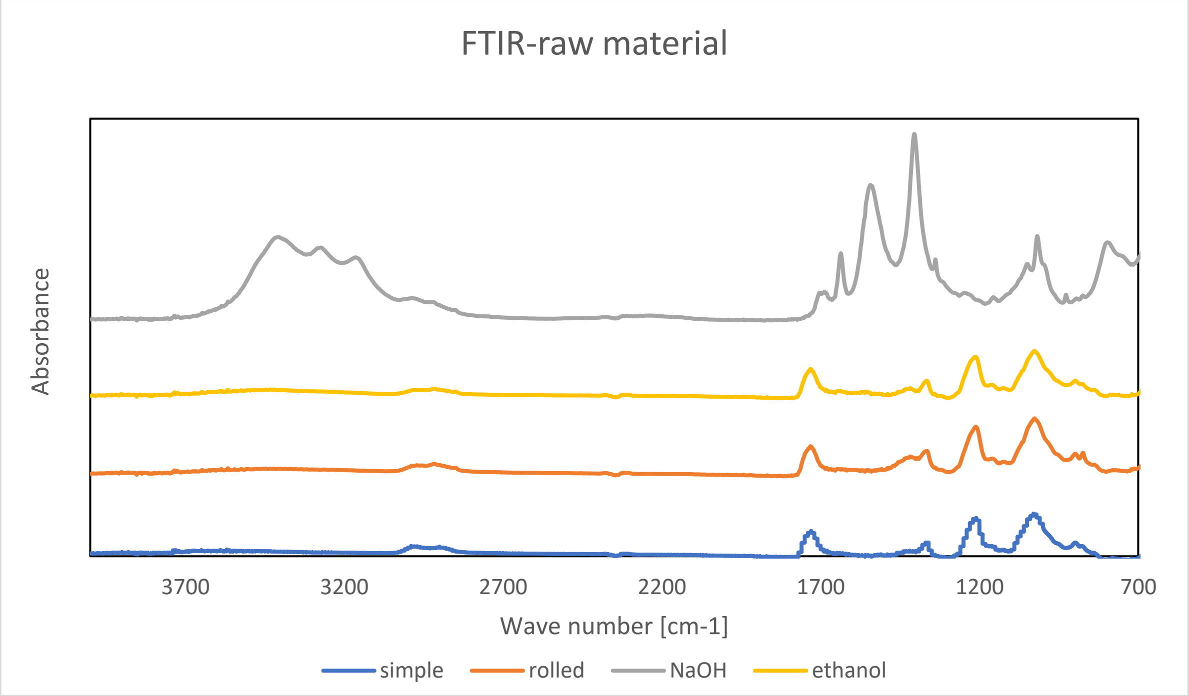


Figure [67], FTIR profiles for raw materials, author's elaboration.

From this graphic it is possible to see that the simple, rolled and ethanol filters had more or less the same behaviour. These presented:

- The 1072 cm^{-1} peak corresponded to O–C=O–CH_3 and it is typical of cellulose acetate bonds
- C=O peak at 1710 cm^{-1} (of ketones, aldehydes, lactones or carboxyl groups)
- The bands in the region from 1650 to 1500 cm−1 were characteristic of C=C aromatic bonds
- Bands around 1000 cm^{-1} are usually associated to C–O
- Bands around 1200 cm^{-1} can be associated to C–O and to C–H
- A band at 1300 cm $^{-1}$ that represents C=O in phenol, ether or ester
- weak absorption peak at 873 cm^{-1}, which is attributed to the bending vibration of the C–H bond in the high degree of substitution of the aromatic ring

On the other hand, the NaOH pre-treated filters (represented by the grey curve in Figure [67]) presented a completely different profile, which included:

- C–OH stretch band at circa 3430 and at circa 3700 cm^{-1}
- C–O vibration at 1380 cm^{-1}
- C=O peak at 1710 cm^{-1}
- Peaks from 1650 to 1500 cm^{-1}, which are characteristic of C=C aromatic bonds
- A peak at 1072 cm−1 corresponded to O–C=O–CH_3 typical cellulose acetate bonds
- A band at 1300 cm $^{-1}$ that represents C=O in phenol, ether or ester

From these findings we can state that the NaOH filters contain alcohols, esters, ketones, aromatics and carboxylic acids. The most interesting finding is that there are the C=C aromatic bonds, as most probably this comes from the smoking activity, as reported in the bibliographical part. Moreover, the bands of NaOH were much more detailed and intense than for the others.

Then, we analysed the produced carbons. To do the comparisons between the untreated and the treated carbons, we chose to analyse the filters pyrolysed at 800°C for 30 minutes (F800C30min), that were called simples. This was a difficult sample to analyse at it was a really fine and granulose powder: when pressed with the tools of the machine, as of its fragile nature, it broke into pieces. This is the reason why many tests were made, but even of this, the results are not the best possible. From the figure below (Figure [68]), it is clear to see that there is a pattern, but there were also tests that failed (as test 1 in the image). The spectrum that was chosen to be the comparison for the other samples was test number 5.

It is important to remark that all these samples, as the tests for the raw materials, report a peak around 2340 cm^{-1}: this represents the carbon dioxide. When we proceed with the analysis, we do a subtraction of the blank, that is the air in the room and the CO_2 is then seen as a peak. Unfortunately, it is not always possible to completely well subtract the blank, so this peak is present.

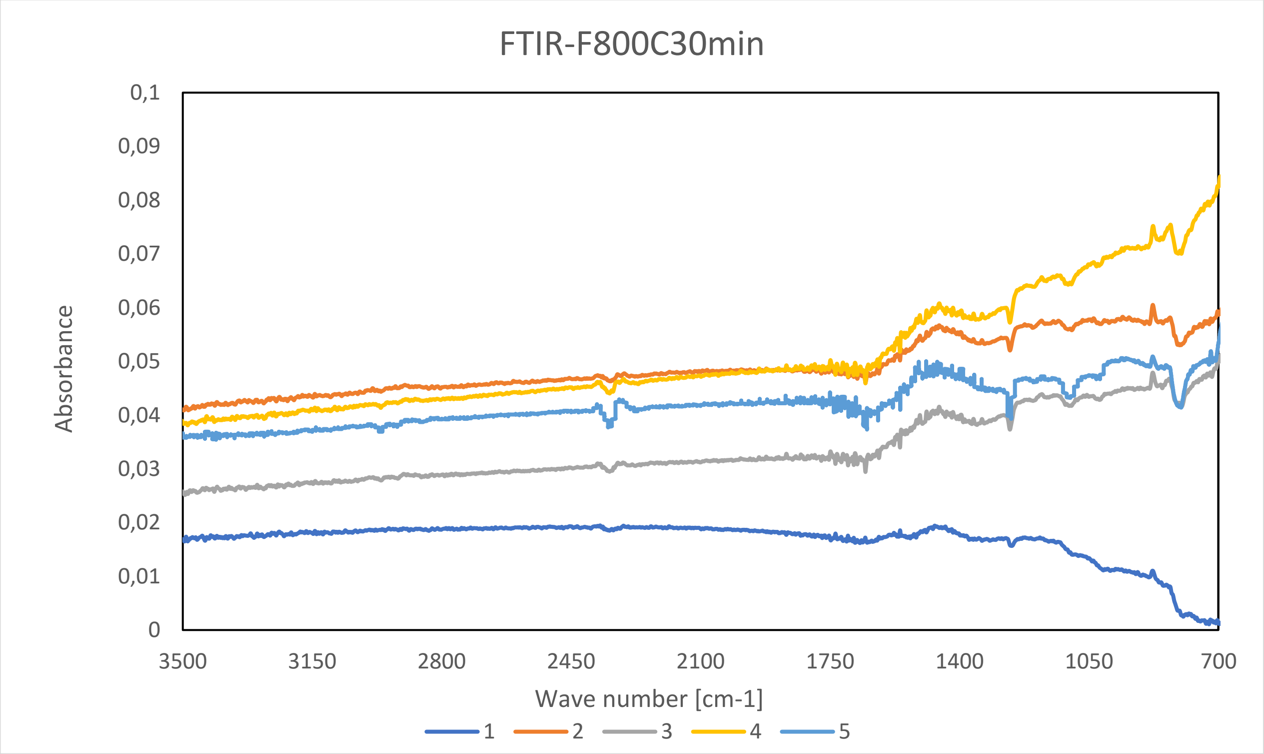


Figure [68], FTIR profiles for F800C30min, author's elaboration.

This spectrum is much more difficult to analyse, as it is not as clear as the others. The chosen test to be compared with the others was test 5. This test presents:

- A weak peak at 1710 cm^{-1} , that represents C=O
- The broad band between 1000 and 1300 cm^{-1} that is usually found with oxidized carbons and has been assigned to C–O stretching in acids, alcohols, phenols, ethers and/or esters groups
- The bands between 800 and 900 cm^{-1} are due to C–H

Anyways, as of the really bad shape of the spectrum it is not really correct to analyse it; this is why it will be used only as a comparison to other samples.

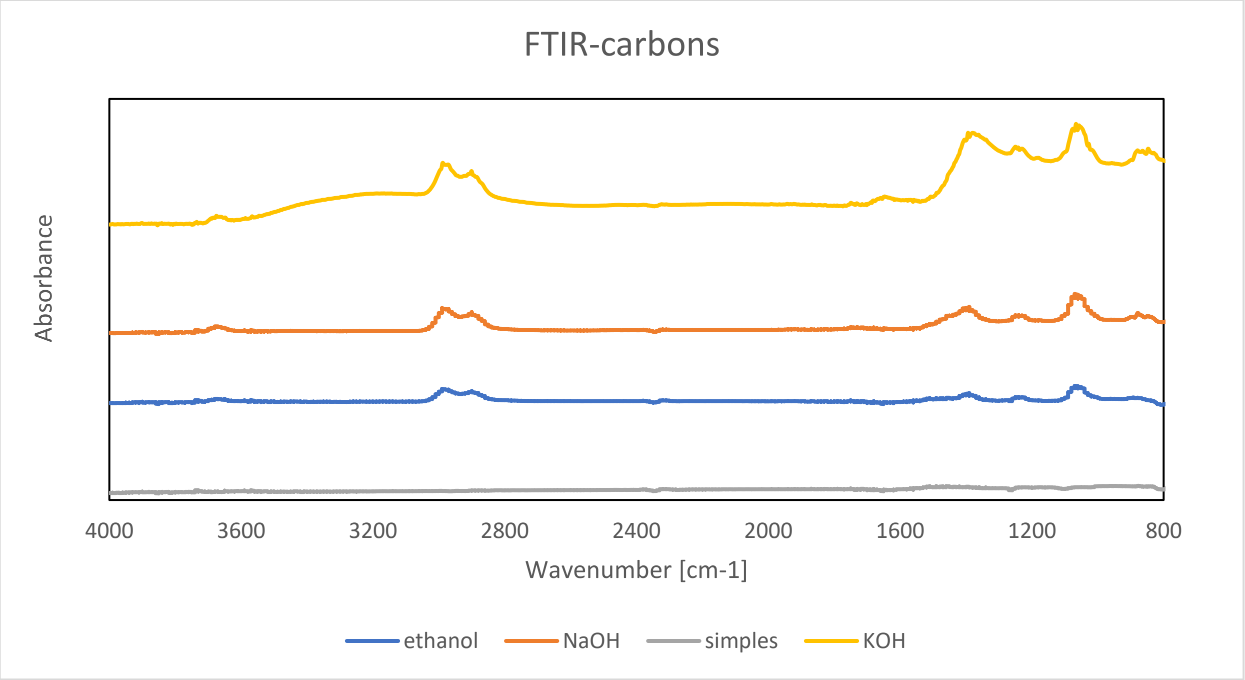


Figure [69], FTIR profiles for manufactured carbons, author's elaboration.

The spectrums for these products are more or less the same, but the peaks for the KOH sample are much more intense (and even more evident when we put the mon the same level). Therefore, the filters pre-treated with KOH, NaOH, ethanol have a spectrum that can be described with the followings:

- At approximately 3000 cm^{-1}, the bands observed were associated with stretches of C–H bonds in CH_2 groups
- C–H peaks at ca. 2850 and 1450 cm^{1}
- C=O peak at 1710 cm^{1}
- The bands in the region from 1650 to 1500 cm−1 were characteristic of C=C aromatic bonds (but only for KOH)
- KOH also presents wide band between 3000 and 3500 cm^{-1} that can be also associated to O–H, it was be reconducted to some KOH that stayed there and recrystallised
- 3584–3700 cm^{-1} that represents O–H in alcohol
- The band 1300 cm^{-1} that represents C=O in phenol, ether or ester
- Absorption peak at 873 cm−1, which is attributed to the bending vibration of the C–H bond in the high degree of substitution of the aromatic ring (not for ethanol)

4.2.4 Scanning Electron Microscopy and EDX analysis:

The SEM analysis was performed with the methodology described before. The images will be reported in the chronological order of analysis, which was also the logical way: the raw materials first and the produced carbons after. In the following figure (Figure [70]), there are the SEM images of normal filters (a) and NaOH pre-treated filters (b). It is clear to see that the cellulose acetate fibres, as expected, have a "Y" form and the images corresponded to the images of our references. On the other hand, the NaOH fibres, even if presented more or less the same shape, had some white grains on it.

