



## INTRODUCTION

Large amounts of pollutants in the world threaten the humans, animals, and plants life. The World Health Organization (WHO, 2017) has reported that tobacco and related products threaten many resources on the Earth. According to the WHO, there are many pollutants that pose damage to the environment during the tobacco product life cycle. Although tobacco processing and production take place in particular regions of the world, its use and waste are widely dispersed around the globe. Since the produced wastes can be found in everywhere, their collection and disposal are considered a complex problem. Approximately, 967 million smokers in the world used 6.25 trillion cigarettes in 2012 (Ng *et al.*, 2014). However, the smoked cigarettes were reported to be decreased to 5.7 trillion in 2016. Considering the rapid development of this market, this rate is expected to rise to 9 trillion by 2025 (Mackay *et al.*, 2006). Cigarette butts (CBs) are the main residue of tobacco around the world, and they account for a large share of pollutants collected in urban clean-ups (Curtis *et al.*, 2017, Conservancy 2018). The cigarette consumption waste in the world is estimated to be 340–680 million kg. Approximately, 2 million tons of ink, paper, foil, cellophane, and glue are used for cigarettes packaging. The CBs have a share of over 40% in urban clean-up items (Novotny and Slaughter 2014, Bonanomi *et al.*, 2015). According to WHO (2017), around 2/3 of the CBs are left in the environment. Moreover, Patel *et al.* (2013) reported the exact number of the left CBs as 76%. The uncontrolled distribution of CBs is a bigger problem because they are not biodegradable and release more than 7,000 toxic chemicals into the environment (Marinello *et al.*, 2020). While the adverse impacts of smoking on human's body are widely studied, the negative effects of tobacco on the environment are not well understood. The use of insufficient land and water for tobacco farming, application of hazardous pesticides in tobacco plantation, erosion, carbon pollution from manufacturing and processing systems, and production of toxic and non-biodegradable waste are among these negative effects. Inappropriate CBs dumping has led to a number of domestic and wildland fires with disastrous consequences (Kadir and Sarani 2015). Many countries ratify some rules against

using tobacco and advocate the policies on raising the price of the tobacco-based products (Smith and McDaniel 2011). Considering the inefficiency of the conventional disposal techniques, such as landfilling and incineration which are not feasible for CBs, an effective solution for management and disposal of this waste seems to be essential (Barnes 2011, Bandi *et al.*, 2018). An efficient disposal method for this waste could reduce the release of toxic chemicals into the environment and lead to some benefits such as energy supply from the huge volume of waste material. There are several methods for recycling and reusing the CBs to ensure a hazardless procedure for their life cycle. CBs are mainly made up of cellulose acetate which has attracted the attention of many researchers. A single cigarette filter contains about 12,000 fibers of cellulose acetate (Novotny *et al.*, 2009). These fibers consist titanium dioxide and are connected together by a triacetin (glycerol triacetate) surfactant (Kabir and Hameed 2017). The molecular formula of cellulose acetate is  $C_{76}H_{114}O_{49}$  and its average molecular weight is 1,811.7 g/mol (Sayers *et al.*, 2010). High amounts of carbon atoms in the cellulose acetate structure make it a good candidate to be used as a raw material for producing the porous carbon derivatives. The primary element of CBs, cellulose acetate, is a desirable organic carbon source for conversion into useful liquid finished goods using the thermal cracking techniques (Lam *et al.*, 2017). The pyrolysis method has been successfully used for degradation of cellulose to furans, (Long *et al.*, 2017), carboxylic acid and aldehydes (Al Shra'ah and Helleur 2014), and hydrocarbons/aromatics (Zhang *et al.*, 2011, Karanjkar *et al.*, 2014). The main goal of these conversions is to achieve sustainable energy from waste. The direct combustion of raw materials to provide heating energy is called thermal combustion which is usually performed to generate steam and electricity. The main principle of gasification technology is producing synthetic fuel gas to be combusted for heat generation or used as a turbine or engine fuel for electricity generation. The liquid fuel produced by the pyrolysis method can be used as a fuel oil in static heating and applied for electricity generation. Interestingly, pyrolysis can directly produce a liquid fuel which is a good option when the resources are far from the energy-required place. Pyrolysis process has received much

attention due to its ability to produce high amount of liquid oil (up to 80 wt%) at moderate temperature of about 500 °C. Moreover, it is very flexible as its parameters can be manipulated to optimize the product yield based on preferences. The liquid oil produced can be used in furnaces, boilers, turbines and diesel engines without any upgrading or treatment. The oil produced by biomass pyrolysis is considered as a highly environmentally friendly fuel because it contributes to the reduction of CO<sub>2</sub> in the atmosphere (Sharuddin *et al.*, 2018). Although many studies have focused on the risk of CBs being released into the environment, a few studies have been done on converting the CBs into valuable products through the pyrolysis process. In this study, it has been attempted to give a short review of CBs and the pyrolysis method for recycling and converting them to sustainable energy. The review is focused on distribution, structure, and toxicity of the CBs. It also covers the methods for recycling of CBs, a brief review of pyrolysis technology, and a comparative discussion on the pyrolysis methods used for the disposal and recycling of CBs. The obtained results can be used by researchers and industries to perform an optimized method for controlling this waste. This study has been carried out in Biofuel Research Laboratory, Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshahr, Iran during 2019-2021.

### *Cigarette butts*

#### *Distribution*

CBs production is directly affected by the production of tobacco and its use. China has the highest share in this industry around the world. The CBs account for about 22-46% of visible wastes in the municipal discharges (González Alonso *et al.*, 2012) and have a variable distribution in all the urban areas. A study performed in Berlin indicated that different areas had different concentrations of the CBs. The maximum and the minimum mean values were 5.2 CBs/m<sup>2</sup> and 0.29 CBs/m<sup>2</sup>, respectively. In the mentioned study, the maximum value of CBs concentration (about 48.8 CBs/m<sup>2</sup>) belonged to a nearby train station (Green *et al.*, 2014). In another study in San Diego, Merah and Novotny (2011) investigated the probability of the CBs existence in different places. They reported the mean values of 38.1 CBs/m<sup>2</sup> and 4.8 CBs/m<sup>2</sup> for the highest

