Politecnico di Torino

Corso di Laurea Magistrale
in Ingegneria Chimica e dei Processi Sostenibili
A.a. 2022/2023
Sessione di Laurea Ottobre 2023

Valorization of cigarettes butts for their ability to produce high surface area supports.

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Contents

1. Introduzione

Lo scopo della ricerca, in merito alla valorizzazione dei mozziconi di sigaretta, è stato portato avanti soprattutto sulla considerazione che è uno dei principali rifiuti solidi presenti nel mondo. Rifiuti dannosi e inquinanti, presenti in tutti gli ambienti come: asfalto, mari e terreni coltivabili.

Rispetto al tipo di ambiente si è preso nota che il comportamento degradativo dei mozziconi di sigaretta cambia in termini di componenti rilasciati e tempi di degradazione. 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, causando problemi al suolo e alle acque circostanti.

Lo sviluppo della ricerca presso l'università degli studi di Compiègne ha seguito un protocollo ben preciso, in prima analisi è stata effettuata un grande approfondimento bibliografico sui rischi e pericoli attuali dei mozziconi di sigarette nei vari ambienti possibili, dalla quale si è riuscito a capire quanto sia di vitale importanza, per l'uomo, ricercare soluzioni alternative che possano valorizzare questo rifiuto anziché continuare ad accumularlo come se il problema non esistesse mentre parallelamente avvelena il mondo e con esso chi ci vive.

Successivamente si è analizzata la propagazione del calore all'interno del filtro stesso, considerando le principali leggi termodinamiche che governano il processo e riuscire a capire come gestirlo per ottenere alte efficienze e informazioni necessarie per la costruzione di un modello che possa meglio predire e descrivere il processo in oggetto.

Presso l'università di Compiègne è stato possibile lavorare a questa tematica utilizzando un reattore a letto fisso recentemente costruito, il quale era circondato da una fornace che permetteva di raggiungere anche elevate temperature senza le quali non si sarebbe potuto ottenere delle curve sperimentali che permettessero di comprendere lo sviluppo termico del campione.

A seguito di questi esperimenti è stato doveroso considerare anche il punto di vista cinetico, ossia costruire un modello basato sui dati sperimentali ottenuti mediante analisi termogravimetrica, per modellizzare al meglio la cinetica di reazione.

Una grande ricerca bibliografica è stata sviluppata per comprendere la vastità dei componenti che sono presenti nei mozziconi di sigaretta. Da ciò si è compresa la complessità del campione e la difficoltà nel determinare con accuratezza i vari componenti del singolo mozzicone.

Mediante il processo di pirolisi, si è avuta l'opportunità di misurare, seppur in maniera poco precisa, la quantità di prodotti formati, i quali si differenziano principalmente in due parti: una matrice solida compatta molto dura che grazie alle proprietà intrinseche del campione può essere utilizzato a sua volta come catalizzatore per processi di purificazione e inoltre una quantità considerevoli di gas di pirolisi, ossia H_2, CO e CO_2.

2. Bibliografia

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,come riportato da Tobacco Atlas [1] ma dobbiamo segnalare che dopo molti anni il numero di sigarette fumate nel mondo sta finalmente diminuendo negli adulti, con un leggero incremento nei giovani.
Inoltre, come riporta Tobacco Atlas [1], il processo di fabbricazione dei prodotti del tabacco genera un'enorme quantità di rifiuti: 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 quanto concerne la parte bibliografica, essa è stata suddivisa in più fasi: una prima parte per la comprensione dei componenti, o delle macro-famiglie dei componenti all'interno della sigaretta, successivamente nella comprensione dal punto di vista ambientale, e infine i metodi di valorizzazione già esistenti per il riutilizzo di questo rifiuto.

3. Componenti presenti nelle sigarette

Le caratteristiche delle sigarette cambiano dai vari produttori, i componenti chimici pericolosi che verranno elencati successivamente possono essere presenti nelle foglie di tabacco raccolte o in seguito inserite nel processo di fabbricazione della sigaretta.

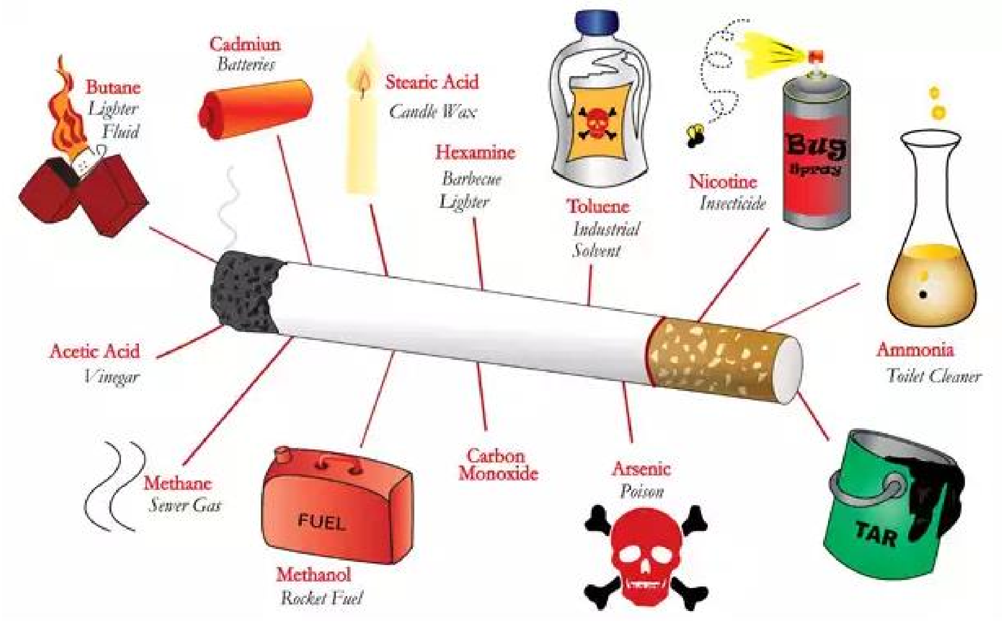


Figura 1: Componenti delle sigarette [1]

Generalmente la sigaretta viene suddivisa in quattro parti come spiegato nell'articolo di Linda Bianchi, 2018, [2]:

- Miscele di tabacco essiccate molto sottili
- La carta che avvolge la sigaretta, composta principalmente da cellulosa e aditivi
- Il filtro: composto anch'esso da cellulosa
- Il rivestimento del filtro

L'oggetto d'interesse di questo studio riguarda la parte finale del ciclo di vita di una sigaretta, ovvero il filtro rimanente dopo la combustione definito CB (cigarette butt).
Dagli studi sviluppati da Kurmus e Mohajerani ,2016, [3] si evince che il componente maggioritario presente nel CB è l'acetato di cellulosa, una molecola complessa, la quale presenta una grande presenza di atomi di carbonio. L'utilizzo di tale composto risiede nella grande capacità filtrante, caratteristica posta d'obbligo dopo che sono state bandite, nella maggior parte dei paesi, le sigarette senza filtro. Dato che 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.
Oltre all'acetato di cellulosa, all'interno del filtro sono presenti molti composti di varia natura: come la nicotina, metalli, composti organico volatici, catrami, e altri composti tossici per l'ambiente, Lombardi C. C. et al, 2009, [4].

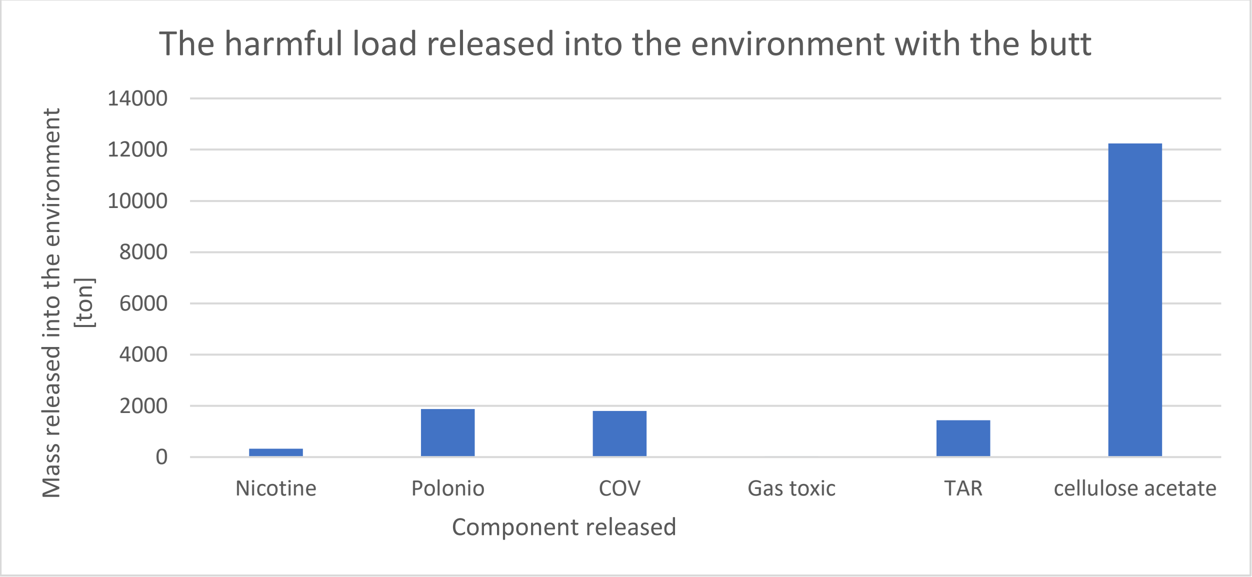


Figura 2:Sostanze tossiche rilasciate in ambiente, elaborazione dell'autore

4. Punto di vista ambientale

I mozziconi di sigaretta sono uno dei principali rifiuti solidi presenti in natura, è un materiale che richiede molto tempo per degradare, dovuto alla sua natura chimica. La peculiarità di questo rifiuto è la sua abbondanza, lo si può trovare ovunque, persino nei fondali marini.

La causa di tale abbondanza risiede nel comportamento sconsiderato dei fumatori, un esempio è riportato dagli studi del DOXA ISS (istituto superiore di sanità), 2018, [5] si stimano oltre 13 milioni di fumatori in Italia, i quali fumano in media 15 sigarette al giorno, delle quali la maggior parte vengono gettate, in maniera sconsiderata, in qualsiasi suolo.

Col progredire del problema la maggior parte degli stati ha preso dei provvedimenti per contrastare la diffusione e propagazione di tale comportamento con, ad esempio, delle sanzioni oppure dei divieti ai fumatori di fumare all'interno di luoghi al chiuso come aerei o locali.

La situazione è complicata persino per i fondali marini, nei quali i mozziconi rappresentano il 40% dei rifiuti complessivi, come viene riportato da Maocai Shen et al ,2020,[6]

Figura 3: Processo di diffusioneo delle sostanze tossiche presenti nelle sigarette rilasciate in mare [6]

I filtri di sigaretta contengono delle microplastiche e numerose sostanze chimiche cancerogene per gli organismi che vivono in questi habitat, i quali assorbono queste sostanze cambiando la loro natura in maniera irreversibile.

5. Valorizzazione dei mozziconi di sigaretta

Per contrastare il pericolo dei mozziconi di sigaretta, come rifiuto solido presente in ogni tipo di suolo, negli anni numerosi ricercatori e aziende si sono premurati di trovare altri metodi per valorizzare e riutilizzare tale rifiuto. Oggi giorno le soluzioni esistenti non sono numerose né ampliamente utilizzate, la causa risiede nel fatto che la lavorazione di tale rifiuto genera una quantità non trascurabile di gas che, se non trattati finirebbero direttamente nell'atmosfera.

Non tutti i metodi valorizzatori esistenti danno un contributo innovativo, alcuni sono stati creati con il solo scopo di eliminare tale rifiuto come mostrato nell'articolo di Samuele Marinello, 200, [7].

La maggior parte dei componenti presenti nel mozzicone di sigaretta sono non biodegradabili, per questo motivo oltre che escogitare metodi di valorizzazione dei mozziconi di sigarette molti stati hanno preso la decisione di aumentare i prezzi delle sigarette per scoraggiare i fumatori nel comprarle.

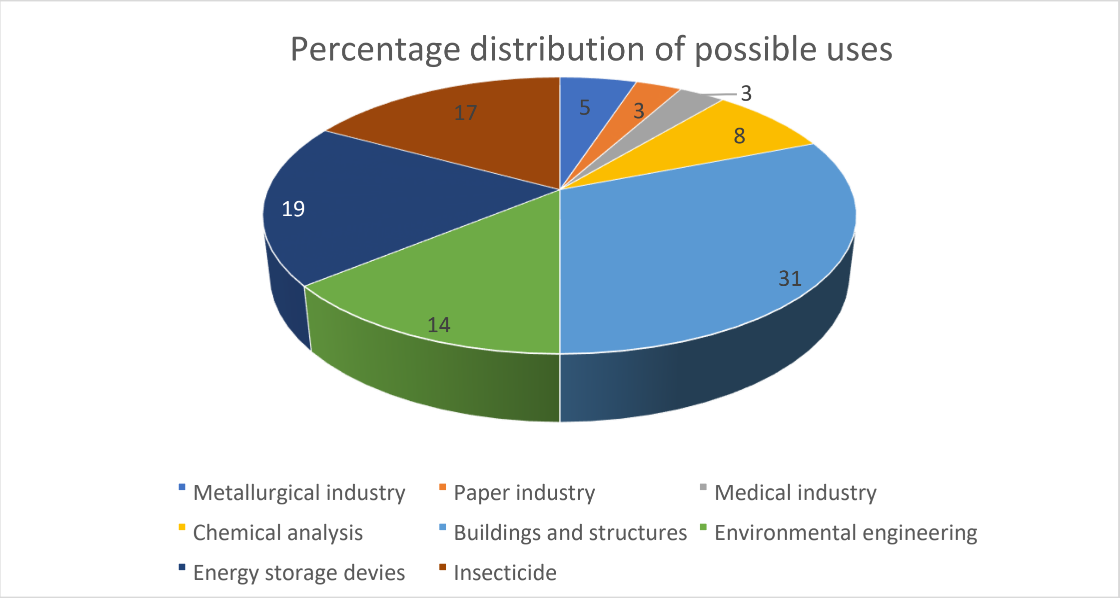


Figura 4: Grafico riassuntivo dei possibili usi industriali dei mozziconi di sigaretta, elaborazione dell'autore

5.1 Produzione di mattoni

Uno dei primi metodi scoperti per la valorizzazione dei mozziconi di sigaretta è stato quello di utilizzarli per la produzione di mattoni, spiegato dal signor A. Mohejerani,2016,[3] per i quali non è richiesta una grande quantità di energia. Il processo richiede l'utilizzo di alte temperature, le quali permettono le volatizzazioni dei componenti pericolosi cambiando le caratteristiche chimiche. Il processo in questione, quindi, permette di immobilizzare le sostanze tossiche che possono essere dannose per l'ambiente.

Per cui tale processo non solo genera un prodotto utilizzabile ma cerca di contrastare l'aumento dell'inquinamento ambientale.

5.2 Produzione di asfalto

Il progresso dei materiali avanzati ha dato al settore della pavimentazione una nuova dimensione grazie allo studio di Md. Tareq Rahmen et al ,2020, [8] le tecnologie innovative sono state implementate nel settore delle strade e delle autostrade per la produzione di asfalti con materiali di scarto. Gli asfalti si differenziano in tre categorie: Denso, Gap e Aperto (permeabile all'acqua).

La prima tipologia è la più comune ed utilizzata, richiede un grande quantitativo di bitume da ciò si è ricercato un modo per produrre la stessa tipologia di asfalti, aventi le stesse caratteristiche meccaniche, ma prodotto da fonti alternative. Con l'aggiunta dei mozziconi di sigaretta si è scoperto che è possibile ridurre la quantità di bitumi presenti negli asfalti densi ottenendo caratteristiche paragonabili con prezzi meno elevati, ed ovviamente, un minor impatto ambientale.

5.3 Re-cig

La Re-cig è una giovane start-up italiana produttrice di materiali polimerici derivati dal riutilizzo dei mozziconi di sigaretta. Attualmente produce occhiali, custodie per smartphone e oggetti per stampe 3D come riportato dal brevetto Re-Cig, 2019, [9]. Una giovane realtà che è riuscita prima di tutto a installare in varie parti d'Italia delle stazioni di raccolta per riuscire a collezionare in maniera più veloce i mozziconi di sigaretta e sensibilizzare la popolazione nel corretto riciclaggio di questo rifiuto.

6. Progetto

Obiettivo del progetto è la valorizzazione dei mozziconi di sigaretta mediante un processo di degradazione in assenza di ossigeno, ossia la pirolisi.

Processo poco costoso è di facile utilizzo, la pirolisi permette di far avvenire una degradazione termica del campione con conseguente produzione di matrice solida e composti gassosi. Tutto ciò è stato effettuato in un reattore a letto fisso recentemente costruito presso l'università di Compiègne.

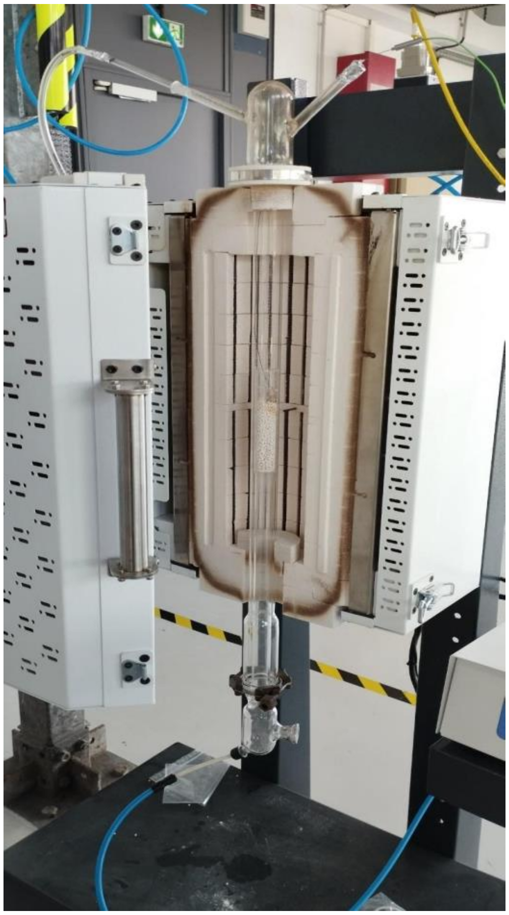


Figura 5: Reattore a letto fisso, elaborazione dell'autore

Durante gli esperimenti si è cercato di capire e determinare:

- La composizione del mozzicone di sigaretta
- Lo sviluppo termico e cinetico del processo
- Costruzione di un modello termodinamico e cinetico

6.1 Esperimenti

Durante la fase sperimentale è stato seguito un protocollo ben definito per la corretta riuscita degli esperimenti.

- Misurare il campione prima che questo venga messo all'interno del forno
- Essiccare il campione per eliminare l'acqua al suo interno
- Porre il medesimo all'interno del reattore collegato ad una termocoppia
- Impostare la temperatura target a cui voler far avvenire l'esperimento
- Controllare il processo mediante la strumentazione a disposizione
- Misurare i gas in uscita dal reattore
- Una volta terminata la reazione aspettare che il reattore si raffreddi
- Misurare il campione una volta esso estratto dal reattore

Grazie ai dati sperimentali ottenuti si è stati in grado di costruire delle curve qualitative che hanno permesso di comprendere meglio il processo.

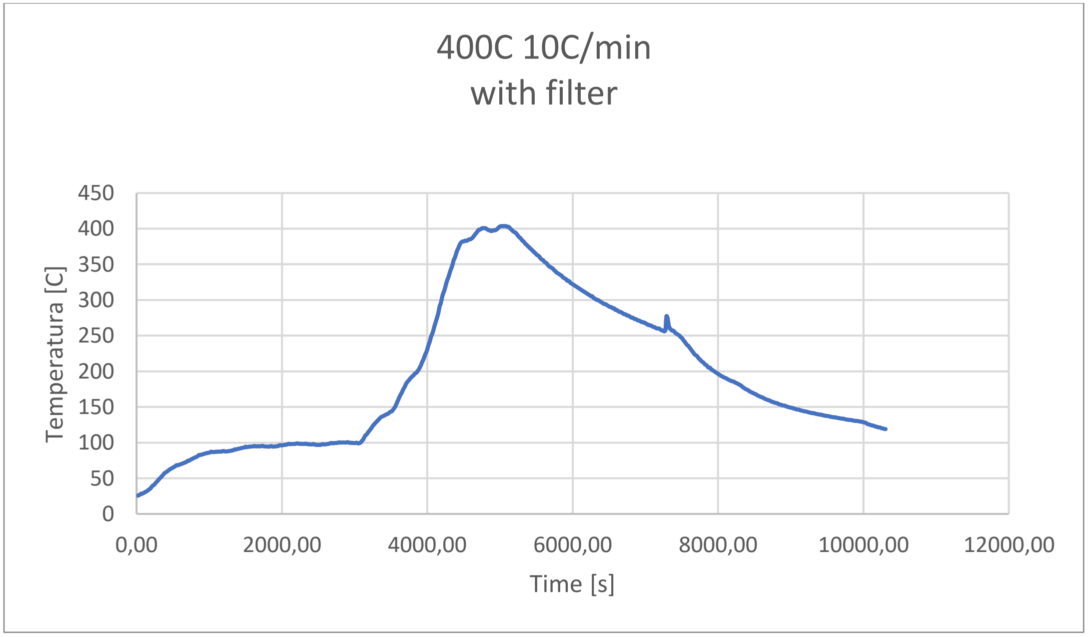


Figura 6: Andamento della temperatura nel tempo del campione durante il processo di pirolisi, elaborazione dell'autore

Una prima importante scoperta, all'inizio non considerata, è stata la comprensione che dopo un certo lasso di tempo all'interno del nostro campione non vi era alcun gradiente termico, per cui si potevano trascurare gli effetti di conduzione all'interno del filtro stesso. Ciò successivamente confermato dal numero di Biot.

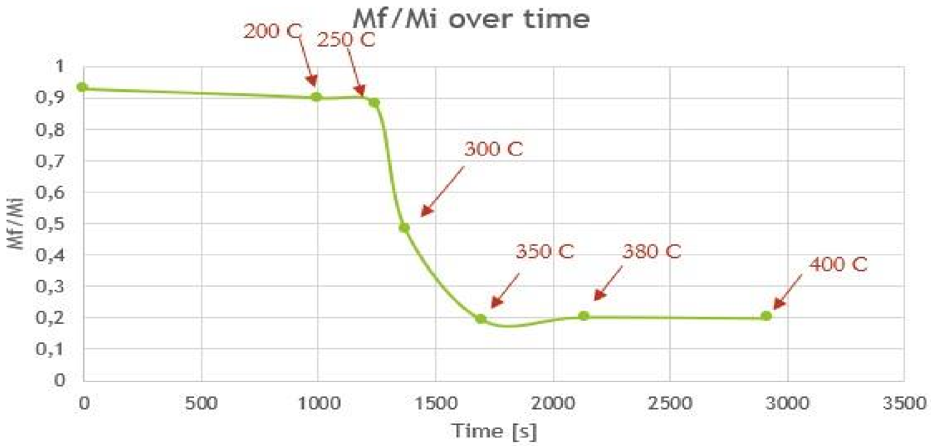


Figura 7: Conversione nel tempo, elaborazione dell'autore

Le misurazioni eseguite, hanno permesso di tracciare un grafico qualitativo della conversione del nostro campione durante l'intero processo così da poter studiare e comprendere il fenomeno fisico e ottenere una buona approssimazione del fenomeno degradativo a cui è soggetto il campione. Il grafico in questione può essere suddiviso in tre macroaree:

- La prima che è la fase in cui avviene il riscaldamento e parallelamente l'evaporazione della percentuale di acqua presente nel campione.
- Una seconda zona dove avviene la reazione, questa parte è il cuore centrale dell'esperimento in cui si è misurata la più alta percentuale di fumi emessi, in particolar modo gas di pirolisi.
- Una terza parte in cui, dopo un certo tempo di esposizione si è misurata una maggiore percentuale di metano prodotto.