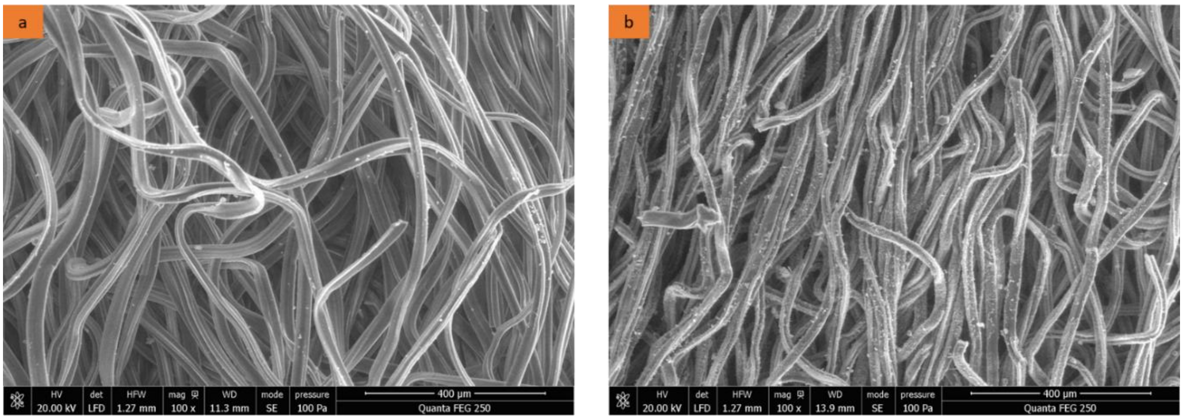


Figure [70], SEM of normal filters (a) and NaOH pre-treated filters (b), author's elaboration.

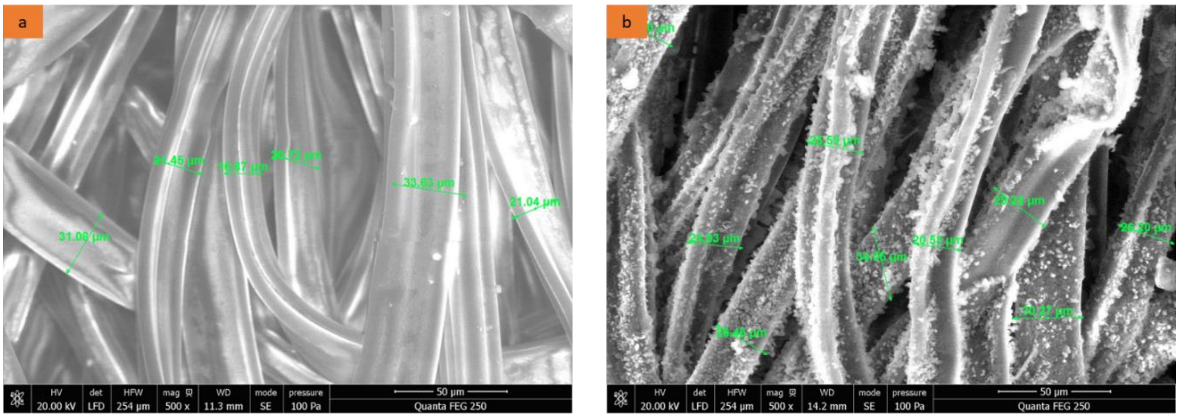


Figure [71], SEM of normal filters (a) and NaOH pre-treated filters (b), author's elaboration.

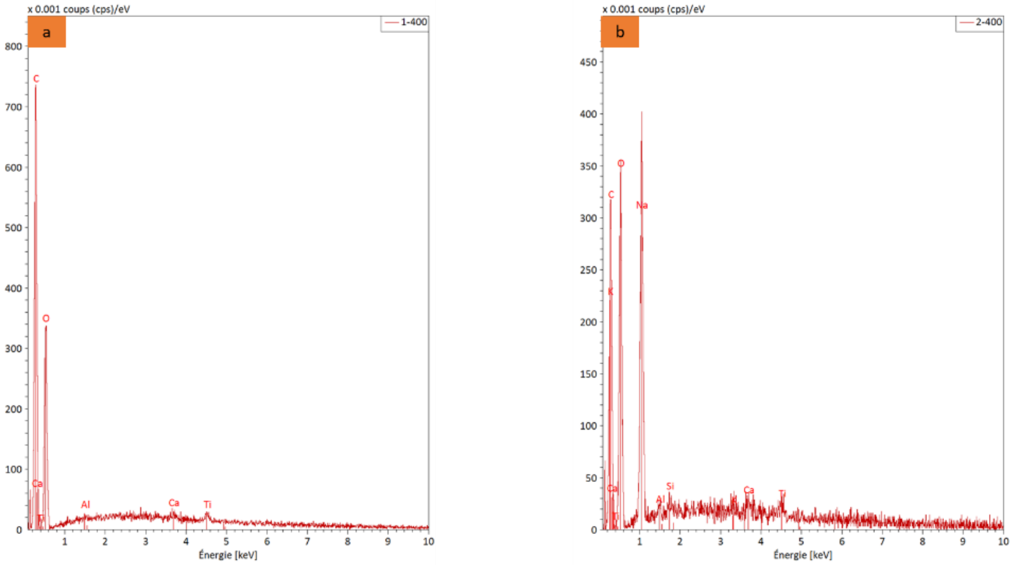


Figure [72], EDX of normal filters (a) and NaOH pre-treated filters (b), author's elaboration.

When comparing the pair of images at 50 µm (Figure [71]), it was possible to see that the NaOH fibres were a little bit swollen, having an average width that was a bit lower than the average width of the NaOH filters. This result, although not as obvious, is in agreement with the findings of the study by Koochaki et al. (2019) [5]. However, as already said the present study and the reference cannot be really compared, as the concentrations that were used are really different. From Figure [71] is it possible to better see the presence of white grains, therefore a zoom was made and it is reported in Figure [73] (a) and (b). From this image it is clear that there are some crystals on the surface. Having done an EDX spectrum (in Figure [72]) it was clear that these are Sodium crystals. As a result, we understood that during the immersion in NaOH and the following drying of the filters, the sodium crystals get on the surface of the fibres and stay attached there. This will surely influence the production of carbons, as it will be clearer in a moment.

From the EDX, apart from the finding that the shown crystals are Na crystals. It was also clear that in the filters we can find other compounds as aluminium, calcium, titanium and silicon, alongside the most present elements: carbon and oxygen, which indeed are the constituents of cellulose acetate, the main material that makes cigarette filters.

Furthermore, it was chosen to analyse the filters from rolled cigarette butts, which appeared quite different from the industrial ones.

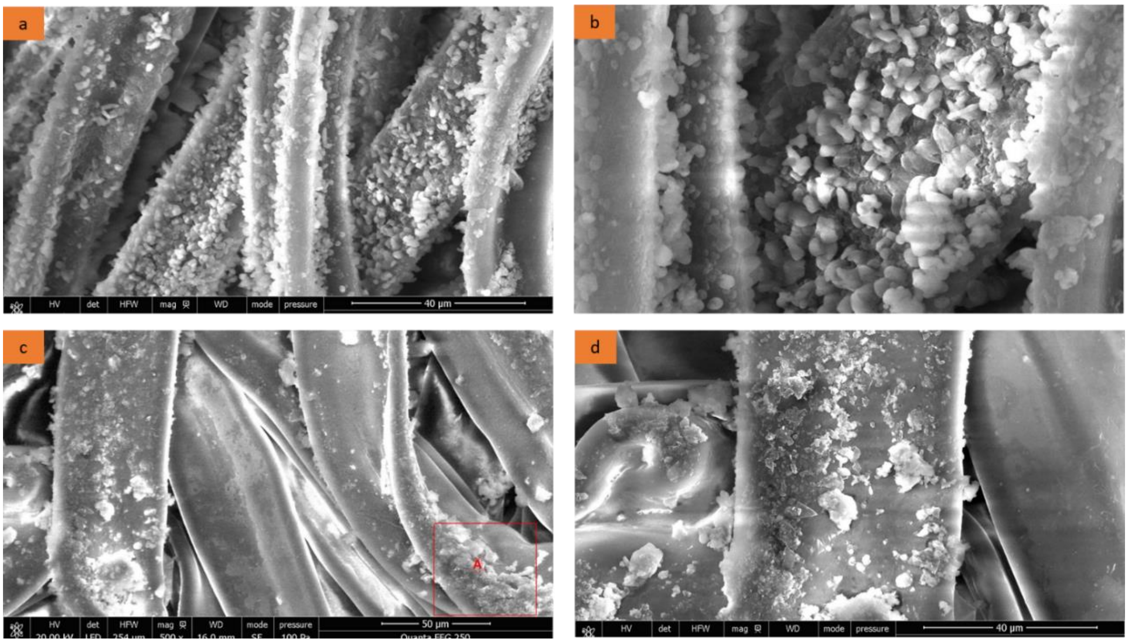


Figure [73], SEM of NaOH pre-treated filters (a, b) and rolled filters (c, d), author's elaboration.

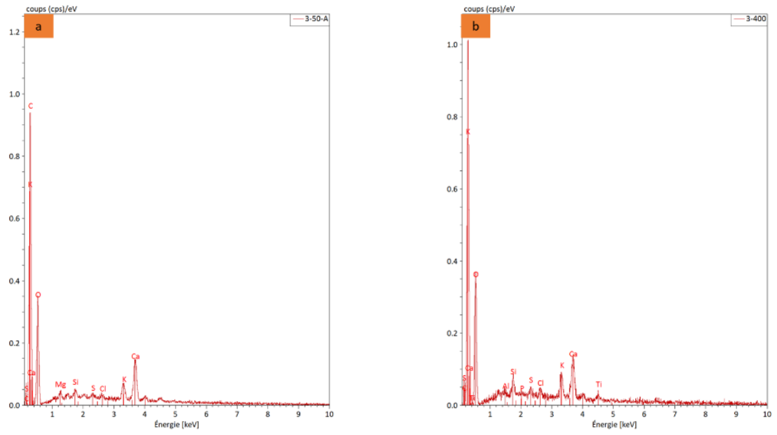


Figure [74], EDX of rolled CB's filters at 50µm (a) and 400µm (b), author's elaboration.

As it appears clear from the SEM image in Figure [73] (c) and (d), also the filters from rolled cigarette butts present some crystals, differently from the industrial ones. Therefore, an EDX was done (Figure [74]) and it showed that these crystals are mostly made of calcium, potassium and magnesium, and that these filters also showed the presence of sulphur, titanium, chlorine and phosphorus. By zooming at 50µm we saw that essentially in a certain area the granules were crystals of calcium.

Finally, we analysed the carbons. In the following images there are the SEM of F800C5min and F800C20min (both Figure [75]) and SEM of NaOH800C10min (Figure [76]) at different magnifications.

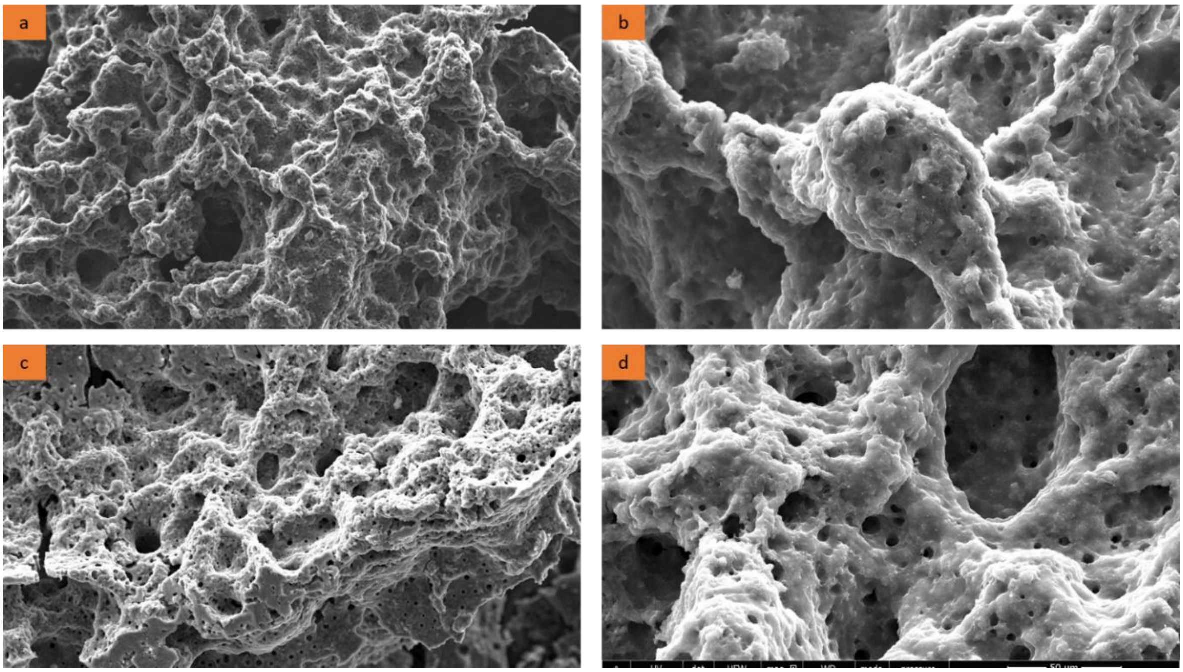


Figure [75], SEM of F800C5min (a, b) and F800C20min (c, d), author's elaboration.