and the lowest probabilities, respectively. They finally showed that only 6 places were devoid of CBs contamination (Marah and Novotny 2011). There are some correlations between the concentration of CBs and the parameters such as density of population and cigarette market availability (Araújo and Costa 2019). The places around the malls, bars, restaurants, gas stations, grocery stores, liquor stores, cafés, traffic signals, and convenience stores have a higher probability of CBs existence (Green *et al.*, 2014). Merah and Novotny (2011) reported that the CBs concentration around the venues was nearly 8 times higher than their concentration in other places. They applied the graphic information system to indicate the CBs distribution density in municipal fields. In another conducted study by Asensio-Montesinos *et al.* (2019), 56 Mediterranean coastal sites were selected for the CBs density measurement. They found different CBs concentration in various beach topologies. This value was measured as 54 CBs per 100 m of the beach, 67 CBs per 100 of village areas, and 121 CBs per 100 of urban areas (Elliott 2014, Asensio-Montesinos *et al.*, 2019). In different seasons, there are different numbers of CBs in a single area, especially in touristic regions. However, there is no data about the specified correlation between these parameters (Green *et al.*, 2014). In another coastal area, the tourism season showed 46% growth in CBs pollution, which was two times greater than the same value in other seasons (Martinez-Ribes *et al.*, 2007). Another study showed that the CB contaminants were significantly higher in summer than in fall (Simeonova *et al.*, 2017). Evaluation of the pollutants collected from Bulgaria indicated that CBs (with total amount of 4496) had the highest share in the detected litter and accounted for 29.7% of the total waste. However, a significant variation in the amount of these CBs was observed in different seasons. For instance, in the study area, 2637, 1072, 454, and 333 CBs were detected in summer, autumn, winter, and spring respectively (Simeonova and Chuturkova 2019). Consumption rate and presence of people in public spaces can also affect the volume of the waste. The amount of CBs on public beaches was greater than other sites (Taffs and Cullen 2005). Moreover, the rate of the disposed CBs could vary among different points in different times of the week. Volume of CBs/m<sup>2</sup> in the studied areas was twice in vacations (Oigman-

Pszczol and Creed 2007). Patel *et al.* (2013) found that the majority of the 219 smokers littered their cigarette butts. Butt littering was more common among those who did not extinguish their cigarette (94.4% vs 4.5%,  $p=0.003$ ). It was also more common in the evening than in the lunchtime periods (85.8% vs 68.1%,  $p=0.002$ , logistic regression analysis). Most of the smokers (73.5%) did not extinguish their butts and some of them threw their lit butts into the trash bins (Patel *et al.*, 2013).

#### Structure of cigarette butts

CB is a cigarette filter which has some tobacco with some chemical compounds and contaminants (Parker and Rayburn 2017). The key material used in the CBs is cellulose acetate which is resistant to biodegradation compounds (Ariza *et al.*, 2008, Velzeboer *et al.*, 2014) and remains undegraded in the environment for 18 months in usual conditions (Novotny and Zhao 1999). While it is non-biodegradable, it can be converted to lighter elements under ultraviolet (UV) irradiation, remaining for 10-15 years (Dieng *et al.*, 2013). To create a cigarette cartridge, titanium dioxide is exposed to the cellulose acetate fibers with a thickness of about 20  $\mu\text{m}$  and 15,000 of them are densely packed along with glycerol triacetate as a binder (Slaughter *et al.*, 2011). Production of cellulose acetate by acetylation (combination of acetic acid and acetic anhydride) is quite well known. Plasticizers (e.g. polyethylene glycol) may be applied before the treatment. Although cellulose has a low capacity for biodegradation owing to the chemical alteration of the materials, it is effectively digested by the cellulase enzyme. The conversion of synthetic cigarette filters is inhibited by the extreme compactness of the fiber and additives (Araújo and Costa 2019). Such factors make the CBs a potential candidate for environmentally harmful problems (Ariza and Leatherman 2012). Although each CB's pollution is not significant due its tiny size and distribution, it has the potential to cause local contamination (van Dijk *et al.*, 2011). The effect of CB pollutants on aquatic life has been studied and approved (Slaughter *et al.*, 2011). The CBs in the public areas, if swallowed, can cause health problems in children, birds, and animals (Novotny *et al.*, 2011). The harmful chemicals in CBs have encouraged the researchers to track and validate

their influence on such species (Dieng *et al.*, 2013).

#### Cigarette butt contaminants

CB contamination in various places induces the environmental hazards and introduces toxins into the ecosystem (Moerman and Potts 2011). 75 % of cigarette smoke compounds are verified to be gaseous, with the rest being in the tar form (Aeslina and Mohajerani 2012). Nitrates, hydrogen cyanide, polycyclic aromatic hydrocarbons (PAHs), acetaldehyde, N-nitrosamines, ammonia, carbon monoxide, formaldehyde, phenol, benzene, pyridine, aromatic amines, and metal ions like chromium, nickel, cadmium, and arsenic are some of the contaminants in cigarette smoke (Micevska *et al.*, 2006) and all of them are trapped in the filter (Dieng *et al.*, 2013). CB is one of the key sources of pollution in urban areas and it can disperse many pollutants, including toxic metal ions, into the marine ecosystem (Dobaradaran *et al.*, 2017). Due to the penetration of such pollutants into the freshwater supplies, CB has been classified as a hazard to marine life and environment (Patel *et al.*, 2013). Since CB contains cadmium, tar, arsenic and lead, it can pose a serious threat to ecosystems and marine species (Pon and Becherucci 2012). Metal ions are among the most significant pollutants discovered in CBs and they can cause pollution in the aquatic species, if discharged into the marine ecosystems (Dobaradaran *et al.*, 2017). The value of heavy metal ions, such as arsenic, nickel, cadmium, lead, zinc and copper, in CBs is known to be from some  $\mu\text{g/g}$  to many hundred  $\text{g/g}$  (Chevalier *et al.*, 2018). Extraction of the heavy metals packed within CBs could be occurred by penetration into the ecosystem (Aeslina and Mohajerani 2012). The leakage of heavy metals from CB in roadways with an estimate of 150 butt/km/month was calculated as 0.02–1.7  $\text{mg/km/month}$ . Cadmium, lead, copper, arsenic and chromium leaks, for example, were recorded to be 0.02, 0.59, 1.7, 0.81 and 0.15  $\text{mg/km/month}$  (Moriwaki *et al.*, 2009). Fig. 1 illustrates the different heavy metal ions existing in the CBs.