Ogni parte del processo è stata studiata dando delle conclusioni che hanno permesso di approfondire il comportamento degradativo, e i limiti termodinamici oltre la quale non otteniamo alcun benefit ne aumento in resa come, ad esempio, effettuare un esperimento settando il forno a una temperatura al di sopra di 400 °C.

Precedenti esperimenti effettuati con mozziconi pretrattati sono stati effettuati a temperature molto elevate, fino a 800 °C, questo comporta un costo oneroso in termini di tempo e denaro.

Il processo studiato presenta invece un andamento asintotico già per temperature intorno ai 400 °C.

Con ulteriore cura e precisione verranno di seguito spiegati i dati sperimentali ottenuti.

7. Modello cinetico

Grazie ai dati delle analisi termogravimetriche si è potuto creare un modello che prevedesse la cinetica di reazione che governasse il processo.

Come precedentemente discusso il campione utilizzato per gli esperimenti presenta una grande vastità di composti, ciò ha portato una complessità nel capire il tipo di cinetica da cui partire. Dopo un'attenta ricerca bibliografica, basata in particolar modo sugli studi di E.Daouk, 2020, [10] e C. Herce Fuente; R. Mecozzi , 2010, [11] si è deciso di considerare come ipotesi iniziale una cinetica del prim'ordine del solo acetato di cellulosa.

Non si è stati in grado di determinare un modello cinetico che fosse paragonabile ai dati sperimentali mediante l'ipotesi iniziale, da ciò ne è comportato un cambiamento di considerazioni fino ad aver ottenuto il seguente modello cinetico in cui è prevista la presenza di due reagenti: acetato di cellulosa e catrame.

Di seguito è riportato un grafico comparativo che confronta i dati sperimentali (curva in verde) con il modello costruito, basato sul modello di Arrhenius (curva tratteggiata blu). In ordinata riportata $\frac{dX}{dt}$ dove X sta ad indicare la conversione.

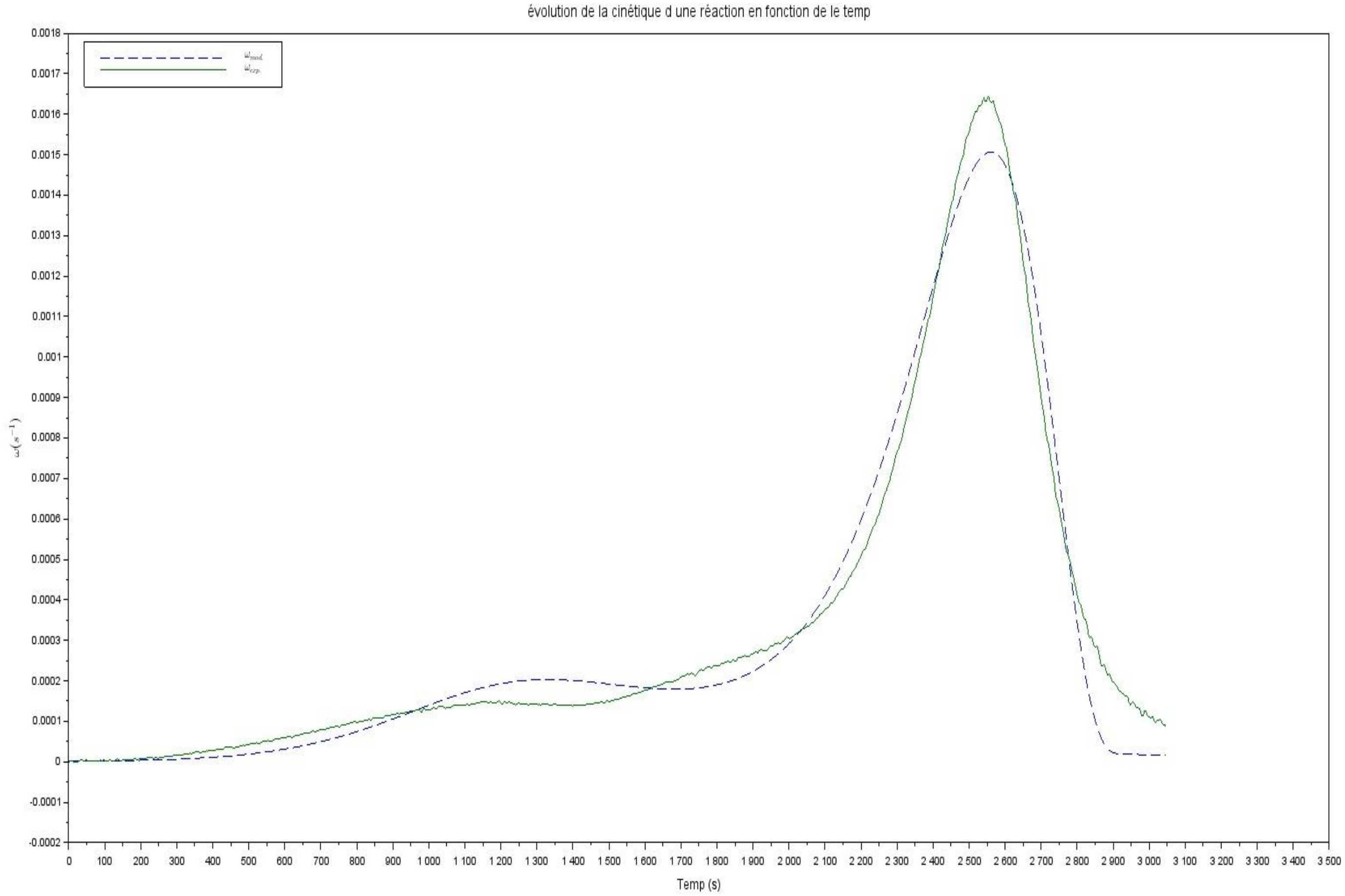


Figura 8: Modello cinetico vs dati speriemntali

8. Conclusione

L'obiettivo della ricerca in oggetto era quello di determinare un metodo innovativo e poco dispendioso per ridurre, riutilizzare e riciclare i mozziconi di sigaretta.

Dopo un'attenta analisi bibliografica si è cercato di utilizzare delle tecnologie e dei metodi già conosciuti, perfezionare le medesime tecnologie per ottenere un processo che possa generare una matrice solida porosa utilizzabile come catalizzatore per l'assorbimento della CO_2 e inoltre i gas di pirolisi, sostanzialmente (CO e H_2).

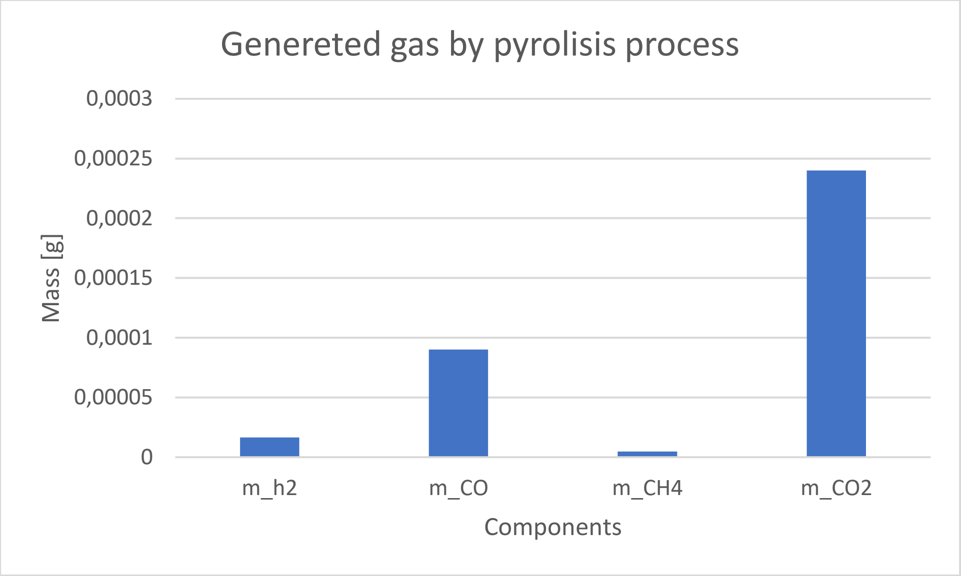


Figura 9: Risultati della gas cromatografia, elaborazione dell'autore

La ricerca, oggetto di questa tesi, ha permesso di concretizzare la creazione di un processo industriale che permetta la produzione di materiali utilizzabili in diversi settori, con il principale scopo di diminuire l'impatto ambientale e l'aumento dell'effetto serra cui i mozziconi di sigaretta concorrono insieme ad altri protagonisti inquinanti come si evince dall'articolo di Samuele Marinello et al, 2019, [7].

La volontà di migliorare la qualità della vita e di rispettare il nostro pianeta hanno orientato la mia ricerca nel tentativo di dare un contributo e proporre una soluzione innovativa.

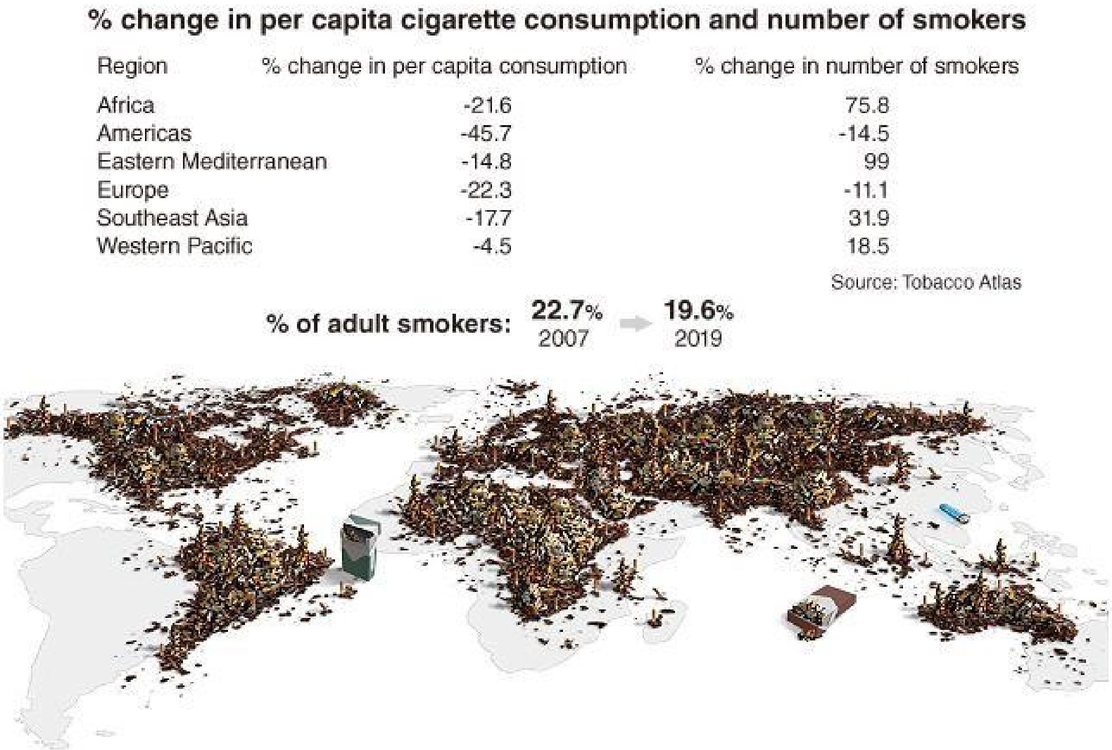
Il cambiamento climatico è un fenomeno che l'uomo non può più trascurare, dal momento che quest'ultimo ne è artefice, mentre il nostro pianeta succube, per questa ragione è auspicabile che l'uomo assuma un comportamento risolutivo.

Scopo del lavoro è stato quello di adottare una visione ciclica iniziando dal prelevare i campioni di mozziconi di sigaretta dai posaceneri pubblici, proprio come potrebbe avvenire in un ipotetico processo industriale, e sottoporli a un trattamento degradativo in modo da valorizzare gli stessi rifiuti rendendoli un valore aggiunto per la società e non più un pericolo per il sistema.

I risultati ottenuti sono una chiara evidenza dell'opportunità di riutilizzo e rinascita di un rifiuto solido che ai nostri tempi si trova in tutti gli eco sistemi e invece di essere abbandonato, facendo parte di un paesaggio infausto quale quello del cambiamento climatico, potrà essere utilizzato per migliorare la qualità della vita stessa fornendo prodotti utili per tutte le aree dell'industria.

1. Introduction

Approximately 4,5 trillion cigarette butts are being scattered across the world over the more than 5,5 trillion cigarettes manufactured according to Tobacco Atlas [1]. These cigarettes are considered one of the most hazardous wastes and environmental threats in the world. This number will increase too according to WHO (world health organization), considering the percentage of smokers in the world, one can estimate that 967 million daily smokers consumed approximately 6,25 trillion cigarettes According to the Tobacco Atlas the number of cigarettes smoked will increase to nine trillion in 2025. Nowadays there are more than 1,13 billion smokers in the world, and 200 million more who use tobacco products after the pandemic (following the 7th edition of Tobacco Atlas).



% change in per capita cigarette consumption and number of smokers

Region	% change in per capita consumption	% change in number of smokers
Africa	-21.6	75.8
Americas	-45.7	-14.5
Eastern Mediterranean	-14.8	99
Europe	-22.3	-11.1
Southeast Asia	-17.7	31.9
Western Pacific	-4.5	18.5

Source: Tobacco Atlas

% of adult smokers: 22.7% 2007 → 19.6% 2019

Figure 1: Percentage of smokers in the world [1].

The challenge of this report is to describe and explain the characteristics of cigarettes that are a problem for everybody, from the small particles in the ocean to human beings and environmental pollution. Shows the different ways to evaluate and reuse this waste, which is not so common in comparison to the popularity of smokers. Moreover, the object of this work is to explain the reason for this type of research, which is the pyrolisis of cigarette butts to generate renewable gas and a porous solid particle useful for generating carbon active catalyst.

The pyrolysis process is one of the cheaper processes in which is possible to reevaluate organic substances. The same substance that may, after a certain range of time, release unconscious number of lethal and harmful substances.

2. Bibliography

Approximately 4,5 trillion of cigarette butts are being scattered across the world over the more 5,5 trillion cigarettes manufactured, Tobacco Atlas, [1] . These cigarettes are considered one of the most hazardous wastes and environmental threats in the world, for this reason they have been developed throughout time a different way to recycle and valorize cigarette butts.

2.1 Composition of cigarette

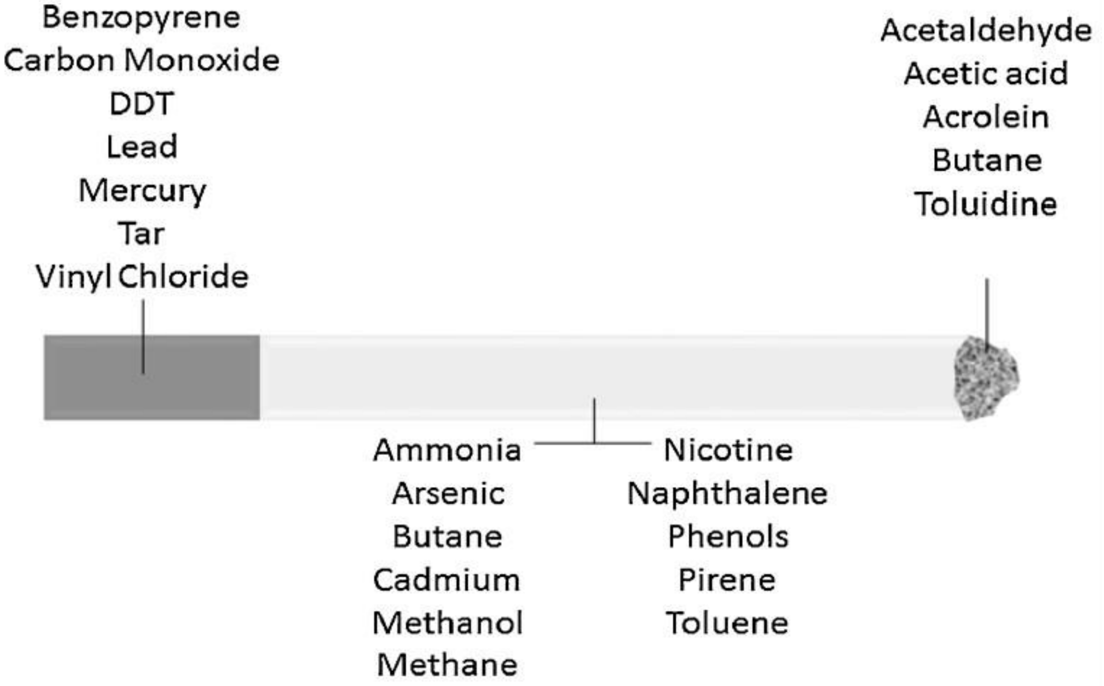


Figure 2: Representation of cigarette compoundsé[7]

A cigarette is built like a small cylinder in which there are a thin leaf of tobacco rolled.

Commercially manufactured cigarettes are showed in (Fig.3):

- Tobacco blend dried and cut into thin one-millimeter-thick strips.

The characteristics of tobacco changes from manufacturer to manufacturer. Basically, the harmful behavior of cigarettes depends on the dangerous chemicals that are deposited inside of the cigarettes and also in the paper rolled, according to Samuele Marinello et al, 2020, [7]. When the cigarettes are burned more compounds are generated by the combustion and most of them remain in the filter.

There are hundreds of possible additives, however, these are not declared on the cigarette packages on the market.

- Rolling paper to cover the tobacco is composed of cellulose and more additives, that enhance the combustion to produce more ash.
- Also, the filter is composed of cellulose.
- Typically, there is another paper that covers the filter, this is composed of polyvinyl acetate.

Since September 2003, the European Union has changed the standard smoking machine specifications to make them as like actual smoke as possible and has outlawed the use of the terms "light," "ultralight," and "mild.", Jean-François Etter et al, 2003, [12]

Compared to conventional cigarettes, "light" cigarettes have less tar and nicotine. However, because the smoker desires nicotine due to addiction, it aspirates more often, changing the combustion process and increasing the creation of fine particles (0.1m). These particles caused a higher risk of bronchopulmonary carcinogenicity due to their deeper lung penetration. But many smokers have always been deterred from quitting because they believe that smoking cigarettes with a filter will lessen, if not completely eliminate, the harm to their health. This myth, along with other causes, keeps the number of smokers in Italy at a high level (13 million, or 25.2% of the population), with everything that has to do with morbidity (about 186,000 admissions per year), death (around 80,000/year), and healthcare costs (about 6 billion euros, or 6.7 percent of health expenditure).

Several hazardous substances, such as polycyclic aromatic hydrocarbons, benzo(a)pyrene, benzene, arsenic, cadmium, tar, formaldehyde, ammonia, polonium-210, acetaldehyde, hydrocyanic acid, acetone, and many others are released into the environment when we discard gum, in addition to the filter and tobacco residue that are attached to it. Because it comprises gases, vapors, liquids, and solid particles, most of which are very minute and have diameters between 0.01 and 1 μm, tobacco smoke is typically referred to as the ideal aerosol. The following tables summarize some components of cigarettes.

Table 1: Gas component emitted during the combustion of cigarettes express in mg/cig.

Gas components	**mg/cigarette**
COx	17
Toluene	0,15
formaldehyde	0,09
acrolein	0,08
acetone	0,18
acid cyanide	0,45
ammonia	0,1
Nox	0,4
acetic acid	0,57
Benzene	0,28
pyridine	0,09
acetaldehyde	0,7

Table 2: Some particulate matter emitted during the combustion of cigarettes express in mg/cig.

Particulate matter	**mg/cigarette**
Powder	40
Nicotine	1,8
Phenol	0,08
cathecol	0,23
hydroquinone	0,2
lactic acid	0,12
glycolic acid	0,08
Benza(a)pyren	0,07
Nichel	0,03
Arsenic	0,0013
Polonium210	0,5
Cadmium	0,002

Tobacco must be carefully dried for its smells to emerge. During this process, the leaf goes through a particular fermentation and several chemical agents are formed. Several additional ingredients are added to tobacco to give it a distinctive flavor; these ingredients were chosen for their non-toxic dietary properties. Nobody, save the producers, is aware of which additives, and in what proportions, are used in each brand of cigarette. As far as we are aware, this is not exactly how cigarettes are often used, so the only certain thing is that the ingredient must be safe to consume. When combustion is combined with various additions, hundreds of hazardous chemical agents can be created, including burning sugars, for instance, raises the proportion of tar; Glycerin creates acrolein, a chemical that prevents the cilia's ability to vibrate at the bronchial level to filter the air, while caramel produces catechol, one of the most harmful carcinogens in smoking. To be more precise, it’s been proven that there are more than 7,000 toxic substances identified in cigarette smoke.

2.2 Cathecol

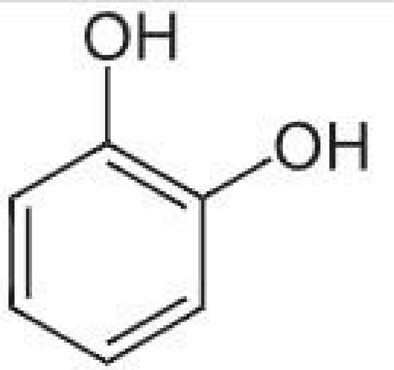


Figure 3: Cathecol[13]

Catechol exposure can happen both during production and usage. Humans who come into touch with catechol get eczematous dermatitis. In humans, skin absorption leads to a condition similar to that brought on by phenol, but with more violent convulsions. Animals exposed to high dosages of catechol may have sustained blood pressure increases and central nervous system (CNS) depression. It is unclear if these health effects were seen following acute (short-term) or chronic (long-term) exposure because the above studies did not provide information on the length of exposure. In oral-exposed rats, tumors in the glandular stomach were seen. But the concentration of cathecol in the smoked cigarettes doesn’t allow immediate effects according to the National Library of medicine, [13]

2.3 Nicotine

The principal and more famous component of cigarettes is nicotine.

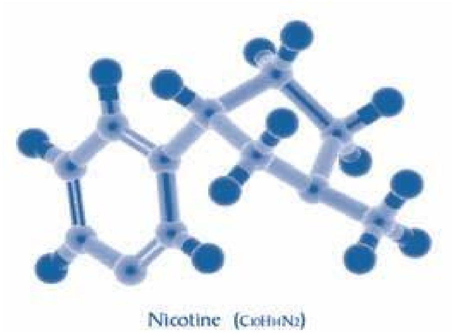


Figure 4:Nicotine molecules[4]

A water-soluble volatile alkaloid. It is an extremely potent toxin, and even just 50–60 mg injected intravenously may be fatal to people. A typical cigarette contains 10-15 mg, of which 20% is lost as smoke and 50% is broken down during combustion. In this instance, we may estimate that 4.5 mg of nicotine is still trapped in the gum. Nicotine is swiftly processed by the body and is also rapidly absorbed by it (half-life 2 hours). This implies that a smoker regularly inhales large amounts of alkaloids without experiencing severe poisoning symptoms.