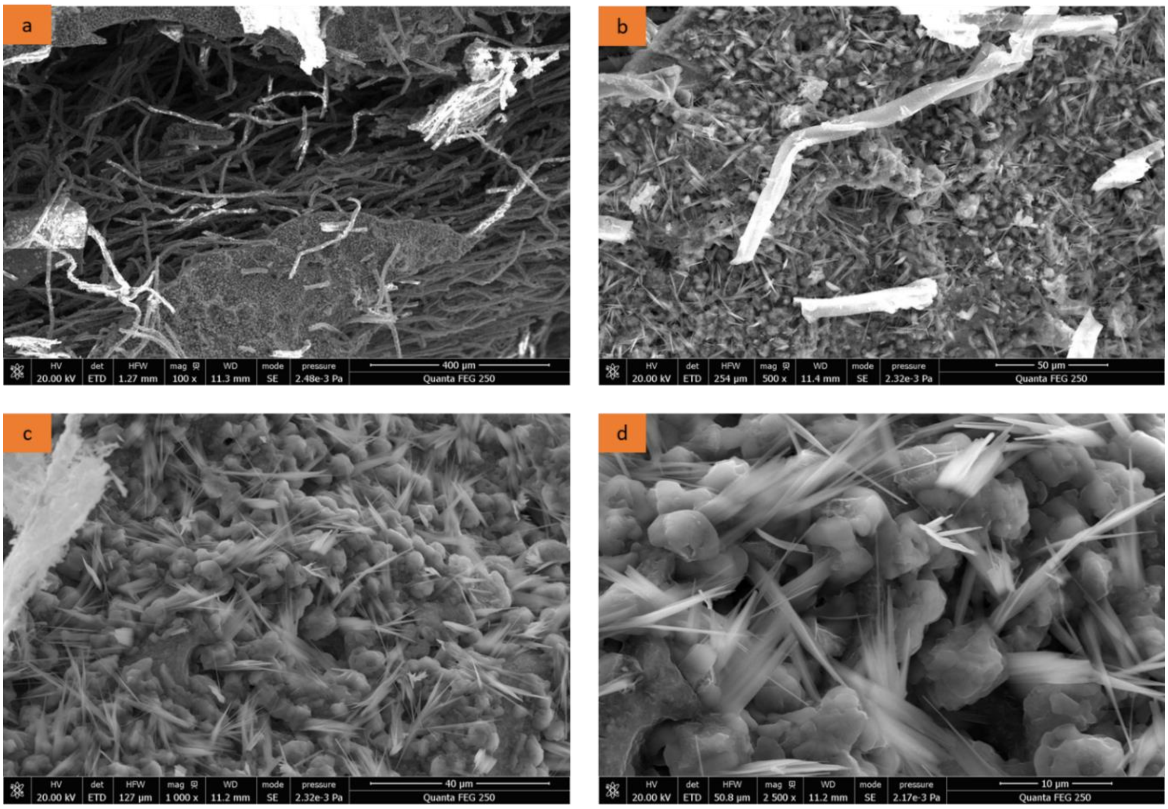


Figure [76], SEM of NaOH800C10min at different magnifications, author's elaboration.

From these figures we can see two really different things. If F800C20min and F800C5min showed a really good morphology with many pores (in particular, from Figure [75] (b) and (d) it is clear that at 20min there are more pores that at 5min), the NaOH carbons did not have a nice result at all. It appears that the fibres did not carbonise and many of them are still intact (therefore this explains why the NaOH samples kept their original shape after having been thermally treated). The comparison between the two sets of samples is quite easy and also in the case of the difference between F800C20min and F800C5min, it is evident that the 20 min presented a bigger number of pores and smaller pores too.

In Figure [76] we can see that there are some intact fibres and others that were partially transformed. Overall, there are sodium crystals and some of them appear to be molten one into another. As these elements were on the surface of the filters, probably they received the heat at first and impeached the fibres to get a complete thermal treatment, also impeaching the formation of pore, therefore of activated carbon. From Figure [76] (d) these phenomena are clear: there are some crystals that appear as the ensemble of multiple smaller crystals and there are spikes of fibres that were partially destroyed but not transformed into carbon. The Na granules made the sample keep its shape and not get carbonised. As a result of all these, as it will be better explained later, there are no pores, so the specific surface area of these samples was most likely to be really low or zero.

Then, the untreated filters heated at 400°C for 2 hours and 30 minutes were analysed. From the following image (Figure [77]), it is able to se the result. The carbon appears to be porous and presenting many macropores, therefore it was considered to be a good sample to analyse on the BET, which results will be described later. On the sample it is possible to see that there are some white granules, that are again calcium crystals. The resulting morphological texture is much smoother and plain than the samples treated at 800 °C.

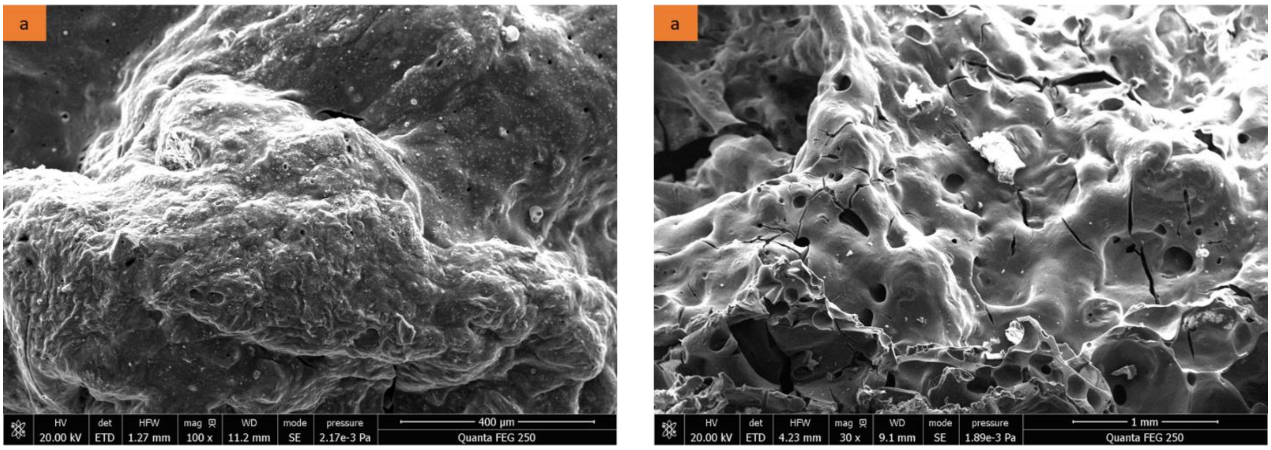


Figure [77], SEM of F400C2h30 at different magnifications, author's elaboration.

Finally, the microwaved carbons and the KOH post-treated carbon were analysed.

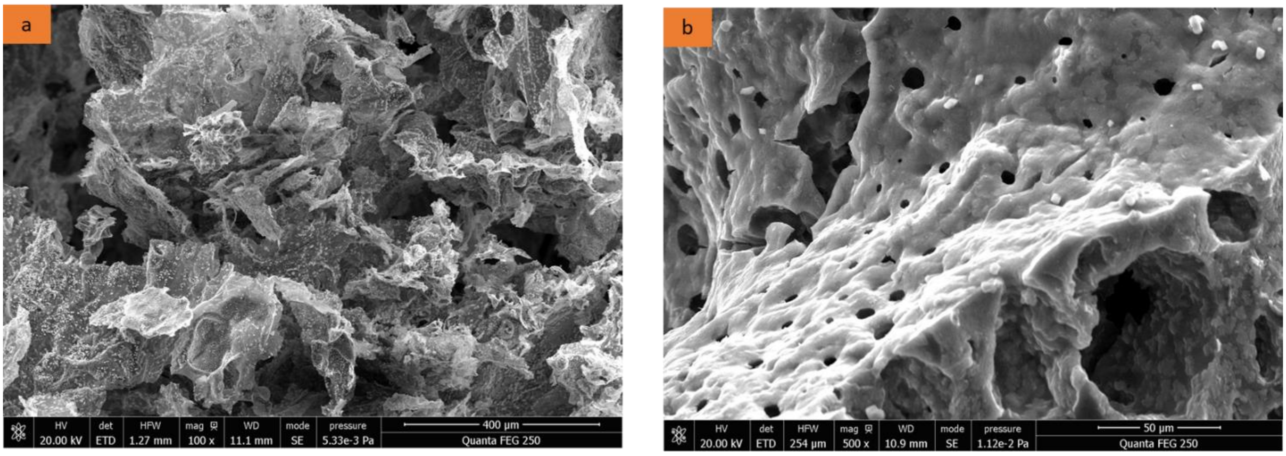


Figure [78], SEM of microwaveKOH800C5min (a) and F800C5min + KOH, author's elaboration.

As of the above image, Figure [78], the microwaveKOH800C5min, represented in (a), did not achieve any good results. There are many potassium crystals as one would expect, but there are absolutely no pores. There are the granules of potassium that probably formed during the immersion phase and that were helped to fix with the microwaving treatment. Probably, during the microwave phase the fibres were damaged, as they do not have the same morphology as the NaOH sample that was presented above (Figure [76]). In Figure [79] it appears even more clear that the crystals are present on the material, but these, even if it is chemically carbons (as seen from the EDX, which was not reported here), it does not have the form of a carbon.

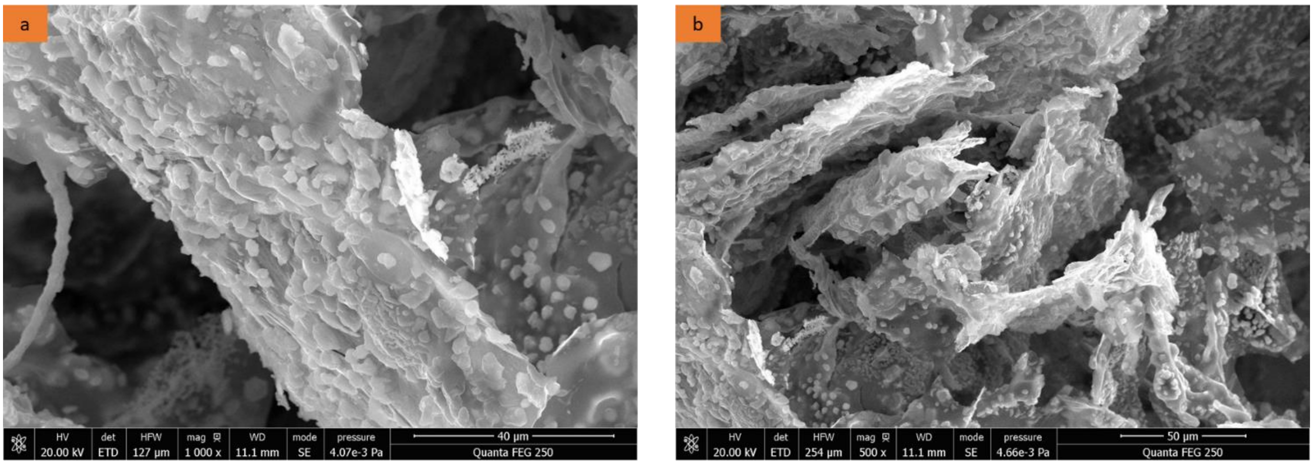


Figure [79], SEM of microwaveKOH800C5min at 2 different magnifications, author's elaboration.

Therefore, to conclude, from the SEM analysis we obtain a great result: we can say that a pre-treatment of the filters by immersion in a liquid solution of NaOH does not work as an activating treatment. Our hypothesis is that, when the pyrolysis starts there are reactions between the fibres, that thanks to their surface's proprieties make them react. Instead, when we have the NaOH treatment, something else happens. We already sae that there are the granules of sodium deposed on the surface and our hypothesis, to be confirmed, is that the sodium, which melts at 97 °C and evaporates at 882 °C, melts on the fibres at a temperature that has not yet allowed the fibres to degrade. This creates a coating of sodium, which remains liquid, on the fibres and thus prevents the fibres from reacting with each other, maintaining a fibrous structure and hindering the formation of pores. This is why, after pyrolysis (as reported in Figure [80]), there are still the granules of sodium.

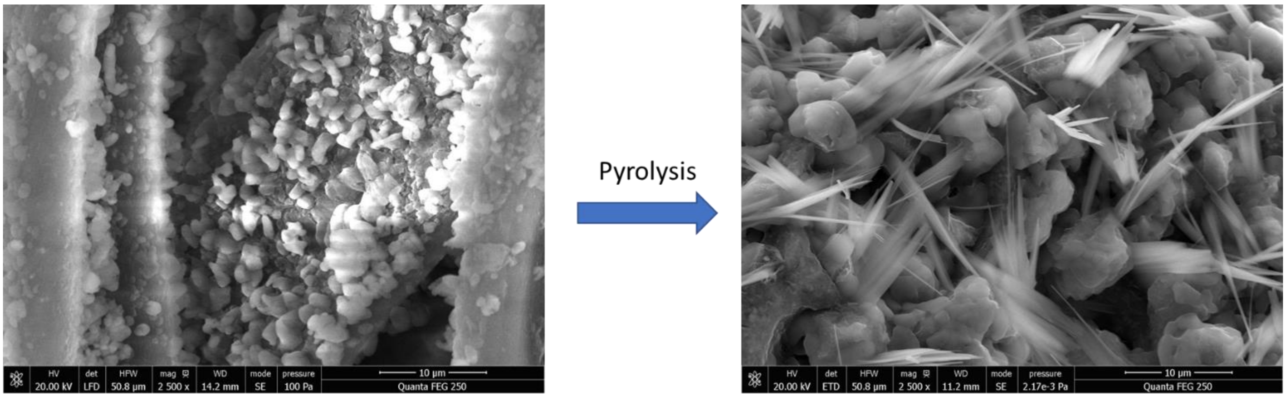


Figure [80], SEM of NaOH filters before and after pyrolysis, author's elaboration.

4.2.5 Methylene blue and Rhodamine B adsorption

The methylene blue and rhodamine B adsorption, as already said, have been performed only as a proof of concept. Even if with a spectrophotometer it could have been possible to state the variation of the concentration and possibly evaluate the specific surface area.

The first test was the Rhodamine B one and it was done almost in a random way: the colorant was in the laboratory and the produced active carbon (F800C30min) was put into the beaker. The solution was about 80 mL in volume and the carbon had a mass of about 0,3 g. Unfortunately, no data was measured, but this was also the point of doing a proof of concept: it was only expected to see if the test worked or not. The before and after images are reported in the following figure, Figure [81].