CBs have a capability to release PAHs which can cause cancer in the living organisms in the ecosystem. In a roadway survey, although the volume of each PAH in a CB was 0.0065 to 0.0078  $\text{mg/kg}$  and the overall volume PAHs in all the CBs was 0.039  $\text{mg/kg}$ , the mean probable exposure of

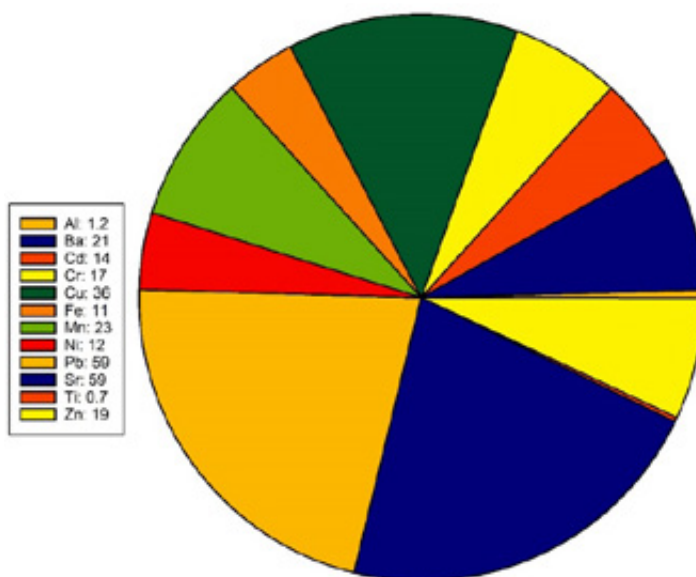


Fig. 1: The leakage percentage rate of different heavy metals from cigarette butts (Moerman and Potts 2011)

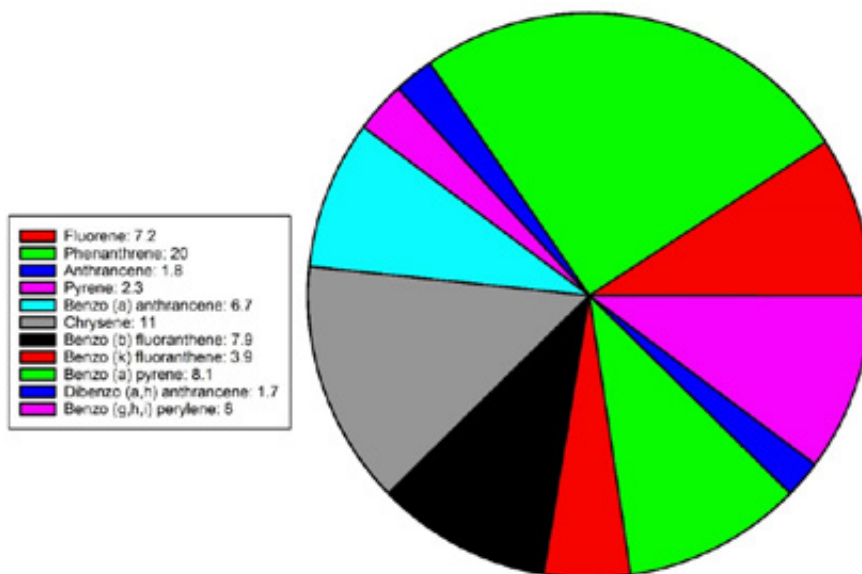


Fig. 2: The percentage of polycyclic aromatic hydrocarbons in cigarette butts (Moriwaki et al. 2009)

PAHs in the littered CBs was 0.032 mg/km/month. In the mentioned survey, the factors such as weather and wind were found to be effective in determining the concentration of such contaminants (Moriwaki et al., 2009). Various amounts of PAHs are detected

in CBs. In a CB, the maximum PAH rate is related to phenanthrene with a frequency of 20% and the minimum PAH rate belongs to anthracene and dibenzoanthracene with less than 2% (Fig. 2).

CBs also include polycyclic aromatic compounds

(PACs), such as nicotine, which have an adverse effect on humans (Green et al., 2014). The nicotine leaked from CB into the water resources can be immediately absorbed by skin, small intestine, bladder and lung alveoli, potentially causing heart failure and neurological effects. Nicotine leakage from CBs into aquatic environments happens very quickly, and this applies to both precipitation on CBs and submersion of CBs in the marine environment. When a cigarette is washed in standing water, nicotine rapidly starts to leach [7.3 mg/g (equivalent to 2.5 mg/L) leaking exceeded 1,440 min], half and 90% of which occur in the first 26 min and 651 min respectively. An average of 3.8 mg/g nicotine exposure was observed in a 21.6-mm accumulation substrate, and almost half of this amount leached with 1.6 mm of precipitation from the soil (Green et al., 2014). The fast nicotine release into the aqueous medium is attributed to its interaction and dosage left in the structure. Other factors, such as chemical composition of the soil and filtration of the bed, can influence the level of nicotine leakage into the water supplies. The amounts of nicotine and other toxins, which are basically determined by smokers,

can be influenced by the characteristics (mass and amount of total tobacco) of the dispersed CBs. Each cigarette can contaminate 1000 liters of water (Green et al., 2014). The nicotine leaking level as been registered as 3.8 mg/L. The precise release of nicotine by natural runoff and the species' response to it have not been determined, but its hazard has been well studied (Moriwaki et al., 2009). Considering the huge volume of discarded CBs, their potentially poisonous and environmentally harmful compounds should be taken seriously. The toxic effects of this waste on fish and other aquatic organisms have been already identified, and the adverse effects of cigarettes have been approved by many studies (Lee and Lee 2015, Dobaradaran et al., 2019). For example, 100% of *Aedes aegypti* died after 24 h during the first period of larvae due to the CB toxicity in 100 ml of water (Dieng et al., 2013). CB termination in the larval step for *Aedes albopictus* and its impact on the decomposition of *Aedes aegypti* were also observed (Dieng et al., 2014). Moreover, the effectiveness of CB on *Aedes albopictus*, the risk of fish mortality owing to the toxins in CB (86), the antibacterial activity in the