In Italy, people smoke roughly 72 billion cigarettes a year, which results in 324 tons of nicotine being emitted into the atmosphere according to the article of Carmine Ciro Lombardi, 2009,[4]

2.4 Polonium

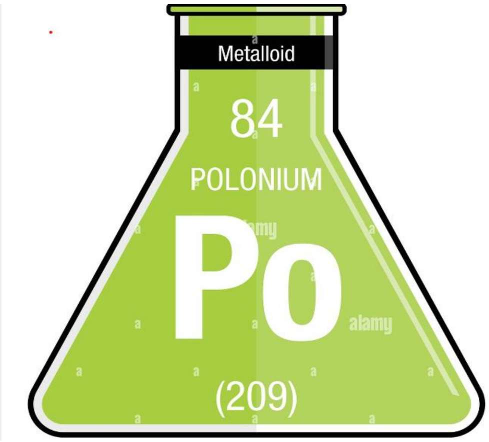


Figura 5:Configuration of Polonium's electrons.[14]

Alpha emitter, a radioactive element, has a significant propensity for cancer. The amount of Polonium-210 (Po-2110) in each cigarette varies depending on where and how the tobacco was grown. The finding was made in the early 1960s.

The presence of alpha radioactivity is partly caused by the roots' direct uptake of radionuclides from uranic soils, partially by the trichomes of leaves' uptake of lead and polonium-210 from air precipitation, and ultimately by polyphosphate fertilizers. The distribution of a cigarette's radioactive burden from polonium 210 has been the subject of several investigations like the article of Farshid Soleimani, 2021, [15]. One of these studies, conducted by the

Society of Tobacco Addiction with the US of Chemical Sciences, Radiochemistry and Metallurgy of the Faculty of Pharmacy of the University of Bologna and with the ENEA of Bologna, has shown that the smoke from a western cigarette contains an alpha radioactivity from Polonium-210 of about 75mBq, which is variously distributed between active and passive smoke. It was possible to determine the Po-210's distribution in the various fractions by using Parfenov's considerations and the assumption that its average concentration is equal to 75mBq: 26.0 mbq in the stub, 11.5 mbq in the ash, and 37.5 mbq in active and passive smoke. The entire yearly load of radioactive alpha released with the buttresses in the environment is equivalent to roughly 1.872 million Bq, given that around 72 billion butts are created in Italy each year.

2.5 VOC

Volatile organic compounds are compounds that have high vapor pressure and low water solubility. Mostly used for paints or pharmaceutical purposes, they are industrial solvents, such as trichloroethylene; fuel oxygenates, such as methyl tert-butyl ether (MTBE). VOCs are often components of petroleum fuels, hydraulic fluids, and other industrial compounds. VOCs are common ground-water contaminants. That theory it was explained by the United States Environmental Protection Agency, [16] and also express in the article of Lombardi C.C [4] and used in this research to obtain a better view of this compounds.

VOCs are prevalent in many places, but residences are particularly common. Such substances may become trapped in structures and have an impact on both the environment and human health. Substances like methylene chloride may be fatal and are exceedingly poisonous. Numerous clinical investigations, specifically concentrating on the VOC levels in cigarette smoke and show that smoking can raise the quantities of carcinogenic polycyclic aromatic hydrocarbons in lung tissue. Keep in mind that one of the best free search engines, PubMed, has millions of scientific publications in it.
Combustion of tobacco generates a huge quantity of VOC, mostly:

- Benzene
- Aceton
- Formaldehyde
- Toluene
- Xylene

Taking into account that each cigarette emitted above 50 mg of VOC and that more of 50% remain in the filter, this means that more of 1800 ton of VOC are release in the environment.

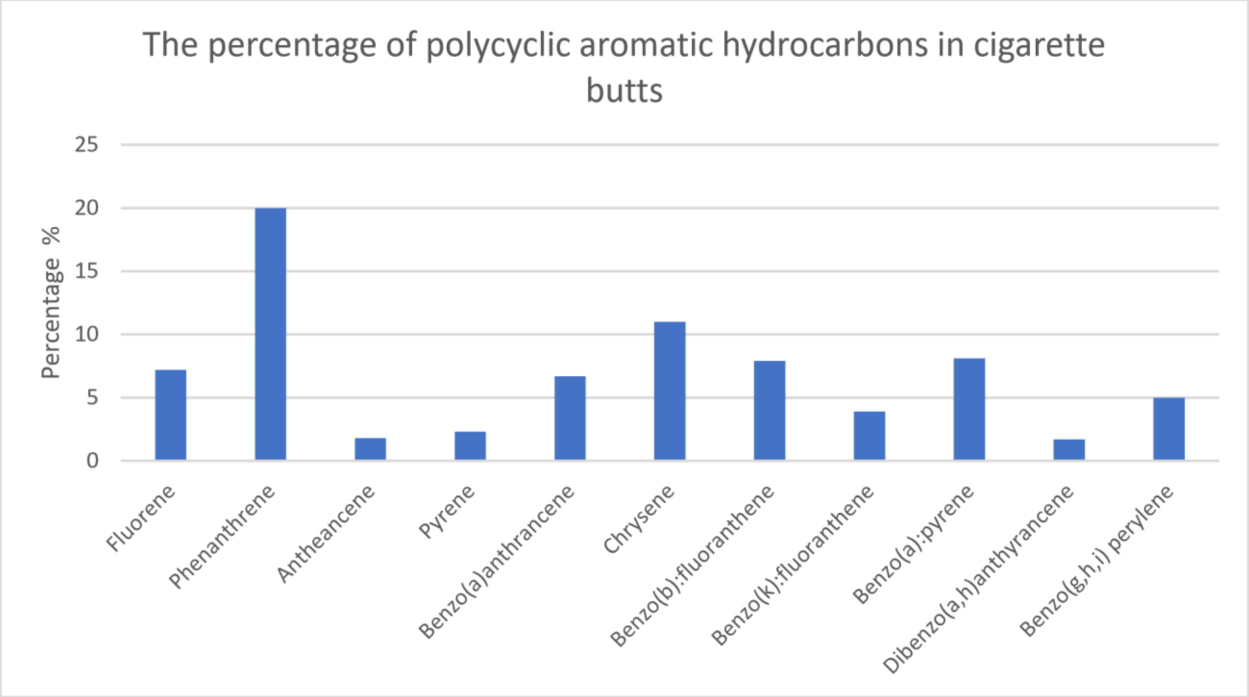


Figure 6: Resume of PAH in cigarette butts, author's elaboration

2.6 Ammonia and hydrocyanic acid

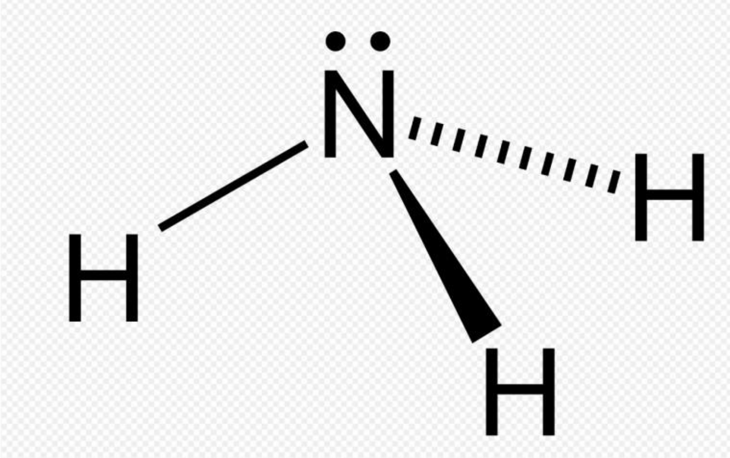


Figure 7: Ammonia [17]

Gases like hydrocyanic acid and ammonia are also released by smoke.

These are classified as hazardous gases by Royal Decree No. 147 of 1927 and any changes or additions thereto. About 0.6 mg are released by each cigarette, of which 50% pass through the filter. Thus, together with the gum, we contribute to the emission of 21.6 tons of these hazardous gases into the atmosphere each year.

2.7 Particulate matter

Each cigarette emits about 40 milligrams of particulate matter on average. Particulate matter also includes the portion known as "condensate," which is made up of several chemical substances, including tar, benzopyrene, chromium, cadmium, and other metals. The numerous substances that make up tar give it its carcinogenic potential. Farshid Soleimani et al, 2021, [15]

For every gram of that, we release 20 mg of particles into the atmosphere, assuming that 50% of the particulate material created by cigarette combustion remains in the gum. Approximately 1,440 tons of gum end up in the environment as little particles, many of which are poisonous, dangerous, and carcinogenic.

2.8 Cellulose acetate

Additionally harmful to the environment is cellulose acetate, a component of the filter. Although this material is not biodegradable, it is photodegradable. As a result, explained on the article of M.Schiling et al, 2010, [18] and the research off Bao. C, 2015, [19] it gets disseminated in soil and water after being exposed to UV radiation. Each filter has a 170 mg content.

It indicates that a total of 12,240 tonnes of cellulose acetate end up in the environment based on the yearly cigarette use in Italy. In conclusion, considering the aforementioned factors and the residual tobacco column's and the filter's filtration capacity, we can claim, albeit roughly, that the toxic load delivered into the environment with the buttresses is relevant.

2.9 Metals

Taking to account that different smoke conditions can cause changes in the emission, one to say that long-term passive smoking could potentially increase human exposure to harmful toxic metals (loid)s including: Pb,Cd,Ni,Cr and Hg to nonsmokers. Every metal present in the cigarette and after the combustion presents in the butt burned is explained by Füsun Okçu Pelit, Ruken Esra Demirdöğen et al, 2018, [20].

The amounts of chemical compounds, including metals, may be different in each of the components. Several factors, including smoking behavior, how CBs are collected(fresh or old), cigarette types and brands, and the source, cultivation, and growth of tobacco would influence the metal concentration across cigarette components.

During cigarette combustion, the metals present in the tobacco are released in smoke and CBs Metals present as toxicants are associated with particles. Due to this association, it is unlikely that metals are emitted into the air from cigarette butts. Nonetheless, there is some potential for organometallic compounds (i.e., nickel tetra carbonyl) to volatilize. Moreover, heavy metals and chemicals in CBs could reach water bodies and pollute aquatic environments, posing potential toxicity for marine and/or limnic species. In this report will speak about the effects of butts on the ocean environment.

The table below shows the number of metals present in the cigarettes before combustion. Metals will be emitted into the air and absorbed in the filter.

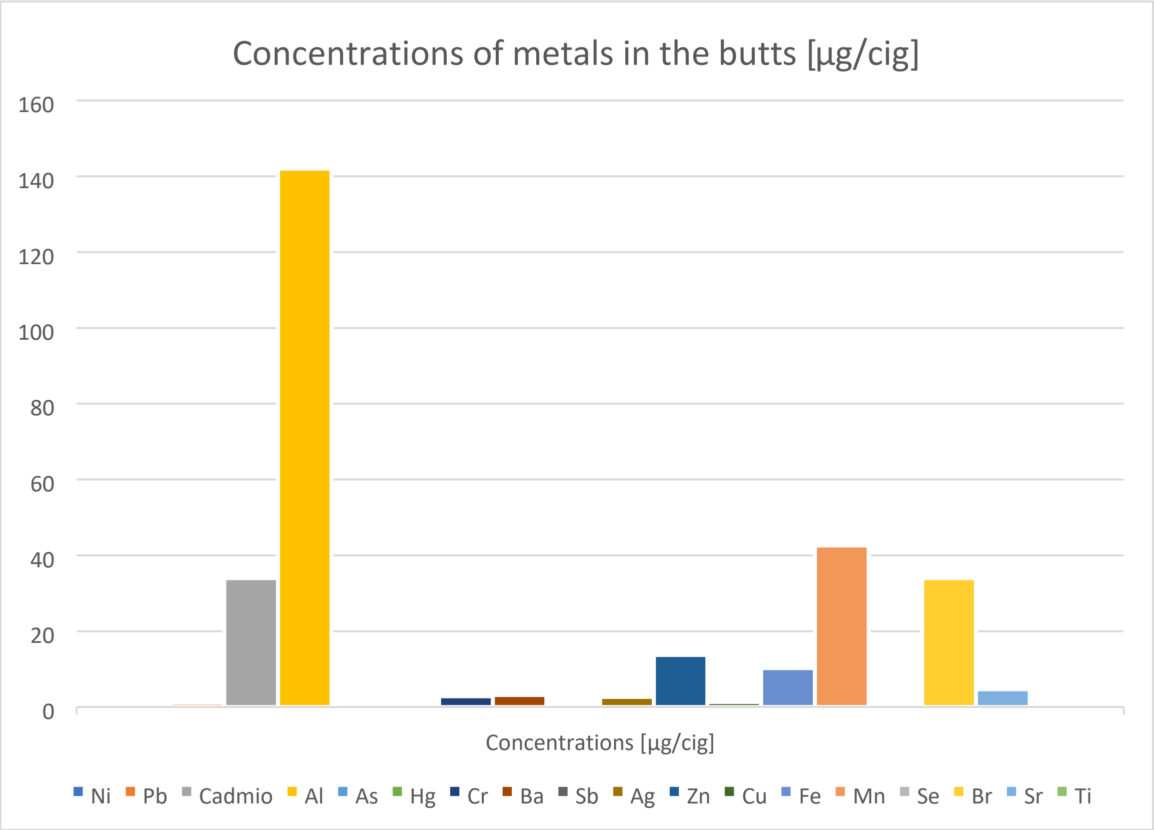


Figure 8:Concentration of metals in the butts, author's elaboration.

Studying the whole process of tobacco industries, from the field of Tobacco plants to the finished product, can analyze the percentage of different metals in each example studied. Table 7 shows the analysis of four metals, copper, zinc, cadmium, and manganese, in tobacco leaves, cigarette ash, butt, and smoke were made by atomic absorption spectrometry.

Table 4:Average of metals

Average concentration(microgram/g)				
	Cd	**Zn**	**Cu**	**Mn**
Tobacco leaves	1,5	29	48,8	47,4
Cigarette ash	0	20,7	12,21	32,8
Cigarette butt	0,84	8,7	4,21	10,8

To sum up the characteristic of gases emitted are:

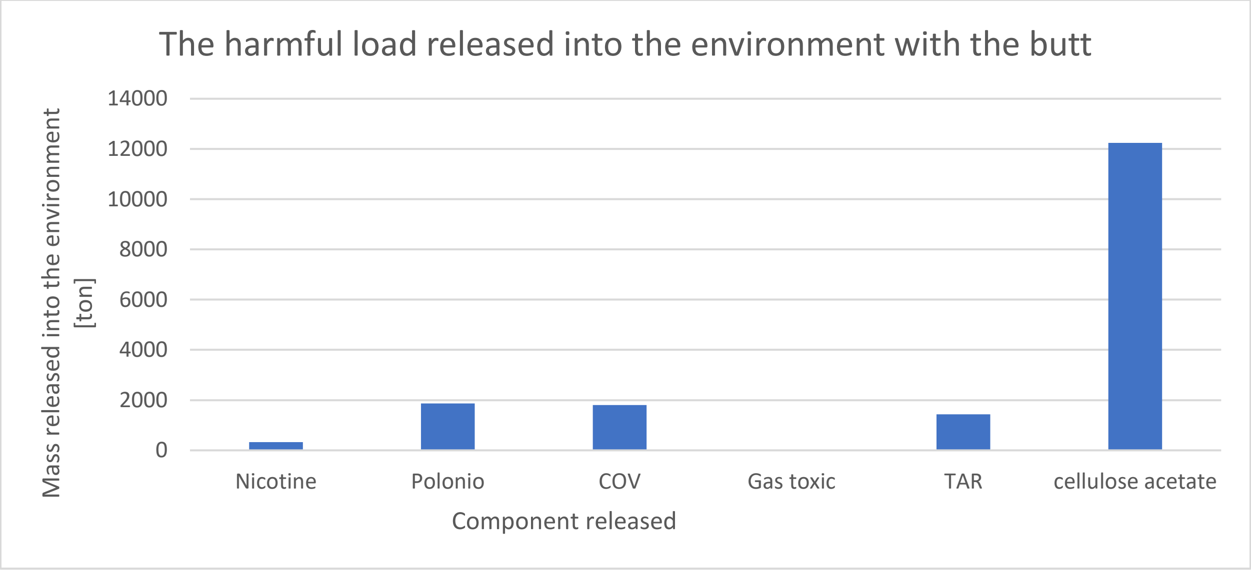


Figura 9:The harmful load released into the environment

2.10 Environment

The disposal of waste is even one of the most important problem of environmental pollution, however more important is the quantity of waste that every day can be found on the floor or in normal life. The butts of cigarettes remain the most popular waste that everyone can find in every city or even in natural environments. The following is one table that can resume the percentage of waste found in the Mediterranean Sea. This research did not take into account any waste other waste but cigarette buttresses. Although each buttock has just a little amount of risk, the large number of smokers magnifies the issue.

There are approximately 1.5 billion smokers around the globe, and each year, 4.5 million billion cigarettes, or 845,000 tons, are released into the atmosphere.

We have worldwide contamination of 7,800 tons of hazardous chemicals released into the environment with the buttocks if we take into account only the precaution that of the 6.5 kg of tobacco consumed annually on average by each smoker (World Bank data), at least 10% of the harmful products remain in the cigarette butts. According to the DOXAISS study,), 2018, [5] there were an estimated 13 million smokers in Italy in 2009, and each person smoked an average of 15 cigarettes per day. Because of this, 195 million butts are produced in Italy every day, totaling more than 71 billion per year. These butts are largely dumped everywhere they can be (on roads, pavements, in parks, along beaches, on railroad tracks, etc.), without regard for any criteria and with little thought given to potential environmental harm. After declining after the Sirchia law (Law 3/2003, Art. 51) went into effect (10 January 2005), cigarette smoking progressively grew again, which led to a rise in the buttocks as well. With the change of the law, it is not allowed to smoke inside of the public local so the smokers are obligated to smoke outside in as evidenced by the fact that the buttocks are at the top of the list of so-called urban dirty in the absence of ashtrays, buttocks is eradicated in the environment.

Table 5:Major wastes found in the Mediterranean Sea

Waste	%
Butt	40
Plastic bottle	9,5
Plastic bags	8,5
Aluminum bottle	7,6
Lids of plastic bottles	7,3
Glasses, dishes, and disposable cutlery	5,8
food packaging products	2,5
plastic straws	2,1
pulls rings of cans	1,9

2.11 Butts and Fires

Fires and/or explosions are examples of "side effects" of unattended, discarded, or abandoned cigarettes in the house or outdoors. Smoking cigarettes has traditionally been seen as a risky habit due to the potential for fires to start, which can have terrible results. As a result, deaths from smoking cigarettes are correctly included in worldwide figures of deaths from tobacco smoke.

In the following tables is summarized the number of fires according to Carmine Ciro Lombardi et al, 2009, [4] .

Table 6:Number of fires due to cigarettes butts

Year	**number of fires due to cigarettes butt**
2007	6000
2008	6331

2.12 The potential effect of smoked cigarette butts on the environment

Figura 10: Smoked cigarette butts: Unignorable source for environmental microplastic fibers[6]

The main component of cigarette butts, that we have already spoken about, is a common plastic pollutant present in the environment.

Cigarette butts are really dangerous mostly because the complexity of the harmful compounds present in the cigarettes is almost unknown, more of 15.000 compounds are present in the cigarettes according to the article of Mr. Maocai Shen et al [6]. In this article he explains the presents of this solid material in our environment and also the development of the way into rivers, lakes and finally the ocean. In this way this waste continues to release microplastic fibers that can affect the ocean environment and could change it. Moreover, during the path of this waste in the ocean more toxic substances, for instance nicotine or worst compounds like tar come absorbed by the fish and poisoned.

The problems related to this environmental pollution are several, which one depends on the hearth and environment conditions. After several years of reckless behavior that led an increase of microplastic production this became one of the most problematic wastes of the word, also because it is difficult to quantify the percentage of microplastic presents in the marine environment, researchers have estimate that about 4.8–12.7 million tons of plastic waste flow into the ocean and it is destinated to grow.

The critical point reached of microplastic pollution, due to the small particle size, made it possible to understand that we must find a solution, to reduce the impact of smoking on human health.

This problematic situation is move on the characteristic of the filters, that is not sustainable given by the molecular structure of the cellulose, the tobacco industry's produce around 6 trillion of cigarettes per year and most of them are throw away without any consideration. To sum up has been described the generally composition of the cigarettes butts that it is not only the cellulose acetate, that it is not biodegradable, but also tar and polycyclic aromatic and all of them are harmful compound for the ocean environment and also for who live there.

3 Methods to exploit this waste.

Trillions of cigarettes are smoked every year, becoming cigarette butts one of the most common types of waste in the word, according to Mr.Samuele Marinello et al [7] . The harmful property of this material is due to the toxic substances that they contain that are a risk to the environment and organism that live there. Taking into account that this waste is not biodegradable and it is really present in our daily lives they make the cigarette a big problem. For this reason, several scientist and entrepreneurs decided to find some opportunity to exploit this waste. Below it is reported a cake diagram in which is showed some industry that already use this waste to produce and re use this solid waste.

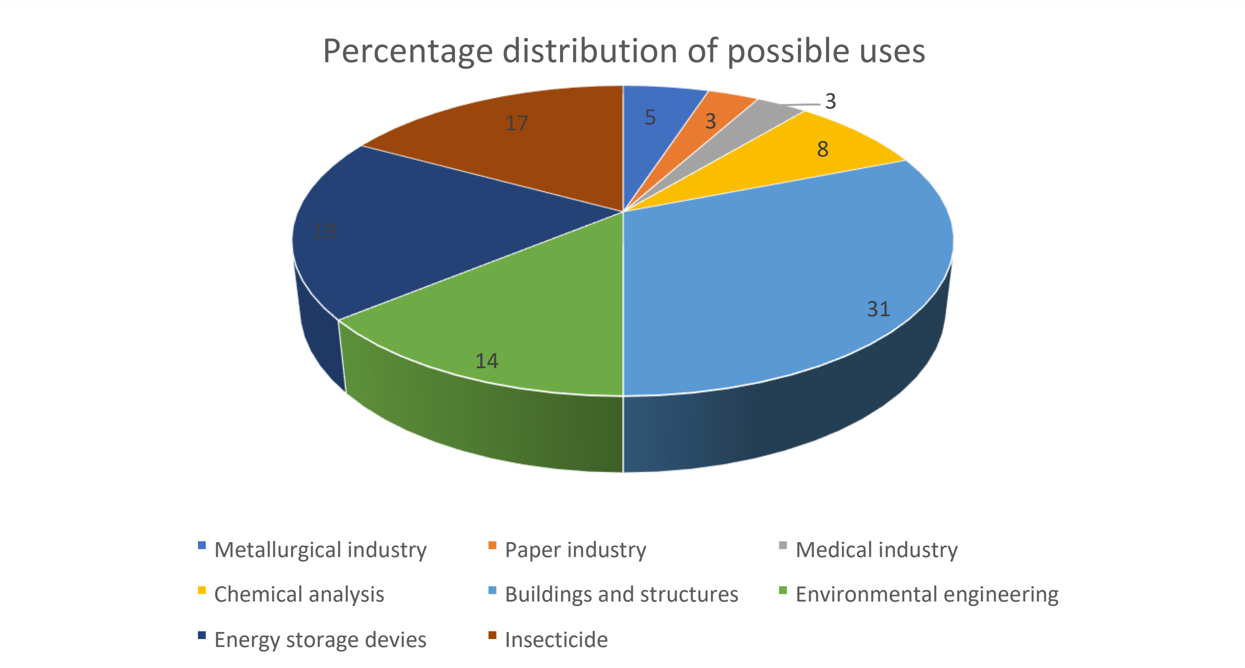


Figure 11:Percentage distributions of possible uses, author's elaboration

3.1 Firing bricks

Bricks are one of the most common masonry units due to their various properties. Attempts have been made to incorporate waste in the production of bricks thanks to the discovery of the process by A.Mohejerani, 2016, [3] . Recycling such wastes by incorporating them into building materials is a practical solution to the pollution problem. However, issues waste teaching is still relevant and require testing. The utilization of waste materials in clay bricks usually has a positive effect on the properties; however, a decrease in performance in certain aspects has also been observed.