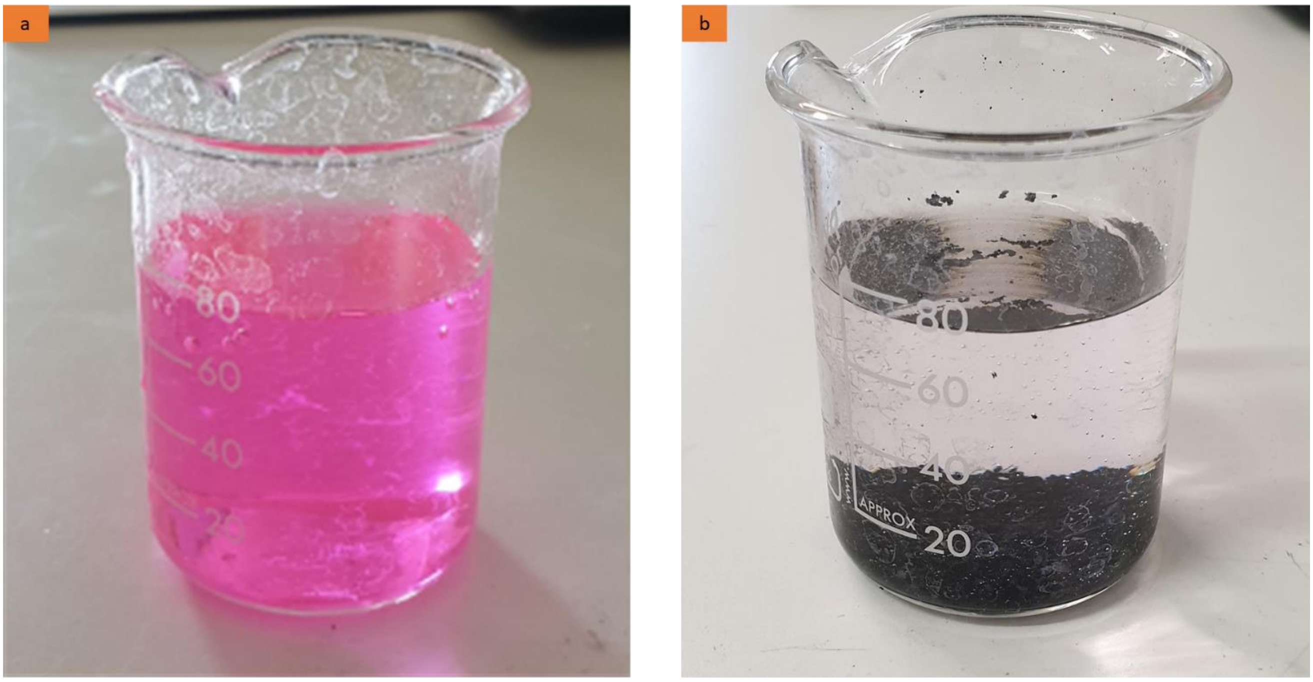


Figure [81], Rhodamine B adsorption test, author's elaboration.

It was clear that the carbon completely cleaned the solution from the colorizing material. The picture of the pink solution was done at the end of one afternoon and the picture of the decoloured solution was taken the following morning. It was therefore possible to say that in about 12 hours the solution was fully decoloured. This meant that the carbon F800C30min had a decolouring potential of the pink dye, meaning that it had an adsorption capacity and as a result it could perform well in the BET adsorption test.

Moreover, a methylene blue adsorption test was performed, by using the F800C5min carbon. This time it was better organised, as described in the methodology. This time the times were taken, to have a more complete analysis, even if in the end it was always only a proof of concept. From the image reported below (Figure [82]), it is clear that already at a time of 15 minutes after the start, there is a small decrease in the concentration of methylene blue. This decrease is also present after 30 minutes and one hour, although it should be noted that in reality the colour change is not substantial. Instead, a large difference in the shade of blue was found after a time of two hours. Proceeding in time, it is clear that the sample was completely discoloured after 4 hours, which is obviously even more evident after 24 hours.

We must also point out to the reader that it is evident from the photo that not all volumes in the containers are equal. This is due to the fact that in the process of extracting the carbons from the solution (obviously to keep the solution at the desired colour it was necessary to remove the activated carbons to avoid further discolouration), small parts of the liquid either fell into the laboratory sink or remained in the filter to remove the carbons.

It must be understood that the initial volumes were all the same, otherwise the meaning of the test is somewhat lost, despite the fact that it is only a proof of concept and does not require real rigidity in compliance with pre-established protocols. The following image (Figure [82]) shows all the samples:

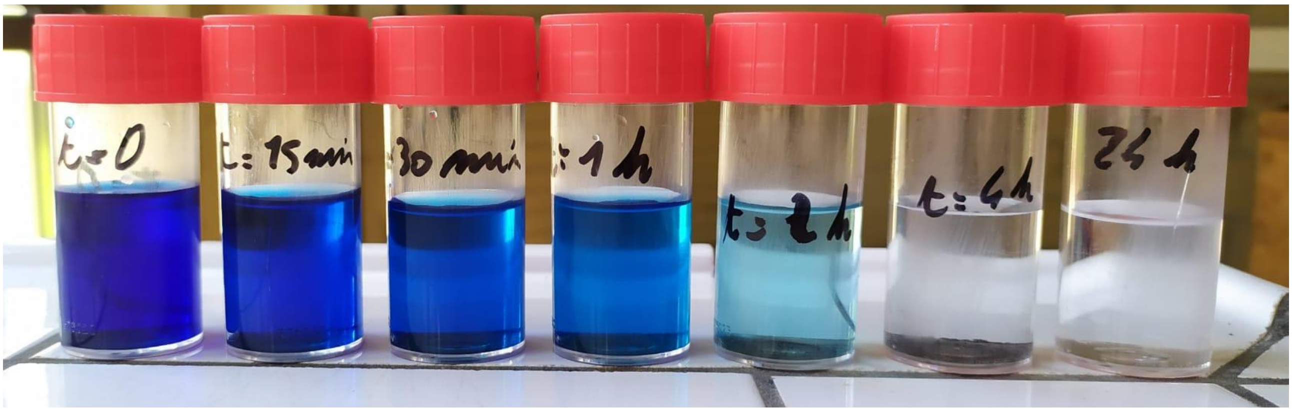


Figure [82], Methylene blue adsorption test, author's elaboration.

Therefore, from these two tests we can understand that both the F800C30min and the F800C5min have a certain specific surface area, therefore both had an adsorption capacity and as a result could perform well in the BET adsorption test. Hence, the BET tests were performed.

4.2.6 BET analysis and N_2 adsorption-desorption

BET stands for Brunauer–Emmett–Teller and as already said it is thus very used to measure the specific surface area of adsorbing materials. It was therefore done for understanding the specific surface area of some of our produced carbons.

The isotherm we obtain from the BET analysis for sample F800C20min is as follows. The red curve is the adsorption curve and the blue curve is the desorption curve. It is possible to see that the result is quite satisfying and that the sample presents micropores (seen in the left side of the graph) and mesopores (given, in simple words, by the distance between the adsorption and desorption curves in the right side of the graph).

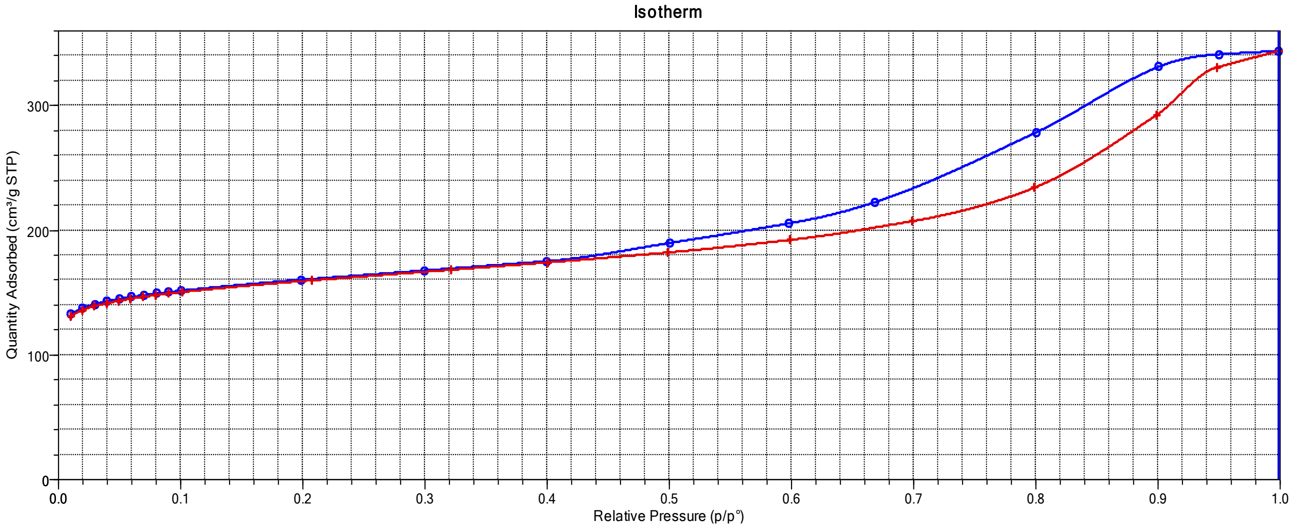


Figure [83], F800C20min isotherm adsorption-desorption curve, author's elaboration.

To make a first comparison of the samples, without looking to the BET area, we can look at the isotherm N_2 adsorption curves.

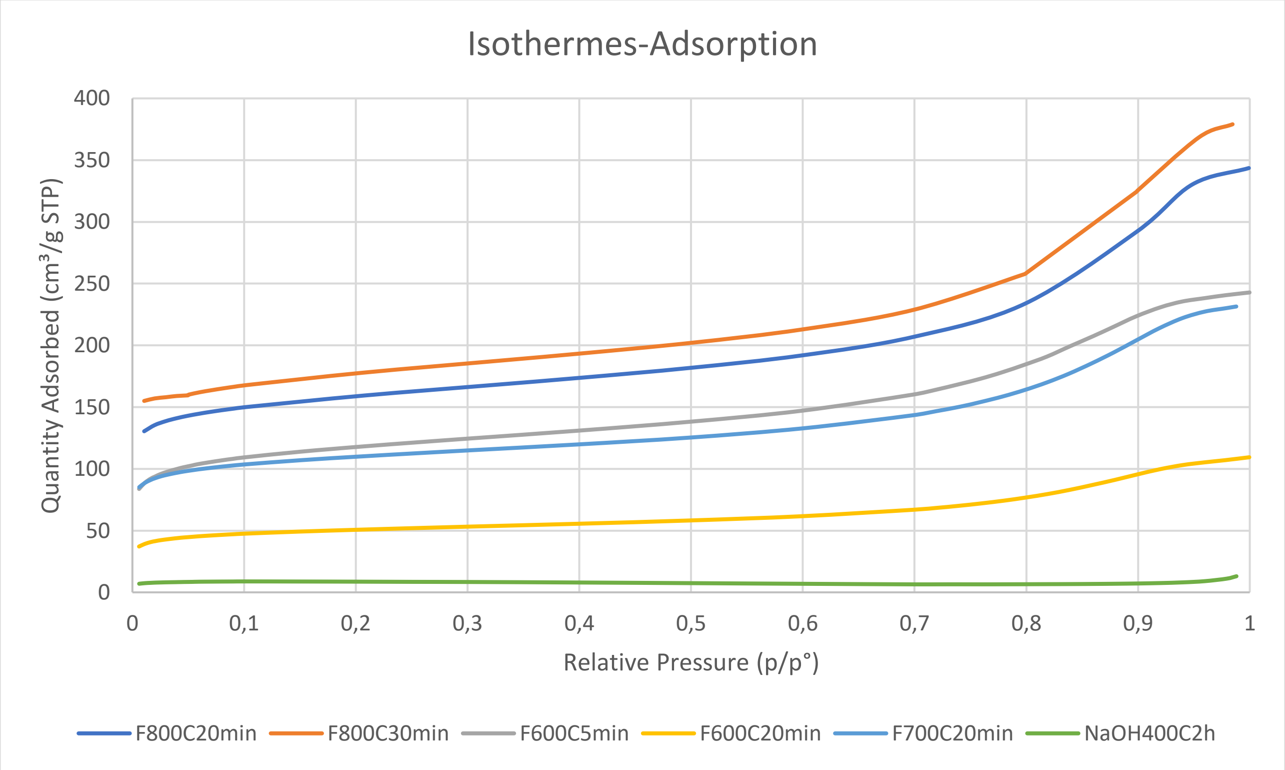


Figure [84], N_2 adsorption isotherm curves, author's elaboration.

From these curves we can see that we had the most various results. The F800C30min and F800C20min had the best curves (being higher on the y-axis, the curve adsorbes a greater volume of nitrogen). Moreover, it can be remarked that the filters at 800 °C performed better that the ones at 700 °C, which performed better than the ones at 600 °C, implying that the higher the heating temperature, the better the nitrogen adsorption (and thus the greater the specific surface area). Then we can see that the samples treated at 600 °C gave results that were a bit different between them and not in line with the ones found for the other temperatures.

Another result is that, as expected from the SEM analysis (reported in Figure [76]), the NaOH pre-treated samples performed much worse than the untreated samples. As the curve is very low on the y-axis, we decided to plot the curves of other NaOH samples, to better see the trending. The curves not only are almost flat, but have a really low maximum volume of adsorbed gas. This confirms the suspects that we had on the SEM analysis: as the carbonisation did not go as according to plan and there are no pores, the adsorbing power is almost none.

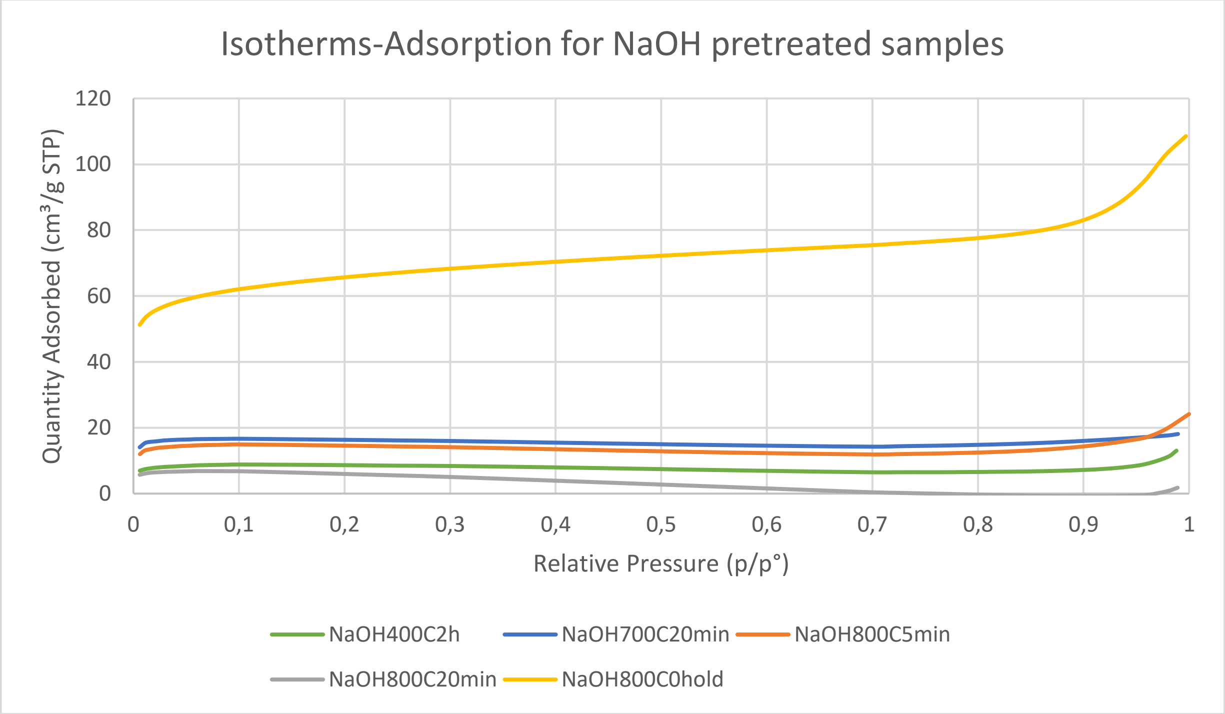


Figure [85], N_2 adsorption isotherm curves for NaOH samples, author's elaboration.