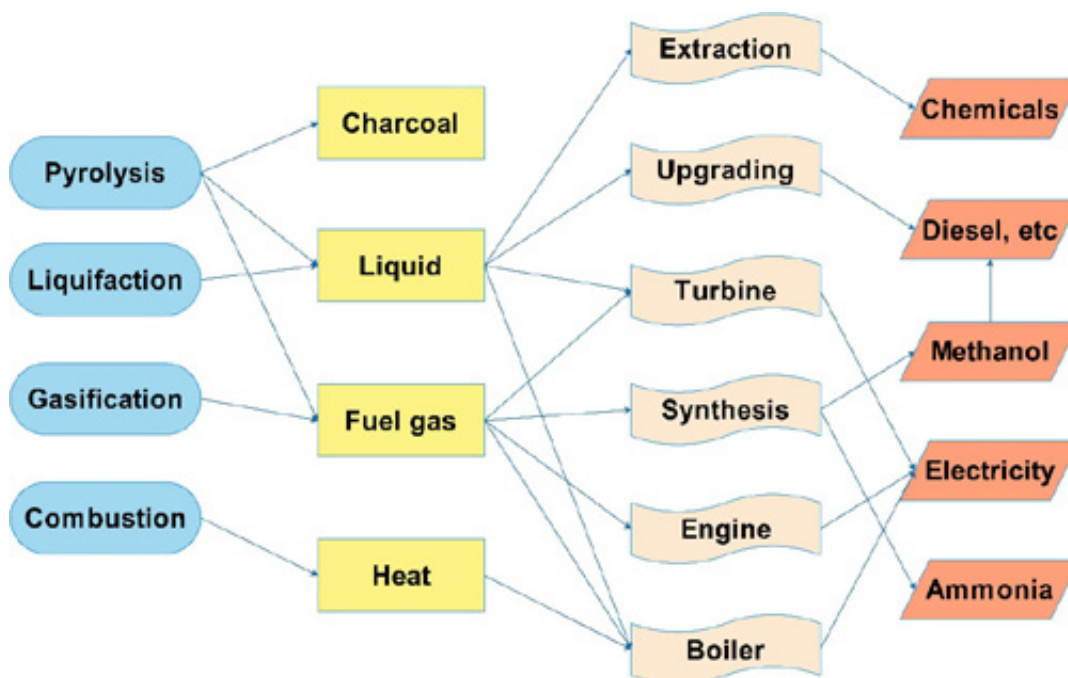


Fig. 3: Thermochemical biomass processes and products (Bridgwater and Peacocke, 2000)

Aedes aegypti larval time, and the impact of CB on Dafina and Daphnia Magna water flea were reported (Dieng *et al.*, 2013). Three types of CB were studied for their potential hazards by Rebischung *et al.* (2018). These hazards were labled as HP 4 (irritant – skin irritation and eye injuries), HP 5 (particular target area toxicity/aspiration toxicity), HP 6 (acute toxicity), HP 7 (cancer causing), HP 8 (irritant), HP 10 (toxic to recombination), HP 11 (mutagenic), and HP 13 (sensitizing). The CBs’ nicotine has been reported as the main hazard corresponding to HP 6 (acute toxicity) (Rebischung *et al.*, 2018).

**Methods for cigarette butts recycling**

The researchers efforts to recycle CBs were

influenced by the physical structure and chemical properties of CBs. CB recycling processes are examined in brick manufacturing, cement production, mosquito handling, porous carbon and absorbent production, voice insulating materials, paper performance, and biofilm drivers in wastewater treatment. CB refining is not requires in some fields such as bricks or asphalt manufacturing, and cigarette could be used in the original form. CB, however, needs to be processed by extraction procedure, pyrolysis, and filter rod extraction for other purposes. Fig. 3 illustrates some conventional thermal conversion methods for producing energy from biomass.

In most of the studies, CBs are disinfected and

Table 1: The CBs recycling methods

Recycling method	Process	References
Vector control	Doping CB for 24 h in 100 mL of deionized water and using the substances discharged from it	(Dieng <i>et al.</i> , 2013)
	Dope the CB in tap water within 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 days	(Dieng <i>et al.</i> , 2011)
	Doping CB for 24 h in 100 mL of deionized water and using the compounds leaked from it	(Dieng <i>et al.</i> , 2014)
	Doping 5 g CB in 250 mL of distilled water for 24 hours, then centrifuging the solution and using the supernatant	(Mondal <i>et al.</i> , 2015)
	Using the CB extract for constructing nano silver structures in the presence of AgNO <sub>3</sub> solution	(Murugan <i>et al.</i> , 2018)
Asphalt production	Encapsulated in paraffin and bitumen	(Mohajerani <i>et al.</i> , 2017)
	Without process	(Kadir and Mohajerani 2011)
	Without process	(Mohajerani 2012)
Production of clay brick	Without process	(Kadir <i>et al.</i> , 2015)
	Without process	(Mohajerani <i>et al.</i> , 2016)
	Without process	(Sarani 2013)
	Heating in vacuum at 230 °C for 3 h and pouring out the carbon to 100 µm	(Masoudi Soltani <i>et al.</i> , 2015)
	Simple pyrolysis with 900 °C for 3 h and with a continuous nitrogen gas equivalent to 100 cm <sup>3</sup> /min and 5 °C/min heating rate	
Activated carbon	Single-stage carbonisation with pyrolysis fuel equivalent to 900 °C for 1 h at 5 °C/min heating	(Yazdi <i>et al.</i> , 2012)
	Impregnated with NaOH, then pyrolysis	(Koochaki <i>et al.</i> , 2019)
Biofilm barrier application	The filter rod extracting	(Sabzali <i>et al.</i> , 2012)
	The filter rod extracting	(Sabzali <i>et al.</i> , 2011)
Production of super hydrophobic fibers	Doping the cigarette filters in NaOH solution and then in Hexadecyltrimethoxysilane-ethanol solution	(Ou <i>et al.</i> , 2016)
	Doping in about 4% hexane solution at room temperature	(Liu <i>et al.</i> , 2015)
Porous sound absorber	Cellulose acetate extracted manually from cigarette filter	(Murugan <i>et al.</i> , 2018)
	Without process	(Maderuelo-Sanz <i>et al.</i> , 2018)
Paper pulp	Pulping the cigarette at boiling point for 3 h and with 1% NaOH	(Teixeira <i>et al.</i> , 2017)
Corrosion inhibitors for metal surface	Water extracts of CBs	(Lucatero <i>et al.</i> , 2016)
Application in lithium-ion batteries	Packaging and any remaining tobacco and chars were removed, and the cellulose acetate filters were soaked in purified water before being sonicated with ethanol using an ultrasonic UP400S	(Huang <i>et al.</i> , 2015)
Ester-rich bio-oil production	Microwave assisted pyrolysis	(Wang <i>et al.</i> , 2020)

dried before being used. CB reuse techniques and their products are presented in [Table 1](#).

Reuse of CBs in various mechanisms can contribute to the production of functional items. It was proved that CBs contain a number of recyclable materials owing to their physicochemical properties. The use of CBs in some reusing techniques may have unfavorable impacts on the characteristics of the finished product as listed in [Table 1](#). The data provided in [Tables 1](#) and [3](#) indicate that it is necessary to recycle CB regardless of its structural properties or contaminants captured in its filter. While the usage of whole CBs in re-enactment without eliminating the components has been explored in a few processes, such as production of building products, application of the chemicals adsorbed onto CBs and also cellulose acetate are the most important methods for CBs recycling. Distilled water and chemical solvents may be used to remove the contaminants contained in the CB. Utilization of these chemical compounds for prevention of corrosion in metals and vectors needs some serious health and environmental attention ([Mondal et al., 2015](#)). Upon clearance of contaminants without any physical deformation, tobacco cellulose acetate filters are used in supercapacitor industries. Cellulose acetate is chemically converted into pulp and adsorption products ([Yazdi et al., 2012](#)), which eventually produce contaminant gases and wastewater emissions ([Teixeira et al., 2017](#)). The quality of the final product is a key element in the CB reuse for development of construction materials such as bricks and asphalt. Application of CBs in the raw materials influences the finished product's properties including strength, density, porosity, and thermal conductivity ([Murugan et al., 2018](#)). The variability of such features is beneficial, but the strength increase in bricks is known to be a negative property. The reuse cycle contributes to the development of high-quality materials under appropriate working conditions such as correct mixing period ([Torkashvand et al., 2020](#)). While the application of CBs in raw resources, owing to their adsorption ability, decreases the heavy metals release in the manufacturing process of bricks, it induces pollutant emission in the gas or liquid phase in all the strategies for CBs re-utilizing. In some cases, researchers, despite using chemical treatment methods, could not reduce the