Positive effects, such as lightweight bricks with improved shrinkage, porosity, thermal properties, and strength can be obtained with recycled waste. Moreover, lower energy consumption during firing through the contribution of the high calorific value provided by many types of waste has also been achieved. Furthermore, the high temperature in the firing process allows volatilization of dangerous components, changes the chemical characteristics of the materials, and eliminates the toxic components through the fixation process Incorporating CBs in fired bricks could provide a sustainable method to immobilize toxic chemicals that pose a very high risk to the environment. The cellulose acetate content in CBs is an organic content that could make a positive contribution to the firing process. Therefore, a secondary environmental impact from CB incorporation can be achieved through the reduction of firing energy.

3.2 Asphalt

The progress of advanced materials has given the pavement industry a new dimension. New approaches and procedures have been implemented to ensure the long-term viability and performance of roads and highways. Research works are currently underway to assess the suitability of various waste materials, like polymer and plastic for use in road construction, like asphalt. Plastic was previously integrated into the binder, which improved rutting and fatigue efficiency. For medium-traffic conditions, quarry waste has also proved to be an adequate substitute for conventional aggregate. Building demolition waste in the asphalt foundation and sub-base layer minimized emissions and gave the materials a second life.

One of the largest asset management sectors is roads and highways. Based on the gradation, asphalt pavements are classified in Dense Graded Asphalt, Gap Graded Asphalt (e.g., Stone Mastic Asphalt) and Open Graded Asphalt (water permeable asphalt). Dense graded particle distribution is maintained in DGA, and a gap graded particle distribution is maintained in SMA. DGA is the most popular type of asphalt. This type of asphalt is used both in the base layer and top layer. DGA requires less amount of bitumen Compared to SMA. SMA is popular due to its interlocking skeleton. While gap-graded aggregates are used in SMA, finer aggregates fill up the gap between the coarse aggregates and provide excellent performance in the long run. However, this type of asphalt requires a higher percentage of bitumen, and due to cost issues, only heavy-duty pavement requires SMA, for this reason, is important to make more not expensive asphalt. With the add of CB is possible to fix some problems related to environmental and the cost of asphalt production, according to Md. Tareq Rahman et al, 2020, [8].

3.3 Re-Cig

The characteristic of CB allowed Re-Cig to find an innovative process to obtain from the filter of the cigarettes a polymer useful for a lot of fields, in this case the production of eyeglass, mobile phone covers, object for 3D printers. Following a circle economy philosophy it allows to reuse and reevaluate this type of waste, according to Re-Cig brochure, [9].

4 Project

The complexity and harm of cigarette butts bring us to continue the research to find a new method to re-use this problem that affects the whole world. The goal of this research is to find optimization of the process of pyrolysis, using different instruments the most important is the reactor in which is possible to make different experiments with several conditions of temperature. The research was carried out following different steps, first of all, to understand the composition and thermodynamics quantities of the filter.

4.1 Thermodynamics and chemical kinetics

Before starting the experimental part of this work, was important to find the principal thermodynamics quantities that take place in the equations. The first part of the project was the study of heating rate and temperature development. According to the article of Michael Schiling, 2010, [18] the molecular formula of cellulose acetate is:

$$C_{76}H_{114}O_{49}$$

And the principals' thermodynamics properties are:

$\mathrm{PM} = 1811.7\,\frac{g}{mol}$

$\rho = 60\ Kg/m^3\ \ it\ is\ the\ density\ of\ cellulose\ acetate$

$k = 0{,}0251\ \frac{W}{m*K}\ ;\ it\ is\ the\ thermal\ conductivity\ of\ cellulose\ acetate$

$Cp = 1480\frac{J}{K};\ it\ is\ heat\ capacity\ of\ cellulose\ acetate$

$\alpha = \frac{k}{\rho * C_p} = 2.83 * 10^{-6};\ thermal\ diffusivity\ of\ cellulose\ acetate$

$\mu = 0{,}11\ Pa \cdot s;\ it\ is\ the\ viscosity\ of\ cellulose\ acetate$

With these values were possibly evaluated and understood, for the first time how may is the behavior of the butt. Previously studied by literature according to Ralph S. Jessup, 2010, [21] and also Chiung-Fen Chang, 2000, [22].

The first calculating method involved creating a MATLAB code that contained the errors' function. That is the solution of the heating equation:

With some hypotheses:

$$\frac{\delta T}{\delta t} = \alpha \frac{\delta^2 T}{\delta x^2}$$

$$\theta = 1 - \mathrm{erf}\,(\frac{x}{\sqrt{4\alpha t}})$$

Where:

$\theta = \frac{T(t)-\mathrm{T}\infty}{T^{wall}{}_{-\mathrm{T}\infty}}$ is the adimensional temperature.

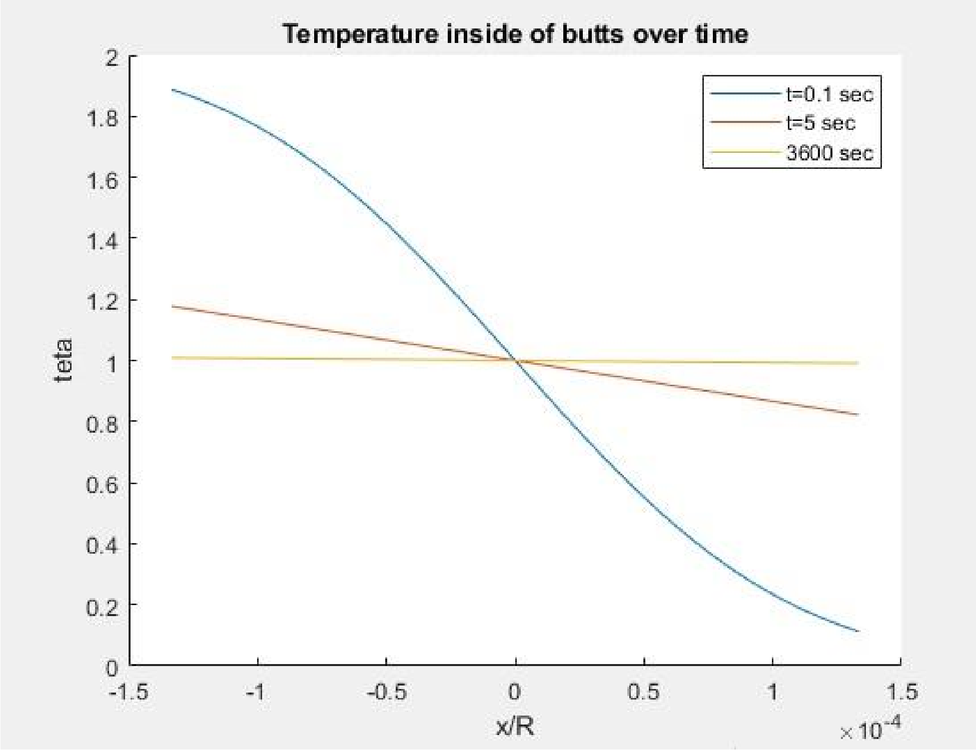


Figure 15: shows the development of Temperature inside of the butt

4.3 Equations

This process is described by a system of equations in which are including the variables that take place and characterize the process. Each equation takes place together for this reason our process si not easy to evaluate.

The general form of balance:

$$A + E \leftrightarrow G + U$$

In this system is not possible the approximation of steady state, our purpose is to evaluate the heat transfer and mass transfer also over time.

Heat balance

$$mCp\frac{dT}{dt} - k\nabla^2 T = q_{convective} + \Delta H_{reaction} * \frac{dX}{dt}$$

Where X is used to express the conversion

In the heat equation, we can find the conduction flow and convective flow. This project aims to describe the behavior inside of our test in order to solve this problem iteratively or using modeling. Subsequently will explain how to find the value of $\Delta H_{reaction}$.

Kinetic

$$dX_1/dt = \mathrm{A}_1 * \exp\left(-\frac{Ea_1}{RT}\right) * (1-X)^{n_1}$$

$$dX_2/dt = \mathrm{A}_2 * \exp\left(-\frac{Ea_2}{RT}\right) * (1-X)^{n_2}$$

$$\frac{dX}{dt} = \alpha_1 \frac{dX_1}{dt} + \alpha_2 \frac{dX_2}{dt}$$

At the beginning of the experimental part was thought to consider only the cellulose acetate like promoted reaction, after some calculations that will explain in Chapter 7 multiple factors have to be considered.

Thanks to this first analysis it is possible to understand that after a certain value of time won't be any difference in temperature inside the example. But the hypothesis is too strong, the reaction exists and it is not negligible. The determination and assessment of the thermodynamic quantities involved in the physical phenomena form the basis of the first thesis study. Prior to implementing the mathematical model, it was important to determine which reaction kinetics was most appropriate.

The reaction should generally take the following form:

$$aA + bB \rightarrow cC + dD$$

In this work is considered the reaction of the butt, in the pyrolysis process, and to study this process is essential to find the reaction enthalpy.

$$C_{76}\,H_{114}O_{49} \rightarrow 27C_{Solid} + 49CO + 57H2$$

Considering the above reaction is it possible to determine the value of the enthalpy reaction. The temperature value is set equal to 400 $°C$.

Table 7: Resume of enthalpy formation for each component

	Enthalpy formation [T=25 °C]	
Cellulose acetate	-58,8	KJ/Kg
CO	-3928,58	KJ/Kg
H2	0	KJ/Kg
C(solid)	0	KJ/Kg

According to thermodynamic theories, the value of heating reaction is a linear combination of stoichiometric coefficients and formation enthalpies.

$$\Delta H_{Ro} = \sum v_i \Delta H_{oformazione}$$

$$\Delta H_{R^o} = c\Delta H_f{}^C + d\Delta H_f{}^D - (a\Delta H_f{}^A + b\Delta H_f{}^B)$$

Basically the value of ΔH_{R^o}indicates the energy variation required, under the reference circumstances, for the full creation of the products and the transformation of the reagents.

We may distinguish between two alternative definitions of reaction enthalpy depending on the enthalpy value.

If the value of ΔH_{R^o} is:

- Positive, the reaction will be termed endothermic, meaning that the reaction leads to substances with a higher energy contribution so it will result in energy absorption from outside.

- Negative, the reaction will be termed exothermic, meaning that the reaction leads to substances with a lower energy contribution. You will be releasing energy outward.

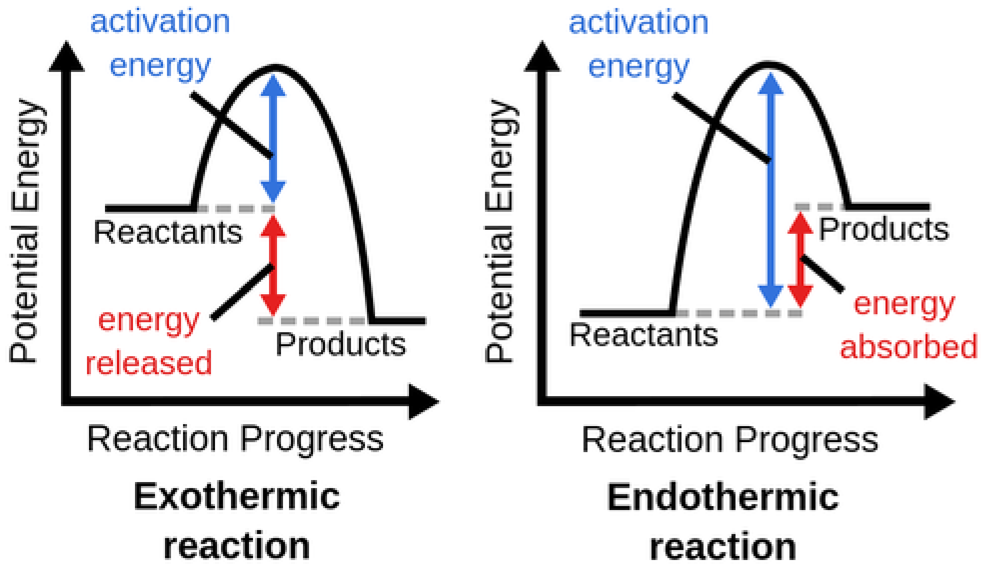


Figure 16: Graphs representation of enthalpy reaction[23]

$$\Delta H_{Ro} = 5{,}76\ e^{6}\ \frac{KJ}{Kg}$$

The value is positive, so the reaction is endothermic, it means that is favored by an increase in temperature, so we are not limited by a high level of temperature. By the way, we cannot use too high temperature because we are working with carbon, we don't want to crack of carbon.

4.4 Reactor

The reactor supplied to the University of Compiegne, in which this experiment took place, was in **a fixed bed reactor.**

This is divided into three different parts:

i. The top of the reactor has two different pipes in which the gases come out, one of these guests is the thermocouple.
ii. The middle of the reactor may be represented as a cylinder in which one component, activated alumina, is put, that is our fixed bed.
iii. The final part is composed of a chain and two different holes, in which we will send the gases.

Figure 17:Fixed bed reactor author's elaboration

The composition of this reactor is quartz (SiO_2), that allows reaching high values of temperature, indeed the maximum temperature that is possible to reach is over 1000 ℃. Anyway, in this work is never crossed the value of 450 ℃.

The dimensions of this reactor are resumed in the table below.

Table 8: Reactor sizes

Reactor size		
Diameter	4,00E-02	m
Length	1	m
Area	1,26E-03	m^2
Volume	1,26E-03	m^3

4.5 Nitrogen

The pyrolysis process is led under nitrogen control to ensure that the process of degradation continues without any oxygen present. For the thermal conditions, the thermodynamics quantities of Nitrogen are found in the literature.

Table 9:Thermodynamics quantities of Nitrogen

Nitrogen		
Density	1,1606	kg/m^3
Cp	1036	J/KgK
Viscosity	1,74E-05	Pas
k	2,58E-02	W/mK
Molecular weight	28	g/mol

After having evaluated the principal quantities that take place in the equations is the time to find the value of the convective coefficient, according to the transfer phenomena to discover the regime of this experiment it is necessary to calculate the value of the dimensionless number of Reynolds, which describes the rate of inertial forces in comparison to viscosity forces.

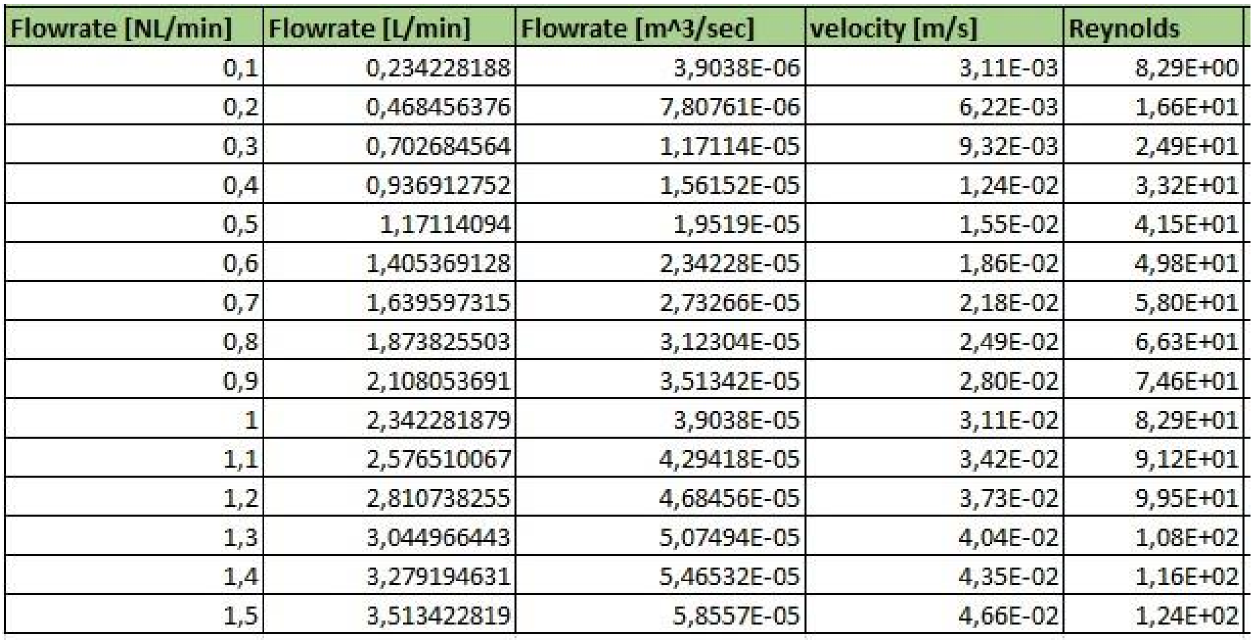
$$Re = \frac{\rho_{fluid} v D_{reactor}}{\mu_{fluid}}$$

If the value of Re is higher than a certain value that is already determined the regime will be turbulent, so will have a different value of Temperature inside the reactor.

4.6 Fluid's Velocity

A flow rate controller was used to set the experiment's volumetric flow rate at various settings. Making numerous calculations with different amounts of volumetric flow rate was crucial since it was vital to understand how the fluid velocity influenced the computations at the beginning of the process.

Table10: Values of Reynolds number



Flowrate [NL/min]	Flowrate [L/min]	Flowrate [m^3/sec]	velocity [m/s]	Reynolds
0,1	0,234228188	3,9038E-06	3,11E-03	8,29E+00
0,2	0,468456376	7,80761E-06	6,22E-03	1,66E+01
0,3	0,702684564	1,17114E-05	9,32E-03	2,49E+01
0,4	0,936912752	1,56152E-05	1,24E-02	3,32E+01
0,5	1,17114094	1,9519E-05	1,55E-02	4,15E+01
0,6	1,405369128	2,34228E-05	1,86E-02	4,98E+01
0,7	1,639597315	2,73266E-05	2,18E-02	5,80E+01
0,8	1,873825503	3,12304E-05	2,49E-02	6,63E+01
0,9	2,108053691	3,51342E-05	2,80E-02	7,46E+01
1	2,342281879	3,9038E-05	3,11E-02	8,29E+01
1,1	2,576510067	4,29418E-05	3,42E-02	9,12E+01
1,2	2,810738255	4,68456E-05	3,73E-02	9,95E+01
1,3	3,044966443	5,07494E-05	4,04E-02	1,08E+02
1,4	3,279194631	5,46532E-05	4,35E-02	1,16E+02
1,5	3,513422819	5,8557E-05	4,66E-02	1,24E+02

As already said the volumetric flow rate is determined and controlled by a flow rate control, therefore this value is not the really flow rate that is inside of the reactor for this reason, thank to perfect gas's law, is possible to change the normal value in the really volumetric flow rate

$$V_{\text{Treactor}} = V_{\text{Tnormal conditions}} * \frac{T_{reactor}}{T_{\text{normal conditions}}}$$

Which normal conditions is:

$$\{\, T \;=\; 25°\text{C} \;\; P = 1\, atm \,\}$$

The velocity of nitrogen inside of the reactor was determined by the definition of volumetric flow rate.

$$V_{Treactor}{=}S * v$$

Where S is the area of reactor, already evaluated in Table 12.

Reynolds number calculations allow us to conclude that our system's flow is laminar, not turbulent. For which there are no vortex and different values of temperature inside of the reactor, that means internal friction forces that control the behavior of the flow. Contrary to turbulent flow, laminar flow allows even minute fluid layers to flow smoothly over one another without intermixing.

4.7 Convective coefficient

It is time to comprehend how the heat behaves within the reactor once the behavior of the heat inside the cigarette butt has been discussed. For this reason, one must calculate the value of h that is the convective coefficients. The article of H.Sandusky et al, 1977, [27] that determines the convective heat of an organic compound allows to determine the value of heat in the environment of this experiment, which is the reactor.

The method to evaluate this coefficient is given by Nusselt theory. In literature and in the whole chemical engineer degree it was already define the expression of the Nusselt number, which is an adimensional number that describes the rate of convection and conduction in the fluid phase.

$$Nu = \frac{(h * D_{butt})}{k_{nitrogen}}$$

Exists another expression of Nu, the function of other adimensional numbers, which are Reynolds and Prandtl. That is a dimensionless number that represents the proportion of a viscous fluid's kinematic diffusivity to thermal diffusivity.

$$Pr = \frac{\mu * Cp}{k}$$

$$Pr = 0{,}698$$

$$Nu = 0{,}989 * Re_{0{,}33} * Pr_{0{,}33}$$

The following table resumes the values of different h with different values of nitrogen velocity, the temperature for these cases is set at 400 ℃

Table 11: Convective coefficient Biot number

Nu	h [W/m^2K]	Bi
1,77	38,20	0,18
2,24	48,12	0,23
2,56	55,08	0,26
2,82	60,62	0,29
3,03	65,29	0,31
3,22	69,38	0,33
3,39	73,03	0,35
3,55	76,35	0,37
3,69	79,41	0,38
3,82	82,24	0,39
3,94	84,89	0,41
4,06	87,39	0,42
4,17	89,75	0,43
4,27	91,99	0,44
4,37	94,13	0,45

Another crucial factor for this work is the evaluation of the Biot number, which describes the interaction of heating and is the first data that might confirm that there is no gradient of the temperature inside the example.

$$Bi = \frac{h}{k_{butt}} * D_{butt}$$

The importance of this number lies in the theory which:

If the number of Biot is less than 1 it means that the conduction, in comparison to the convective flow is negligible, therefore one can consider the temperature, inside of the example**, homogenous.**

5 Experiments

The University of Compiegne's laboratories served as the site for this study's experimental component, and thanks to the teacher Elias Daouk, we were able to make these experiments in whole control and safety.

The experiments were carried out with different instruments like volumetric flow rate control. In which it was possible to set the target flowrate of N_2 needed for the process.

Figure 18: Flow meter author's elaboration

5.1 Themocouple

A thermocouple is an electrical device consisting of two dissimilar electrical conductors forming an electrical junction. A thermocouple produces a temperature-dependent voltage as a result of the Seebeck effect, and this voltage can be interpreted to measure the temperature. Thermocouples are widely used as temperature sensors.

Commercial thermocouples are inexpensive, interchangeable, supplied with standard connectors, and can measure a wide range of temperatures. In contrast to most of the other methods of temperature measurement, thermocouples are self-powered and require no external form of excitation. The main limitation with thermocouples is accuracy; system errors of less than one degree Celsius (°C) can be difficult to achieve.

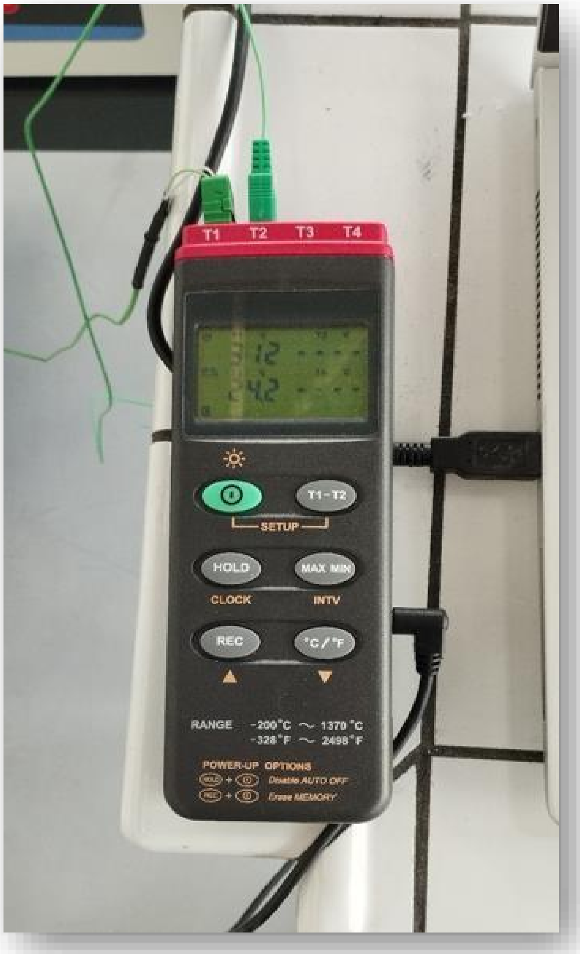


Figura 19: Thermocouple used for this experiment, author's elaboration.