Then, it comes to the comparison of the BET results. The following figure represents the BET Surface Area Plot that the Micromeritics 3Flex gave us for the F800C20min, but it will not be further explained. It is reported only for comprehensiveness of the study

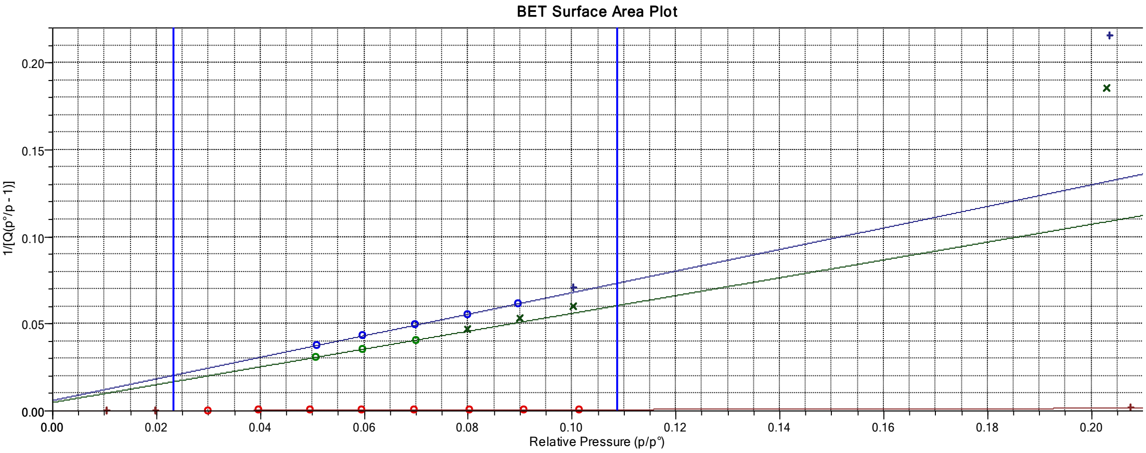


Figure [86], BET Surface Area Plot for the F800C20min, author's elaboration.

Moreover, the comparisons of the BET specific surface area will be reported. At first, an overall graph will be shown, but then the graph will be divided in sections, to better analyse the results.

The overall column graph that shows all the obtained results in the following:

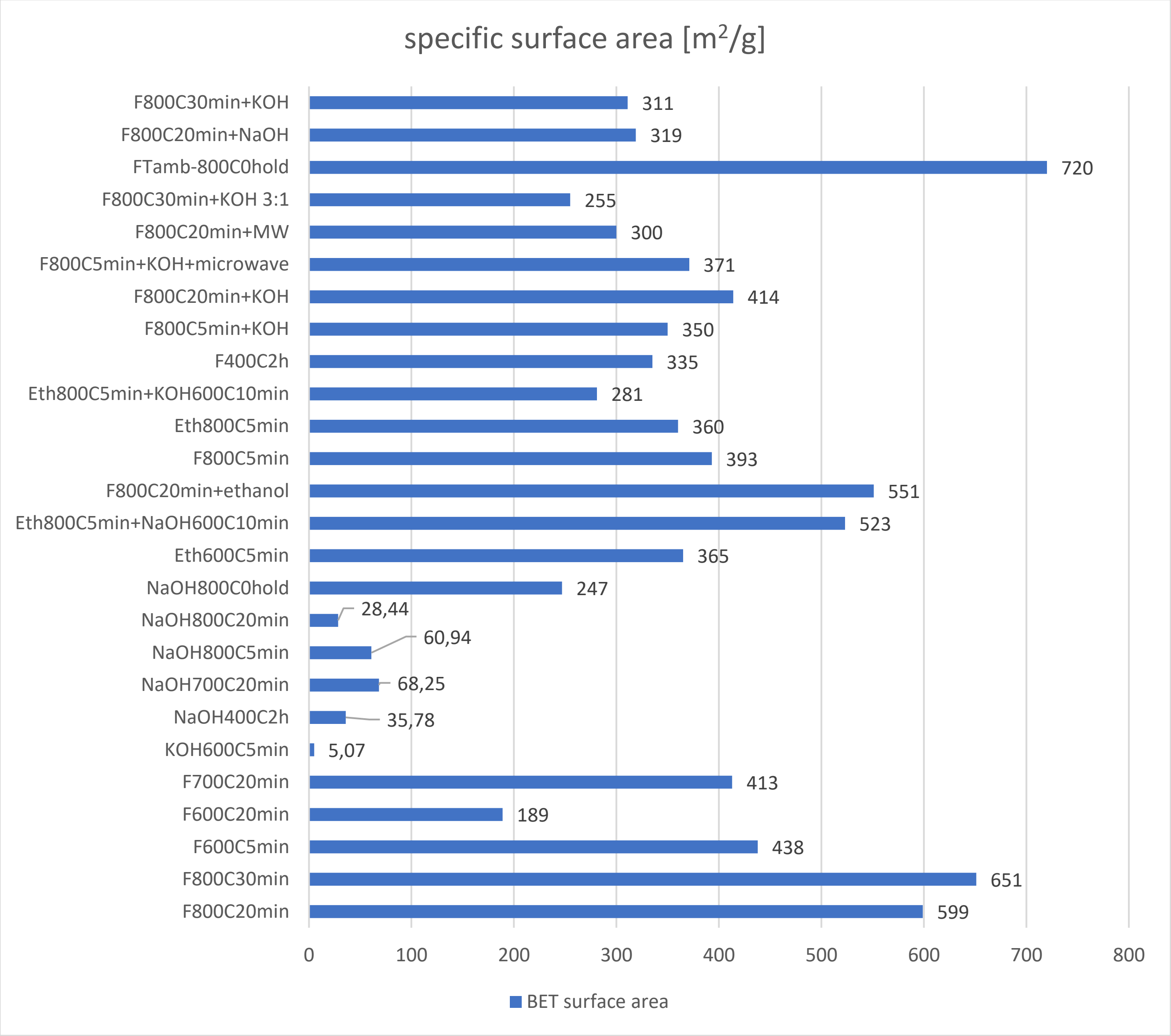


Figure [87], Surface Area of all the analysed samples, author's elaboration.

It is already possible to see the enormous difference that there is between the untreated filters or the post-treated of ethanol-washed filters and the ones pre-treated with NaOH or KOH. For the KOH6005min, the area was so small that the machines had problems in evaluating the surface area and gave a final value of 5 m^2/g.

However, the great result is that there are some carbons that performed well, confirming that it is possible to transform the cigarette butts in active carbons with a good specific surface area. The best carbon, which gave a result of 720 m^2/g, was the FTamb-800C0hold, that was treated with a ramp from ambient temperature to 800 °C. It is to be remarked that this sample was done by not following any reference, but only to see what could possibly happen and gave us the best result of the study. Then, some other good results, were given by the F800C30min and F800C20min, as anticipated from the adsorption isotherms: from this graph we see that they have a specific surface are of about 650 and 600 m^2/g, respectively.

To better understand how the different carbons performed and how the time and temperature differences influenced the final result, we need to look at more detailed and less concentrated graphs.

But before, it seems logic to show that much of the area given by the BET came from micropores. This is shown in all the samples. To show this, we plotted the micropore area in function of the total specific surface area (by excluding all the NaOH and KPH samples, which had some useless and unusable results).

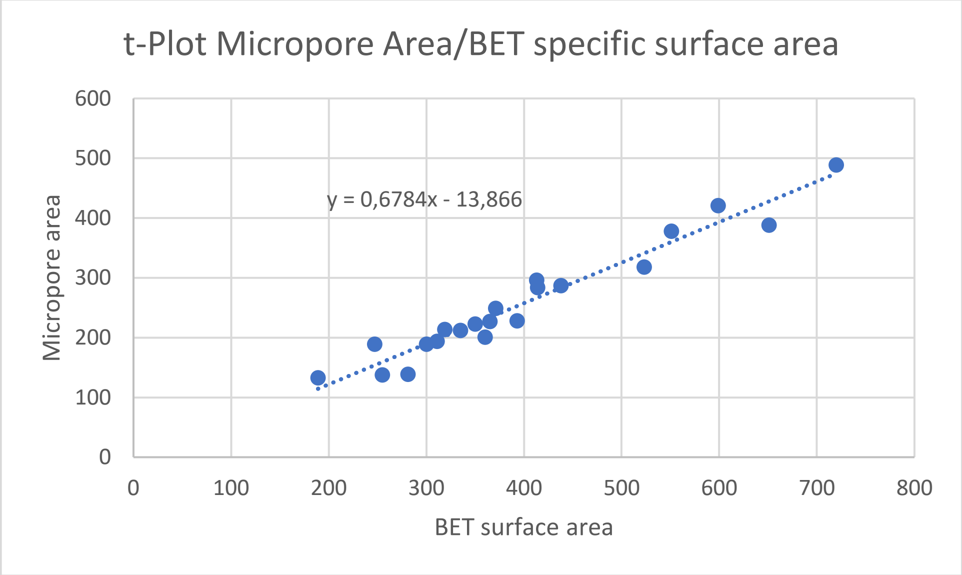


Figure [88], Micropore Area/BET specific surface area, author's elaboration.

The graph shows that the trending is linear and the trend line equation shows that about two thirds of the area is given by micropores. To confirm it again and to show it in another way, we plotted the same figure of Figure [88], but reduced the number of samples and by adding also their micropore area:

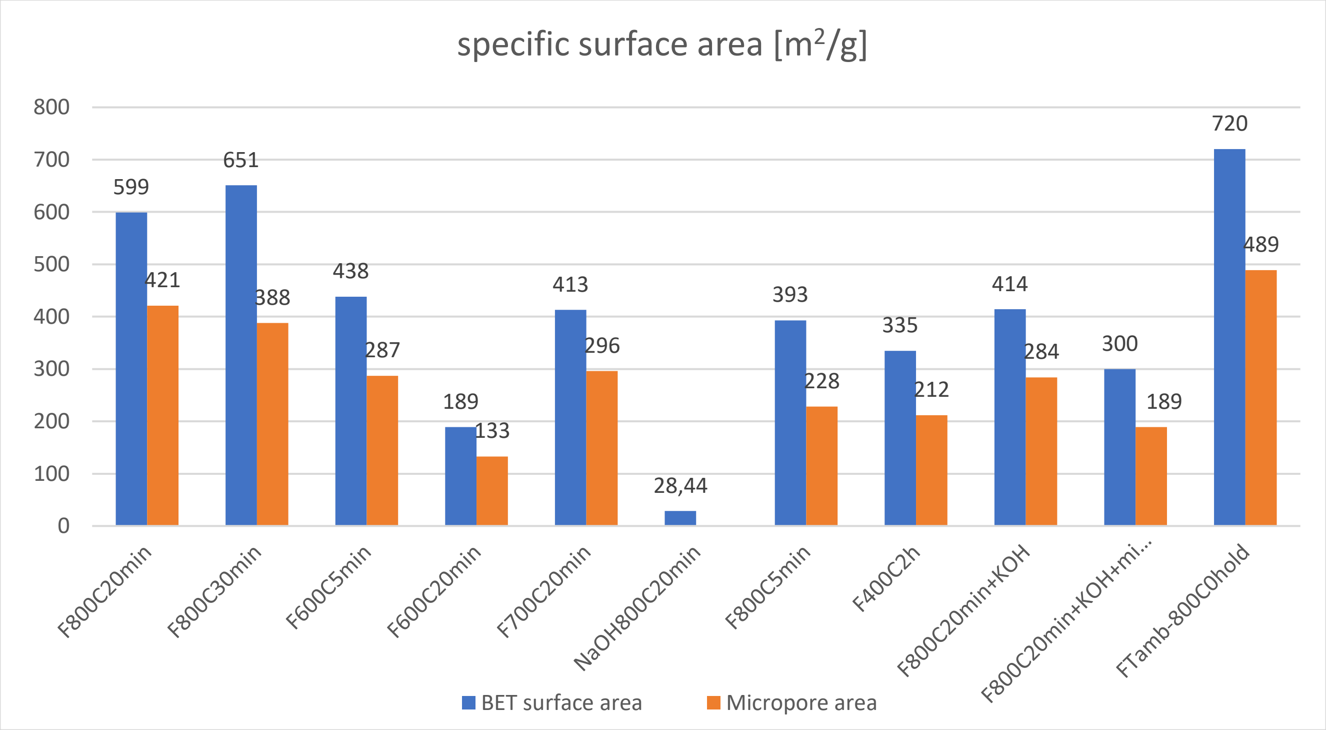


Figure [89], Micropore Area and BET specific surface area, author's elaboration.