contaminants from the wastewater produced by CBs processing to an appropriate degree ([Teixeira et al., 2017](#)). A particular portion of CBs is removed in many systems, but some components remain as waste and need maintenance. The trapped chemicals emitted from CBs could be applied in reuse operations for other purposes, such as management of vector and inhibitors for metal corrosion ([Lucatero et al., 2016](#)). Many studies approve the high quality of the product obtained from the CB recycling processes ([Dieng et al., 2014](#)). Pollutants existing in CBs, for example, are extremely good at controlling the vectors. In particular, the CB-derived carbons have a large number of active sites with a large surface area ( $600 \text{ m}^2/\text{g}$ ) which make them suitable for treatment of wastewater ([Hamzah and Umar 2017](#)). The efficiency of the CB reuse techniques is determined based on the effectiveness of their products (see [Table 3](#)). Despite the improvements in the consistency of bricks following the introduction of CBs and the modest adsorption capability of the carbon extracted from CBs compared to other adsorbents, these approaches may not have the ability to recycle CBs in a large scale. Superoleophilic/Superhydrophobic fiber processing can be a great option for CB reuse due to its product efficiency and no loss of output over many cycles among the suggested methods. CB recycling for manufacturing supercapacitors may also be deemed an appropriate process which can provided the product with consistency when it is incompatible with the commercial forms. Certain recycling procedures, including vector control, anticorrosion production, and paper production, may have some disadvantages due to the use of CB toxins or toxin release during the processing period. Problems of hazardous waste, such as CBs, should be deeply considered in sustainability programs in terms of environmental effects. It is claimed that *Aedes aegypti* has a higher propensity to spawn (egg-laying) in a water containing CBs than in a space lacking CBs, indicating that CBs do not affect the mosquito setting location ([Dieng et al. 2014](#)). Moreover, it was shown that the compounds derived from CBs did not decrease the reproductive behavior of *Anopheles stephensi* ([Murugan et al. 2018](#)). One of the effective procedures for CBs safe recycling is the application of cellulose acetate to produce sound absorbers or supercapacitors following the



recovery of captured compounds for manufacturing corrosion inhibitors or for carrier protection purposes that minimize wastewater and hazardous waste (Torkashvand and Farzadkia 2019). CBs were also used as a strong basis for the development of activated carbons by pyrolysis procedures to create N-doped carbon materials (Lee *et al.*, 2014, Kim *et al.*, 2016). Since cellulose acetate is the key element of CBs, it was applied to manufacture nanocrystalline cellulose (Ogundare *et al.*, 2017) and cellulose-based membranes (Huang *et al.*, 2015). CBs treatments included several effective opportunities to recover them. Nevertheless, the CBs have always been a solid waste despite being utilized as absorbent products. Moreover, these recycled products need to be further destroyed to prevent the production of solid contaminants in an area. The main component of CBs, cellulose acetate, is a highly efficient natural carbon source and could be processed into highly valued liquid fuels using the efficient thermochemical processing techniques (Wang *et al.*, 2018). The pyrolysis process has been widely used for the conversion of cellulose to hydrocarbons/aromatics, furan substances (Mascal 2019), and other organic materials such as aldehydes, carboxylic acid and similar substances (Al Shra'ah and Helleur 2014). Microwave-assisted pyrolysis (MAP), due to its rapid temperature increase, targeted processing, volumetric and standard heating in growing heat flux, and improving the reaction efficiency, has advanced as a possible method to replace the regular pyrolysis (Zhao *et al.*, 2019). MAP of cellulose was conducted in earlier studies to produce the phenol-rich fuel (Wenliang *et al.*, 2018, Wang *et al.*, 2019). Some researchers (Nieva *et al.*, 2015) have also approved the efficiency of the MAP of cellulose in producing significant yields of useful liquid products (Veerabagu *et al.*, 2021).

#### Pyrolysis

Pyrolysis is a thermal disintegration of compounds where there is no oxygen or slightly less oxygen full combustion. A precise description of pyrolysis is difficult, particularly when it is applied to biomass. Earlier studies typically correlate pyrolysis with the carbonization process, of which a solid char is a primary ingredient. The term pyrolysis defines processes where oils are favored materials. In the

latter procedure, the time period for pyrolysis is much faster. The generalized changes that happen during pyrolysis are as follows (Diebold and Bridgwater 1997).

- 1) Transfer of heat from a source of heat to raise the fuel temperature;
- 2) The initiation at high temperature of primary pyrolysis reactions produces volatile and charcoal elements;
- 3) Hot volatile flow to colder solids contributes to heat conversion between hot volatiles and colder unpyrolyzed fuel;
- 4) Tar is generated by the condensation of certain volatile matter in the cooler sections of the fuel, accompanied by side reactions;
- 5) In a competition, catalytic second pyrolysis reactions happen when primary pyrolysis process interactions take place simultaneously;
- 6) Residential cycle, dehydration, radical replication, water gas shift reaction, and reformation occur based on the time/temperature/pressure pattern of further thermal decomposition.

Groundbreaking investigations on flash or fast pyrolysis have demonstrated that carbon-based materials can yield significant amounts of dominant, non-equilibrium liquids and gases, including associated materials, useful materials, oils, and petrochemicals. The lower volume of solid char produced by traditional pyrolysis can have alternatives such as fuel gas with high value, fuel oil, or quick pyrolysis materials (Bridgewater *et al.*, 2001).

#### Types of pyrolysis

The pyrolysis method may be divided into various types according to the configurations of the process. The subsequent sections provide a description of gradual and rapid pyrolysis processes, since they are the most regular approaches. Different types of pyrolysis procedures have been described, and additional details about the pyrolysis cycle's approaches and reactors have been reported in many studies (Czajczyńska *et al.*, 2017, Zaman *et al.*, 2017). The method indicates reactor type which should be used in the process (Roy and Dias 2017). Drum, screw/auger and rotatory kilns are the reactors commonly used in simple pyrolysis. Spinning cones, fluidized beds, vacuum, entrained

stream, and axial reactors are the reactors for rapid pyrolysis (Marshall and Eng 2013). Using auger-type reactors, both fast and slow pyrolysis processes could be handled.