In the continuation of the experiments was chosen to follow a protocol, taken from literature. This allows us to simplify the process since the following can be summarized:

- Take the example, put off the paper and measure it

- The example needs to stay for a certain time in one oven with a temperature of 105 ℃, to allow the evaporation of water.
- Take the example and put it inside the thermocouple, this is important to have some information about the value of temperature inside the butt.
- Putting the example inside of the reactor, here is important to pay attention because the reactor is fragile and thermocouple also.
- Close the pipe in which we put the thermocouple because there must be no oxygen in the reactor.
- Open the bottle of nitrogen, and chose the volumetric flow rate, in the controller, for these cases we started with 1 NL/min .
- Set the temperature target in the Furnace.
- Switch on the Furnace.

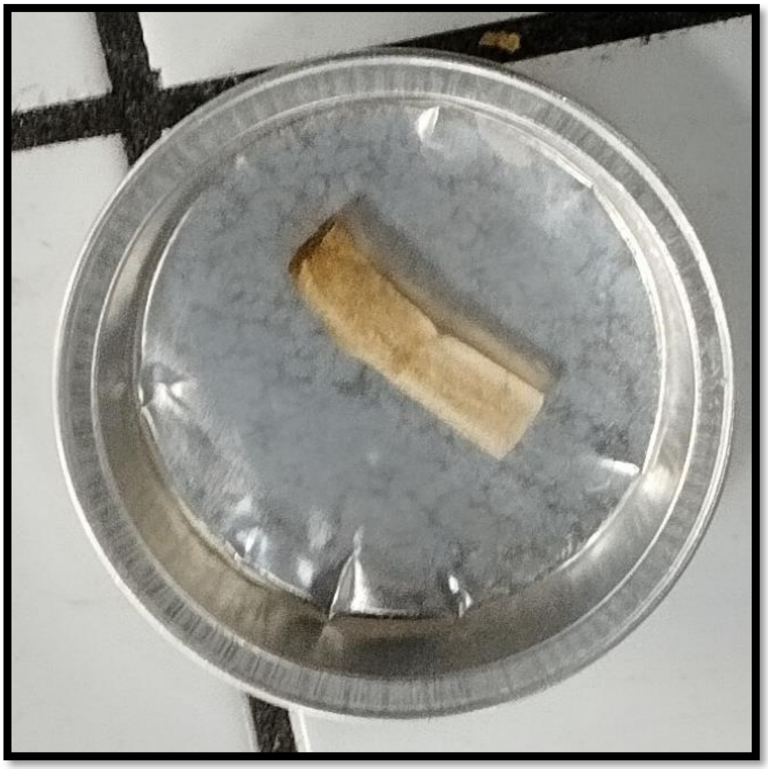


Figure 20: Example before being put inside the reactor

The first results that were observed in the first weeks confirmed the hypothesis in which, after a certain value of time, and with the reaction goes ahead there isn't a range of temperature inside of our experiment.

In particular two experiments were carried out with the same temperature target.

5.2 Pyrolysis

Pyrolysis is a thermochemical breakdown process for organic materials that uses heat but does not use any oxygen (apart from that provided by the structures themselves, as in combustion). Under these circumstances, it experiences thermally induced hemolysis, which causes the original chemical bonds to split. This sets off a series of molecular and radical chain reactions that result in the formation of simpler molecules, primarily vapors, aerosols, and gases, leaving a carbon-rich solid residue (char). The industrial cracking and treatment of thermal waste stand out among the primary pyrolytic processes that are employed on a big scale. Wood pyrolysis was the primary method of producing methanol before to 1925.

The condensed organic components then undergo cooling, forming a black liquid phase (bio-oil or tar) with a calorific value that is roughly half that of conventional fuels.

Various forms of pyrolysis

Different forms of pyrolysis may be realized under the process' experimental circumstances; in general, we can classify them into three categories according to M.Hazbehiean et al, 2021, [24]:

- **Slow pyrolysis** (slow pyrolysis) is characterized by a low heating speed of the fuel with modest reaction temperatures (about 200-350 °C) and with very long residence themes. This particular type of pyrolysis is typically used to produce high amounts of char (over 30%).
- **Conventional pyrolysis** can be achieved with a temperature range not exceeding 600 °C, having a moderate heating rate. Extremely important are the residence times, ranging from 10 seconds to 10 minutes). The products generated between gaseous (syngas), solid (char) and liquid (tar) substances are comparable.
- **Fast pyrolysis**, is characterized by high heating speeds, having a temperature/time ramp higher than 100 °C/s, reaching by a very fine grain size supply, and by very short residence times of the gas phase (less than 2 seconds).

5.3 First experiment

Following the protocol already explained, but for the first cases we didn't put the example inside of the oven, so the example considered having a mass of 0,1532 g, is put in the reactor at the end of the experiment the thermocouple registered this temperature development:

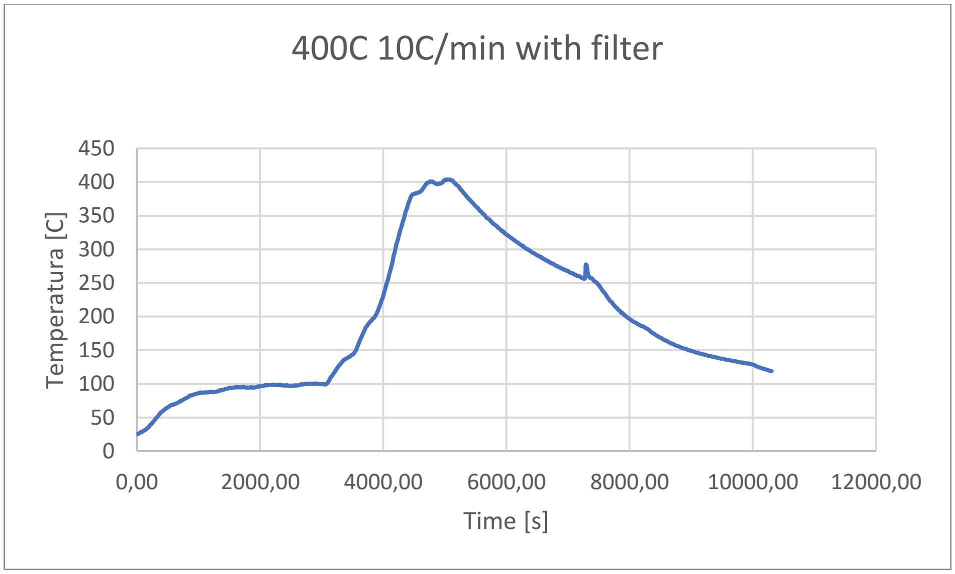


Figure 21: Temperature inside of the example over the time, author's elaboration

We are unable to open the reactor while operating at high temperatures and with this particular type of reactor to track the trend of the mass over time and create a conversion graph, for this reason, was necessary to take the example at the end of the process when the cooling down phases ended.

The mas found was about 0,021 g this means that the percentage of solid phase is about 16%, it means that 16% of the initial mas remained in the reactor and this is approximately the carbon mass present in the example.

The second experiment was carried out with the same condition of flow rate and temperature target but in this case, was not put anything inside of the reactor, the main reason is that we need to discover how is the behavior of temperature in the environment.

The results are given by the thermocouple:

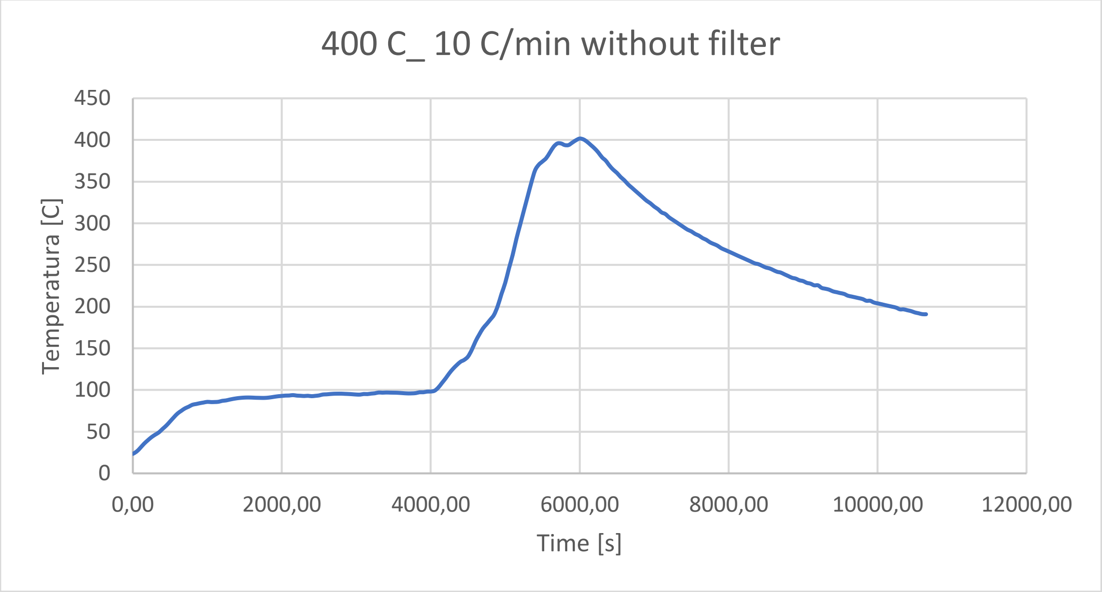


Figure 22: Temperature development in the reactor over time, author's elaboration.

It is evident from this second experiment that the temperature gradient is the same as that previously computed when the cigarette butt was present. This entails that was discovered different important behaviors.

First of all the temperature set in the reactor allows us to say that there is no thermal resistance inside of the experiment, so the heat diffusivity is negligible in comparison to the convective flow. This discovery allows for simplifying the heating equation. The same equation is not possible to solve it because is a partial differential equation of second order, but now the situation is changed.

The experimental phases continued with the intention of discovering and answering some questions, before starting this experiment the study of the bibliography has been of fundamental importance. What has studied the components of each cigarette, but in particular, for cigarette butts are many and varied alike, so it is not possible to refer to individual components, for this reason, was important to understand what there is inside of each buttock.

Parallel to reactor experiments some buttocks were put in the oven at different times, is necessary to make one consideration, the examples were taken from the public ashtray so the initial mass and conditions are not the same or accurate.

5.4 Moisture

To improve heat exchange, it was necessary to put the examples in a specific oven capable of drying them, that is to remove some part of water presents. Below are the first diagrams obtained by the first experiment of drying:

Tabella 12: Moisture 5%

Moisture 5%	
time [s]	m [g]
0	0,133
4200	0,1321
10200	0,128
13800	0,1266

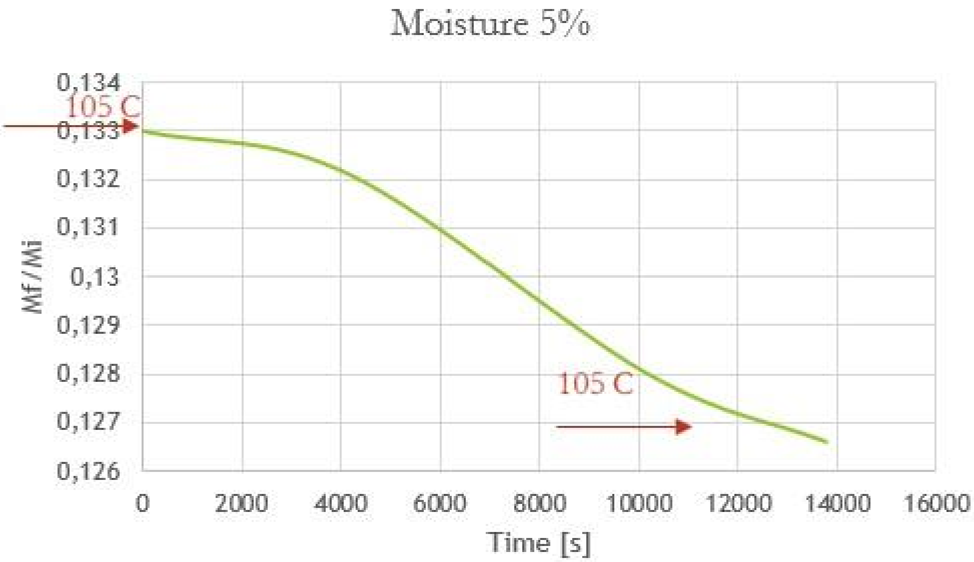


Figure 23: First experiment of water percentage, author's elaboration.

According to the literature, the maximum percentage of water inside of the examples should be around 7-10%, to prove this was carried out monitoring for one day. Each certain value of time was studied in the final mas and built this graph which is evidence that the maximum value of water percentage inside of the example is 5%.

Tabella 23: Moisture 10%

Moisture 10%	
time [s]	**m [g]**
0	0,1222
10800	0,1187
22800	0,1169
33600	0,1147
206400	0,1102

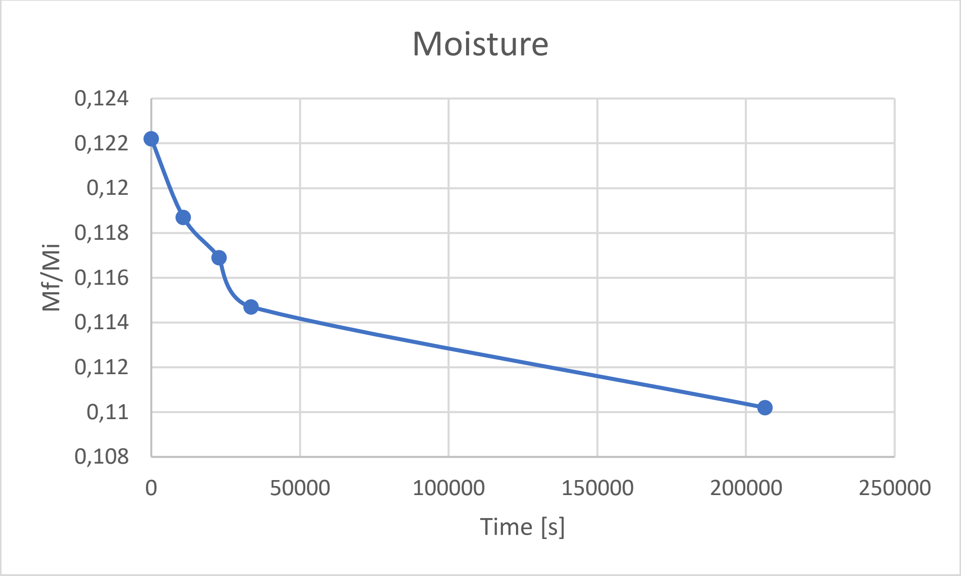


Figure 24: Ultimate experiments of water percentage author's elaboration.

Because the initial curve, Figure17, had not yet reached the plateau, it was decided to continue the research while leaving the cigarette butt inside the oven for more time. The last curve that may describe the moisture inside the experiment is Figure18. In this case, the percentage of water is 10%, this is supported by the fact that no change in mass was seen when the experiment was placed within the reactor for longer after the previous figure was observed.

After some experiments were decided to put the experiment, under target temperatures for more time and observe if the is some variation in the reaction. An example was led to 300 ℃. There is no significant change considering the others experiment. Generally, it is possible to say that pyrolysis process improves the yield at lesser quantities of water are present in the organic material used.

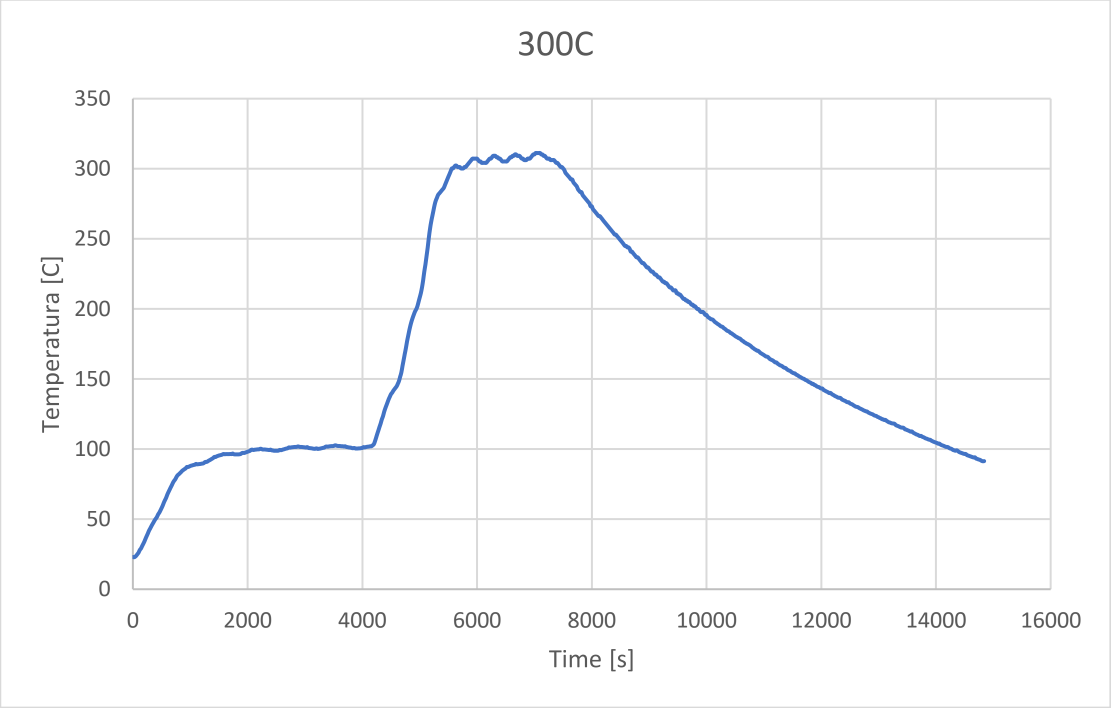


Figure 25: Temperature target 300C with heating velocity 10 ℃/min, author's elaboration.

5.5 Conversion

Different experiments carried out at various temperatures and heating velocities enabled the writing of conversion curves, considering the conversion as the rate of final mass over beginning mass it was possible to built the following curve in which each point indicates a different experiment carried out at different temperature. This graph gives the first idea and first results on which the subsequent experiment was based.

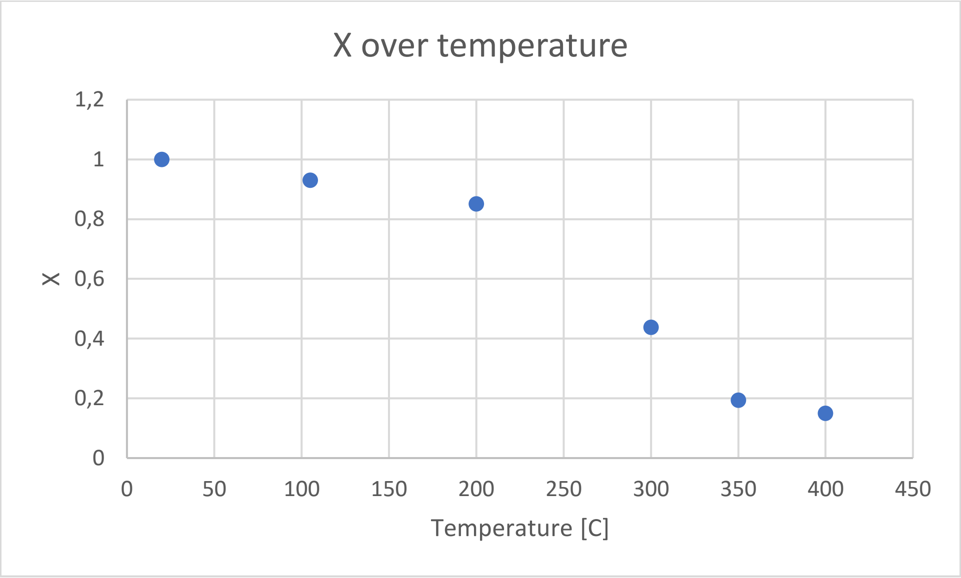


Figure 26: Mf/Mi over temperature at 10 °C/min, author's elaboration

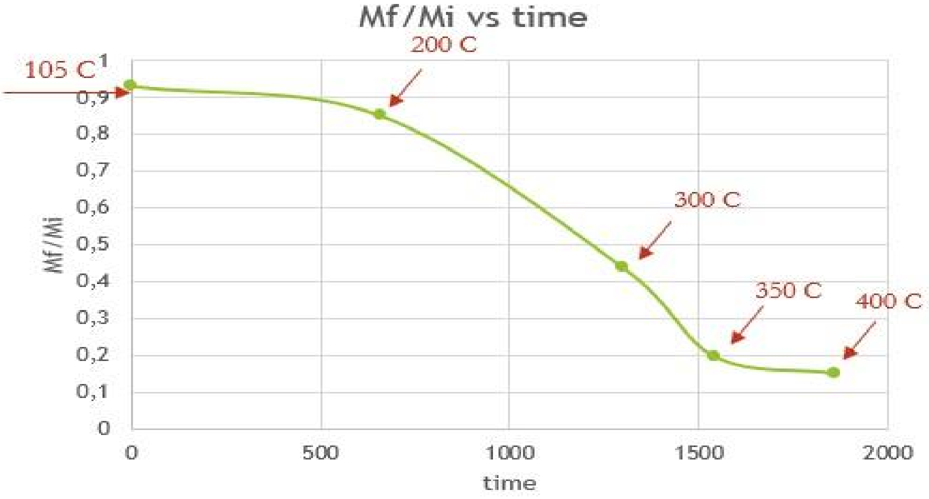


Figure 27: Conversion over time 10 °C/min author's elaboration.

Another important point of this research is to evaluate the conversion of the example with different heating velocities, Figure26 was carried out with one heating velocity of 10 ℃/min. The maximum conversion reached was 16%.

The protocol used for each point is:

- Make the experiment with the value of the temperature target.
- Register the curve for temperature over time.
- Take the range of time for each point.
- Build the curve which has the range of time on the x-axis and the value of remaining mass on the y-axis.

Figure 28: Examples after the pyrolysis process, author's elaboration.

Figure28 shows the first three experiments that we did in the reactor, especially (from right to left) experiments that takes place at 250 ℃, 300 ℃, 400 ℃.

The experimental part continues with the same methodology but different values in order to understand if the heating velocities affect the reaction. The other experiments were carried out with $15\ ^{\circ}C/min,$ because another point of this research is to define the correct heating velocity to reach the optimal conversation whereby the best way to lead these experiments.