This Figure shown again that the orange column, that represents the micropore area, is always about two thirds of the blue column, the total surface area. This is a great result because it means that there is a repeatability and that the behaviour is shown by all the samples, no matter the pre or post treatment (always except for the

NaOH and KOH carbons). The maximum micropore percentages values are given by F700C20min (71,6%) and F800C20min (70,3%), but almost all the other attest well over 60%.

To better analyse the results, now more graphs will be presented. At first, it is interesting to compare how the non-treated filters preformed. In this way we can see the influence of temperature and time. We can well see that the temperature that performs better is 800°C. This effect is clearly visible in the 20 minutes series and it is indicated and pointed out by the arrow in the Figure [90]: at 800°C we have a much greater specific surface area than at 700 and 600 °C. Anyways, the samples at 5 minutes reported a result that is different, as the two analysed surface areas are almost the same or the 600 °C is a bit better. Therefore, once again we state that all these results need confirmations and that are only a first attempt to give directions for the following studies.

On the other hand, we can also analyse the effect of time. From the figure below it appears clear that 30 minutes is the best timing: this is probably caused by the fact that (as it is reported in Figure [57]), the pyrolysis process finishes at about 30 minutes time and this means that above there is still space for more pores and after this time, the oxygenation process begins, degrading the matter and destroying the pores. This trending is reported here and clear for the 800 °C series: the carbon made with a 5 minutes hold time has a lower specific surface area than the ones at 20 and 30 minutes.

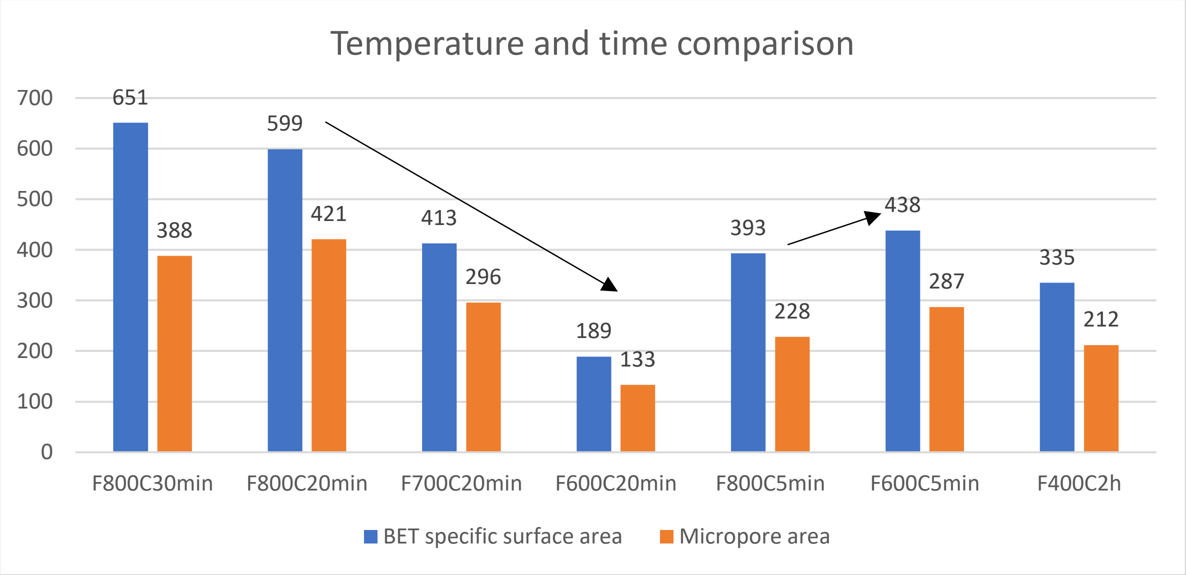


Figure [90], Temperature and time influence in BET specific surface area, author's elaboration.

Now it is the time to analyse the pre-treatments and the post-treatments. First of all the NaOH will be analysed:

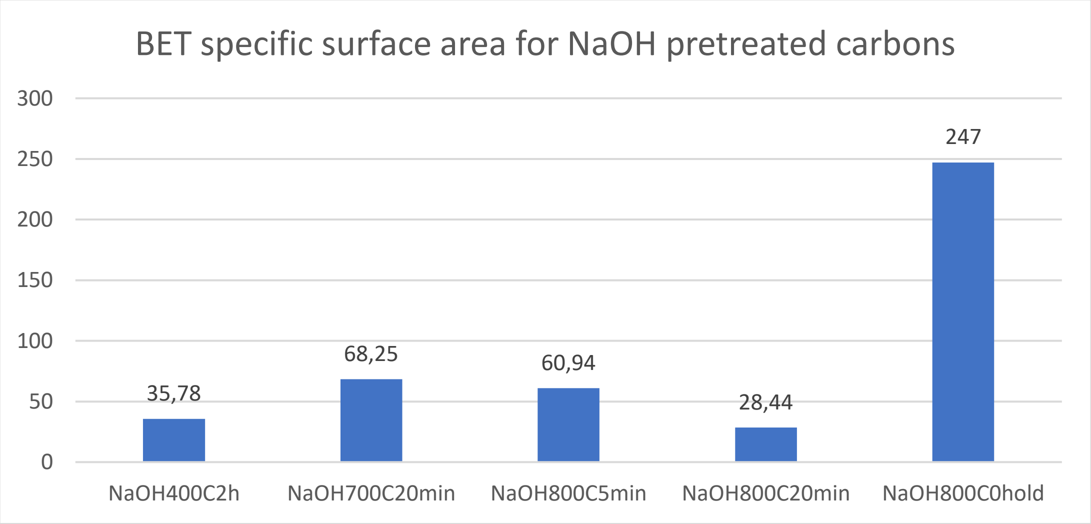


Figure [91], BET specific surface area for NaOH pre-treated carbons, author's elaboration.

The graph shows that these areas are much smaller than the ones obtained with the non-pretreated carbons. The areas are all below 100 m^2/g but the one that was thermically treated with a ramp. As a result this is a second confirmation of what it was stated in the pages before: the sample treated with a ramp, even for the NaOH samples that usually have a much smaller area, had a better performance. Hence, in future works, this information must be taken into account and developed, to get confirmations.

Moreover, we can make some comparisons on all the other pre and post treatments. In the following figure (Figure [92]), we compared the sample F800C5min with all of the variations. Therefore, all the samples were subject to the thermal treatment at 800 °C for 5 minutes, but either the pre-treatment of the filers was different (here are represented the carbons from NaOH and ethanol immersion) or had a modification after carbonisation. the graph shows that when we immerge the made carbon in KOH, then we have a decrease in specific surface: this is most probably caused by the fact that there are some potassium crystals that deposit on the surface preventing access to the pores and thus reducing the specific area. However, when we treat this sample in a microwave we have a augmentation of the specific surface: even if the total area is smaller than the original one (but not that small), the micropore area has increased (even if not that much). This phenomenon could be caused by the fact that the KOH introduces the creation of some oxygenated functional groups on the surface, that with the heating help forming more pores (and micropores in particular). Nevertheless, this is only an assumption and this idea should be verified. However, in future studies, this route of post-treatment of the carbons, with immersion in KOH or NaOH and then a second heat treatment, should and could be developed and improved.

From the image below (Figure [92]), we can again see the huge difference between the NaOH immerged filters and all the others: once again the failure of this method is confirmed. Finally, there is another good point to analyse. Even if a washing with ethanol has proved to be useless and unnecessary. But this idea is to be review if we look at the problem from the point of view of the pyrolysis gas: if certain substances that could end up in the pyrolysis gas were removed by ethanol scrubbing, perhaps the slight reduction in the specific surface area of the activated carbon produced would be a good compromise to avoid subsequent gas purification. However, from this study we can see and prove only that the ethanol-washed filters give a smaller specific surface. Nevertheless, if we place them in sodium hydroxide and then heat them at 600 °C for 10 minutes, the result is much better. Once again there is a confirmation: a chemical and thermal post treatment might be a good idea.

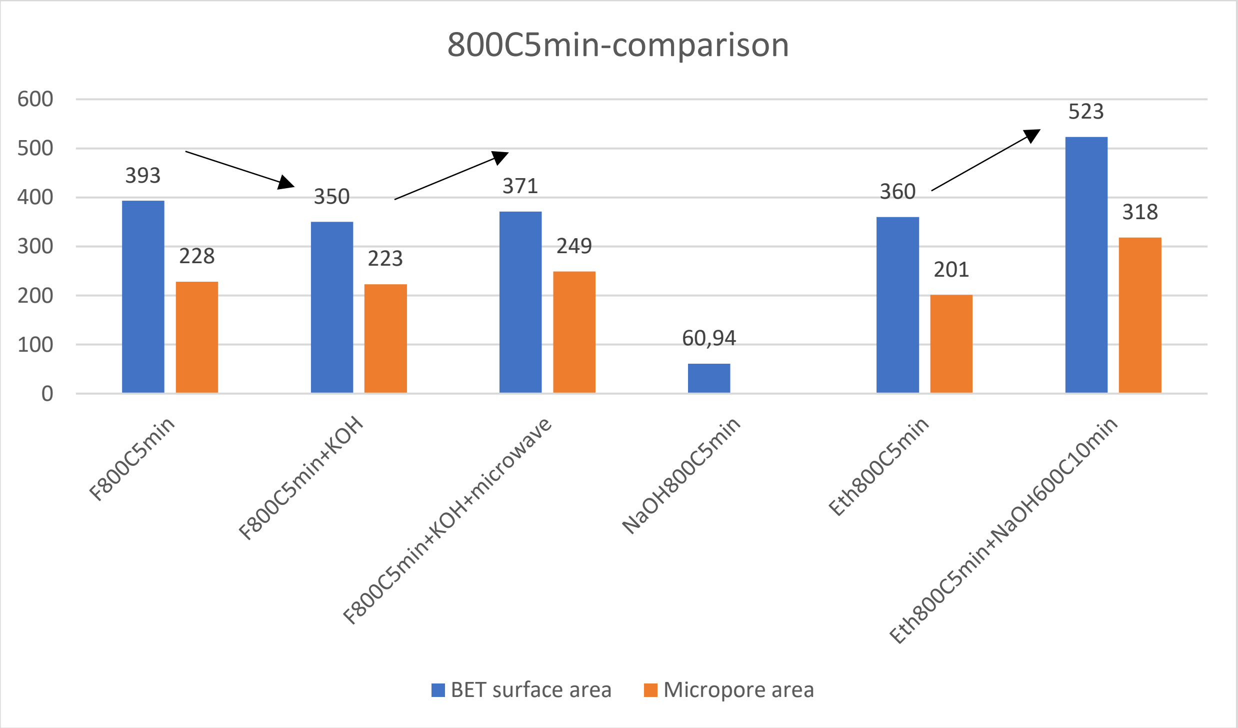


Figure [92], Comparison of the BET specific surface area for 800°C and 5 minutes samples, author's elaboration.

Then, to conclude, the same comparisons have been made for the 20 minutes and 800 °C samples.

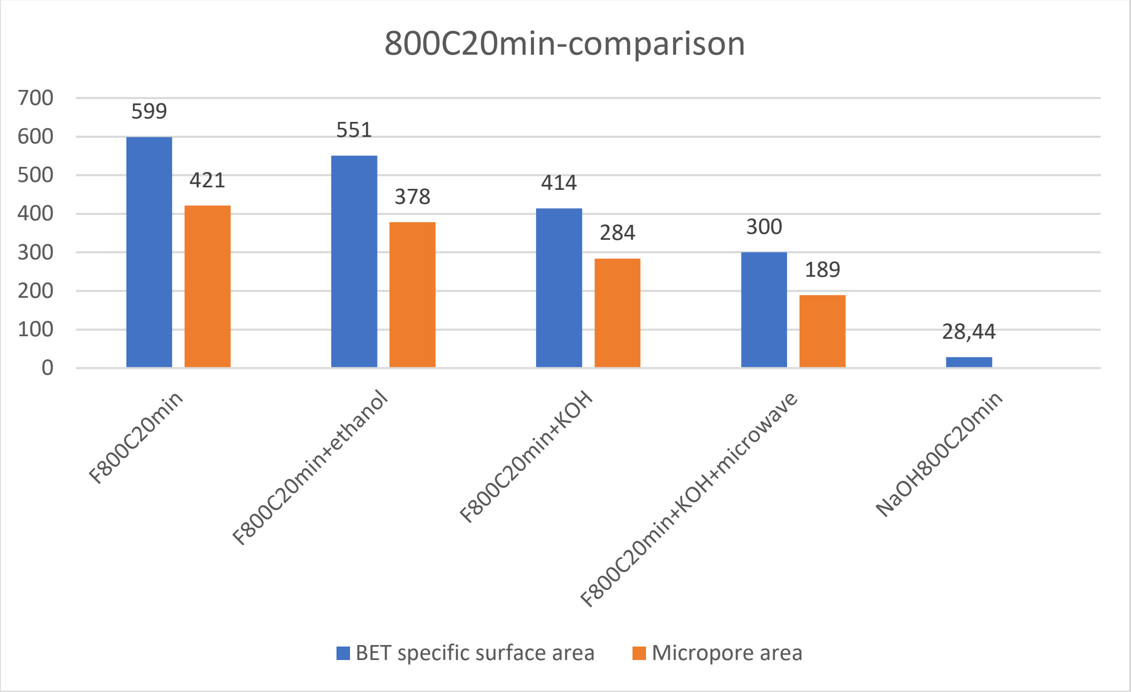


Figure [93], Comparison of the BET specific surface area for 800°C and 20 minutes samples, author's elaboration.

These samples confirm the fact that the pre-treatments did not work, but state that a microwaving test after the carbonisation does not help increasing the specific surface area: this is again to be verified in the following studies.

5. Conclusion

To conclude the analysis of the problem, we presented here some statistics on cigarette consumption and cigarette butt pollution. Cigarette production is huge: multiple sources report that each year the average production of cigarettes is about 5.7 trillion. These figures represent an incredible amount of waste. Unfortunately, many smokers have the bad habit of throwing their cigarette butts on the ground, without caring about the significant environmental damage this can cause. Cigarette butts are not biodegradable and contain over 7,000 toxic components. When cigarette butts are discarded in the environment, significant amounts of toxic chemicals are leached and potentially accumulated, posing a serious threat to the environment. To solve this huge problem, we need to find a smart way to collect and store this waste and, most importantly, find a sustainable way to recycle it. This process will not only bring economic benefits, as we will be able to make a product out of waste, but it will also help us to clean up the environment.

I was interested in the thermal way for making activated carbons. The aim of this study was therefore to be a preliminary research for other studies to follow in the field of the valorisation of butts. Activated carbons are the easiest and, for our means, also the most feasible way of recovery. The results of the BET tests show us that there is a good performance on average of untreated filters. The best ones are at 800°C with the samples held for 20 and 30 minutes (where it was estimated that the pyrolysis was finished), with specific surfaces of 600 m^2/g, which are already good figures. The average of the coals made from untreated filters was about 500 m^2/g. There is the carbon treated with a temperature range from ambient temperature to 800°C, with a specific surface of 720 m^2/g. Another result is that the surface given by the micropores is always around two thirds, which is a very good result. Secondly, these results show us that the pre-treatments done on the filters do not work. In particular the immersion of the filters in NaOH or KOH gave very bad results. The treatment with ethanol also shows lower results compared to the untreated filters (with an average of 350 m^2/g). We have seen that there is a possibility to improve the post-treatment, but unfortunately we have not been able to do all the necessary analyses to confirm these effects.

Although there are results to be confirmed, we can say with certainty that soaking the filters in NaOH or KOH does not lead to activated carbon and therefore does not work as a chemical activator, as we thought. So we wanted to try to understand why, and the SEM analysis helps us. As we saw from the SEM of the untreated filters, a change in morphology is clear. The development of a hierarchical pore structure during the carbonisation process is most likely a consequence of the acetate modification. The produced activated carbon has in general a high specific surface area and a porosity ranging from micrometre to nanometre. In contrast, for filters pre-treated with NaOH, there is no change in morphology (in fact the filters keep their shape). In the picture on the left, there are sodium crystals deposited on the fibres. When we do the heat treatment there are some fibres that are intact and others that have been partially transformed. Overall, there are sodium crystals and some of them seem to be fused together. As these elements were on the surface of the filters, they probably received the heat first and prevented the fibres from undergoing a complete heat treatment, also preventing the formation of pores, and thus activated carbon. Our hypothesis, to be confirmed, is that the sodium, which melts at 97 °C and evaporates at 882 °C, melts on the fibres at a temperature that has not yet allowed the fibres to degrade. This creates a coating of sodium, which remains liquid, on the fibres and thus prevents the fibres from reacting with each other, maintaining a fibrous structure and hindering the formation of pores. As they melted, they prevented the fibres to be jointed and melted together, therefore preventing the pyrolysis.

We also need to think about an integrated way forward. Here we offer an example of what we think a more comprehensive exploitation of the material might look like. Pyrolysis can be carried out on butts, but it would be intelligent to also exploit the pyrolysis gases and after using activated carbons to carry out a second thermal treatment. The ashes would be buried, but in much smaller quantities than the materials used in the process. Moreover, the produced gas could be the fuel for the furnace and therefore the process would be really integrated and circular. The process, reported in a scheme in the following graph (Figure [94]), graphically represents the way of thinking that we want to give to the reader. The process that was study in the present analysis could be easily expanded, especially if it could be taken to an industrial scale. Indeed, on an industrial scale (or even just pilot scale) it would be necessary to recover the pyrolysis gases. Obviously, studies need to be carried out on this stream, since we do not know its specifications, but from our analyses we know that it represents almost 90% of the mass entering it (since we managed to make coals with a weight that was 10% of that of the mass entering the process). Anyways, further work and analysis will have to be done to expand these results as this was only a preliminary study.

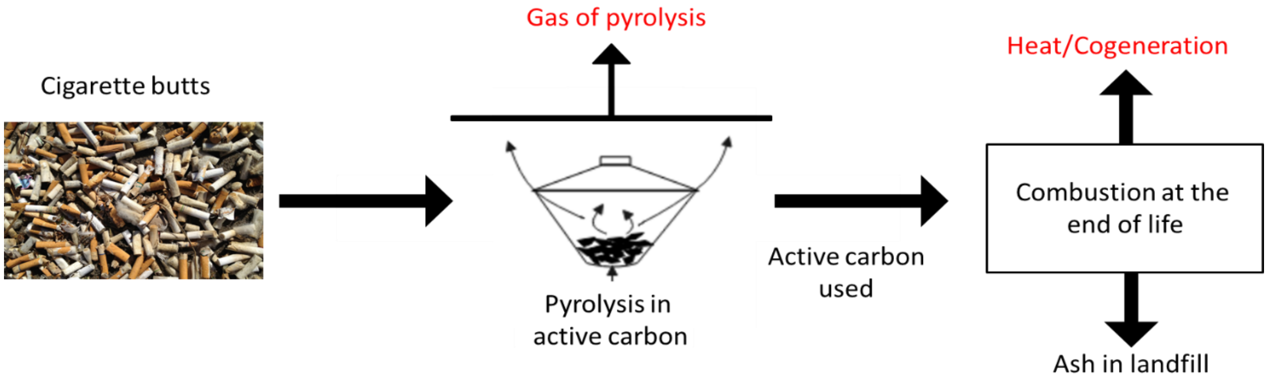


Figure [94], Proposition of process improvement, author's elaboration.

In the actual situation, sometimes the combustion is done directly, which is the easiest but also dumbest way to recycle, as we do not giver a second life to a product. By producing active carbons, we could give a second life to the product and use also the produced gas and only at the end of the life of the recycled product, increasing the productivity.

So, we can now draw the final conclusions. The study that was carried out was only the beginning of a larger project. All these results are preliminary and need to be confirmed, but they can be developed further and open the way for future studies. The points we will need to focus on will be the repeatability of the tests (remember that we only carried out one test, to test as many temperatures and residence times as possible) and the variability of the raw material. The repeatability will be fundamental to better understand the kinetics of the pyrolysis, to identify the optimum times and also to try to maximise the specific surface area. As we have multiple results, moreover, it will be easy to tell if the results are constant and if the areas that we reported in this study are realisable on an industrial scale. For now, as an exploring study, we can only say that there is a great possibility to make active carbons starting from cigarette butts as a raw material. In addition, we did not consider the variability of cigarette butts (burnt regions, humidity, differentiations in the brands) that might or might not interfere in the valorisation pathway.

Furthermore, it is important to say that in the first part of the present study, many valorisations have been reported and many solution were thought to be really interesting and foreseeable, however we concentrated on the valorisation option that we thought more immediate and easier. Nevertheless, solutions like mixing in fired clay bricks or asphalt concrete could be really interesting as they are brute-force solutions without much added value or technological cost, but which could employ large quantities of cigarette butts. On the other hand, there are more technological solutions that could represent a real advantage in the future, like the use as biofilm carrier or a cellulose acetate aerogel to manufacture a thermal insulator.

With this study we aimed at giving the reader an inspiration, reviewing and reporting different valorisation opportunities and ways, obtained by exploring the bibliography and by trying to reproduce one of these valorisations, explaining that a recycling of cigarette butts in a new product is possible and feasible.

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Annex:

[1] **The FDA list** is reported here, to give the idea of the number of dangerous compounds that are present in cigarettes and cigarette butts. To identify the categories, we have 5 indexes: Carcinogen (CA), Respiratory Toxicant (RT), Cardiovascular Toxicant (CT), Reproductive or Developmental Toxicant (RDT), Addictive (AD). A compound can be identified with more than one index, if presents the danger indicated by the index.

Constituent	Category		Constituent	Category
Acetaldehyde	CA, RT, AD		Benzene	CA, CT, RDT
Acetamide	CA		Benzo[b]fluoranthene	CA, CT
Acetone	RT		Benzo[k]fluoranthene	CA, CT
Acrolein	RT, CT		Benzo[b]furan	CA
Acrylamide	CA		Benzo[a]pyrene	CA
Acrylonitrile	CA, RT		Benzo[c]phenanthrene	CA
Aflatoxin B1	CA		Beryllium	CA
4-Aminobiphenyl	CA		1,3-Butadiene	CA, RT, RDT
1-Aminonaphthalene	CA		Cadmium	CA, RT, RDT
2-Aminonaphthalene	CA		Caffeic acid	CA
Ammonia	RT		Carbon monoxide	RDT
Anabasine	AD		Catechol	CA
o-Anisidine	CA		Chlorinated dioxins/furans	CA, RDT
Arsenic	CA, CT, RDT		Chromium	CA, RT, RDT
A-α-C (2-Amino-9H-pyrido[2,3-b]indole)	CA		Chrysene	CA, CT
Benz[a]anthracene	CA, CT		Cobalt	CA, CT
Benz[j]aceanthrylene	CA		Coumarin	Banned in food

Crotonaldehyde	CA		Nicotine	RDT, AD
Cyclopenta[c,d]pyrene	CA		Nitrobenzene	CA, RT, RDT
Dibenz[a,h]anthracene	CA		Nitromethane	CA
Dibenzo[a,h]pyrene	CA		2-Nitropropane	CA
Dibenzo[a,i]pyrene	CA		N-Nitrosonornicotine (NNN)	CA
2,6-Dimethylaniline	CA		N-Nitrososarcosine (NSAR)	CA
Ethyl carbamate (urethane)	CA, RDT		Nornicotine	AD
Ethylbenzene	CA		Phenol	RT, CT
Ethylene oxide	CA, RT, RDT		Polonium-210	CA
Formaldehyde	CA, RT		Propylene oxide	CA, RT
Furan	CA		Quinoline	CA
Hydrazine	CA, RT		Selenium	RT
Hydrogen cyanide	RT, CT		o-Toluidine	CA
Indeno[1,2,3-cd]pyrene	CA		Selenium	RT
Isoprene	CA		Styrene	CA
Lead	CA, CT, RDT		Toluene	RT, RDT
Mercury	CA, RDT		Uranium-238	CA, RT
Methyl ethyl ketone	RT		Vinyl acetate	CA, RT
5-Methylchrysene	CA		o-Toluidine	CA
Naphthalene	CA, RT		Uranium-235	CA, RT
Nickel	CA, RT		Vinyl chloride	CA

[2] **Management**
As we were thinking about the possibilities of the cigarette butts' collection, Mr. Saleh and I decided to star an association, linked to the Université de Technologie de Compiègne, based on the valorisation of cigarette butts. Our goal is to firstly to raise awareness of the danger of this waste, and secondly to create teams of students to implement promising recycling and collecting ideas.

The association's name is Recyclope, crossing the word "recyle" and "clope", the French slang word for "cigarette", with a jeu de mots as many associations related to the university do. The association was created to raise awareness among young students of the UTC about the great problem of cigarette butts and to try to bring ideas and knowledge for possible recycling. The principles of this association are those of the circular economy, where a waste becomes a raw material for a new process and sustainable development. The project of the association is to study and put into practice, within the UTC, the studied valuations and thus to propose a model of environmental sustainability.

The initial objective of the association will be to highlight the importance and necessity of evaluating cigarette butts. To do this, it will be necessary to change the paradigm, ingrained in the minds of many, that butts are not a hazardous waste and can therefore be treated more superficially. It is therefore necessary that the members of the association understand the problem and have the firm intention to help the association to make this change of mindset. Subsequently, another very important objective of this nascent association will be to propose and verify ideas for possible valorisation. This will be a fundamental work over the years and will become the main objective.

Moreover it is also necessary to consider that the association being open to multidisciplinarity and deeply anchored in the social context of Compiègne, so another objective will be to establish and study the optimisation of the points of collection and storage of cigarettes, putting in motion the ingenuity and the great practical qualities of the students of the UTC.

As you can thus understand, the association was born from the recognition of an urgent need to act and to sensitize the student population and not the UTC on a non-trivial and gigantic problem. To this end, the possible improvements that can be put into practice will be the cornerstone of our activity.

Activities:
At first, we had to set up the association. I assumed the role of vice-president and Mr. Saleh assumed the role of president. We then proceeded to find UTC students willing to join our association. Another fundamental step to create an association was to write a statute, a formal establishing letter and to follow the rules presented by the university. The statue and the formal letter are attached in the Annex (Annex [3] and Annex [4], respectively).

Logo:
After finishing the long bureaucratic process, we finally could start our association and start planning our future activities. One really important thing was the logo, that I personally designed with Hugo Fayolle, a fellow member of the association. After brainstorming some ideas, we came up with the following:

Figure [1_Annex], Recyclope's logo, author's elaboration.

Sampling:
The association will start its activity next year, but some ideas already came to mind. As we decided in our first meeting, we thought that the essential first step was to take a sample of the various cigarette butts found in the area of Compiègne, in order to make a general study on the average CB found on the streets of our city. Thanks to this activity we will manage not only to find what the average CB looks like, but also we could acquire more cigarette butt samples for the laboratory tests that I described before.

In order to do our research in the best possible way we had to select areas in which to collect. Given the fact that the number of members of the association is not very high, being a new reality among the other associations present at the UTC, we could choose few areas in which to collect. For this reason it was necessary to make a very careful and considered choice.

The chosen areas are representative of three different categories. With our approach, after a collective decision during a meeting, we decided to identify the areas in:

- the city centre, including the square and the main street of Compiègne;
- residential areas, i.e. made up essentially of blocks of flats and with some green space;
- parks, i.e. areas with a lot of trees where students often meet.

After this classification we managed to identify the key spots for our sampling campaign. The chosen spots are marked on the following map of the city:

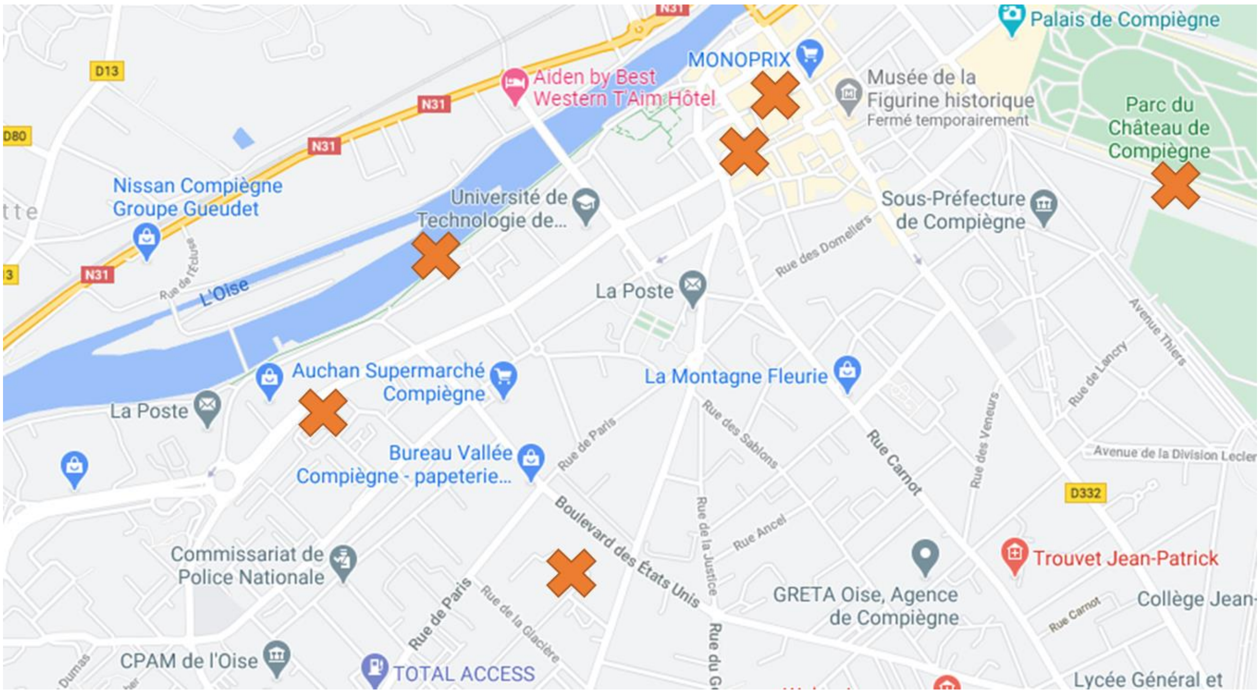

Figure [2_Annex], Compiègne's collecting spots, author's elaboration.

The choses spots were 2 streets in the city center, were the biggest shops are, a street next to the parc of the "Château de Compiègne", an area called "Bord de l'Oise", the area next to the river Oise and near the UTC very popular with UTC students and 2 residential areas.

Then, with the help of Professor Saleh and Professor Bals, new techniques will be tested, but for now it is all in the hypothetical.

[3] Here is reported the statute of the association Recyclope, that I founded, as a more managerial part of my master's thesis. The statue was written by me in French and it will be reported in the original version.

STATUT ASSOCIATION Recyclope

ARTICLE PREMIER – NOM

Il est fondé entre les adhérents aux présents statuts une association régie par la loi du 1er juillet 1901 et le décret du 16 août 1901, ayant pour titre : Recyclope, valorisation des mégots de cigarette à l'UTC.

ARTICLE 2 - BUT OBJET

Cette association a pour objet de sensibiliser les jeunes étudiants de l'UTC au grand problème des mégots de cigarettes et de créer des équipes d'étudiants pour réaliser des idées prometteuses de recyclage.

Si l'on considère que les mégots de cigarettes sont l'un des déchets les plus produits dans le monde et, pour l'instant, sans aucune forme de valorisation, on peut comprendre la gravité du problème. C'est pourquoi l'association vise d'abord à sensibiliser au danger de ces déchets, puis à créer des équipes d'étudiants pour étudier des idées de valorisation.

Les principes de cette association sont ceux de l'économie circulaire, où un déchet devient une matière première pour un nouveau processus et le développement soutenable. Le projet de l'association est d'étudier et de mettre en pratique, au sein de l'UTC, les valorisations étudiées et donc de proposer un modèle de durabilité environnementale.

ARTICLE 3 - SIÈGE SOCIAL

Le siège social est fixé à Rue Roger Couttolenc, 60200 Compiègne.

Il pourra être transféré par simple décision du conseil d'administration.

Article 4 - DUREE

La durée de l'association est illimitée.

ARTICLE 5 - COMPOSITION

L'association se compose de :
a) Membres actifs ou adhérents ;
b) Membres bienfaiteurs.

ARTICLE 6 - ADMISSION

L'association est ouverte à tous, sans condition ni distinction.

« Pour faire partie de l'association, il faut être agréé par le conseil d'administration, qui statue, lors de chacune de ses réunions, sur les demandes d'admission présentées. »

ARTICLE 7 - MEMBRES – COTISATIONS

Sont membres actifs ceux qui ont pris l'engagement de verser annuellement une somme de 5 € à titre de cotisation.

Sont membres bienfaiteurs, les personnes qui versent un droit d'entrée de 10 € et une cotisation annuelle fixée chaque année par l'assemblée générale.

ARTICLE 8. - RADIATIONS

La qualité de membre se perd par :
a) La démission ;
b) Le décès ;
c) La radiation prononcée par le conseil d'administration pour non-paiement de la cotisation ou pour motif grave, l'intéressé ayant été invité à fournir des explications devant le bureau et/ou par écrit.

ARTICLE 9. – AFFILIATION

La présente association est affiliée à l'Université de Technologie de Compiègne et se conforme aux statuts et au règlement intérieur de cet institut.

Elle peut par ailleurs adhérer à d'autres associations, unions ou regroupements par décision du conseil d'administration.

ARTICLE 10. - RESSOURCES

Les ressources de l'association comprennent :
1° Le montant des droits d'entrée et des cotisations ;
2° Les subventions de l'Etat, des départements et des communes ;

3° Toutes les ressources autorisées par les lois et règlements en vigueur.

ARTICLE 11 - ASSEMBLEE GENERALE ORDINAIRE

L'assemblée générale ordinaire comprend tous les membres de l'association à quelque titre qu'ils soient. Elle se réunit chaque année au mois de Décembre. Quinze jours au moins avant la date fixée, les membres de l'association sont convoqués par les soins du secrétaire. L'ordre du jour figure sur les convocations.

Le président, assisté des membres du conseil, préside l'assemblée et expose la situation morale ou l'activité de l'association. Le trésorier rend compte de sa gestion et soumet les comptes annuels (bilan, compte de résultat et annexe) à l'approbation de l'assemblée. L'assemblée générale fixe le montant des cotisations annuelles et du droit d'entrée à verser par les différentes catégories de membres.

Ne peuvent être abordés que les points inscrits à l'ordre du jour. Les décisions sont prises à la majorité des voix des membres présents ou représentés.

Il est procédé, après épuisement de l'ordre du jour, au renouvellement des membres sortants du conseil. Toutes les délibérations sont prises à main levée, excepté l'élection des membres du conseil. Les décisions des assemblées générales s'imposent à tous les membres, y compris absents ou représentés.

ARTICLE 12 - ASSEMBLEE GENERALE EXTRAORDINAIRE

Si besoin est, ou sur la demande de la moitié plus un des membres inscrits, le président peut convoquer une assemblée générale extraordinaire, suivant les modalités prévues aux présents statuts et uniquement pour modification des statuts ou la dissolution ou pour des actes portant sur des immeubles.

Les modalités de convocation sont les mêmes que pour l’assemblée générale ordinaire.

Les délibérations sont prises à la majorité des membres présents.

ARTICLE 13 - CONSEIL D'ADMINISTRATION

L'association est dirigée par un conseil de 3 membres, élus pour 1 année par l'assemblée générale. Les membres sont rééligibles.

En cas de vacances, le conseil pourvoit provisoirement au remplacement de ses membres. Il est procédé à leur remplacement définitif par la plus prochaine assemblée générale. Les pouvoirs des membres ainsi élus prennent fin à l'expiration le mandat des membres remplacés.

Le conseil d'administration se réunit au moins une fois tous les six mois, sur convocation du président, ou à la demande du quart de ses membres. Les décisions sont prises à la majorité des voix : en cas de partage, la voix du président est prépondérante.

Tout membre du conseil qui, sans excuse, n'aura pas assisté à trois réunions consécutives sera considéré comme démissionnaire.

ARTICLE 14 – LE BUREAU

Le conseil d'administration élit parmi ses membres, un bureau composé de :
1) Un-e- président-e- ;
2) Un-e- vice-président-e;
3) Un-e- secrétaire et, si besoin est, un-e- secrétaire adjoint-e- ;
4) Un-e- trésorier-e, et, si besoin est, un-e- trésorier-e- adjoint-e-.

Les fonctions de président et de trésorier ne sont pas cumulables.

ARTICLE 15 – INDEMNITES

Toutes les fonctions, y compris celles des membres du conseil d’administration et du bureau, sont gratuites et bénévoles. Seuls les frais occasionnés par l’accomplissement de leur mandat sont remboursés sur justificatifs. Le rapport financier présenté à l’assemblée générale ordinaire présente, par bénéficiaire, les remboursements de frais de mission, de déplacement ou de représentation.

ARTICLE - 16 - REGLEMENT INTERIEUR

Un règlement intérieur peut être établi par le conseil d'administration, qui le fait alors approuver par l'assemblée générale. Ce règlement éventuel est destiné à fixer les divers points non prévus par les présents statuts, notamment ceux qui ont trait à l'administration interne de l'association.

ARTICLE - 17 - DISSOLUTION

En cas de dissolution prononcée selon les modalités prévues à l'article 12, un ou plusieurs liquidateurs sont nommés, et l'actif net, s'il y a lieu, est dévolu à un organisme ayant un but non lucratif ou à une association ayant des buts similaires, conformément aux décisions de l'assemblée générale extraordinaire qui statue sur la dissolution. L'actif net ne peut être dévolu à un membre de l'association, même partiellement, sauf reprise d'un apport.

Article – 18 LIBERALITES :

Le rapport et les comptes annuels, tels que définis à l'article 11 (y compris ceux des comités locaux) sont adressés chaque année au Préfet du département.

L'association s'engage à présenter ses registres et pièces de comptabilité sur toute réquisition des autorités administratives en ce qui concerne l'emploi des libéralités qu'elle serait autorisée à recevoir, à laisser visiter ses établissements par les représentants de ces autorités compétents et à leur rendre compte du fonctionnement desdits établissements.

« Fait à Compiègne, le 05/04/2021 »

Khashayar Saleh, président

Matteo Burdese, vice-président

[4] In this part is reported the letter to UTC's official committee that supervises the formation of student lead associations. Thus, to form an association we had to write a letter explaining why the association was created and which were our founding principles. The letter is reported in French as it was written, by me, in French.

Matteo Burdese
Rue Roger Couttolenc
Compiègne 60200

Compiègne, le 12 Avril 2021

Madame et Monsieur,

L'association Recyclope est créée pour sensibiliser les jeunes étudiants de l'UTC au grand problème des mégots de cigarettes et pour essayer d'apporter des idées et des connaissances au service d'éventuelles valorisations.

Si l'on considère que les mégots de cigarettes sont l'un des déchets les plus produits dans le monde et, pour l'instant, sans aucune forme de valorisation, on peut comprendre la gravité du problème. C'est pourquoi l'association vise d'abord à sensibiliser au danger de ces déchets, puis à créer des équipes d'étudiants pour réaliser des idées prometteuses de recyclage.

Les principes de cette association sont ceux de l'économie circulaire, où un déchet devient une matière première pour un nouveau processus et le développement soutenable. Le projet de l'association est d'étudier et de mettre en pratique, au sein de l'UTC, les valorisations étudiées et donc de proposer un modèle de durabilité environnementale.

L'objectif initial de l'association sera de souligner l'importance et la nécessité de l'évaluation des mégots. Pour cela, il sera nécessaire de changer le paradigme, ancré dans l'esprit de beaucoup, selon lequel les mégots ne sont pas un déchet dangereux et peuvent donc être traités avec plus de superficialité. Il est donc nécessaire que les membres de l'association comprennent le problème et aient la ferme intention d'aider l'association à opérer ce changement d'état d'esprit.

Par la suite, un autre objectif très important de cette association naissante sera de proposer et de vérifier des idées de valorisation possible. Il s'agira d'un travail fondamental au fil des ans, qui deviendra l'objectif principal.

Par ailleurs, il faut aussi considérer que l'association étant ouverte à la pluridisciplinarité et profondément ancrée dans le contexte social de Compiègne, un autre objectif sera d'établir des points de collecte et de stockage de cigarettes, mettant en mouvement l'ingéniosité et les grandes qualités pratiques des étudiants de l'UTC.

Comme vous pouvez donc le comprendre, l'association est née de la reconnaissance d'un besoin urgent d'agir et de sensibiliser la population étudiante et non de l'UTC sur un problème non trivial et gigantesque. À cette fin, les améliorations possibles qui peuvent être mises en pratique seront donc la pierre angulaire de notre activité.

Cordialement,

Matteo Burdese, vice-président

Acknowledgements

I would like to thank my supervisors, Professor Stefania Specchia and Professor Khashayar Saleh, for the theoretical and technical support of this study. Thanks to their trust, this analysis was much easier to do, as they facilitated my path giving me directions and helping me improving the results.

Furthermore, I would like to thank Vivi, who helped me every day keeping me mentally sane and being the best person I’ve ever met. You have been a precious help in the most delicate moments. A huge thank you to my family for the constant support in the past 23 years and the continuous help that they’ve given me: without them I would not have achieved this goal. Thank you to the bois for the jokes and the witticisms: it has been fundamental, and you know it. Here between me not to think about anything.

I would also like to thank the whole team of the Centre de Recherche for their welcome and in particular Professor Daouk, Professor Guénin and Professor Bals, who have facilitated my work by helping me with continuous advice and guidance on how to proceed with the work on a variety of things.

Finally, I would like to thank all the people who advised me during the writing of this report and read it, my PoliTo classmates and my UTC classmates and especially Adrien Pot for the time spent together in the lab and the help during the tests.

I would like to thank all the people who contributed to the success of my analysis and who helped me during the writing of this report. I wrote these words, I wrote what I thought most painfully, I wrote them but then I realised it was better if I kept quiet. Alone and silent.