#### Fast pyrolysis process

The “fast pyrolysis” term refers to heating carbon-based materials at a heating rate of 100-1300 °C/s for 1 to 10 s (Tripathi et al., 2016). This process is typically applied for producing bio oil because the pyrolysis process oil content is significantly higher than the char and gas output. 60–75% liquid biooil, 10–20% volatile gas compounds, and 15–20% biochars are common commodity yields in rapid pyrolysis (Bridgwater 2003). The primary aim of the rapid pyrolysis procedure is to heat carbon-based feedstock to reach the thermal degradation, thus shortening the release time and facilitating the char forming (Mohan Jr et al., 2006). Besides, by using high heating speeds through rapid pyrolysis to convert the feedstock into liquid biooil products, the unexpected generation of char is avoided.

#### Slow pyrolysis process

The standard form of pyrolysis is slow pyrolysis which usually requires low levels of heating and high periods of residency (Tripathi et al., 2016). Approximately, a 400-500 °C average temperature, with a thermal intensity of 0.1-1 °C/s is used for 5-30 min as an optimal period. The slow pyrolysis cycle favors the carbonaceous char output but liquid, while gas fuel compounds are often generated in comparatively limited amounts (Demirbas and Arin 2002).

#### Pyrolysis; Benefits and Limitations

Pyrolysis is a more environmentally sustainable

option compared to incineration. Compared to other thermo-chemical and biochemical processes, pyrolysis is often thought to be the best option for time saving and have the least environmental footprint (Jo et al., 2017). The high capacity to manage all types of feedstock and manufacture a broad array of products is among the advantages of using the pyrolysis technique (Foust et al., 2009). Unlike biochemical processes, the process needs less reaction time and can be quickly upgraded as short retention periods. Considering the disadvantages of using pyrolysis, it is possible to mitigate the wet and high moisture feedstock issue by integrating the low cost predrying methods before reaction which can be measured using the model and simulation. Sufficient sunlight and low humidity, especially in arid environments, allow the solar greenhouse methodologies to offer a low-cost pretreatment drying. Gasification and pyrolysis are the techniques for producing biochar, but pyrolysis generates greater biochar outputs and emits less toxic gases such as SO<sub>x</sub> and NO<sub>x</sub> (Tripathi et al., 2016). Another advantage of pyrolysis versus gasification is its versatility in managing various raw materials and various operational situations which allows the final products to produce the necessary specifications. Comparison of the different processes of converting materials into energy sources is presented in Table 2.

#### Pyrolysis of cigarette butts

Some experiments are focused on the pyrolysis of CBs aiming to develop the valuable items such as biochars and fuel oils. Bio char is regularly used to modify the soil, and bio oil can be applied for energy supply and as additive in asphalt industries (Vakalis et al., 2017). Biochar is an organic material

Table 2: Comparison of thermochemical conversion processes (Pourkarimi et al., 2019)

Conversion Process	Temperature (°C)	Pressure (MPa)	Liquid		Gas content (% dry wt.)	Solid content (% dry wt.)
			Content (wt.% dry)	HHV (MJ/ Kg)		
Gasification		-	13.74	15.18	28.08	58.18
Gasification	500	35	15	-	69	7
Liquefaction	350	36	43	39	-	-
Liquefaction	350		39.9	39.9	23.2	-
Pyrolysis	450	0.101	57.9	41	32	10.1
Pyrolysis	502	0.101	55.3	39.7	36.3	8.4

Table 3. The CBs pyrolysis methods and results

Objective of study	Product(s)	Highlights	Reference
Manufacture of ester-rich bio-oil by pyrolysis of used cigarette filters	Ester-rich bio-oil	<ul style="list-style-type: none"> <li>Due to the high heating frequency under MAP conditions, the pyrolysis output was greatly improved with the the help of microwave absorber silicon carbide in the reactor as well as the application of methanol to N<sub>2</sub> carrier gas;</li> <li>MAP heating method led to 29.17% bio-oil from CBs compared to to the conventional tubular muffle furnace heating method which yields 0% of bio-oil. The bio-oil yield from CBs increased from 29.17% to 46.71% due to the introduction of methanol.</li> <li>Gas chromatography/mass spectrometry findings showed that esters, particularly methyl acetate (over 12%). were the major components of bio-oils (over 40%)</li> <li>The UCF bio-char showed mesoporous properties (e.g., over 500 m<sup>2</sup>/g of specific surface area).</li> </ul>	Wang <i>et al.</i> , 2020
Treatment of the recycled CBs to produce electrically conducted materials	Conducting material	<ul style="list-style-type: none"> <li>In a simple process, the conductive substances were produced through heat treatment of the recycled cigarette filters.</li> <li>Since no pretreatment of the used cigarette filters was needed prior to the carbonization phase, it was cost-effective.</li> <li>The current-voltage curve of the product showed a marked improvement in conductivity, supporting the application of the substance in electronic conduction.</li> </ul>	Ghosh <i>et al.</i> , 2017
The effect of carbonization temperature of waste CBs on Na <sup>+</sup> storage capacity of N-doped hard carbon anode	N-doped hard carbon anode	<ul style="list-style-type: none"> <li>Waste CBs for the sodium ion battery anode was reused through the pyrolysis carbonization process at 700 °C and 800 °C.</li> <li>The morphology and electrochemical efficiency of N-doped waste CBs hard carbon (NWHC) were influenced by the temperature of the carbonization process.</li> <li>The reversible discharge power of NWHC-700 anode was 300 mAh/g at 25 mA/h/g for 200 cycles and 135 mA/h/g even at 1500 mA/h/g for 2000 cycles, higher than 241 mA/h/g and 105 mA/h/g of NWHC-800 anode, respectively.</li> </ul>	Hou <i>et al.</i> , 2019
Lead removal by charred carbon from the pyrolysis of used cigarette filters	Nitric acid modified charred carbon	<ul style="list-style-type: none"> <li>Charred carbon was produced by the simple pyrolysis of the CBs.</li> <li>The effects of the pH of the lead solution, the adsorbent dosage, the initial lead concentration and the contact time of the two carbons were studied.</li> <li>The adsorbent dosage impact was virtually equivalent for both modified and unmodified carbons with an average value of 0.1 g</li> <li>The adsorption results were fitted with the Freundlich and Langmuir isothermic models.</li> <li>The removal performances for non-modified and HNO<sub>3</sub>-modified carbons were calculated at an initial lead concentration of 600 mg/L at 66 and 74.5 mg/g, respectively.</li> </ul>	Masoudi Soltani <i>et al.</i> , 2015
Effects of pyrolysis conditions on the porous structure construction of mesoporous charred carbon from used cigarette filters	Mesoporous charred carbon	<ul style="list-style-type: none"> <li>One-step pyrolysis was used to synthesize mesoporous charred carbon from the used cigarettes filters.</li> <li>Complete factorial configuration of experiments, including heating intensity, soaking period and pyrolysis temperature, was used at three rates for each factor.</li> <li>The temperature and heating volume of the synthesized coal had the most important impact on the overall surface area.</li> <li>At a pyrolysis temperature of 900 °C, the maximum surface area (597 m<sup>2</sup>/g) was achieved when the substrate was heated at 5 °C/min and kept at this level for 3 h.</li> <li>The N<sub>2</sub> adsorption – desorption isotherm generated showed some degree of mesoporosity in charred carbon at an average pore size of 3.32 nm.</li> </ul>	Soltani <i>et al.</i> , 2014
The effect of pre-swelling on activated carbon from CBs	Activated carbon	<ul style="list-style-type: none"> <li>CBs were impregnated with various proportions of NaOH solutions and then pyrolyzed.</li> <li>Phenol and carboxyl were evaluated using FTIR.</li> <li>The activated carbon specific surface area was about &lt; 900 m<sup>2</sup>/g.</li> <li>The iodine number verified the maximum activated carbon capacities (1143.34).</li> <li>Tests revealed that filter fiber pre-swelling can raise the average activated carbon surface by 47%.</li> </ul>	Koochaki <i>et al.</i> , 2019
Dry physical mixing of cigarette filters with KOH prior to porous carbon synthesis	Porous carbon	<ul style="list-style-type: none"> <li>This analysis measured the impact of physical mixing of cigarette filters with KOH powder on the final characteristics of carbonated porous carbon</li> <li>Dry KOH functional mixing of cigarette filters has been observed to minimize the specific surface area of Brunauer, Emmet and Teller by about 79%.</li> <li>This indicated that dry KOH impregnation to CBs as a carbon precursor for porous carbon synthesis would not be an acceptable method for achieving a higher surface area.</li> </ul>	Soltani and Yazdi 2012

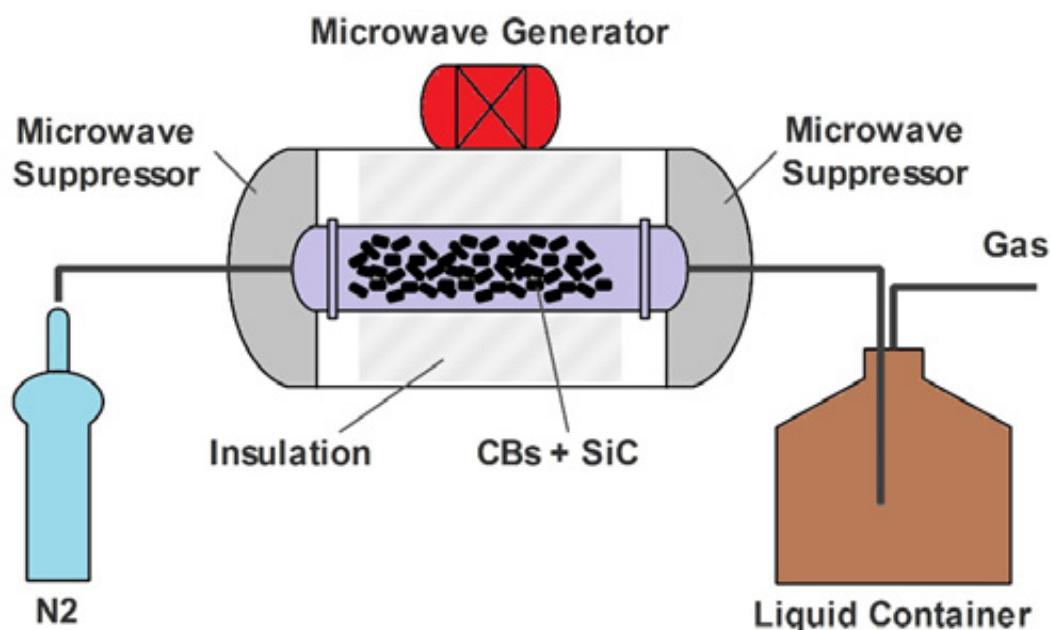


Fig. 4: The reactor of microwave-assisted pyrolysis (Wang et al., 2020)

produced by pyrolyzing carbon-based feedstocks and is better characterized as a “soil conditioner.” The addition of biochar to soil would act as a carbon sink. The characteristics of biochar have been considered to be extremely heterogeneous, both inside the independent bio-char grains and among the biochars derived from different feedstocks and/or under different pyrolysis conditions. Bio-oil can be easily preserved and shipped as it is a green liquid fuel. It can be used as an alternative to fuel oil or diesel in a variety of stationary cases such as boilers, furnaces, generators, and electricity-generating turbines. Alternatively, the crude oil could be used to make adhesives, phenol-formaldehyde-type resins, wood flavors (Xiu and Shahbazi 2012). Table 3 provides a summary of the studies yet have been conducted on the pyrolysis of CBs, and elaborates on the methods, properties, yield, etc, related to the extraction of bio oil and biochar from CBs. The used cigarette filters (UCF) were utilized to produce ester-rich bio-oil via a cleaner production process, namely MAP. The pyrolysis efficiency was significantly enhanced owing to the high heating rate under MAP with the help of microwave absorber silicon carbide

(SiC) in reactor and addition of methanol. Compared to the traditional tubular muffle furnace heating method yielding 0% of bio oil, the MAP heating method extracted 29.17% of bio oil from UCF. Using the MAP, the bio oil yield from UCF increased from 29.17% to 46.71% due to the introduction of methanol. N<sub>2</sub> with a flow rate of 800 mL/min was passed through the MAP reactor for 10 min at the beginning of the experiment. The heating was then achieved by a steady stream of 800 mL/min N<sub>2</sub> using a 1000 W microwave (about 80 °C/min). To complete the operation, the temperature was eventually increased to 600 °C and maintained at this temperature for 10 min. Fig. 4 shows a schema of the system employed for the pyrolysis method. The results of this study showed that by adding methanol to the mobile phase, the bio oil yield would be 17.54% higher. If the projected CBs are fully exploited, about 358065 m<sup>3</sup> of bio oil would be produced annually (Wang et al., 2020).

The products of CBs pyrolysis, are mostly in solid-phase for different applications. The electrically conductive substrates (Ghosh et al., 2017) were developed, and it has been shown that addition of

12 wt% of pyrolyzed CBs to DI water increases its conductivity by at least one order. The results of N-doped hard carbon anode preparation (Hou *et al.*, 2019) indicated that the reversible discharge power of NWHC-700 anode was 300 mAh/g at 25 mA/g for 200 cycles and 135 mAh/g even at 1500 mA/g for 2000 cycles, higher than 241 mAh/g and 105 mAh/g of NWHC-800 anode, respectively. Nitric acid-modified charred carbon (Masoudi Soltani *et al.*, 2015) was utilized to lead ion removal, and the results showed that at an initial lead concentration of 600 mg/L, the removal efficiencies were 66.74.5 mg/g and 74.5 mg/g for non-modified and HNO<sub>3</sub>-modified carbons, respectively. Mesoporous charred carbon (Soltani *et al.*, 2014) was developed and at a pyrolysis temperature of 900 °C, the maximum surface area (597 m<sup>2</sup>/g) was achieved when the substrate was heated at 5 °C/min and maintained at this level for 3 h. The generated N<sub>2</sub> adsorption-desorption isotherm showed some degree of mesoporosity in charred carbon at an average pore size of 3.32 nm. Moreover, pre-swelled activated carbon (Koochaki *et al.*, 2019), and KOH treated porous carbon were obtained as solid products by using the pyrolysis method for CBs recycling.

## CONCLUSIONS

Compared to other biochemical and thermochemical methods, pyrolysis is an economically efficient alternative disposal system for biomass waste. Considering the large amount of CBs waste produced globally, the pyrolysis of CBs with the objective of generating different valuable items holds a promising potential. Biochars can be further processed into valuable materials such as activated carbons. System parameters and activation strategies have a significant impact on biochar properties and performance. A number of recent experiments have shown the advantages of using the pyrolysis of CBs for the development of valuable products, particularly biochars. Although the biggest problem of the pyrolysis process is the moisture of the input feed, its most important advantage is the conversion of feed into valuable materials in a one-step process at moderate temperatures. The following issues can be addressed as part of future study: a) the recycling and integration of

the gas portion again into the pyrolysis reaction, including certain heat requirements for the thermal decomposition of CBs into biochar product can improve the efficiency of pyrolysis system and economic feasibility; b) the co-pyrolysis of CBs with various materials and biomass waste and their effects on the enhancement of the target product yield while reducing the production of undesirable products; c) further examination of the application of microwave-assisted technologies to transform CBs waste into high quality products such as liquid fuel oils; and d) using models and experiments to attain products with the specific properties and yielding required for the final potential use (e.g. capacitors, pollutant adsorbents) and enhancing the manufacturing structures and processes (such as pyrolysis pressure, temperature and retention time). Tackling the technical issues associated with the pyrolysis of CBs to produce valuable goods would help to develop its use in waste handling and recycling of different compounds which can directly be used or converted into the other final products. Adequate economic and thermodynamic evaluation should also be done on methods of converting CBs into valuable products. The results of this study can mitigate the hazards of spreading CBs in the environment and create added value in the pyrolysis process.

## AUTHOR CONTRIBUTIONS

M. Hazbehian performed investigation, data collection, and also done the partial analysis. N. Mokhtarian and A. Hallajisani performed data analysis in the study. All authors contributed to literature, supervision, and writing the original draft. A. Hallajisani edited and corrected the manuscript.

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## CONFLICT OF INTEREST

The ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

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**ABBREVIATIONS**

%	Percentage	<i>KOH</i>	Potassium hydroxide
°C	Degrees Celsius	<i>L</i>	Litre
°C /min	Degrees celsius per minute	<i>m</i>	meter
°C /s	Degrees celsius per second	<i>m<sup>2</sup>/g</i>	Square meter per gram
µg/g	Microgram per gram	<i>mAh/g</i>	Milliamper hours per gram
<i>AgNO<sub>3</sub></i>	Silver nitrate	<i>MAP</i>	Microwave assisted pyrolysis
<i>Butt/Km/month</i>	Cigarette butts per kilometer per month	<i>mg/g</i>	Miligram per gram
<i>CBs</i>	Cigarette butts	<i>mg/Kg</i>	Miligram per kilogram
<i>CBs/m<sup>2</sup></i>	Cigarette butts per square meter	<i>mg/Kg/month</i>	Miligram per kilogram per month
<i>Cl</i>	Chlorine	<i>mg/L</i>	Miligram per litre
<i>Cm<sup>3</sup>/min</i>	Cubic centimeter per minute	<i>min</i>	Minute
<i>et al.</i> ,	And others	<i>mL</i>	Mililitre
<i>FTIR</i>	Fourier-transformed infrared spectroscopy	<i>mL/mm</i>	Mililitre prt millimeter
<i>g/g</i>	Gram per gram	<i>mm</i>	Milimeter
<i>g/mole</i>	Gram per mole	<i>N<sub>2</sub></i>	Nitrogen
<i>h</i>	Hour	<i>NaOH</i>	Sodium hydroxide
<i>HHV</i>	High heat value	<i>NO<sub>x</sub></i>	Nitrogen oxides
<i>HNO<sub>3</sub></i>	Nitric acid	<i>nm</i>	Nanometer
<i>HP</i>	Hazardous properties	<i>NWHC</i>	N-doped waste cigarette butts hard carbon
<i>J/g</i>	Joule per gram	<i>PACs</i>	Polycyclic aromatic compounds
<i>Kg</i>	Kilogram	<i>PAHs</i>	Polycyclic aromatic hydrocarbons
		<i>pH</i>	Power of hydrogen
		<i>S</i>	Second
		<i>SO<sub>x</sub></i>	Sulfur oxides
		<i>UCF</i>	Used cigarette filters
		<i>UV</i>	Ultra violet
		<i>W</i>	Watt
		<i>WHO</i>	World Health Organization

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#### AUTHOR (S) BIOSKETCHES

**Hazbehian, M.**, Ph.D. Candidate, Department of Chemical Engineering, Islamic Azad University, Shahreza Branch, Shahreza, Iran.  
Email: [haz\\_mohamad@yahoo.com](mailto:haz_mohamad@yahoo.com)  
ORCID: [0000-0000-0000-0000](https://orcid.org/0000-0000-0000-0000)

**Mokhtarian, N.**, Ph.D., Associate Professor, Department of Chemical Engineering, Islamic Azad University, Shahreza Branch, Shahreza, Iran. Email: [mokhtarian@iaush.ac.ir](mailto:mokhtarian@iaush.ac.ir)  
ORCID: [0000-0002-1307-926X](https://orcid.org/0000-0002-1307-926X)

**Hallajisani, A.**, Ph.D., Assistant Professor, Biofuel Research Labotary, Caspian Faculty of Engineering, College of Engineering, University of Tehran, Rezvanshar, Guilan, Iran. Email: [hallaj@ut.ac.ir](mailto:hallaj@ut.ac.ir)  
ORCID: [0000-0003-3793-9129](https://orcid.org/0000-0003-3793-9129)

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