By using the 15 $°C/min$ heating velocity it was possible to obtain the following data:

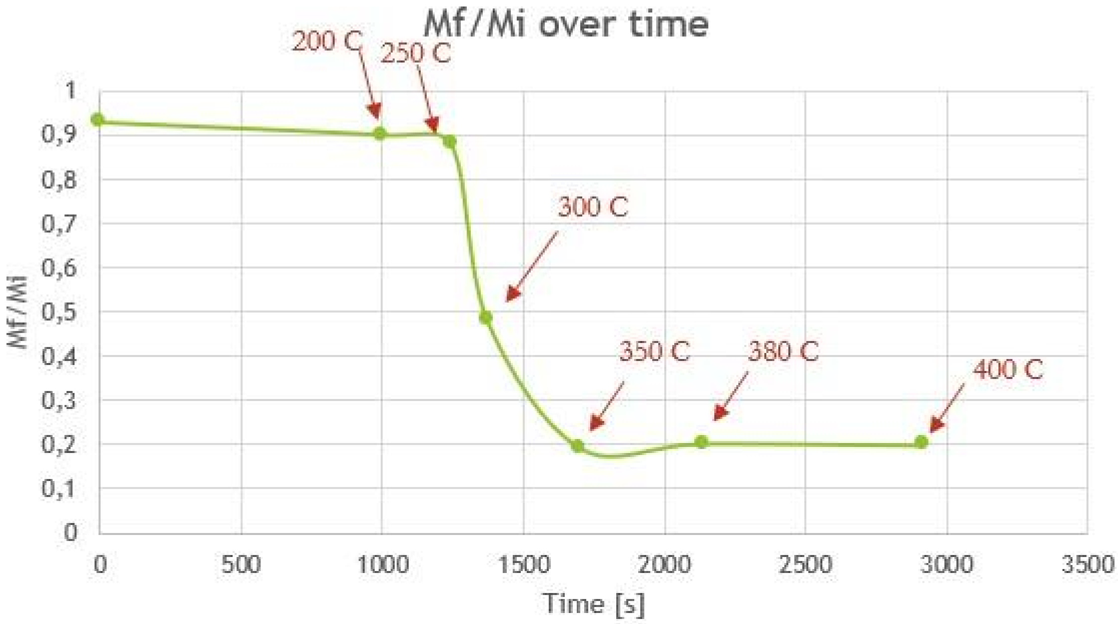


Figure 29: Conversion over time with 15°C/min author's elaboration.

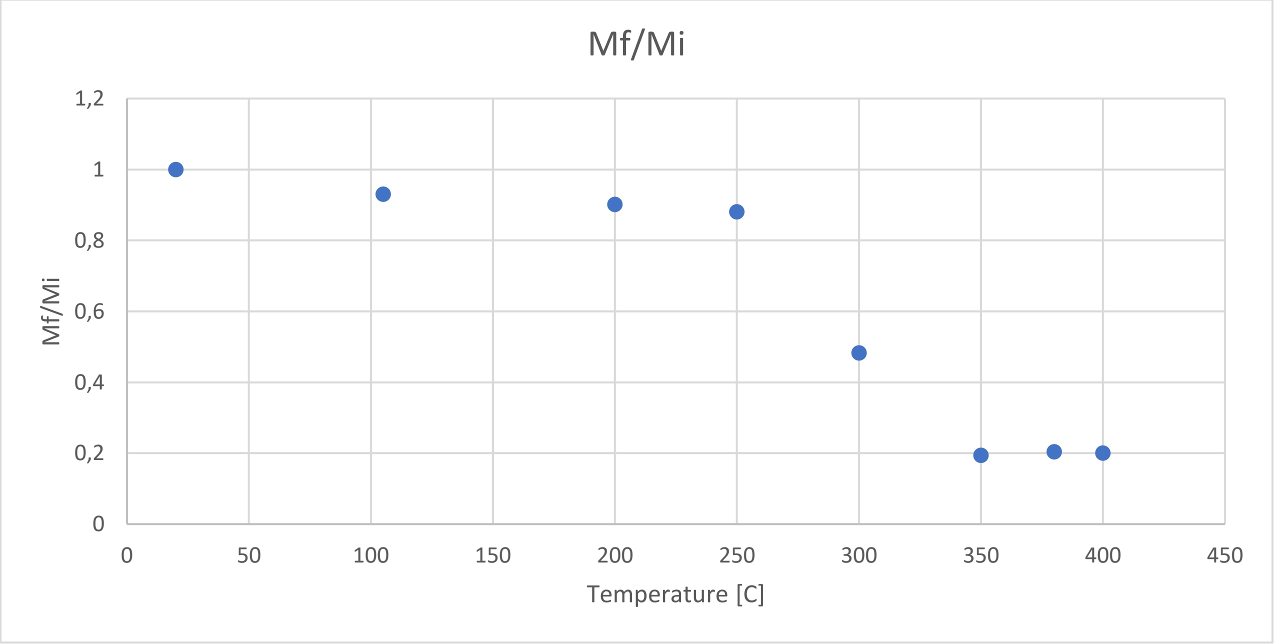


Figure 30: Conversion over temperature with15°C/min author's elaboration.

The results established in these circumstances varied; the greatest conversion rate was approximately 20 percent. Additionally, some ash was established in these cases; the presence of oxygen is what caused this.

Figure 31: Examples after the pyrolysis process author's elaboration.

Below it is showed the comparison between the two curves of conversion obtained by experiments:

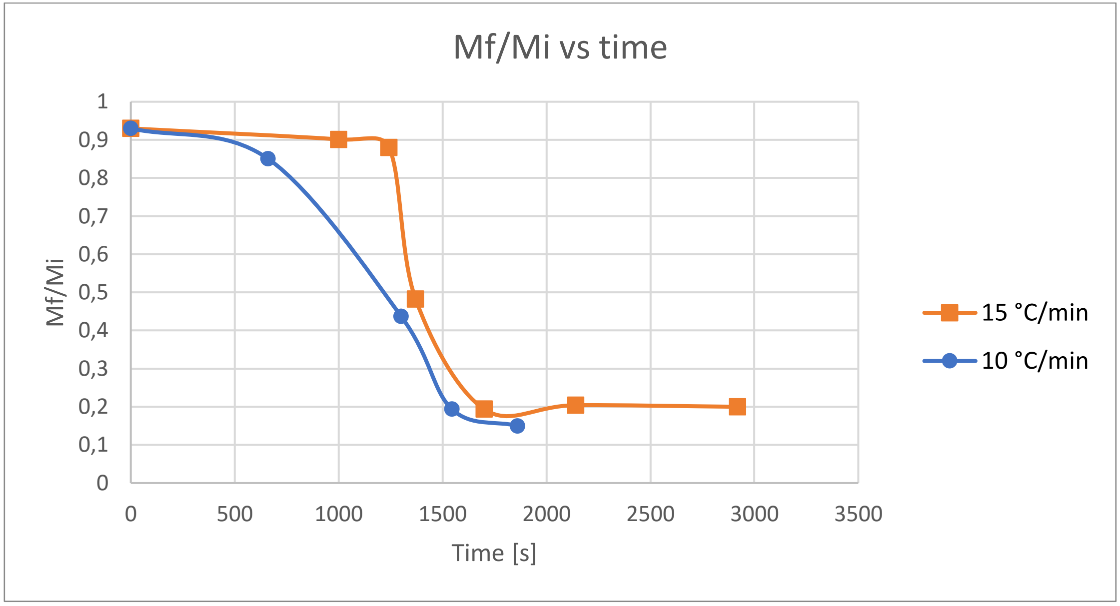


Figure 32: Comparison. Between the two curves of conversion, author's elaboration.

5.6 BET

During this research were addressed different things related to this process, like temperature control. An essential characteristic that describes our results is given by the BET (Brunauer-Emmet-Teller) analysis.

5.6.1 Results

After having done different experiments with the different conditions of temperature and heating velocity. The significant value that allows understanding of the structure of the generated material is precisely the value of the surface area and the porous zone in which the example is found. Is possible to describe the different zone by the adsorption that is red curve and desorption brown curve. In this case for each example, the desorption curves don't have correct behavior, this allows us to say that it is better to make another experiment of BET analysis, for the lack of time in this research is not present any other results.

The development of the desorption curve is not normal, but this experiment is useful because thank to the adsorption, the curve is found to show the value of the surface area.

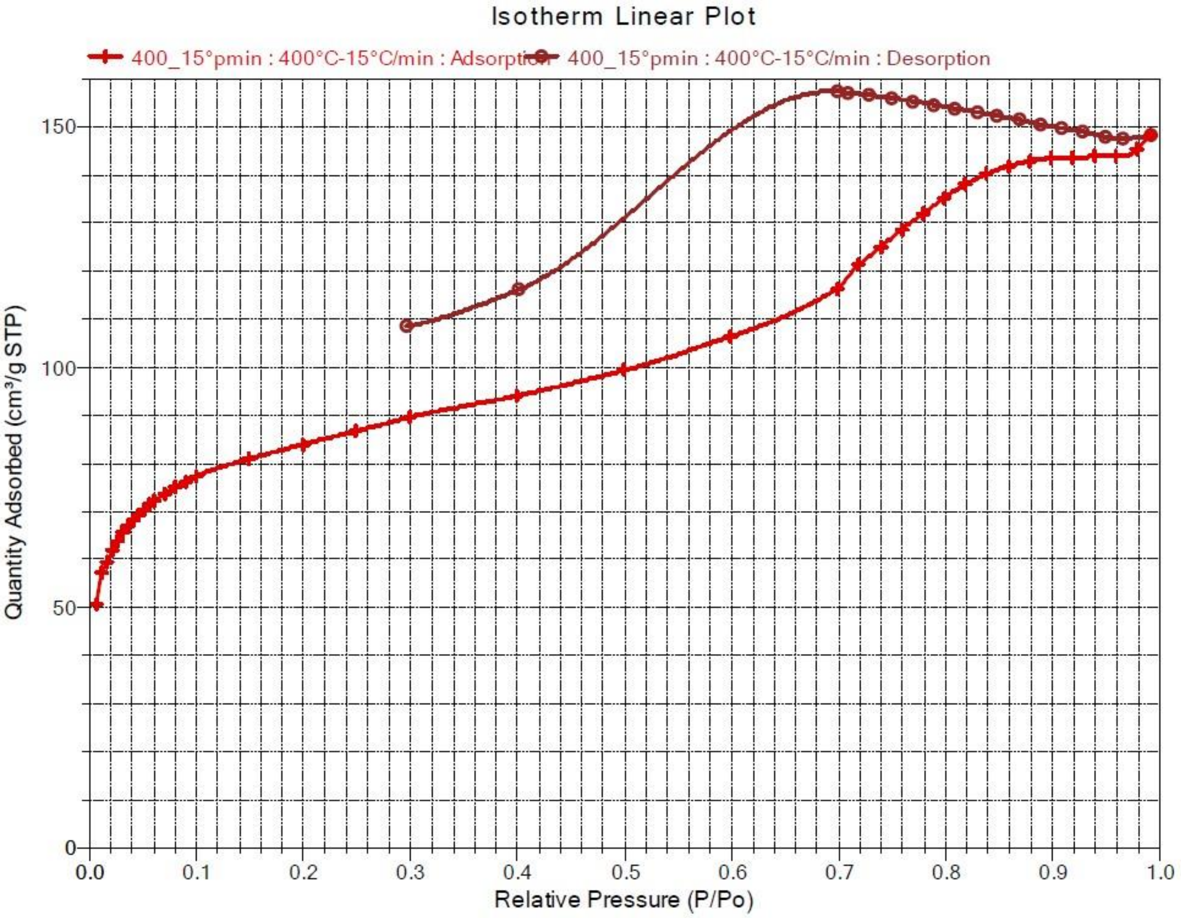


Figure 32:Adsorption and Desorption curves in BET analysis T=400 °C 10 °C/min, author's elaboration.

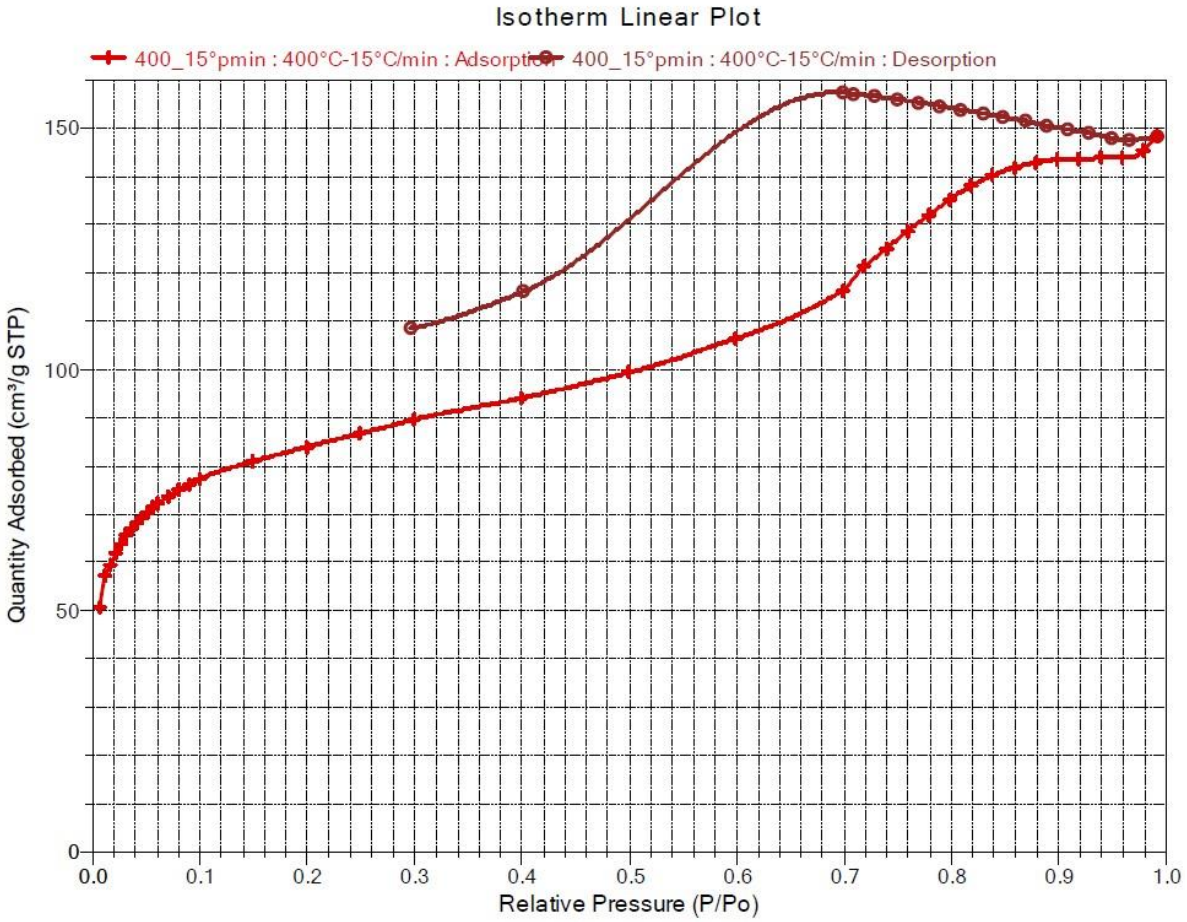


Figure 33: Adsorption and Desorption curves in BET analysis T=400 °C 15 °C/min,author's elaboration.

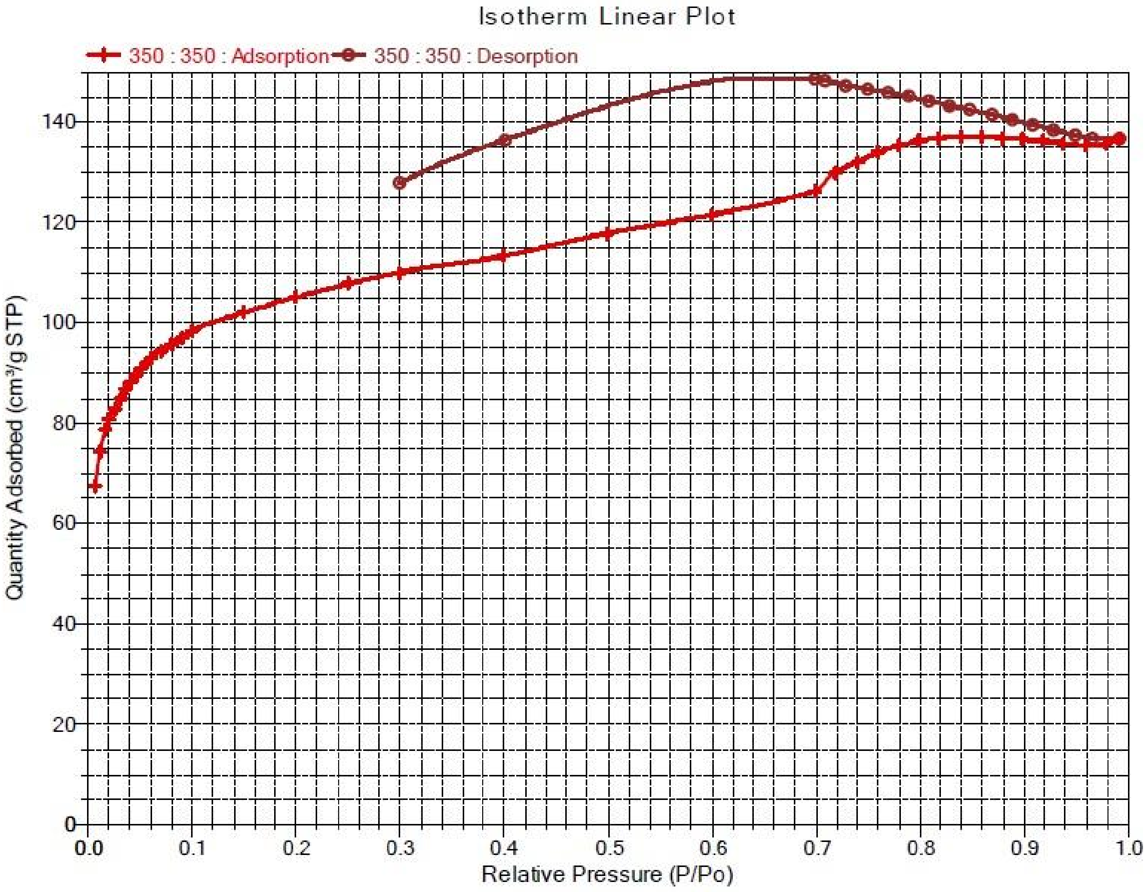


Figure 34: Adsorption and Desorption curves in BET analysis T=350 °C 15 °C/min, author's elaboration.

Table 12: Value of specific surface area for each example

Examples	**Temperature [C]**	**Specific surface area [m^2/g]**
Butt_400C_10C/min	400	420
Butt_400C_15C/min	400	315
Butt_350C_10C/min	350	365
Butt_200C 10C/min	200	0
Butt_250C 10C/min	250	0

Is possible to see that, after a certain value of temperature it does not generate any specific surface area and for the same reason the example is not porous. That is because the heart of reaction is after 250 °C. With the adsorption curves we can calculate the value of surface area but at the same time is important to obtain good desorption curves.

At the same time, thank the different type of experiment made, different heating velocity is easy to see the dependence of that heating velocity to generate an example more porous than the others, the physics reason lies in the fact that a lower value of heating velocity allows more time of the heating exposition which generates a more porous example.

The arrow shows the decrease of surface area respectively different values of heating velocity.

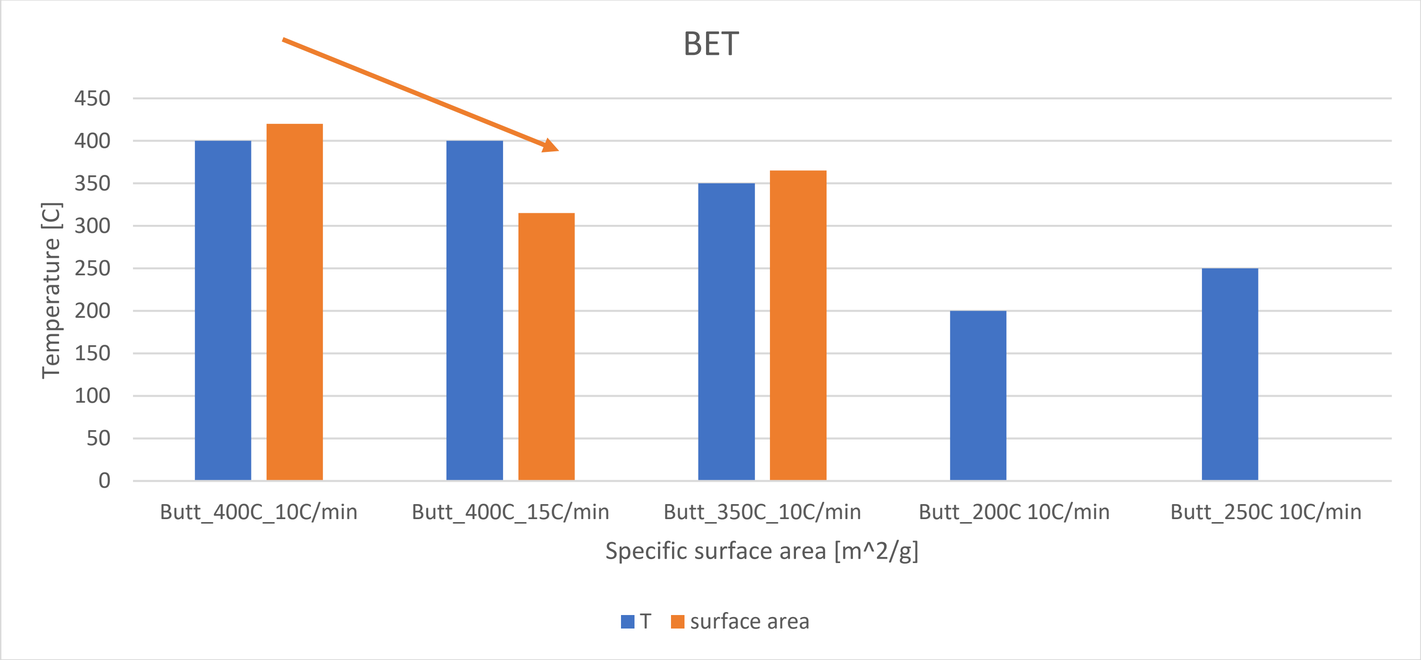


Figure 35: Specifi surface area related to temperature.

From these results of surface can say that the example generated after the pyrolysis process are useful examples to be treated as catalysts since they have a microporous surface. Subsequently, it will explain how to produce a catalyst from these examples.

5.7 TGA (Thermogravimetric analysis)

At the beginning of the experimental part of this report, it was said that it is not easily obtain the correct values of conversion. TAG analysis has been used to prevent this problem.

Figure 36: TGA machine in the University of Compiegne, author's elaboration.

Was used this machine to perform the process of pyrolysis, using nitrogen as gas, for the raw material which is a small particle of filter never used. Another type of experiment was carried out with particle of filter already used. All of that with the purpose of obtaining the curve of conversion and understanding what is happening and comparing the results with our results given by the experimental part. 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 our tests under a nitrogen atmosphere, to try to better understand the pyrolysis mechanism of our raw material. The machine used is called SETSYS-1750 CS.

5.7.1 Functioning

After being measured, the sample will be put inside the apparatus so that mass balance may occur. To calculate and take into account the temperature change over time and determine if there should be fluctuations because of the chemical reaction itself, it is compared to the same volume of an experiment without the experiment itself.

Since the cigarette filter already in use is loaded with several substances, we are unable to determine the composition of the example with true accuracy, and chromatography would produce ambiguous findings, it is not possible to quantify the amount of gas produced after the operation.

Before the main experiment can begin, the system must go through further intermediary processes after the nitrogen delivery.

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

- 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).

  A vacuum is created by a process that gradually eliminates oxygen from the air, which is not the case for the reactor that is used to detect temperature trends.

- A stabilization phase under a flow of nitrogen (20 °C for 600 seconds and with a flow of nitrogen of 100 mL/min).

  Again, since there is no temperature variation, we will just take into account the fixed gas flow rate of 100 ml/min for 10 minutes to ensure that the sample will remain stable during the experiment.

- The sequence for the samples (going up to 600°C and then back to 20 °C).

- Another stabilization phase is under a flow of nitrogen (20 °C for 600 seconds and with a flow of nitrogen of 100 mL/min).
- The sequence for the blank (going up to 600 °C and then back to 20 °C).

Will repeat the experiment for two time.

5.7.2 Results

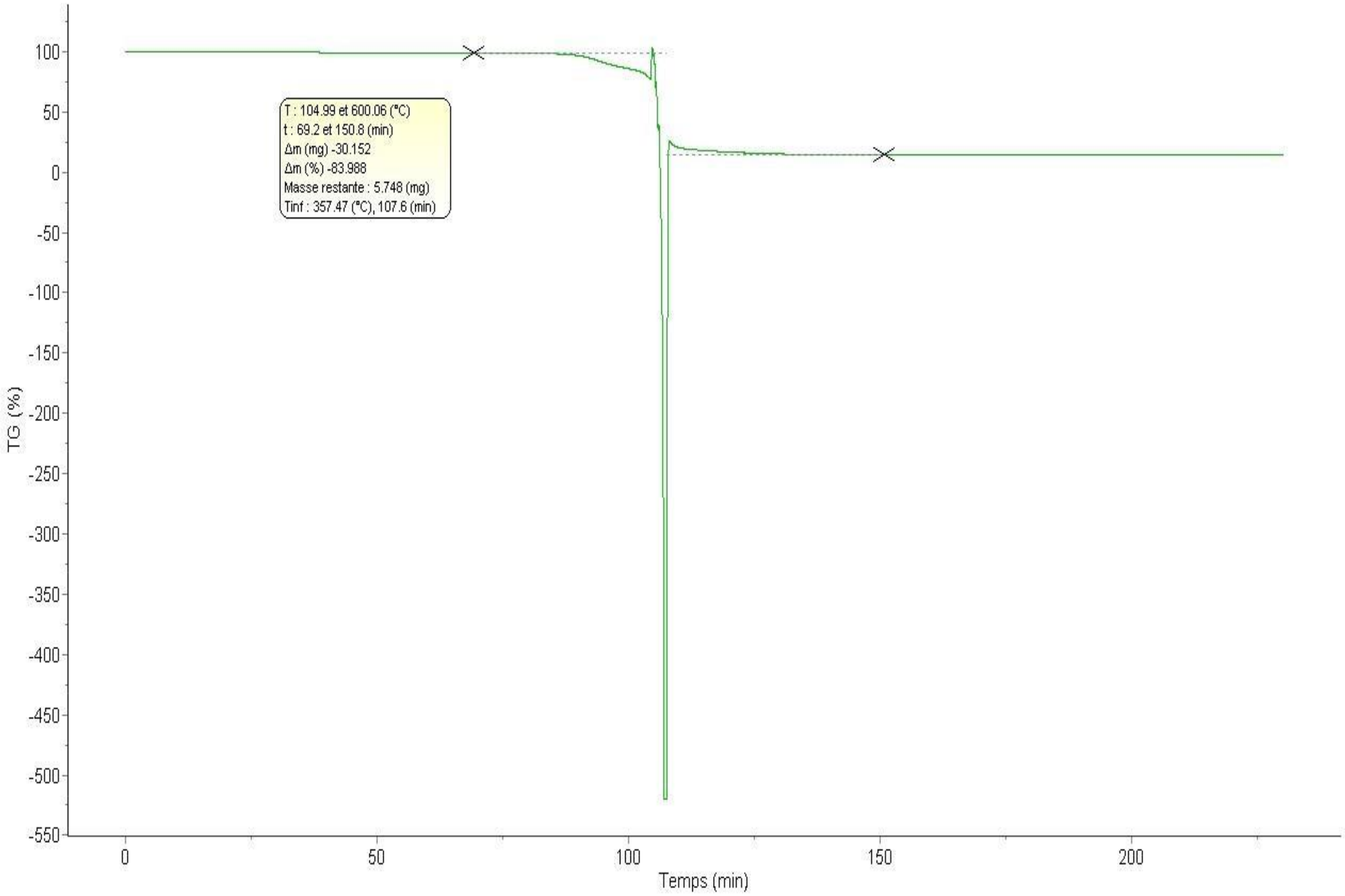


Figure 37: TGA of black example.

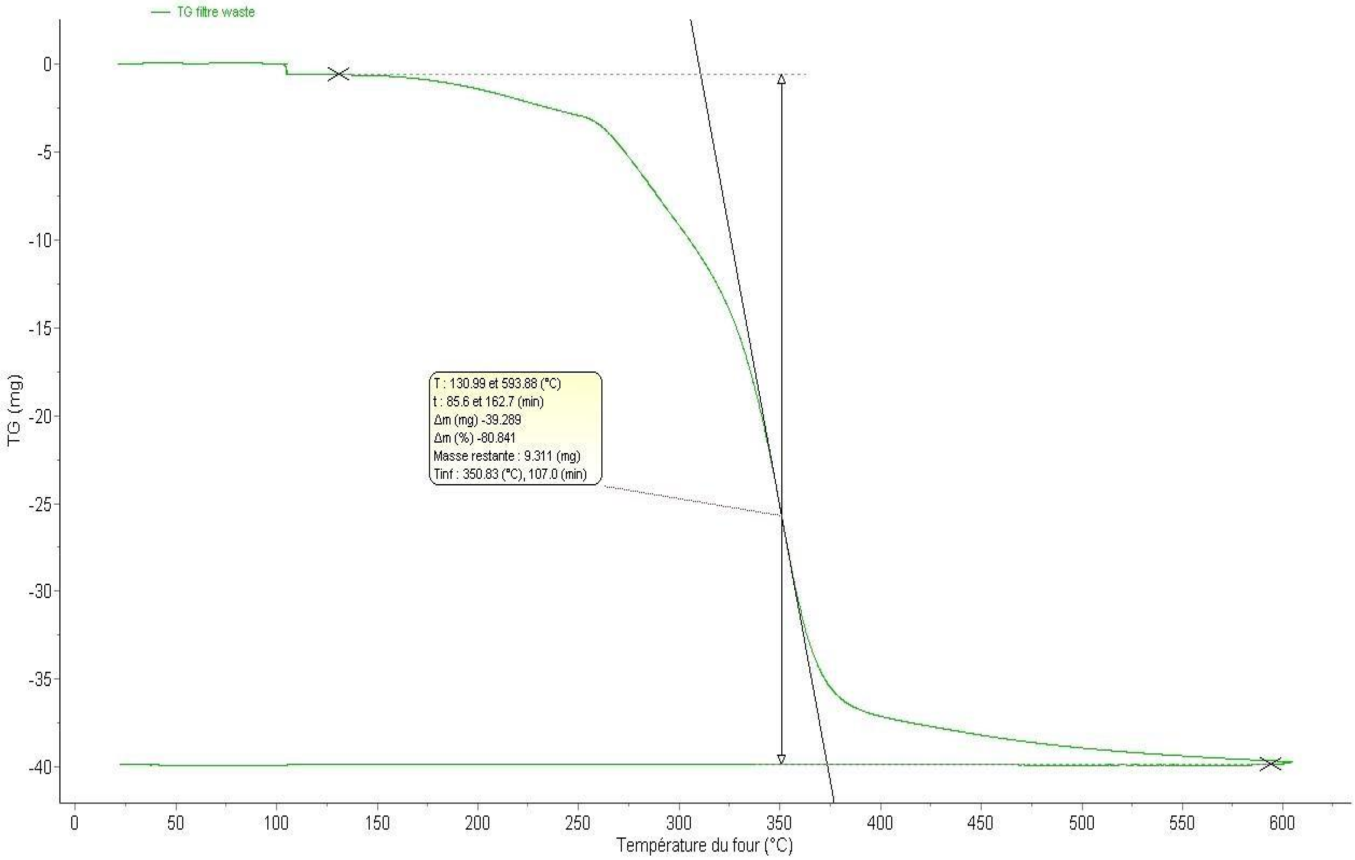


Figure 38: TGA of the used example

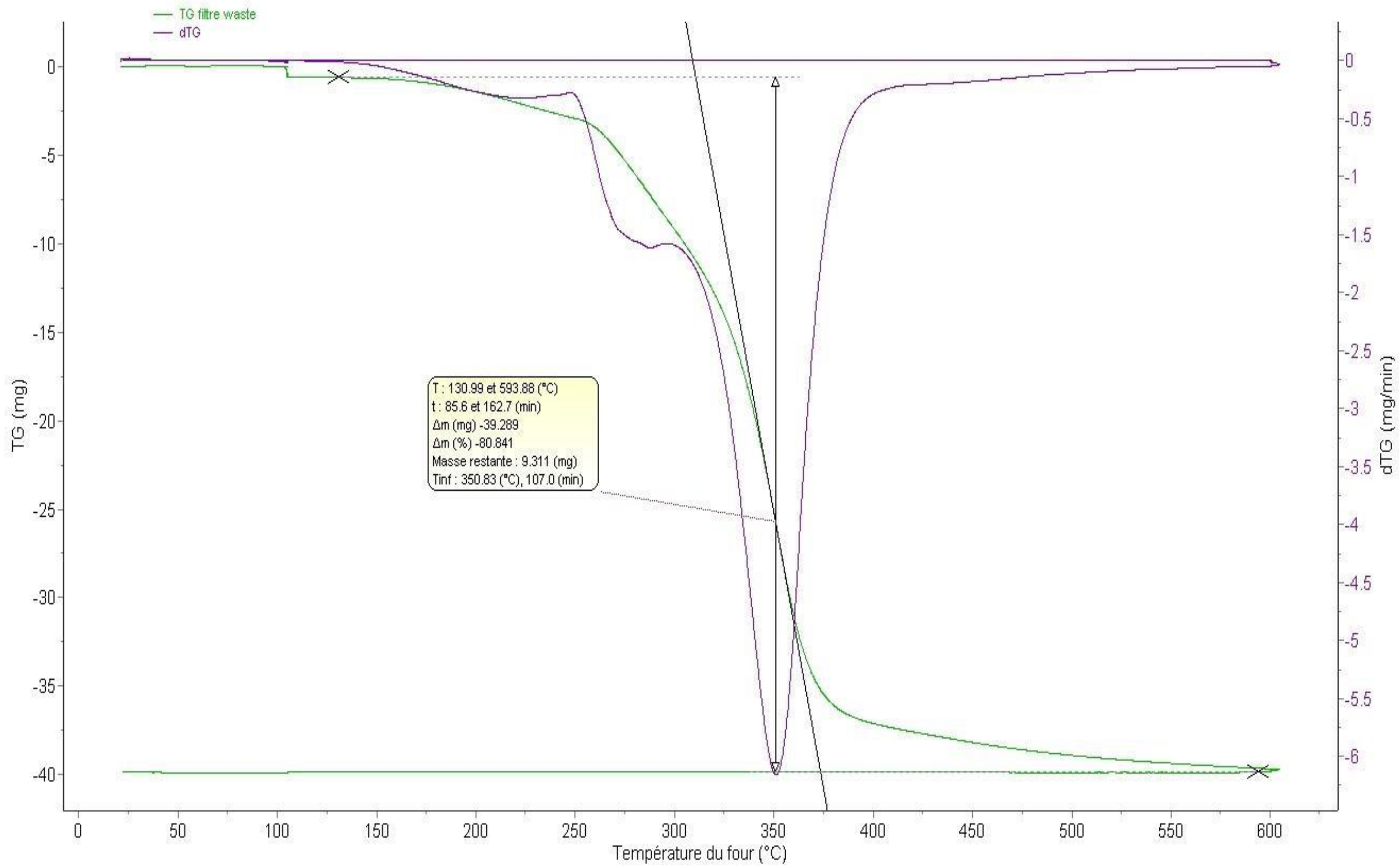


Figure 39: TGA of used example with the velocity of mass loss.

In figure 32 the curve agrees with the experimental results obtained with the provided reactor. The maximum percentage of mass loss is around 20% like our results.

6 Gas

In this report is explained the whole process, in which, the buttock is subject, at the beginning was saw the maximum percentage of water and carbon calculated, and now is the time to answer the question of how much and which type of gases are produced. The experimental part was carried out following a protocol that may be summed up:

- To link the pipe of gas' out with two different glass bottles in which
- The first is fill of isopropanol.

- The second is filled with silicium.
- To start the process with the wish conditions
- To take the time from the start point, in which the gas came out, until the end of the gases
- To fill some bags, in which was carried out the cleaning.
- Put the bags in the Gas Chromatography to see the results.

Figure 40: System of pipes, glasses and bags, during the process, author's elaboration.

The choice of this system is given by the property of two components that are inside of the glasses, the isopropanol has the task of capturing the TAR particles while the other one, the silicium, has the task to take the isopropanol that is dragged by the gas, at the same time the silicium adsorb the vapor and the other TAR that was not absorbed by the isopropanol.

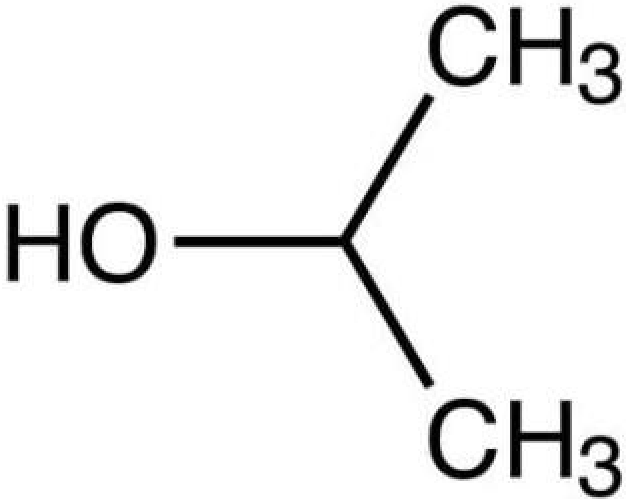


Figure 41: Isopropanol

The right time to begin taking the gases with bags and beginning the timer is when the gas came out of the pipe and the reactor's interior temperature was about between 200 and 250 °C. At this point, the gases were filling the glass bottles with gas. The observation of this experiment was in according to what one thought, the heart of the reaction is more moved in the range of temperature higher than 250°C. In this case, after 20 minutes 8 bags were filled, ready to be studied and for the Gas Chromatography.

Figure 42:One bag in which to put the gas author's elaboration.

6.1 Gas Chromatography

Numerous significant benefits of gas chromatography include:

- Rapid examination, usually taking only a few minutes.
- Effective, offering excellent resolution
- Sensitive, easily revealing levels in the ppm and frequently ppb range .
- Mass spectrometry is an example of a non-destructive technique that enables inline coupling.
- Another is very accurate quantitative analysis, with an RSD (Standard Deviation Relative) of 1 to 5 percent.

- Requires modest sample sizes, usually in the order of l;
- Is trustworthy and straightforward;
- Is affordable

6.1.1 Results

The results of the gases taken by the microgc are resume in the table below.

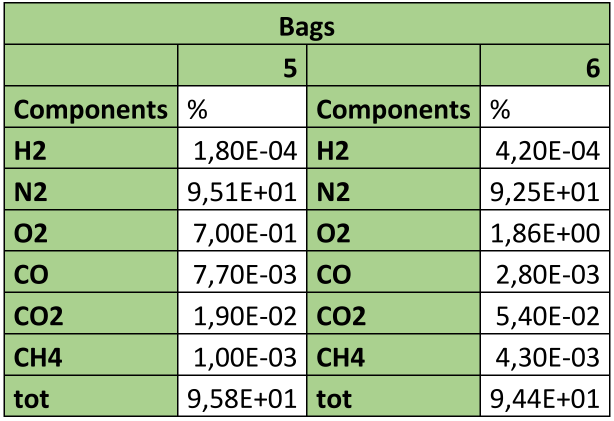
Table 13: Percentage of components of first two bags.

Bags			
	1		**2**
Components	%	**Components**	%
H2	0,00E+00	**H2**	0,00E+00
N2	9,42E+01	**N2**	9,40E+01
O2	1,08E+00	**O2**	8,70E-01
CO		**CO**	
CO2	4,70E-03	**CO2**	4,70E-03
CH4		**CH4**	
tot	9,52E+01	**tot**	9,49E+01

Table 14: Percentage of components for 3th and 4th bags

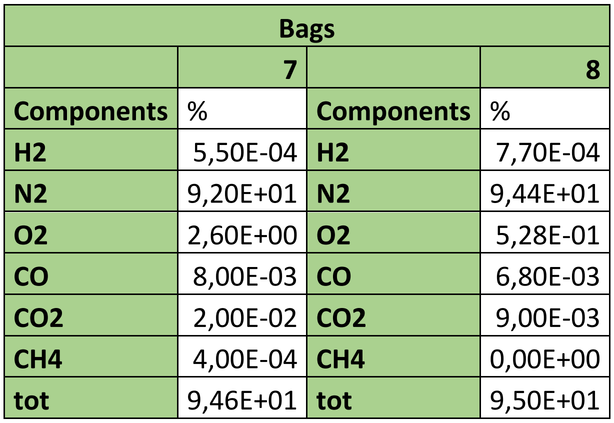
Bags			
	3		**4**
Components	%	**Components**	%
H2	0,00E+00	**H2**	0,00E+00
N2	9,37E+01	**N2**	9,43E+01
O2	1,05E+00	**O2**	7,30E-01
CO	3,70E-03	**CO**	3,00E-03
CO2	5,30E-03	**CO2**	8,80E-03
CH4	8,00E-04	**CH4**	9,00E-04
tot	9,48E+01	**tot**	9,50E+01

Table 15: Percentage of components for 5th and 6th bags.



Bags			
	5		6
Components	%	**Components**	%
H2	1,80E-04	**H2**	4,20E-04
N2	9,51E+01	**N2**	9,25E+01
O2	7,00E-01	**O2**	1,86E+00
CO	7,70E-03	**CO**	2,80E-03
CO2	1,90E-02	**CO2**	5,40E-02
CH4	1,00E-03	**CH4**	4,30E-03
tot	9,58E+01	**tot**	9,44E+01

Table 16: Percentage of components for 7th and 8th bags.



Bags			
	7		8
Components	%	**Components**	%
H2	5,50E-04	**H2**	7,70E-04
N2	9,20E+01	**N2**	9,44E+01
O2	2,60E+00	**O2**	5,28E-01
CO	8,00E-03	**CO**	6,80E-03
CO2	2,00E-02	**CO2**	9,00E-03
CH4	4,00E-04	**CH4**	0,00E+00
tot	9,46E+01	**tot**	9,50E+01

Considering only one bag, the 7th is possible to describe and speak about the gases generated by the process.

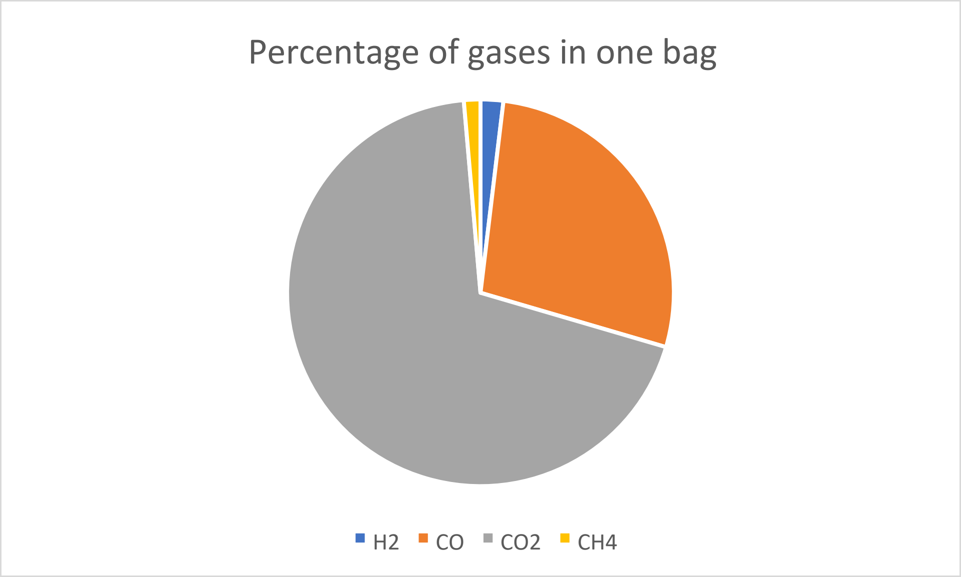


Figure 43: Percentage of gases in 7th bag author's elaboration.

Is evident the presence of CO_2 in the bags, which was not expected, the reason is that in our reactor there is oxygen and for the same reason we are not the partial oxidation of carbon. Oxidation is promoted and favored by oxygen.

These values of gases are not accurate because the integral method used to obtain this value is not accurate.

7 Model

The crucial aim of this research was to predict a model of this process, first of all, it was mandatory to study some model already exist and a path to follow to built a correct structure that may predict the pyrolysis reaction, according to T.Favarelli et al, 2013, [25] and also thanks at the article of E.Daouk, 2020, [10] it was possible to obtain a more knowledge of the the kinetics model of the reaction that takes place in this reactor and at the same time the thermodynamics model.

Thanks to the experiments and the TGA results we can write a code in which make optimization of our kinetic model.

The first hypothesis was carried out thinking that there is only one component, the main component which is cellulose acetate, which takes place during the reaction. The reaction is according to Arrhenius's law, which has the form:

$$\frac{dX}{dt} = A * \exp\left(-\frac{E_a}{RT}\right) * (1-X)^n$$

The optimization is carried out with the Scilab software, which are defined:

- The main equations that take place during the reaction.
- The variables
- The iteration to find the value of our kinetic closer.
- The residuals, that allow the function of iteration.

7.1 First result

In the following graph is shown the comparison between the experimental data given by the TGA (green curve) and the model that follows the Arrhenius law (blue curve). Both relationships using the equation:

$$\frac{dX}{dt} = A * \exp\left(-\frac{E_a}{RT}\right) * (1-X)^n$$

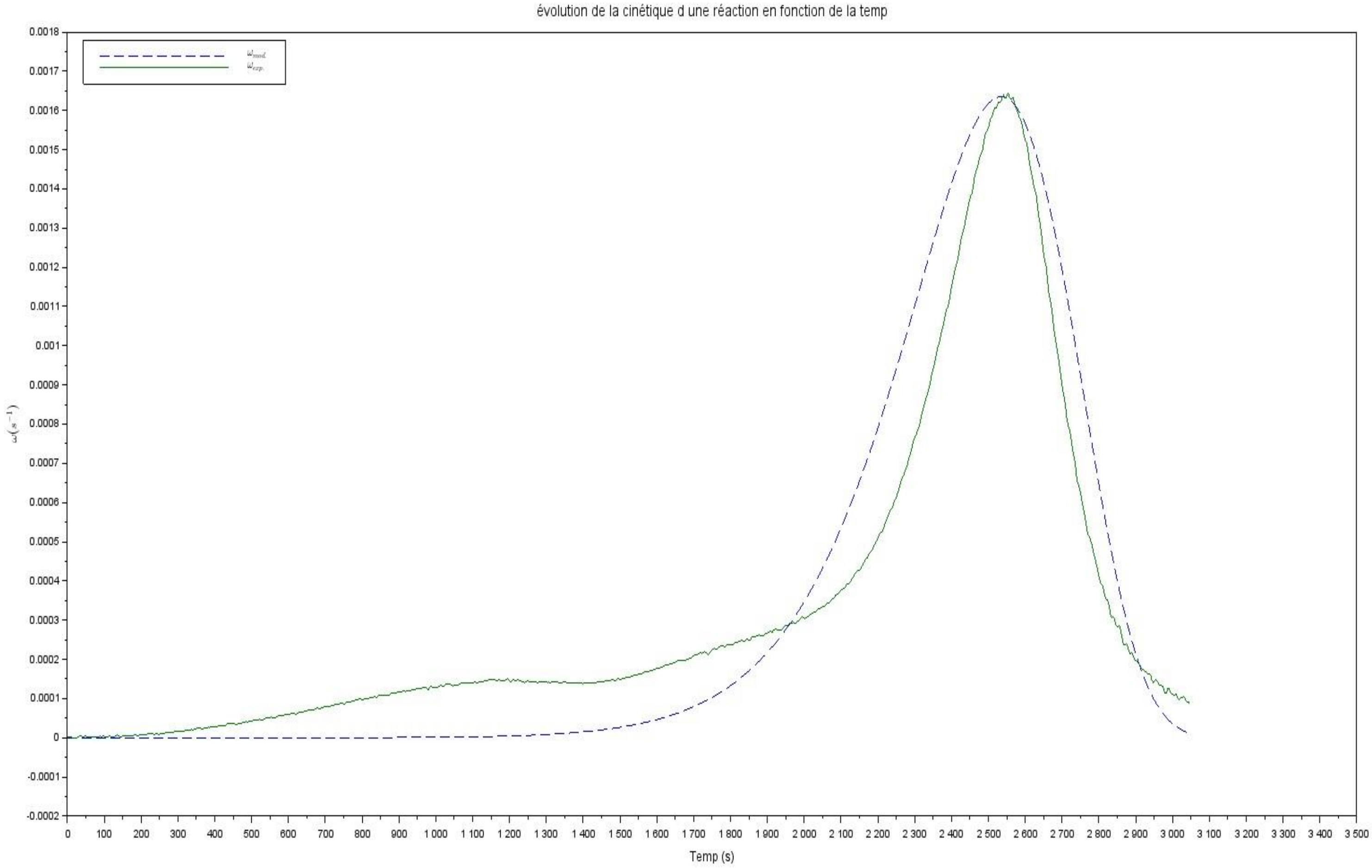


Figure 44: Optimization with kinetic's law of first order, author's elaboration

The results of this optimization are:

$$Ea = -162000 * 0.9252823;$$

$$A = 10^{11.76} * 0.0847394;\ n=1$$

The graph above shows, the blue curve, is our optimization and the green curve that is the experimental conversion. It is evident that the blue curve does not predict and follows the experimental curve.

According to the bibliography and the experiments was thought that the component presents in the buttock area are many and varied, one of that is the TAR. This term depicts a family of organic compounds with a huge quantity of carbon. In our process, when the temperature reaches a certain value of temperature, that is found in a range between 250℃-400 ℃, was evident the presence of fume, all of that is characterized by the TAR reaction that generates, with a parallel reaction, a lot of smokes. The form of the kinetic law is the same but with another relationship that unites both. Moreover it was important to go into detail the kinetic of this organic compound as explained in the article of Mr.Salem ,2020, [26].

7.2 Optimization of the kinetic model

The approximation was carried out with the same software, Scilab, gave us this type of curve:
The blue curve is our approximation and the green one is relative to the experimental data.

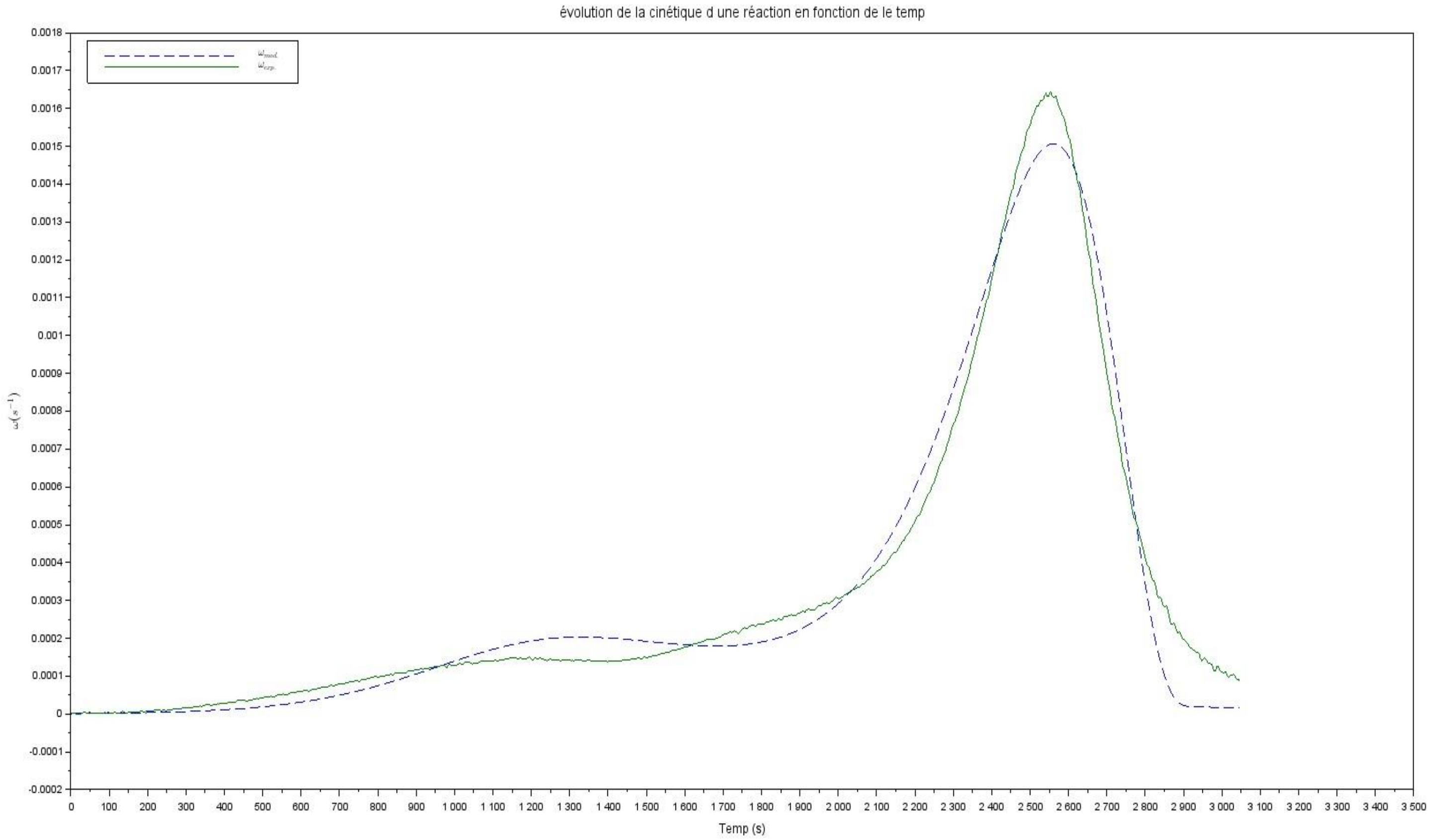


Figure 45: Approximation with two components, author's elaboration

The difference between the two approximations is evident, is not possible to predict the physical phenomena with only degradation of cellulose acetate because is not according to physics and the kinetic results won't be accurate.

The results obtained with these other hypotheses are:

For the cellulose acetate:

$$Ea_1 = -162000 * 1.5940565$$

$$A_1 = 10^{11.76} * 1.0163588$$

$$n_1=0,8$$

For the TAR:

$$Ea_2 =-111000* 1.0036575$$

$$A_2 = 10^8 * 1.0036575$$

$$n_2 = 3,2$$

The value of $alpha$1 and $alpha$2 are:

$$alpha_1 = 0{,}76;\ for\ the\ cellulose\ acetate$$
$$alpha_2 = 0{,}24\ for\ the\ TAR$$

Is possible to say that the reaction is not of the first order as thought but is more complex. Are more reactions, we took into consideration only two by the way the chemical phenomena include more species that are not easy to understand given the complexity of the example. Nevertheless, the reaction was described and the value of kinetic was found. The reaction of TAR is almost of the third order.

Although the goal of the project is to reach the best approximation that could explain the process, the real purpose is to predict the progress of the reaction in order to reach a good knowledge of the kinetic and at the same time to be able to use this model to design a good reactor for industrial uses.

Considering the equation of chapter 7, is it possible now to split those equations and to consider more equations as well as data obtained.

The Arrhenius's model assumes the following structure, depending by the quantities of components considered in the previously analysis:

$$\frac{dX_1}{dt} = A_1 * \exp\left(-\frac{Ea_1}{RT}\right) * (1 - X)^{n_1}\ that\ is\ for\ the\ cellulose\ acetate$$

$$\frac{dX_2}{dt} = A_2 * \exp\left(-\frac{Ea_2}{RT}\right) * (1 - X)^{n_2}\quad that\ is\ for\ the\ TAR$$

$$\frac{dX}{dt} = \alpha_1 \frac{dX_1}{dt} + \alpha_2 \frac{dX_2}{dt}$$

8 COMSOL

The study of the chemical phenomena was necessary to understand and describe the thermodynamics that characterize this process of pyrolysis. Generally, the pyrolysis process, as said, is a process easy and fast. In this condition and range of temperature, the pyrolysis is fast, according to the experimental part that has shown and confirmed this theoretical concept.

This work explained the thermodynamics equations that take place and found the values of the principals' variables allow for evaluating and carrying out a model thermodynamic.

The software used is called COMSOL Multiphysics®, which is a cross-platform program for multiphysics simulation and finite element analysis. It enables connected partial differential equation systems and standard physics-based user interfaces (PDEs). For applications in electrical, mechanical, hydraulic, acoustical, and chemical engineering, COMSOL offers an IDE and a unified workflow.

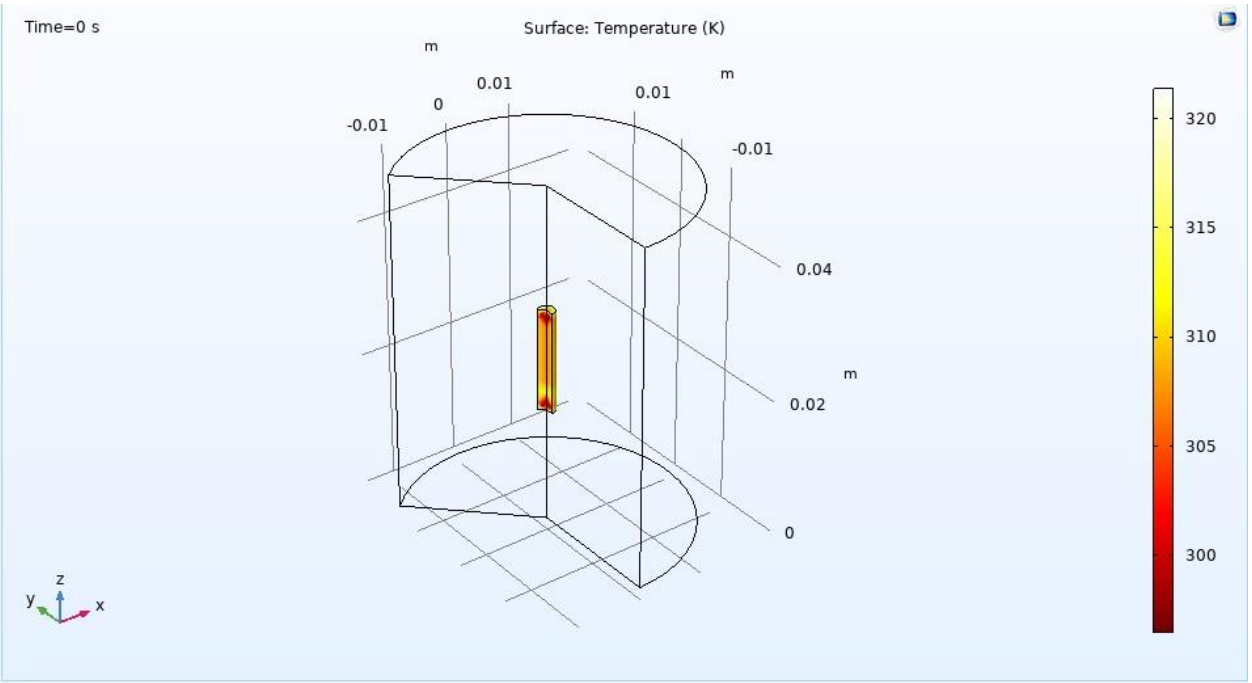


Figure 46: Temperature on the buttock's surface before starting the process author's elaboration

The analysis is carried out following a certain protocol as another computational software, it is mandatory to explain the initial conditions and the materials object of the study. After having put every single parameter to define the whole physics of the process COMSOL starts to calculate and predict what may happen after a certain time under the imposed conditions. At the beginning of the process the reactor and the champion are at ambient temperature as Figure 48 shows.

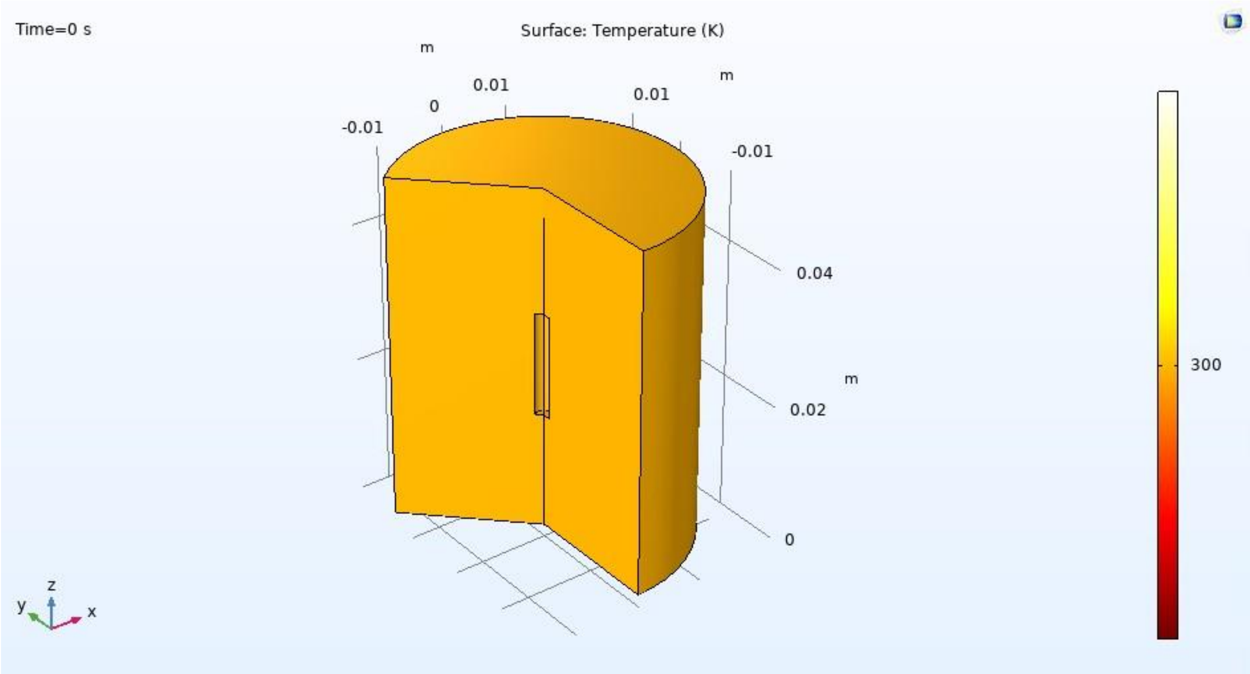


Figure 47: Global temperature in the environment, before the process author's elaboration

Subsequently at a certain time it is possible to verify that there isn't a gradient of temperature as the previously chapter explained and confirmed by experimental part too.

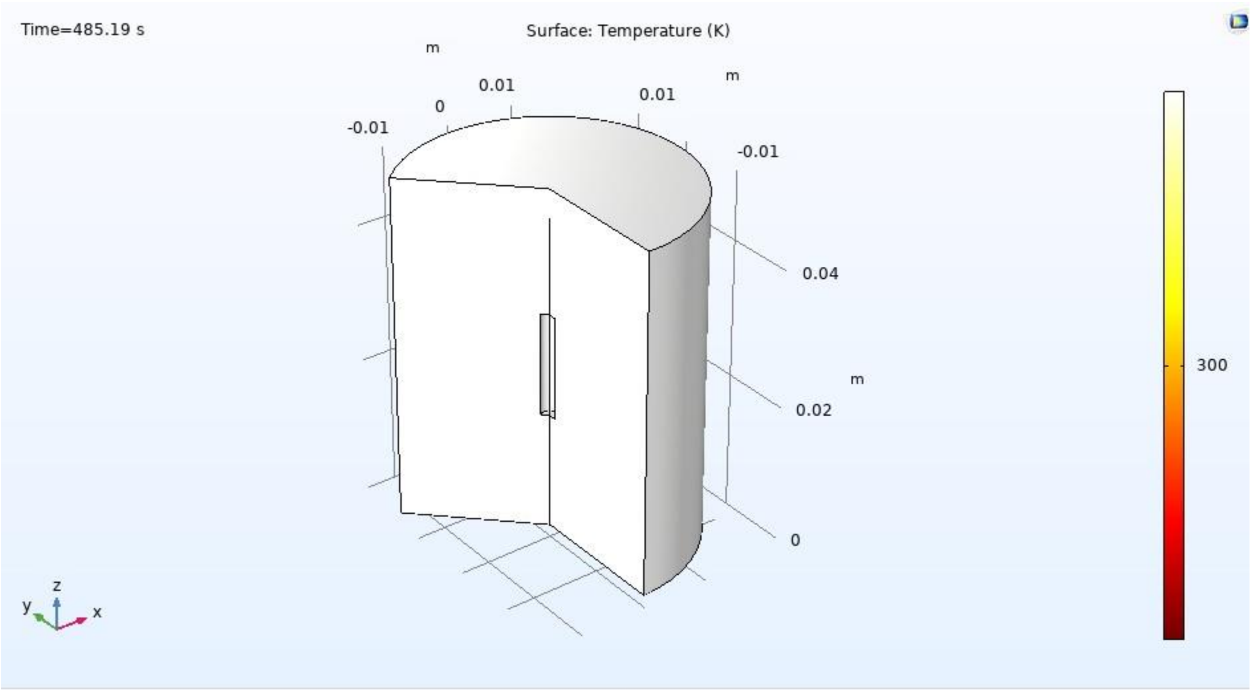


Figure 48: Global temperature in the environment, after the process,author's elaboration.

After almost 8 minutes the gradient of temperature between the champion and the ambient expired. Of course, it is the case in which the reactor is already at the temperature target so after the heating time (first part of the curve shown in Figure 21).

9 Conclusion

In this report, was documented the experimental results obtained with the pyrolysis process of the cigarette butt in a controlled environment of temperature. The behavior of the example was studied, by this study is understood that the reaction is endothermic, so in the process is normal to see that the development of temperature changes in order with the reaction. After that was made clear that higher temperature doesn't allow parallel, high conversion of the example and consequently higher formation of gas.

Additionally, the study of kinetics has brought to light the importance of TAR, the reaction that we want to study is not led by cellulose acetate, although is the main component. The purpose of the project was to build a predictive model able to describe future behaviors. The family of TAR is so big and varied, moreover, each component of this family generates carbon gases. If put in a degradation process, therefore, are cancerogenic and toxic chemical compounds.
This research was thought to be an innovative way to solve the problem of pollution and the presence of solid waste, which is shown, to be one of the most problematic in the world.

Was taken, personally, the examples from the public ashtray that the university of Compiègne leaves for everybody, after that the butts were studied in the laboratory and generated something useful for the whole world.

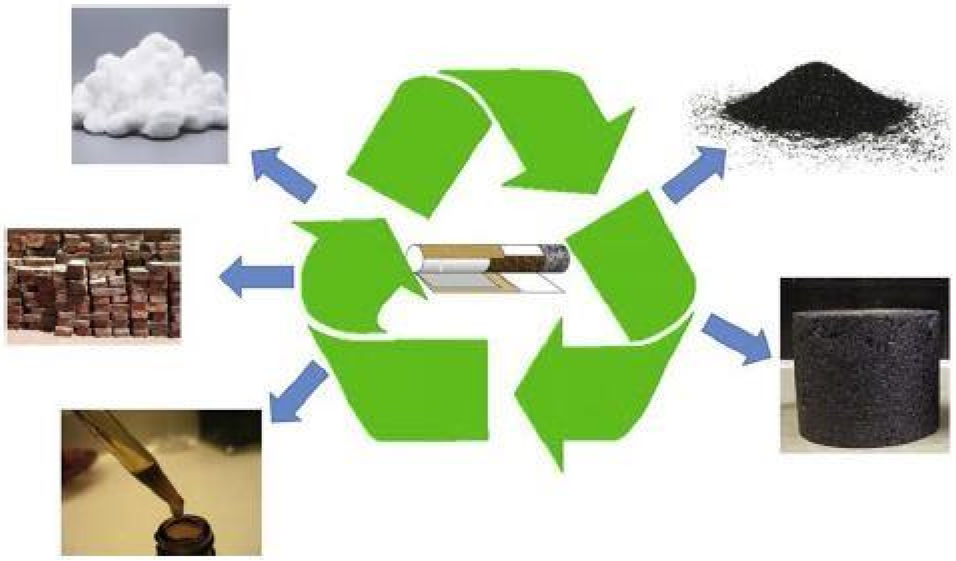


Figure 49: This figure shows the different ways to recycle [7].

Only one butt can generate:

- Solid part: Range of 15% to 20% from the initial mass, a good candidate to make catalyst thanks to the specific surface area registered.
- Gas: were generated gas of pyrolysis and methane.
- Tar: Other compounds that after a certain process could become a good fuel.

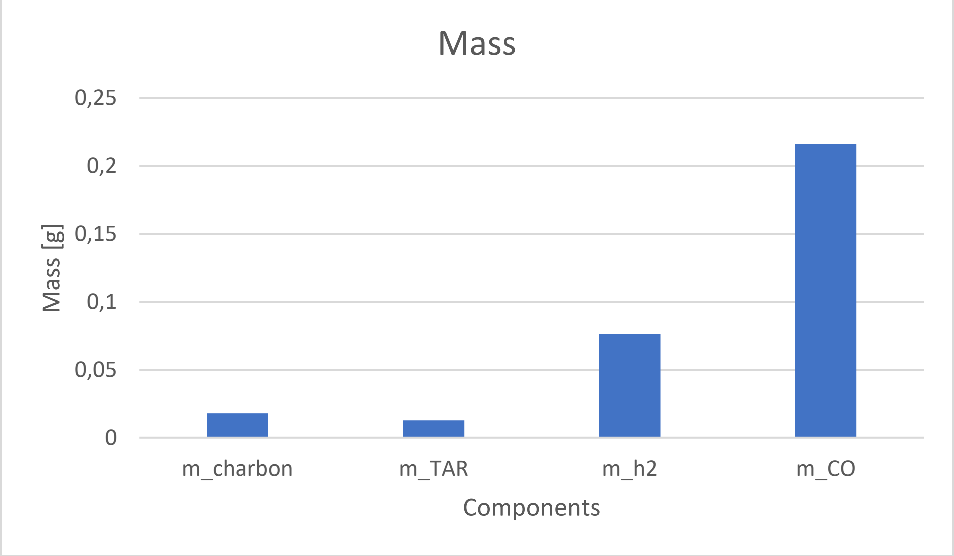


Figure 50 : This figure shows the different ways to recycle, author's elaboration.

Pyrolysis is a more cost-effective alternative disposal option for biomass waste when compared to other biochemical and thermochemical processes. The pyrolysis of a cigarette butt, in order to manufacture various valuable things, has a bright future given the significant volume of CBs waste produced globally. Activated carbons and other useful compounds can be created from biochar through additional processing. The performance and characteristics of biochar are significantly influenced by system settings and activation techniques. Recent studies have demonstrated the benefits of harnessing the pyrolysis of CBs to produce useful goods, notably biochar.

Climate change is a serious problem for the whole world and is a human duty to find a solution that is possible to exploit the waste already created in something new or that might be useful.

Cigarette butts, as said, are an unbiodegradable material that releases a lot of toxic compounds which are dangerous to the environment, whatever it is: air, ocean, or heart.

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11 Table of figures:

12 Tables of Tables: