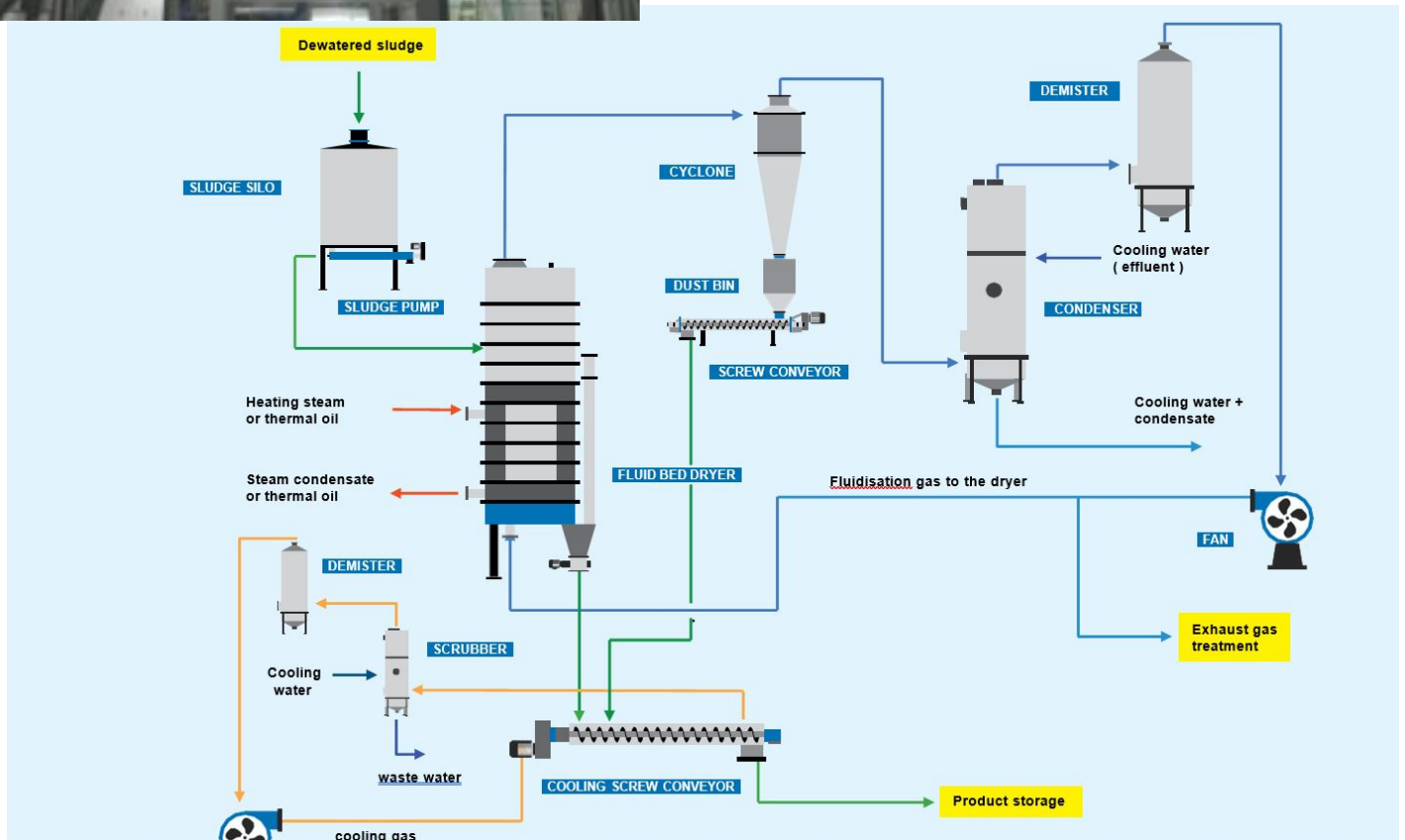
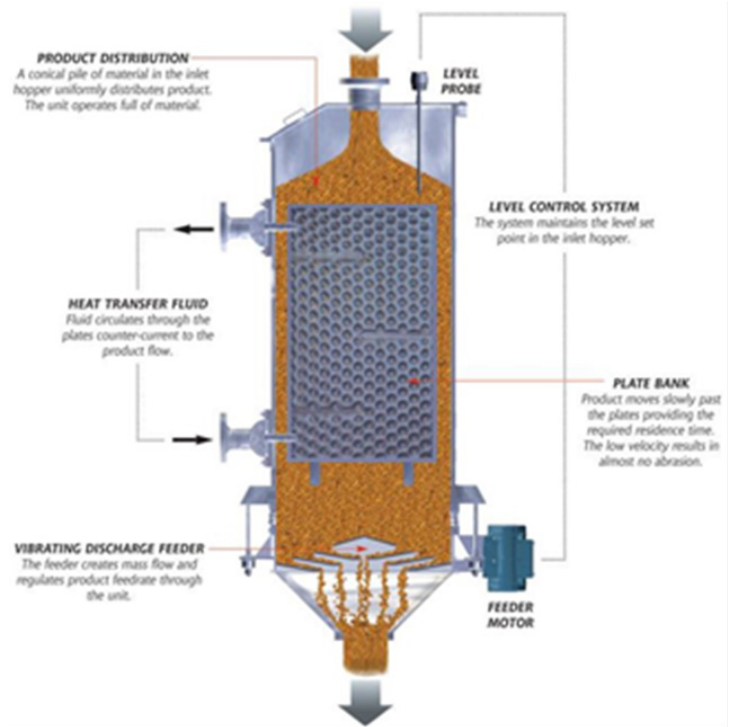


Gasification – Drying – Pfas Destruction and Fertilizer



Thermal Drying 7

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Thermal Drying

- (i) Better product quality
- (ii) Diversified use (biofuel)
- (iii) Faster process & lower volume
- (iv) Lower storage & transportation costs
- (v) Less social impact
- (vi) Operational hazards
- (vii) Risk of fire and explosions
- (viii) Complex operation requiring experience operators
- (ix) Dust and emissions

Types of Pyrolyzation

PYROLYZATION

Pyrolysis is typically defined as the thermochemical decomposition of biomass feedstock at medium (300–800°C) to high temperatures (800–1300°C) in an inert atmosphere [15]. Some similar definitions are reported in other publications [5,8,9,14,16–18].

Pyrolysis is the thermochemical decomposition of organic matter into noncondensable gases, condensable liquids, and a solid residual coproduct, biochar or charcoal in an inert environment (ie, in the absence of oxygen).

From: Environmental Materials and Waste, 2016

PYROLYSIS

Prabir Basu, in Biomass Gasification, Pyrolysis and Torrefaction (Third Edition), 2018

Microwave-Assisted Pyrolysis Conventional Electric Pyrolysis

Conversion of energy Transfer of energy

Noncontact heating Contact heating

Hot spot No hot spot

Selective Nonselective

Lower thermal inertia and faster response Higher thermal inertia and slower response

Lower energy consumption Higher energy consumption

Rapid heating Slow heating

Shorter reaction times Longer reaction times

Volumetric heating Superficial heating

Higher level of control Lower level of control

Improved product yields Lower product yields

5.3.2 Effect of Pyrolysis Temperature

During pyrolysis, a fuel particle is heated at a defined rate from the ambient to a maximum temperature, known as the pyrolysis temperature. The fuel is held there until completion of the process. The pyrolysis temperature affects both composition and yield of the product. Fig. 5.6 is an example of how, during the pyrolysis of a biomass, the release of some product gases changes with different temperatures. We can see that the release rates vary widely for different gaseous constituents.

The amount of char produced also depends on the pyrolysis temperature. Low temperatures result in greater amount of char; high temperatures result in less. Fig. 5.7 shows how the amount of solid char produced from the pyrolysis of a biomass decreases with increasing temperature, but the heating value of the char increases with temperature. This happens because the fixed carbon, which has a higher heating value, in the char increases while the volatile content of the char decreases. The amount of noncondensable gas (CO₂, CO, H₂, CH₄) increases with temperature.

Heating value of the solid char produced increases with temperature.

((Data for grape bagasse (0.63–1.0 mm and HHV=17.2 MJ/kg dry) replotted from Encinar, J.M., Beltran, F.J., Bernalte, A., Ramiro, A., Gonzalez, J.F., 1996. Pyrolysis of two agricultural residues: olive and grape bagasse: influence of particle size and temperature. Biomass Bioenergy 11(5), 397–409.)

Advances in bio-oil extraction from nonedible oil seeds and algal biomass

G. Baskar, ... I. Abarnaebenezer Selvakumari, in Advances in Eco-Fuels for a Sustainable Environment, 2019

7.5.1 Pyrolysis (thermal cracking)

Pyrolysis is the process of thermal conversion of organic matter using a catalyst in the absence of oxygen. Thermal decomposition of triglycerides produces alkanes, alkenes, alkanes, aromatics, and carboxylic acids. The liquid fractions of the thermally decomposed vegetable oils are likely to be used as diesel fuels. The pyrolyzate is observed to have a lower viscosity and flash point than diesel fuel [30]. Based on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis. Many researchers have studied the pyrolysis of nonedible vegetable oils and their cakes such as Babassu, Karanja (*Pongamia pinnata*), *Jatropha curcas*, Copra, mahua (*Madhuca indica*), and Tung. Castor oil is one of the suitable alternative and renewable fuel for internal combustion engine.

8.4.1.2 Pyrolysis

Pyrolysis involves the decomposition of waste under anaerobic conditions at temperatures ranging between 300°C and 800°C. The pyrolytic products obtained include a gaseous product (syngas), a liquid (tar), and char, with ash as an undesirable residue [21]. The yields of the products depend on the composition of the waste, the pyrolysis temperature, and the heating rate. Lower pyrolysis temperatures lead to the production of more liquid products, whereas higher temperatures yield more gaseous products. The major advantage of pyrolysis is that it is a cost-effective technology and helps curb environmental pollution. However, the production of various pollutants occurs in the exhaust gas during the pyrolysis process such as hydrogen sulfide (H₂S), ammonia (NH₃), SO_x, and NO_x. So strategies for treating the exhaust gas before emission into the environment are extremely important [16].

SUSTAINABLE WASTE-TO-ENERGY TECHNOLOGIES: GASIFICATION AND PYROLYSIS

Serpil Guran, in Sustainable Food Waste-To-energy Systems, 2018

Pyrolysis

Pyrolysis of postconsumer mixed solid waste may provide a promising valorization approach to generate liquid, biochar, and gaseous coproducts. Similar to gasification, mixed food waste has its challenges because of the heterogeneous properties of the feedstock material. Several studies on mixed food waste pyrolysis concluded that food waste can be converted into useful forms of energy (Liu et al., 2014; Grycova et al., 2016a,b; Mahapatra et al., 2012). All these studies demonstrated that properties of the resulting pyrolysis products are dependent on the composition of the feedstock and reaction conditions. To understand mixed food waste thermal decomposition characteristics via pyrolysis, some studies have individually converted food waste components (carbohydrates, lipids, and proteins) and demonstrated that carbohydrates produced furan- and sugar-based products, whereas pyrolysis of proteins resulted mainly in hydrocarbon-based products in the aromatic form. The pyrolysis of lipids produced high amounts of acids and low concentrations of hydrocarbon and alkene products (Collins, 2015). The results also showed that pyrolysis oil from mixed waste is a multicomponent mixture depending on the feedstock. Substances that can serve as feedstocks for other industries can be isolated from the pyrolysis oil and recycled. Some studies showed that pyrolysis of waste cellulose from edible oil production can yield pyrolysis oil-containing substances such as capronaldehyde, valeric acid, caprylic acid, and caprolic acid that can be used in the flavors industry (Grycova et al., 2016a), and the combustible components of the product gas phase can be used for process energy (Grycova et al., 2016b). Microwave pyrolysis is also considered to be a viable technology to convert mixed food waste into upcycled products. Microwave-assisted pyrolysis of coffee hulls resulted in higher oil yields compared to conventional pyrolysis (Luque et al., 2012). Liu et al. (2014) examined the catalytic effect of metals oxides such as MgO, Fe₂O₃, and MnO₂ and chloride salts such as CuCl₂ and NaCl during microwave pyrolysis. Their results showed that the presence of metal salts negatively impacted oil yield and enhanced gas yield, whereas chloride salts provided the opposite effect.

Pyrolysis research has especially concentrated on producing biochar to be used as activated carbon, and Mahapatra et al. (2012) demonstrated that ZnCl₂ was a better activation agent for the biochar produced from pyrolysis of mixed sludge from the food industry. Pyrolysis of postconsumer fats and oils, such as waste cooking oil with animal fat content, resulted in triacylglycerols that were decomposed to fatty acids. Unsaturated fatty acids decomposed to hydrocarbons at temperatures up to 390°C. At higher temperatures, hydrocarbons were formed by decarboxylation of ester groups. The presence of a Pd/C catalyst during the pyrolysis allowed selective decarboxylation to produce light oil fractions (Ito et al., 2012).

PAPER INDUSTRY WASTES AND ENERGY GENERATION FROM WASTES

P.M. Gopal, ... Debabrata Barik, in Energy from Toxic Organic Waste for Heat and Power Generation, 2019

7.4.3 PYROLYSIS

Pyrolysis involves the process of organic matter decomposition in the absolute absence of oxidizing agent that takes place in the temperatures of 280–850°C. With the difference in heating rate and residence time, reaction temperatures, and the relative yields of the solid (bio-char), gaseous (biogas) and liquid (bio-oil) products formed, this process is divided into three main types, namely slow, intermediate, and fast pyrolysis.

In similar to the gasification process, pyrolysis also necessitates the low moisture content feed material [16]. Pyrolysis is a way of thermally upgrading waste and biomass into higher calorific value fuels. Already, a pyrolysis plant which uses plastic fraction

of rejects from the recycling of beverage cartons in paper and board industries as a fiber source was installed and is operational for a number of years in Spain, and it delivers the end products of pyrolysis also to clean aluminum for recycling. Conversely, pyrolysis of sludge is still under development. Numerous examples on this research can be identified in the literatures [22–25]. An approach to incorporate it into paper mill energy system would be the use of oil as fuel on-site and co-firing the gas and char for heat generation to dry the sludge and using steam for generating electricity [16]. From this use of natural gas for combusting, the sludge would thus be eliminated. Yang et al. [26] found that the pyrolysis oil derived from deinking sludge has few characteristics that could possibly restrict its application in diesel engines, but also suggest that these could be toned down by blending with biodiesel. It could also be likely transformed to other liquid fuels or chemicals, but this should first need quality enhancement like sludge pretreating [27]. The char could also find exterior uses in soil improvement or as fertilizer; for example, char obtained from deinking sludge has confirmed its environmental remediation ability on polluted soil with nickel [28]. The sludge pyrolysis also acts as a technique for separation, presenting reclaimed inorganic fillers for reuse in the paper making process [23]. Microwave pyrolysis, believed as an enhanced rapid pyrolysis method, has also been tested on paper and board industry sludge [29].

CHARACTERIZATION OF NOM

Mika Sillanpää, ... Tanja Lahtinen, in *Natural Organic Matter in Water*, 2015

2.5.2.1 Pyrolysis Gas Chromatography-Mass Spectrometry

In pyrolysis, the large complex molecules in NOM are broken down into more analytically available fragments by the application of heat and under anoxic conditions. These fragments are then swept into the analytical column for gas chromatography (GC) and detected by MS. Pyrolysis combined with gas chromatography-mass spectrometry (Py-GC-MS) is a useful technique both for quantitative measurements and for producing structural information about the molecular building blocks of NOM (Bruchet et al., 1990; Schulten, 1993; Fabbri et al., 1998; Christy et al., 1999; Leenher and Croué, 2003; Templier et al., 2005; Chow et al., 2009b). The analysis of complex oxygen-containing macromolecules can be challenging. Polar pyrolysis products are poorly GC amenable and undergo undesirable thermal reactions (Templier et al., 2005). Development in the pyrolysis technique has made it possible to overcome some of these analytical limitations (Parsi et al., 2007).

Microscale sealed vessel pyrolysis is a promising new approach to NOM characterization. This technique promotes the reduction of polar NOM moieties and significantly increases the yield of GC amenable products (Greenwood et al., 2006; Berwick et al., 2007, 2010). This analytical method represents an excellent complement to conventional flash pyrolysis techniques, which may have a limited capacity for chromatographic resolution of polar biochemicals. However, the technique needs to be developed further to enable more advanced NOM characterization.

Major pyrolysis fragments, most commonly yielded from aquatic NOM pyrochromatograms, have been listed by Leenher and Croué (2003) and are summarized in Table 2.3. Besides pyrolysis-MS, the molecular-level structural information can also be obtained by chemical degradation methods such as using a reducing agent (e.g., n-butylsilane) in combination with MS (Nimmagadda and McRae, 2007).

Table 2.3. The predominant pyrolysis by-products from aquatic natural organic matter (NOM)

Type	Common fragments
Polysaccharides	Methylfuran, furfural, acetylfuran, methylfurfural, levoglucosone, hydroxypropanone, cyclopentanone, methylcyclopentanone, acetic acid
Amino sugars	Acetamide, N-methylacetamide, propionamide, acetic acid
Proteins	Acetonitrile, benzonitrile, phenylacetone, pyridine, methylpyridine, pyrrole, methylpyrrole, indole, methylindole (from tryptophan), toluene, styrene (from phenylalanine), phenol, p-cresol (from tyrosine)
Polyphenolic compounds	Phenol; o-, m-, p-cresol; methylphenols; dimethylphenols
Lignins	Methoxyphenols
Tannins	Catechol
DNA	Furfuryl alcohol
Polyhydroxybutyrates	Butenoic acid

Adapted from Leenher and Croué (2003).

Microwave-assisted fast pyrolysis of hazardous waste engine oil into green fuels

A. Santhoshkumar, R. Anand, in *Advances in Eco-Fuels for a Sustainable Environment*, 2019

5.4 FACTORS AFFECTING THE PYROLYSIS PROCESS

The pyrolysis temperature, heating rate, and residence time majorly influence the pyrolysis product and pyrolysis fuel quality. Morin et al. [33] investigated the effect of the biomass nature and the pyrolysis conditions on the reactivity of char and the physicochemical properties. Table 5.1 shows the effect of properties on the pyrolysis product.

Table 5.1. Effect of properties on the pyrolysis product

Sl. No.	Property	Effect on yield with increasing value of the property	Effect on the reactivity of char	Other comments
I.	Heating rate	Decrease the char yield		
II.	Increase the gas and liquid yield	Reactivity of char increased due to higher heating rate	Higher heating rate activates oxygen and hydrogen content and also increases the surface area and the availability of active sites	
III.	Pyrolysis temperature	Increases gas yield; decreases char yield	Decreases reactivity of char	CO ₂ concentration is decreased by increasing pyrolysis temperature; char reactivity reduces due to the enhancement in the presence of a larger aromatic ring and system structural ordering of the char by increasing the temperature of pyrolysis
IV.	Pyrolysis pressure	Increases the yield of char and CO ₂ ; decreases the yield of CO, CH ₄ , and H ₂	Decreases char reactivity	The decrease of reactivity of the char with pyrolysis pressure is due to the rise of the char's carbonaceous structure
V.	Residence time	Increases the yield of char	Decreases char reactivity	Prolonged heating reduced reactivity at the final temperature of pyrolysis, which improves the loss of active sites and structural ordering of the char
VI.	Biomass nature	No effect	No effect	The determining parameter is the initial biomass pertaining to the reactivity of the char as well as its properties and the structure of the char

Pyrolysis processes were divided into three subgroups based on the operating parameters. Each parameter resulted in a different product composition. These subgroups are slow pyrolysis, fast pyrolysis, and flash pyrolysis. The parameters that describe slow pyrolysis are a temperature of 400°C with a residence time of more than 30 min and a heating rate of (0.1–1°C/s). The product composition yield for slow pyrolysis as explained by the investigators is 35% biochar (solid), 30% bio-oil (liquid), and 35% syn-gas (gas) [34].

Slow pyrolysis has the lowest yield of liquid products that is the focus of most experiments. Fast pyrolysis is the second type of pyrolysis that is explained. The operating parameters that describe fast pyrolysis are a temperature of 500°C with a residence time about 10–20 s and a heating rate of (1–200°C/s). The product composition yield for fast pyrolysis is 20% biochar (solid), 50% bio-oil (liquid), and 30% syn-gas (gas) [34]. The yield for bio-oil under fast pyrolysis conditions is better than that of slow pyrolysis. The third operating parameter is flash pyrolysis, which has operating parameters that include a residence time of about 1 s, a temperature of 500°C, and a heating rate that is greater than 1000°C/s. The composition of product yield of flash pyrolysis is 13% syn-gas (gas), 2% biochar (solid), and 75% bio-oil (liquid) [35]. So, fast and flash pyrolysis is proven to be apt for max efficiency.

Miandad et al. [36] state that with the pyrolysis of liquid oil from polystyrene waste at 400°C with 75 min reaction time, the char yield was 16% of the mass, the liquid oil yield was 76% of the mass, and the gas yield was 8% of the mass. Increasing the temperature to 450°C reduced the char production to 6.2%, increased the liquid oil yield to 80.8% by mass, and increased the gas production to 13% by mass. The response time and optimum temperature were found to be 75 min and 450°C. At optimum conditions, the liquid oil had an absolute viscosity of 1.77 mPa s, a pour point of –60°C, kinematic viscosity of 1.92 cSt, a density of 0.92 g/cm³, a flash point of 30.2°C, a high heating value (HHV) of 41.6 MJ/kg, and a freezing point of –64°C; this is similar to conventional diesel.

Compared to conventional electrical pyrolysis, microwave pyrolysis has a higher heating rate and efficiency and provides uniform volumetric heating of the substances. The microwave-assisted pyrolysis increases gas production and decreases char formation due to hot spot formations [37]. Lam et al. [11] reported that microwave-assisted pyrolysis created an 88 wt% income of condensable pyrolysis oil with fuel assets (calorific value, density) practically identical to conventional transport fuels. Inspection of the species of the oils demonstrated that they contain light aliphatic hydrocarbon. The element of pyrolysis oils shows that an excellent recovery (90%) of the quantity of energy from the surplus engine oil is restored in the pyrolysis oil. It is also free from impurities and contains few contaminants of sulfur, oxygen, and dangerous mixtures of PAH. The great return of pyrolysis oil can be recognized in microwave-assisted pyrolysis with appropriate heating in an inert atmosphere. This review amplifies current discoveries on the impacts of pyrolysis process situations on the overall yield and arrangement of the recuperated oils by exhibiting that encouraged addition rate, stream rate of cleansing gas, and warming source impact the focus and the atomic way of the various hydrocarbons shaped in the pyrolysis oils.

Huang et al. [38] investigated whether the corn stover, which is a standout among the most abundant rural deposits over the world, could be changed into significant biofuels and biobased items by a method of microwave pyrolysis. After the response at the microwave control level of 500 W for the processing time of 30 min, the response obtained under the N₂ environment was superior to the CO₂ environment. This might be because of the better heating absorbability of CO₂ particles to decrease the hotness of stover pyrolysis. The more significant part of the metal-oxide impetuses viably expanded the most extreme temperature and mass lessening proportion; however, they brought down the calorific estimations of massive deposits. The more CO gas was formed under the N₂ atmosphere, but higher CO₂ was formed under the CO₂ atmosphere. Catalyst expansion brought down the arrangement of polycyclic aromatic hydrocarbons and, in this way, made fluid items less dangerous.

Lam et al. [39] investigated the pyrolysis of WEO using a metallic char catalyst to increase the heterogeneous reaction such as methane decomposition and attain the required temperature quickly. Moreover, the metals get converted into metal oxides and absorb the sulfur existing in the oil. The high volatile materials Cd and Cr may vaporize at the pyrolysis temperature, which is above 400°C.

INFLUENTIAL ASPECTS IN WASTE MANAGEMENT PRACTICES

Karthik Rajendran PhD, ... Jerry D. Murphy PhD, in Sustainable Resource Recovery and Zero Waste Approaches, 2019

Pyrolysis

Pyrolysis is a technology that breaks down organic materials in the absence of oxygen to produce liquid (bio-oil), gaseous (syngas), and solid (biochar) products, as illustrated in Fig. 5.4. Syngas comprises mainly of CO and H₂ (together 85%) with a small proportion of CO₂ and CH₄. The bio-oil produced through pyrolysis typically has a heating value of around 17 MJ/kg. The pyrolysis process can occur in the temperature range of 400–1200°C. Although the product yield depends on various operating parameters, generally low temperature and high residence time favor biochar production [27]. Pyrolysis has been investigated as an attractive alternative to incineration for waste disposal. The pyrolysis process conditions can be optimized to produce a solid char, gas, or liquid/oil product, indicating that a pyrolysis reactor can act as an effective waste-to-energy converter. When compared with the conventional incineration plant that runs in the capacity of kilotonnes (kt) per day, the scale of the pyrolysis plant is more flexible and the output of pyrolysis can be integrated with other downstream technologies for product upgrading. The existing pyrolysis technologies seldom run alone with gas, bio-oil, and biochar output as end products, most of them are combined with gasification, combustion, and smelting. The combination with gasification produces fuel gas of moderate calorific value, and this will be a competitive choice in the future. However, at the same pyrolysis-based technologies are expensive and may not be affordable compared to commercial waste treatment methods.

GASIFICATION TECHNOLOGIES AND THEIR ENERGY POTENTIALS

Yaning Zhang PhD, ... Roger Ruan PhD, in Sustainable Resource Recovery and Zero Waste Approaches, 2019

Pyrolysis

Pyrolysis is typically defined as the thermochemical decomposition of biomass feedstock at medium (300–800°C) to high temperatures (800–1300°C) in an inert atmosphere [15]. Some similar definitions are reported in other publications [5,8,9,14,16–18].

The overall reaction of biomass feedstock is The products of liquid, syngas, and solid are all actually valuable fuels and are defined as biooil , biosyngas, and biochar, respectively.

The chemical reactions during the pyrolysis process include [19]

When compared with the other thermochemical technologies including liquefaction and combustion, pyrolysis generally has the following advantages: (1) the main product is biooil and the yield may be as high as 75%; (2) the biooil may have a high content of carbon; (3) the biooil may have low nitrogen and sulfur contents; (4) the HHV of biooil may be very high, e.g., 42 MJ/kg, which is comparable with those of fossil fuels; (5) the residence time is generally short, which decreases the operational cost; (6) the desired product (biooil, biosyngas, or biochar) could be produced by adjusting the operational parameters; (7) the biooil could be easily stored or transported; and (8) the biomass feedstock may not need to be processed [20].

According to the operating parameters such as heating rate, pyrolysis temperature, and residence time, conventional electric pyrolysis can be generally classified into three groups: (1) slow pyrolysis, (2) fast pyrolysis, and (3) flash pyrolysis. In some publications, catalytic pyrolysis, microwave pyrolysis, vacuum pyrolysis, and hydropyrolysis are also included [2,8,20]. For slow pyrolysis, the heating rate, pyrolysis temperature, and residence time are <1°C/s, 300–700°C, and >450 s, respectively. For fast pyrolysis, they are 10–300°C/s, 550–1250°C, and 0.5–20 s, respectively. For flash pyrolysis, they are >1000°C/s, 800–1300°C, and <0.5 s, respectively [15,21]. These different conditions generally result in different pyrolysis results. Table 14.2 shows the pyrolysis results obtained from different pyrolysis technologies. It is observed that flash pyrolysis generally favors biooil production, followed by fast pyrolysis and slow pyrolysis.

Table 14.2. Pyrolysis Results Obtained From Different Pyrolysis Technologies [58].

Pyrolysis	Operating Conditions	Results
Slow pyrolysis	Temperature: 300–700°C Vapor residence time: 10–100 min Heating rate: 0.1–1°C/s	Biooil: ~30 wt% Biochar: ~35 wt% Gases: ~35 wt%
Fast pyrolysis	Temperature: 400–800°C Vapor residence time: 0.5–5 s Heating rate: 10–200°C/s	Biooil: ~50 wt% Biochar: ~20 wt% Gases: ~30 wt%
Flash pyrolysis	Temperature: 800–1000°C Vapor residence time: < 0.5 s Heating rate: > 1000°C/s	Biooil: ~75 wt% Biochar: ~12 wt% Gases: ~13 wt%

A new pyrolysis technology, microwave-assisted pyrolysis, has been developed and widely used [22–24], and it has drawn serious attention because of its advantages over the conventional electric pyrolysis, which are shown in Table 14.3. These advantages are due to the different heat and mass transfer mechanisms. For the conventional electric pyrolysis, heat is transferred from high-temperature gas to the fuel particle surface through the convection mechanism and it is then further transferred from the outside surface to the inside core through the conduction mechanism. A temperature gradient from the outside to the inside of the feedstock particle is formed, and the released volatile diffuses from the inside core to the outside surface through a higher temperature region. For the microwave-assisted pyrolysis, microwave penetrates the feedstock particle and the microwave energy is transformed into thermal energy, which constantly accumulates inside the biomass particle and is then transferred outward. A temperature gradient from the inside to the outside of the particle is formed, and the released volatile diffuses from the inside core to the outside surface through a lower temperature region [15].

Chapter 3 - Elemental and Spectroscopic Characterization of Low-Temperature (350°C) Lignocellulosic- and Manure-Based Designer Biochars and Their Use as Soil Amendments

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Abstract

Biochar has multifunctional properties capable of improving the fertility of degraded soils, acting as a sorbent for organic pollutants, and aid in heavy metal sequestration in mine spoils. Biochars are produced using lignocellulosic- and manure-based feedstocks that are pyrolyzed at temperatures ranging from 300 to 1100°C. Thus, the physiochemical characteristics of biochars are dependent on the parent feedstock, blends, and pyrolysis temperature preferences. Manure-based biochars commonly have an alkaline pH and contain higher concentrations of elements than lignocellulosic-based biochars. Biochars produced at low pyrolysis temperatures (<350°C) contain an assortment of organic structures with –OH, OCH₃, C=O, and COOH containing functional groups. This chapter will detail how feedstock selection, blends, and low temperature (350°C) pyrolysis impact biochars properties. Examples will show how this knowledge can be used to design biochars to be more effective soil amendments.

Hydrochar

Hydrochar is another term, when char is made by hydrothermal carbonization (a process where biomass is heated at a temperature range of 200–300°C in the presence of water), and is comprised of two phases: liquid and solid (i.e., slurry) (Manyâ, 2012;

From: Biochar from Biomass and Waste, 2019

4.3.5 Hydrochar

Hydrochar is produced at a relatively low temperature of 180–260°C through hydrothermal carbonization in subcritical water. Though biochar, torrefied wood and hydrochar looks similar there are significant differences between them in terms of how they are produced, product motivation as well as physical and chemical properties. Biochar is produced in dry oxygen starved

ambience, while hydrochar is produced in subcritical water at lower temperatures. Biochar is used primarily for soil remediation and as an agent for carbon sequestration while hydrochar has value added industrial use. Table 4.3 compares some important properties of biochar and hydrochar produced from dry miscanthus processed under similar condition except for the reaction time. Hydrothermal carbonization being a faster process required much shorter residence time than dry torrefaction. Here one notes higher fixed carbon, higher energy density but lower mass yield in hydrochar. An important positive feature of hydrochar is its reduced ash content as the process strips much of inorganic slagging agents of biomass. Additional details of hydrothermal carbonization are given in Chapter 9.

HYDROTHERMAL CARBONIZATION FOR HYDROCHAR PRODUCTION AND ITS APPLICATION

Shicheng Zhang, ... Daniel C.W. Tsang, in *Biochar from Biomass and Waste*, 2019

Abstract

This chapter introduces the hydrothermal carbonization of biomass for hydrochar production and its applications. It starts from production of hydrochar with the influence parameters of feedstock, reaction temperature, reaction time, and catalyst. Hydrochar properties, such as heating value, chemical properties, microcrystalline structure, and surface morphology, have been discussed. Following that, the environmental impact of hydrochar on soil physical characteristics, chemical characteristics, biological characteristics, and the plant growth were reviewed. Modification of hydrochar and its further application for climate change mitigation, pollution control, and remediation, and energy storage were also discussed.

REMOVAL AND RECOVERY OF METALS BY BIOSORBENTS AND BIOCHARS DERIVED FROM BIOWASTES

N.K. Niazi, ... H. Wang, in *Environmental Materials and Waste*, 2016

7.5.3.4 Hydrochars

The hydrothermal carbonization of C-rich biomass in the presence of water results in the production of a solid material that is referred to as hydrochar (Hu et al., 2010). The advantage of hydrothermal carbonization processes over the previously processes is that it usually takes place at relatively low temperatures (150–350°C, at about 2 MPa pressure) and wet feedstock can be directly used, including wet animal manures, sewage sludge, and algae (Xue et al., 2012). The hydrochar process is also eco-friendly because it does not generate hazardous chemical waste or by-products as does dry pyrolysis.

HYDROTHERMAL CONVERSION OF BIOMASS

Prabir Basu, in *Biomass Gasification, Pyrolysis and Torrefaction (Third Edition)*, 2018

9.1.1 Hydrothermal Torrefaction or Hydrothermal Carbonization

Torrefaction, a pretreatment of biomass (see Chapter 4) to produce solid feedstock, is generally carried out in an inert gaseous environment within a small temperature window of 200–300°C. The same process could use even a lower temperature window of 180–260°C if subcritical water is used instead as the inert medium. Hydrothermal torrefaction or carbonization (HTC) produces gases, aqueous chemicals, and solid product, hydrochar. Some of the inorganic products of the process dissolves in hot compressed water. As a result, it produces solid fuels with reduced ash content. Additionally, the water from hydrothermal process contains a host of organic and inorganic materials. Some of these are important value-added chemicals that can be recovered through downstream processing (Gullón et al., 2012). Alkali metals in biomass are major contributors to fouling when it is burnt. In hydrothermal torrefaction these are leached in water resulting in reduced ash as well as reduced alkali in treated biomass. The leachate from sewage sludge treatment could allow recovery nutrients especially potassium, opening up another feed benefits. Compared to dry torrefaction, hydrothermal torrefaction has relatively short residence time for a given level of solid yield or higher mass yield at a given residence time and temperature. Compared to dry torrefied biomass, high temperature carbonized biomass exhibits lower H/C, O/C ratio, and brings them closer to coal or lignite (Kambo and Dutta, 2014). The most important benefit of hydrothermal torrefaction is that it could avoid the energy intensive process of drying of biomass, which is especially expensive for very wet biomass. This option is thus effective for very wet biomass such as animal manures, human waste, sewage sludge (He et al., 2013), municipal solid waste (MSW), and algae residues. HTC greatly reduces the reaction time for torrefaction. Advantage of hydrothermal torrefaction is its ability to produce an energy dense product in a relatively short period (5 min) of residence time. Hydrothermal torrefaction owing to high pressure gives higher mass yield of carbon.

Various water-treatment technologies for inorganic contaminants: current status and future aspects

Richa Soni, ... Dericks Praise Shukla, in *Inorganic Pollutants in Water*, 2020

14.2.3.5 Miscellaneous adsorbent

Various researches are inclining toward the modifications of adsorbents surface chemically in order to increase its efficiency. In one study, magnetic adsorbent derived from walnut shells found to be efficient in the removal of lead from water (Safinejad et al., 2017). Bark obtained from *Tamarindus indica* is been used for the synthesis of BMIOP (bark-based magnetic iron oxide particle) that are found to be an efficient removal of arsenic (As³⁺) from water. Main advantage of this is the ejection of As laden BMIOP by normal magnet (Dhoble et al., 2018). New magnetically modified hydrochar precursors, obtained from pine

wood saw dust after heat treatment in air, show better removal of mercury ion from water (Wang et al., 2018). Indian bael leaves (*Aegle marmelos* tree) and ferric oxide nanoparticles were used to develop a magnetic bioadsorbent capable of removing arsenic from water (Sahu et al., 2019). A bioadsorbent obtained from spent coffee ground is found to have strong affinity toward chromium(VI) and aid in removal process (Mohan et al., 2019). A cross-linked chitosan microsphere was explored and found to be potent adsorbent for iodide ion (Zhang et al., 2019). There are various other materials that are used as bioadsorbents and have been utilized to remove various pollutants and heavy metals from water bodies. Some of them such as eggshells, almond shells, peanut shells, neem bark, black tea residues, coffee residues, and saw dust are summarized and shown in Table 14.1.

Table 14.1. List of various bioadsorbents and metals they removed.

Sr. no.	Adsorbents	Types of pollutants	References
1	Egg shell	Cd, Cr	Park et al. (2007)
2	Almond shells	Fe	Pehlivan et al. (2009)
3	Corncoobs	Cu	Khan and Wahab (2007)
4	Peanut shell	Cu, Cr	Zhu et al. (2009)
5	Tea residues	Zn, Cd, and Co	Amarasinghe and Williams (2007)
6	Coffee residues	Cu, Zn, Cd, and Pb	Utomo (2007)
7	Wheat bran	Pb	Özer et al. (2004)
8	Black gram husk	Pb, Cd, Zn, and Cu	Saeed et al. (2002)
9	Walnut shell	Cr	Orhan and Büyükgüngör (1993)
10	Mango peel	Cu	Iqbal et al. (2009)

Biomass Energy from Revegetation of Landfill Sites*

B. Seshadri, ... R. Naidu, in *Bioremediation and Bioeconomy*, 2016

4.2 Thermochemical Processes

Thermochemical routes of biomass conversion are more attractive and have certain advantages such as higher productivity, complete utilization of feedstocks leading to multiple products, applicability to a wide range of feedstocks, independence of climatic conditions, and better control over the process relative to biological processes (Verma et al., 2012). Thermochemical processes include pyrolysis, liquification, and gasification.

Pyrolysis is the thermal decomposition of biomass to liquid (bio-oil), solid (char), and gaseous products in the absence of oxygen at 350-700 °C (Goyal et al., 2008; Mohan et al., 2006). Changes that take place during pyrolysis reactions are a combination of heat and mass transfer (Bridgewater, 2012; Mohan et al., 2006). Based on the operating temperature (low to high) and residence time (long to short), the process is known as slow pyrolysis, intermediate pyrolysis, or fast/flash pyrolysis (Table 2). Pyrolysis liquids are complex mixtures of oxygenated aliphatic and aromatic compounds (Meier and Faix, 1999) and consist of a tar fraction and pyrolygneous acids. The tar components contain native resins, intermediate carbohydrates, phenols, aromatics, aldehydes, their condensation products, and other derivatives. Pyrolygneous acids consist of 50% acetic acid (CH₃OH), acetone (C₃H₆O), phenols, and water. Biochar generally contains elemental C, H, and various inorganic species including N, P, K, Si, etc. (Goyal et al., 2008). Physical characteristics such as porosity, pH, affinity to metal sorption, and slow release of nutrients make biochar an attractive soil amendment. It helps improve soil quality and reduces cost of plant production by reducing fertilizer requirements. Since biochar has an estimated longevity of 100-1000 years in soil, it can be considered as a significant sequestration of CO₂ from the atmosphere to the soil. Pyrolysis gases mainly contain CO₂, CO, CH₄, H₂, C₂H₆, C₂H₄, and minor amounts of higher organics and water vapor (Goyal et al., 2008). These gases can be either combusted to generate process heat for the feedstock drying process or can be converted into liquid synfuels.

Table 2. Typical Product Yields of Pyrolysis

Yields (%)

Type	Conditions	Liquid	Char	Gas
Slow (carbonization)	Low temperature (300-700 °C), long solids and vapor residence time (600-6000 s), Particle size: 5-50 mm	30	35	35
Intermediate	Moderate temperature (around 500 °C), moderate vapor residence time ~ 10-20 s	50	20	30
Fast	Moderate to high temperature (500-1000 °C), moderate vapor residence time ~ 1 s, particle size (< 1 mm)	12	13	75

Compiled from Maschio et al. (1992), Mohan et al. (2006), and Zhang et al. (2010).

Another thermal approach for bioremediation of waste and biomass is their wet conversion via hydrothermal carbonization (HTC), a process that involves thermal processing of biomass organics in hot, compressed water (175-295 °C and 2-5 MPa pressure) (Libra et al., 2011; Hoekman et al., 2011). This process converts organics and wastes into a carbon-rich solid known as “hydrochar” that has higher energy and mass densities, homogeneity, friability, and hydrophobicity and is easier for handling, transportation, and storage (Hoekman et al., 2011). An advantage of HTC over many dry biomass conversion processes is that heterogeneous wet organic residues and waste streams can be processed without preliminary pretreatment steps such as separating and drying (Libra et al., 2011). The HTC process involves several reactions including hydrolysis, dehydration, decarboxylation, condensation, polymerization, and aromatization, resulting in a loss of some carbon, hydrogen, and oxygen and altering the thermal, chemical, and structural properties (Funke and Ziegler, 2010). The liquid effluents obtained in the HTC treatment can be sterilized, recycled, and reused for further HTC processes or can be used as low-value agricultural uses after inexpensive treatments. The HTC process is also an effective way of densifying the energy content of biomass, changing its physical, chemical, and thermal behavior, and sequestering CO₂ (Funke and Ziegler, 2010; Libra et al., 2011; Sevilla et al., 2011; Román et al., 2012; Reza et al., 2014). A range of feedstocks can be processed using HTC, including woody and herbaceous feedstocks (Yan et al., 2010; Hoekman et al., 2011; Hoekman et al., 2012; Hoekman et al., 2013; Kalderis et al., 2014), algae biomass, (Broch et al., 2013), fecal biomass (Danso-Boateng et al., 2013), agricultural wastes (Román et al., 2012; Oliveira et al., 2013), municipality solid wastes, and food processing waste (Berge et al., 2011), and digested sludge from anaerobic digestion of agricultural residues and wastewater treatment sludge (Mumme et al., 2011). The HTC process results in 40-78% hydrochar that has 20-40% higher energy content than the raw biomass (Hoekman et al., 2011; Reza et al., 2014). The herbaceous feedstocks result in a lower yield of hydrochar than that of the woody feedstocks. However, an overall higher energy densification is reported in HTC in all feedstocks in the literature. The energy contents of HTC hydrochar from woody feedstocks and herbaceous feedstocks were reported as 28-30 MJ/kg and 23-25 MJ/kg, respectively. Another benefit of HTC is its ability to partition inorganic contents in the biomass into the aqueous phase. Large amounts of nitrogen and phosphorous and other organics have been found in the HTC of algae (Broch et al., 2013). A large amount of nonvolatile residues (7-14%) have been reported in the HTC of woody and herbaceous feedstocks (Hoekman et al., 2011). The majority of these nonvolatile components could be due to disposition of inorganic elements (metals and nonmetals) from the biomass. The useful components could be recovered for plant growth and soil application. The HTC of digested sewage sludge has a product yield of 80-94%, an energy yield of ≥ 90%, energy densification of 1.05-1.36, and a fuel ratio (ratio of fixed carbon to volatile matter) of 0.13-0.27 (compared to 0.11 for raw sludge) (Kim et al., 2014). It is also characterized by higher porosity (larger micropores and mesopores) and improved surface area, suggesting it could be a better combustible material and have superior drying properties.

Thermochemical liquefaction (TCL) is the conversion of biomass in sub/supercritical water reactions. TCL resembles the pyrolysis process in some ways, where biomass is heated in an oxygen-free atmosphere in the presence or absence of a catalyst that enhances the hydrolysis, depolymerization, and repolymerization/condensation reactions to produce bio-oil (also called “bio-crude”) as the major product along with gases, water solubles, and char as coproducts (Akhtar and Amin, 2011; Balat, 2008; Yan et al., 2010). However, unlike pyrolysis where the biomass conversion takes place at near or slightly above atmospheric pressure, in TCL, biomass is converted at significantly higher pressures (5-40 atm) and lower temperatures (280-370 °C) (Balat, 2008). A key difference is that TCL can process wet biomass without drying and is therefore energetically more efficient than pyrolysis (Jena and Das, 2011).

Gasification is the conversion of biomass into a combustible gaseous fuel by partial oxidation of biomass at high temperature in the range of 800-900 °C (Goyal et al., 2008). The process can take place in air, oxygen, or steam as the reaction medium (McKendry, 2002). The resulting gas, known as producer gas (or syngas), is a mixture of CO, CO₂, H₂, CH₄, and N₂ gases. The gas is more versatile than the original solid biomass and can be burned to produce heat and steam, or used in internal combustion engines or gas turbines to produce electricity. Syngas can be combusted in boilers or engines to generate electricity or can be converted to liquid synthetic fuels by Fischer-Tropsch reactions.

BIOCHAR AND ITS COMPOSITES FOR METAL(LOID) REMOVAL FROM AQUEOUS SOLUTIONS

Lukáš Trakal, ... Michael Komárek, in *Biochar from Biomass and Waste*, 2019

7.2.3.1 Synthesis of LDH/Biochar Composites

LDH/biochar composites can be synthesized before or after pyrolysis. The prepyrolysis procedure consists of LDH coprecipitation on the biomass surface and subsequent pyrolysis for 2 h at approx. 500–600 °C (Tan et al., 2016b,c; Wang et al., 2016b,c). Alternatively, LDH precoated biomass can also be hydrothermally treated, resulting in the production of LDH/hydrochar composites (Zhang et al., 2014). The postpyrolysis procedure, which is more widely used, consists of pyrolysis of pristine biomass at conditions mentioned above and subsequent coprecipitation of LDHs on the biochar surfaces (Li et al., 2016; Wan et al., 2017, 2016b,c, 2018; Wang and Wang, 2018; Xue et al., 2016; Zhang et al., 2013c). The synthesis prepyrolysis procedure strongly influences the specific surface area of final LDH/biochar composites, namely resulting in a decrease of the

specific surface area (nearly twofold), in a higher amount of nonreacted metal species, and in a lower As(V) adsorption capacity compared to postpyrolysis products (Wang et al., 2016b,c). In general, LDH/biochar composites exhibit a lower specific surface area compared to pristine biochar caused by filling/clogging of pores after the modification procedure, which also results in a notably rougher surface of LDH/biochar composites (Wan et al., 2017; Xue et al., 2016).

To demonstrate the structure of LDH/biochar composites, diffractograms of pristine woody biochar, Mg–Fe LDH (molar ratio Mg/Fe=4) and Mg–Fe LDH/biochar composites are shown in Fig. 7.10A and the SEM images of LDH/biochar composites are shown in Fig. 7.10B. Diffractograms of pristine biochar (with minor phases corresponding to carbonates and/or silicates); pristine LDHs (with characteristic peaks of given intensities); and LDH/biochar composites confirmed the structure of individual materials and the successful synthesis of LDH/biochar composites. The SEM images demonstrated nonhomogeneous distribution of LDH particles on the biochar surface probably caused by the coprecipitation synthesis procedure of LDHs. The morphology of these LDH particles corresponded to pristine LDHs as described in previous studies (Hudcová et al., 2017, 2018). LDHs were also successfully impregnated on the whole biochar surface, as confirmed by the EDX results, suggesting a high affinity of LDHs with the biochar surface that could positively influence the stability/sorption properties of LDH/biochar composites

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Biomass Gasification, Pyrolysis and Torrefaction (Third Edition), 2018

1.1 BIOMASS AND ITS PRODUCTS

Biomass is formed from living species such as plants and animals—that is, anything that is now alive or was alive a short time ago. It is formed as soon as a seed sprouts or an organism is born. Unlike fossil fuels, biomass does not take millions of years to develop. Plants use sunlight through photosynthesis to metabolize atmospheric carbon dioxide and water to grow. Animals in turn grow by taking in food from biomass. Unlike fossil fuels, biomass can reproduce, and for that reason, it is considered renewable. This is one of its major attractions as a source of energy or chemicals.

Every year, vast amounts of biomass grow through photosynthesis by absorbing CO₂ from the atmosphere. When it burns, it releases the CO₂ that the plants had absorbed from the atmosphere only recently (a few years to a few hours). Thus, the burning of biomass does not make any net addition to the earth's CO₂ levels. Such release also happens for fossil fuels, but was the carbon it absorbed millions of years back. So, on a comparative basis, one may consider biomass “carbon-neutral,” meaning there is no addition to the CO₂ inventory by the burning of biomass (see Section 1.3.2.1).

Of the vast amount of biomass in the earth, only 5% (13.5 billion metric tons) can be potentially mobilized to produce energy. Even this amount is large enough to provide about 26% of the world's energy consumption, which is equivalent to 6 billion tons of oil (IFP, 2007).

Biomass covers a wide spectrum: from tiny grass to massive trees, from small insects to large animal wastes, and the products derived from these.

The principal types of harvested biomass are cellulosic (noncereal), starch, and sugar (cereal). Table 1.1 lists the two types of harvested biomass in food and nonfood categories, and indicates the potential conversion products from them. The division is important because the production of transport fuel (ethanol) from cereal, which is relatively easy and more established, is already being pursued commercially on a large scale. The use of such food stock for energy production, however, may not be sustainable as it diverts cereal from the traditional grain market to the energy market, with economic, social, and political consequences. Efforts are thus being made to produce more ethanol from nonfood resources like cellulosic materials so that the world's food supply is not strained by our quest for more energy.

Table 1.1. Sources of Biomass

Farm products Corn, sugarcane, sugar beet, wheat, etc. Produces ethanol

Rapeseed, soybean, palm sunflower seed, Jatropha, etc. Produces biodiesel

Lignocellulosic materials Straw or cereal plants, husk, wood, scrap, slash, etc. Can produce ethanol, bioliquid, and gas

1.1.1 Products of Biomass

Three types of primary fuels could be produced from biomass and are as follows:

- I. Liquid fuels (ethanol, biodiesel, methanol, vegetable oil, and pyrolysis oil)
- II. Gaseous fuels [biogas (CH₄, CO₂), producer gas (CO, H₂, CH₄, CO₂, H₂), syngas (CO, H₂), substitute natural gas (CH₄)]
- III. Solid fuels (charcoal, torrefied biomass, biocoke, biochar, hydrochar)

These biomass products find use in following four major types of industries

- I. Thematic industries for production of methanol, fertilizer, synthetic fiber, and other chemicals
- II. Energy industries for generation of heat and electricity
- III. Transportation industries for production of gasoline and diesel
- IV. Environmental industries for capture of CO₂ and other pollutants

The use of ethanol and biodiesel as transport fuels reduces the emission of CO₂ per unit of energy production. It also lessens our dependence on fossil fuels. Thus, biomass-based energy is renewable and clean from the standpoint of greenhouse gas (GHG) emission, so it can take center stage on the global energy scene. However, this move is not new. Civilization began its energy use by burning biomass. Fossil fuels came much later, around AD 1600. Before the nineteenth century, wood (a biomass) was the primary source of the world's energy supply. Its large-scale use during the early Industrial Revolution caused so much deforestation in England that it affected industrial growth. As a result, from AD 1620 to AD 1720, iron production decreased from 180,000 to 80,000 tons per year (Higman and Burgt, 2008, p. 2). This situation changed with the discovery of coal, which began displacing wood for energy as well as for metallurgy.

1.1.1.1 CHEMICAL INDUSTRIES

Theoretically, most chemicals produced from petroleum or natural gas can be produced from biomass as well. The two principal platforms for chemical production are sugar-based and syngas-based. The former involves sugars such as glucose, fructose, xylose, arabinose, lactose, sucrose, and starch, while the latter involves CO and H₂.

The syngas platform synthesizes the hydrogen and carbon monoxide constituents of syngas into chemical building blocks (Chapter 12). Intermediate building blocks for different chemicals are numerous in this route. They include hydrogen, methanol, glycerol (C₃), fumaric acid (C₄), xylitol (C₅), glucaric acid (C₆), and gallic acid (Ar), to name a few (Werpy and Petersen, 2004). These intermediates are synthesized into a large number of chemicals for industries involving transportation, textiles, food, environment, communications, health, housing, and recreation. Werpy and Petersen (2004) identified 12 intermediate chemical building blocks having the highest potential for commercial products.

1.1.1.2 ENERGY INDUSTRIES

Biomass was probably the first on-demand source of energy that people on the earth exploited. However, less than 22% of our primary energy demand is currently met by biomass or biomass-derived fuels. The position of biomass as a primary source of energy varies widely depending on the geographical and socioeconomic conditions. For example, it constitutes 90% of the primary energy source in Nepal but only 0.1% in the Middle Eastern countries. Cooking, although highly inefficient, is one of the most extensive uses of biomass in lesser-developed countries. Fig. 1.1 shows a cooking stove still employed by millions in the rural areas using twigs or logs as fuel. A more efficient modern commercial use of biomass is in the production of steam for generation of process heat and electricity like in the facility shown in Fig. 1.2.

Heat and electricity are two major forms of energy derived from biomass. The use of biomass for efficient energy production is presently on the rise in developed countries because of its carbon-neutral feature, while its use for cooking is declining because of a shortage of biomass in lesser-developed countries. Substitution of fossil fuel with biomass in existing plants is made simpler with the developments of the torrefaction process (Chapter 4).

1.1.1.3 TRANSPORT INDUSTRIES

Diesel and gasoline from crude petro-oil are widely used in modern transportation industries. Biomass can help substitute such petro-derived transport fuels with carbon-neutral alternatives. Ethanol, produced generally from sugarcane and corn, is used in gasoline (spark-ignition) engines, while biodiesel, produced from vegetable oils such as rapeseed, is used in diesel (compression-ignition) engines.

Pyrolysis, fermentation, and mechanical extraction are three major means of production of transport fuel from biomass. Of these, the most widely used commercial method is fermentation, where sugar (sugarcane) or starch (corn) produces ethanol. The yeast helps ferment sugar or starch into ethanol and CO₂. The production and refining of market grade ethanol, however, take a large amount of energy as explained in Chapter 12.

The mechanical means of extraction of vegetable oil from seeds like rapeseed has been practiced for thousands of years.

Presently, oils like canola oil are refined with alcohol (trans-esterification) to produce methyl ester or biodiesel.

Liquid fuel may also be produced through pyrolysis that involves rapid heating of biomass in absence of air. The liquid product of pyrolysis is a precursor of biooil, which may be hydro-treated to produce "green diesel" or "green gasoline." At this time, ethanol and biodiesel dominate the world's biofuel market.

Thermal gasification and anaerobic digestion can produce methane gas from biomass. Methane gas can then be used directly in some spark-ignition engines for transportation or converted into gasoline through methanol.

1.1.1.4 ENVIRONMENTAL INDUSTRIES

Activated charcoal produced from biomass has major applications in the pollution control industries. One of its extensive uses is in water filtrations. Activated charcoal impregnated with suitable chemicals like zinc chloride is very effective in removing mercury from flue gas from coal-fired power plants (Zeng et al., 2004). Biochar produced from biomass provides viable and less

expensive means of sequestration of carbon dioxide, and thereby provides long-term sink for storage as atmospheric carbon dioxide in ground. Besides this it also helps in soil fertility and increased crop production (Lehman et al., 2006). Thus biochar can retain the carbon naturally buried in ground instead of releasing it as CO₂ to the atmosphere. The potential annual biochar production from agricultural waste materials such as forest residues and urban wastes is 0.162 Pg/year (Lehman et al., 2006). Life cycle analysis for corn stover and yard waste shows a negative CO₂ emission exceeding 800 kg/CO₂ equivalent per ton of dry feedstock (Roberts et al., 2010).

Biochars and Biochar Composites

Rizwan Tareq, ... Md. Shafiul Azam, in *Biochar from Biomass and Waste*, 2019

10.6.2.2 MAGNETIC BIOCHAR COMPOSITES AS ADSORBENT

Adsorption using magnetic adsorbents has emerged as an exigent water remediation technology particularly for wastewater treatment while eliminating filtration shortcomings of nonmagnetic adsorbents. Magnetic separation not only simplifies isolation but also opens the ground for easy washing followed by redispersion. Moreover, mechanisms controlling the adsorption process are also enhanced. Pyrolysis, coprecipitation, and calcination are the methods frequently used for preparation of good-quality and high yield of magnetic biochar (Thines et al., 2017).

Conventional heating and microwave-assisted heating have been used in laboratory scale to generate magnetic biochar adsorbents. Conventional pyrolysis has been successfully integrated in industrial production of magnetic biochars using modified furnace. Cottonwood, pinewood, date pits, pine needles, hydrochar waste, orange peels, and pine bark underwent conventional pyrolysis after being treated with magnetic precursors like FeCl₃·6H₂O, Co(NO₃)₂·6H₂O, natural hematite, Fe(NO₃)₃·9H₂O, etc., to create magnetic biochars (Yang et al., 2016; Zhu et al., 2014; Zahoor and Ali Khan, 2014; Harikishore Kumar Reddy and Lee, 2014; Wang et al., 2015c; Zhang et al., 2013a,d; Theydan and Ahmed, 2012; Chen et al., 2011a; Liu et al., 2010). All these magnetic biochars used for adsorption of phosphate, arsenate, methylene blue, aflatoxin B₁, triclosan, Cd²⁺, Pb²⁺, and metallic Hg showed improved performance in magnetic response and adsorptive removal from aqueous phase due to incorporation of the more active sites required for adsorption and enhanced physical properties. This can be attributed to uniform and dispersive reinforcement of γ -Fe₂O₃, Fe₃O₄, and CoFe₂O₄ forming strong mechanical bonds with biochar matrix. The oxide particles embedded showed particle size within 20 nm to 1 μ m with variable shapes such as cubic or octahedral. However, reduction in surface area (Wang et al., 2015c; Zahoor and Ali Khan, 2014; Chen et al., 2011a) and lowered adsorption capacity upon reinforcement of magnetic oxide (Khan et al., 2015) did not appear significant indicating minimum hindrance in adsorptive removal of pollutants by these composites.

Microwave-assisted pyrolysis has also found its way in the production of magnetic biochars from bamboo and empty fruit branch used for the remediation of Cr(VI), Cd²⁺, methylene blue, and Pb²⁺ from aqueous phase (Ruthiraan et al., 2015; Mubarak et al., 2014; Zhang et al., 2013d; Wang et al., 2013, 2012, 2011). These magnetic biochars containing hydrous Fe₂O₃, cobalt oxide, binary Co–Fe oxide, and metallic Ni crystals adsorbed these contaminants through electrostatic attraction, ion exchange, inner sphere surface complexation, and physisorption. Superparamagnetic cotton fabric biochars were obtained following both conventional pyrolysis and microwave-assisted pyrolysis by ZHU et al. (2014) in order to compare their properties. The authors found that microwave-heated biochar showed no apparent agglomeration and was characterized by more controlled size and dispersion of oxide particles. Modification of magnetic biochar to further improve its functionality has also been reported. For example, chitosan modification of magnetic biochar obtained from invasive species *Eichhornia crassipes* provided more oxygenated functional groups for greater electrostatic interaction and therefore enhanced Cr(VI) remediation (Zhang et al., 2015a).

Coprecipitation is another process by which magnetic biochar can be fabricated. Yu et al. (2013) employed sugarcane bagasse as the raw material for the production of magnetic-modified sugarcane bagasse through the chemical precipitation of Fe²⁺ and Fe³⁺ over the sugarcane bagasse particles in an ammonia solution under ultrasound irradiation at 60°C. A large amount of carboxyl groups found on the surface of biochar, which made the surface more negatively charged. That's why better adsorption was found for the removal of Pb²⁺ and Cd²⁺ due to the ion-exchange mechanism (Yu et al., 2013). A comparison of two synthesis methods including chemical coprecipitation of iron oxides onto biochar after pyrolysis and chemical coprecipitation of iron oxides onto biomass before pyrolysis for preparing magnetic biochars was studied by Baig et al. (2014). The results suggested that the chemical coprecipitation of iron oxides before pyrolysis led to greater Fe₃O₄ loading, higher saturation magnetization, improved thermal stability, and superior As(III, V) adsorption efficiency of the biochars (Baig et al., 2014).

Magnetization in biochar can also be introduced via calcination in which biochar is subjected to heat treatment to remove water and drive off CO₂, SO₂, and other volatile constituents. The simplicity of this process was the main reason behind the wide application of this process in the production of magnetic biochar composites. For instance, calcination of rice hull and ferric acetylacetonate in tube furnace generates magnetic biochar consisting of good dispersion of Fe₃O₄ particles on the

surface. The biochar showed improved lead removal performance through hydroxide precipitation followed by suitable magnetic separation.

A Critical Analysis of Meso- and Macrofauna Effects Following Biochar Supplementation

X. Domene, in *Biochar Application*, 2016

COLLEMBOLANS

Collembolans, together with mites, are the most abundant microarthropod group of any soil ecosystem (Coleman and Wall, 2014), where they carry out a key decomposition role through decomposer population regulation by facilitating the activity of breaking up organic matter particles (Bardgett, 2005), and by promoting soil aggregation (Maaß et al., 2015).

In char-enriched soil layers resulting from wildfires, Bunting and Lundberg (1987) reported intense biological activity and bioturbation, including abundant microarthropod fecal pellets, fungal activity, and fauna reprocessing of those pellets. Uvarov (2000) cited an unpublished study that reported higher abundance and diversity of collembolans in forest soils polluted by historical charcoal kiln smoke emissions. For acid soils, McCormack et al. (2013) predicted reduced collembolan abundance coupled to the expected fungal abundance decreases after biochar addition and liming.

Under laboratory conditions the consumption of biochar by collembolans is ostensible in the collembolan *Folsomia candida* (Fig. 11.2). The potential mechanisms underlying such behavior are unknown, although trophic effects could be potentially involved, as the species may feed on fungi-colonizing biochar (Lehmann et al., 2011). Salem et al. (2013a) reported the consumption of hydrochar particles in two collembolan species, *Coecobrya tenebricosa* and *Folsomia fimetaria*, provided as sole food source, although feeding and reproduction rates were lower than when yeast was provided as food. The relevance of such Figure 11.2. *Folsomia candida* individuals showing biochar in their gut after a 24-h exposure to 1% moist mixtures of a corn stover biochar with quartz sand (Domene et al., 20015a).

In Domene et al. (2015a), a generalized avoidance behavior of the collembolan *Folsomia candida* to a corn stover biochar (0.2–14% w/w) was observed, although after its modeling, such response was shown to be attenuated when a higher microbial biomass was present in soil–biochar mixtures compared to a soil-only control, agreeing with the plausible role of microorganisms in biochar consumption. Amaro (2013) reported no avoidance of *F. candida* to field samples where a wood biochar had been applied (4 and 40 t ha⁻¹), both in the initial mixtures and those collected after 5 months of application. Similarly, Conti et al. (2014) did not record any avoidance of *F. candida* to different gasification biochars below 2–5% (w/w), but reported total avoidance at the 100% (w/w) application rate.

Regarding chronic effects, Hale et al. (2013) recorded no impact on reproduction of the collembolan *F. candida* by a corn stover biochar and two activated charcoals applied at 0.5, 2, and 5% (w/w). For a variety of slow pyrolysis biochars produced from different feedstocks and temperatures, Domene et al. (2015c) recorded no general negative effects on the reproduction of *F. candida*, with the exception of food waste biochars applied at similar and higher (0.2–14%) rates. The authors related the latter trend to this biochar's high soluble sodium content. Similarly, Marks et al. (2014) reported different impacts on *F. candida* reproduction at concentrations from 0.5% to 50% (w/w), in a variety of biochars in terms of feedstock and pyrolysis procedures. While general reproduction stimulation was observed for slow and fast pyrolysis wood biochars and a slow pyrolysis sewage sludge biochar, a strong inhibition was caused by a pine gasification char. The authors linked the significant negative effects of the latter to its high pH but could not explain the positive effects of the other biochars. Since the positive impacts could not be associated to microbial abundance increases, community shifts or the use of some biochar fractions by gut symbionts were hypothesized as explanations.

Regarding field effects, Conti et al. (2014) reported a significant reduction in microarthropod density, and increased diversity and evenness, after 2 years of 30 t ha⁻¹ application of a gasification biochar to a poplar plantation in acidic soil. Specifically, density dropped to 659 collembolans m⁻² in biochar plots from the 1035 collembolans m⁻² present in controls, which agreed with the predictions of McCormack et al. (2013) despite the fact that collembolans exhibit a wide range of species-specific pH optima (Van Straalen and Verhoef, 1997). However, Prober et al. (2014) reported no variation in collembolan density after 2 years of the surface application of a green waste biochar to an acidic soil of a degraded grassy eucalyptus woodland. Similarly, and after 3 years of the application of a corn stover biochar to a corn field (3–30 t ha⁻¹), Domene et al. (2014) did not find variation in fauna activity, measured as feeding rates (partly carried out by collembolans), although modeling of this response together with other soil properties indicated a positive effect of biochar addition rate on fauna activity. On the contrary, Marks et al. (2016) reported feeding rates reduction of a pine gasification biochar 2 and 3 years after its application (12 and 30 t ha⁻¹) to arable land cropped with barley, in a material previously demonstrated to inhibit collembolans reproduction under laboratory conditions (Marks et al., 2014).

Recommended publications

Science of The Total Environment
Bioresource Technology
Waste Management
Journal of Cleaner Production
Featured AuthorsBeta

BIOCHAR

Biochar is a carbon-rich material produced by burning organic biomass under complete absence (pyrolysis) or partial absence (gasification) of oxygen at temperatures ranging from 300 to 1000°C (Lehmann, 2007).

From: Science of The Total Environment, 2018

Biomass and Biofuel Production

C.E. Brewer, R.C. Brown, in Comprehensive Renewable Energy, 2012

5.18.8 FUTURE PROGRESS AND DEVELOPMENT

Future progress in biochar implementation will likely center around addressing the issue of biochar quality standards and performance expectations for development of the market for biochars. As previously mentioned, most companies selling biochar today produce energy as their primary project as they wait for agronomic research data to quantify the value of a given biochar application. As biochar quality varies significantly depending on feedstock and process conditions, the development of some kind of rating system is critical. The IBI currently has an interdisciplinary task force from multiple countries working to draft standards regarding production process sustainability (i.e., a biochar life cycle assessment), characterization methodology, and product labeling. Once this kind of developmental framework is in place, biochar producers, consumers, and policymakers will be able to make more meaningful comparisons between biochars and biochar systems that will influence decisions about what kind of biochar to make, which biochar product to buy, and which biochar systems to support in new legislation. Other critical research areas in the near future will be developing economic models to evaluate and predict the effects of biochar implementation, as well as more fundamental approaches to understand how biochar production conditions and properties are related and the mechanisms influencing biochar's effects on the soil environment.

PYROLYSIS

Prabir Basu, in Biomass Gasification, Pyrolysis and Torrefaction (Third Edition), 2018

5.2.1.2 SOLID

Biochar is the solid yield of pyrolysis. It should not be confused with the fixed carbon measured by proximate analysis. Biochar is primarily carbon (~85%), but it can also contain some oxygen and hydrogen and some inorganic ash if that is present in the parent biomass. The heating value of biochar is in the range 25–32 MJ/kg dry basis, which is substantially higher than that of the parent biomass or its liquid product. As biomass is carbon neutral, the combustion of biochar is considered more environment friendly than coal.

Biochar is characterized by large pore surface area. Hence it has a large number on nonfuel use such as adsorption of chemicals and carbon storage in ground.

Potential Toxic Compounds in Biochar

Hao Zheng, ... Chenchen Zhang, in Biochar from Biomass and Waste, 2019

19.6 CONCLUSION AND RECOMMENDATION

Biochar is promoted not only as a technology that can improve soil quality and productivity and sequester carbon, but also a management tool that can achieve the multiple goals, including mitigation of global climate change, high-value utilization of waste resources, environmental remediation, and food safety. However, not all biochars can obtain the good outcomes, because of the complicated interaction between biochar and soil and the inherent contaminants in biochar. Therefore, the contaminants generated in biochar should be paid more attention. From the published literature, it is clearly shown that the conventional pollutants such as VOCs, PAHs, dioxins, and heavy metals, and the emerging contaminants, such as nanoparticles and PFRs, can be formed during biochar production. The total and bioavailable contents of these conventional pollutants in biochar are dependent on feedstock and pyrolysis conditions, but few general conclusions can be obtained due to the limited studies, especially for the bioavailable contents of these contaminants. For the emerging contaminants in biochar, such as PFRs, it seems that they have negative effects on plant or soil microorganism, but positive effects on organic pollutant degradation. Several studies have proved that the inherent contaminants in biochar may cause adverse influence on organisms, such as plant, soil microbe, and alga, and even one study reported showing direct observation of the cytotoxicity of biochar particles. These studies highlighted the environmental risk that resulted from biochar. Consequently, several quality

guidelines of biochar and possible strategies to mitigate biochar contamination are highly proposed to minimize the risk of biochar exposure during its production and application.

In summary, the content and composition of contaminants in fresh biochar must be thoroughly considered before biochar application, together with the interaction between biochar and soil biota. Currently, there are insufficient data in the literature to draw conclusions concerning contaminants in biochar, and thus further studies need to be fill these gaps. First, the content and composition of contaminants should be thoroughly characterized for more biochars derived from various feedstock and pyrolysis conditions. This will help to elucidate the link between thermal conversion of biomass and resulted biochar that contained contaminants. Meanwhile, it is also very beneficial for testing the content and composition of contaminants in the biochar-based functional materials, such as biochar-based nano-composite, magnetic biochar, composted biochar. Moreover, besides the total content of the contaminants in biochar, the bioavailable fractions must be well measured. Second, it is urgent to develop standard methods for extracting and measuring these contaminants. Various methods that were used to extract and detect VOCs and PAHs in biochar resulted in difficulty in comparison of the available data in the published literature. Third, biological tests, which were frequently treated as an alternative to chemical analyses, should be mandatorily performed before biochar application. The biological tests with more species of organisms may permit knowing the possible toxic effect on organisms induced by the contaminants that are contained in biochar. Additionally, several simple and fast biological tests, such as germination test and earthworm avoidance test, should be proposed to check quickly the quality and safety of biochar in practical applications. Moreover, long-term risk assessments of biochar contained contaminants such as PAHs and VOCs in soils are needed. Based on the above-mentioned aspects, last but not the least, the guideline or standard for biochar related to the inherent contaminant should be developed, which should involve all the contaminants reported in biochar.

Elemental and Spectroscopic Characterization of Low-Temperature (350°C) Lignocellulosic- and Manure-Based Designer Biochars and Their Use as Soil Amendments

J.M. Novak, Mark G. Johnson, in *Biochar from Biomass and Waste*, 2019

3.8 CONCLUSIONS

Biochars can be produced from a variety of lignocellulosic and manure feedstocks utilizing a range of pyrolysis temperatures. To further expand biochar usage as an amendment, designer biochars can be created through blending feedstocks, residence time, and temperature selection. Effective use of biochars requires examination of their elemental and spectroscopic properties because these characteristics control their interaction with target materials and their performance as an amendment or sorbent for contaminants. Low pyrolysis temperature biochars have unique properties that make them suitable as soil amendments for fertility improvement, nutrient retention, and stimulation of microbial activity. These soil improvements are further enhanced when a specific parent feedstock is selected for biochar production.

On the Carbon Abatement Potential and Economic Viability of Biochar Production Systems

Siming You, Xiaonan Wang, in *Biochar from Biomass and Waste*, 2019

ABSTRACT

Biochar production systems are regarded as one of the promising candidates to tackle the triple crisis of increasing energy demand, waste pileup, and climate change. Economics and environmental sustainability are essential indexes to evaluate biochar production. In this chapter, we have an overview of the economic and environmental analysis methods, that is, life cycle assessment (LCA) and cost-benefit analysis (CBA) and their applications to the evaluation of biochar production systems. The products of biochar production systems are evaluated in terms of their economic and environmental impacts. The major factors associated with the carbon abatement potential and economic viability of biochar production are identified to guide the design of biochar production systems. The complication of biochar pricing systems is discussed with an emphasis on the balance between economics and carbon abatement. Finally, the cases of uncertainty analysis are introduced followed by the future development directions of LCA and CBA of biochar production systems.

Biochars and Biochar Composites

Rizwan Tareq, ... Md. Shafiul Azam, in *Biochar from Biomass and Waste*, 2019

10.7 CONCLUDING REMARKS AND FUTURE PERSPECTIVES

Biochar and biochar-based adsorbents have become the focus of many environmental remediation studies today. Their wide availability, low cost, and environmental viability along with relatively high adsorption capacity make them suitable for the adsorption of a wide range of pollutants from heavy metals to pesticides, synthetic dyes to antibiotics. However, their adsorption capacity appreciably depending on the type of pollutant and the synthesis route for the biochar. Hence, selecting the right biochars for the right pollutants is crucial. Furthermore, one single type of biochar may not be appropriate for the removal of all types of contaminants. Physicochemical properties including surface area, porosity, pH, surface charge,

functional groups, and mineral contents influence the ability of biochars to adsorb contaminants. Thus, the properties of biochars need to be well understood and planned.

The complex nature of soil systems compared to aquatic systems has constrained the applications of biochar to soil. The relationship between biochar properties and its potential to enhance agricultural soils is still unclear. For this reason, enhanced collaboration among researchers working in different fields such as agriculture, materials science, and soil science is needed to develop specific biochars and measure their environmental and agronomical benefits to agricultural soils. At present, there are few studies of using biochar to remove heavy metals or other pollutants from contaminated wastewater for field application. Contaminated water is more complicated than the simulated water used in current studies. To ensure the suitability of biochar to treat wastewater, simulating the physicochemical conditions of contaminated water or using actual contaminated water for studies is needed.

The adsorption capacity of biochars also needs to be further studied due to a lack of consistency in the literature. Sorption capacities have been reported for different pHs, temperatures, adsorbate concentration ranges, biochar doses, particle sizes, and surface areas. Biochars have been used to treat groundwater, drinking water, synthetic industrial wastewater, and actual wastewater. Moreover, the types and concentrations of interfering ions reported are different and often not reported. Some adsorption capacities have been reported in batch experiments and others in column modes making the comparison of adsorption capacities difficult. Another reason biochar adsorbents are hard to compare is that they are often prepared under different conditions (temperature, time, atmosphere, etc.). Nevertheless, Mohan et al. (2014), keeping all these limitations and inadequacies in mind, selected some of the best biochars with the highest adsorption capacities for selected contaminants and compared them using a bar diagram. This could be a good starting point for the biochar researchers and the International Biochar Initiative (IBI) to propose a common platform for the comparisons of biochars.

Despite biochar being known as a low-cost adsorbent, cost estimation for the production of biochars from different precursors is mostly unknown. Individual biochar costs depend on local precursor availability, processing requirements, pyrolysis conditions, reactor availability, recycling, and product lifetime. Although the costs for biochars vary in different countries these data are not even available in current literature. Costs depend on whether pyrolysis is part of an existing biorefinery and if value-added coproducts are included. Sometimes the biochar is the product and sometimes it is a byproduct as in the case of biorefineries. Therefore, serious economic studies on biochar production in various-sized biorefineries connected with agriculture and forestry is required.

There are also serious concerns for modified biochars or biochar composites. Various modification and impregnation methods have been introduced to increase the adsorption capacity and mechanical strength of biochars and thus economical assessment of modifying or impregnating biochars should be considered. For example, while physical activation of biochar would increase energy consumption costs, chemical activation and production of biochar-based composites would also include the price of reagents (Banerjee et al., 2016). In these cases, a particularly challenging aspect of future optimization is to decrease the quantity of the chemicals required to activate or modify the biochar produced to minimize costs of production while maintaining maximum sorption capacity by optimizing the biochar:modifying agent ratio. The stability of biochar-based composite modifications over time should be monitored in future experiments as some of the materials imbedded in the biochar matrix (e.g., metal compounds, C nanotubes, organic compounds) can leach away from the biochar if they are not tethered strongly. To address this issue, leaching tests are required. One scenario worthy of investigation is the stability of metal-biochar composites at low pH (pH 4–5), to determine whether metals are released from the biochar matrix. Another concern is the ecotoxicology of these new biochar formulations. Biochar itself has been shown to be good for environmental applications, but sometimes it can contain toxic compounds (Soudek et al., 2017). Modifying or activating the biochar leads to chemical and physical changes that could potentially increase the toxicity (reactivity, presence of nanoparticles, metals, etc.). For example, Shim et al. (2015) noted that activated biochars can induce toxicity to *Daphnia magna*. To ensure environmental protection, the toxicity of modified biochars needs to be evaluated to avoid undesirable impacts to aquatic organisms.

Physicochemical technologies for HRP and risk control

Haidong Hu, Ke Xu, in *High-Risk Pollutants in Wastewater*, 2020

8.1.2.2 BIOCHAR

Biochar is a porous carbonaceous material that is produced from a variety of biomass by different thermal decomposition methods including carbonization, hydrothermal treatment, and pyrolysis. Considering the large porous structure, abundant functional groups, low cost, and solid waste recycling, biochar is regarded as a potential alternative adsorbent for use in wastewater treatment. With the increase of research on biochar adsorption technology, the adsorption mechanisms of biochar on various pollutants are becoming clearer (Fig. 8.1). Rational use of these adsorption mechanisms can make biochar more effective in removing HRP from wastewater. Abdelhafez and Li prepared two biochars using bagasse and orange peel as raw materials and investigated the adsorption characteristics of lead ions by these two biochars (Abdelhafez and Li, 2016). The results showed that the adsorption capacity of these two biochars for lead ions varied greatly. By analyzing the chemical

composition and morphological structure of the two biochars, it was found that the major adsorption mechanisms of both biochars were a specific ion-exchange mechanism and surface precipitation. Because bagasse biochar has a larger specific surface area, it has a stronger adsorption capacity than orange peel biochar.

Similar to most porous carbon materials, biochar also has a high adsorption affinity for organic HRP and can be adsorbed through various mechanisms. For example, as the main site of adsorption of biochar, the pore structure has an important influence on the adsorption of organic HRP by biochar. Wang et al. evaluated the sorption behavior of acetochlor, dibutyl phthalate, 17 α -Ethinyl estradiol, and phenanthrene with biochars produced from three feedstocks (maize straw, pine wood dust, and swine manure) at seven heat treatment temperatures (Wang et al., 2016). The results showed that the organic carbon-normalized CO₂-specific surface area of biochars significantly correlated with the sorption coefficients, suggesting that pore filling could dominate the sorption of tested biochars. In addition, due to abundant surface functional groups, strong hydrophobicity, and graphitized lamellar structure, biochar can also adsorb organic HRP through hydrophobic action, hydrogen bond, and π - π interaction. Chen et al. studied the interfacial interaction between carbamazepine and peanut-shell-derived biochar (Chen et al., 2017). They found that the adsorption of carbamazepine (CBZ) on amorphous (loose) carbon was lower than aromatic (condensed) carbon, but the former mainly contributed to the fast adsorption of carbamazepine, indicating the hydrophobic and π - π interactions were likely the predominant adsorption mechanisms of CBZ on biochar. Through acid treatment experiments, it was proved that the mineral component on the surface of biochar could also generate hydrogen bonding with carbamazepine.

Technologies for bHRPs and risk control

Jinbao Yin PhD, Xuxiang Zhang PhD, in High-Risk Pollutants in Wastewater, 2020

10.5.2 BIOCHAR

Biochar is a heterogeneous black carbon remnant of plant biomass pyrolysis, and it is a relatively new research field. Biochar is a porous material that has rich mineral elements and large specific surface area, and thus provides the most sites to be filled by sorption of contaminants. The main treatment mechanism of biochar is sorption. Moreover, electrostatic repulsion is another sorption mechanism that is attributed to complex properties of biochar (Gwenzi et al., 2017).

Biochar filters are more effective than other filters in removal of *Salmonella* spp. (3 logs reduction) but are less effective in removal of bacteriophages. The capacity of biochar to remove pathogens and indicator organisms depends on biochar type and operating conditions particularly hydraulic loading rates, and presence of potentially interfering concomitants in aqueous systems. The biochar filters can achieve a 1.4, 1.5, 2.0, and 1.3 logs reduction for *E. faecalis*, *E. coli*, *Saccharomyces cerevisiae* yeast, and Phix-174 phage, respectively, and the smaller the particle size of the biochar, the better the straining of bacterial and virus particles (Barancheshme and Munir, 2018).

Biochar Is a Potential Source of Silicon Fertilizer

Muhammad Rizwan, ... Arooj Bashir, in Biochar from Biomass and Waste, 2019

12.5 CONCLUSION AND PERSPECTIVES

Biochar produced from Si-accumulating crops, such as wheat, rice, and sugarcane residues might be a good source of plant-available Si. The release of bioavailable Si depends upon the producing temperature of biochar. The use of biochar prepared from Si-rich feedstocks could be a practical strategy to alleviate Si deficiency in soils and ultimately in crops. Overall, Si-rich biochar would be good source of organic fertilizer for bioavailable Si in the soil. However, Si in biochar and the connections between Si and carbon have been ignored. Further studies are worth investigating regarding the morphology, transformation, and dissolution about Si and their relation with carbon. More studies are required to understand the relation between Si and carbon in biochar.

Modeling the Surface Chemistry of Biochars

Md. Samrat Alam, Daniel S. Alessi, in Biochar from Biomass and Waste, 2019

ABSTRACT

Biochar is a complex carbonaceous material with numerous physical and chemical parameters that control its reactivity toward inorganic and organic species in aqueous solution. Key to understanding the ways in which solutes will behave toward biochar is the development of models that consider the underlying mechanisms of complexation at the surface of biochar particles. In this chapter, we compare and contrast empirical and theoretical approaches to solute adsorption modeling to biochar. Later, we discuss the development of surface complexation models (SCMs) for biochar, including the collection and modeling of potentiometric titration and solute adsorption data, and how these SCM can be complimented by spectroscopic and calorimetric investigations to constrain the mechanisms of solute binding at biochar functional groups. Finally, we discuss the state of biochar surface chemistry science, including the need for further application of SCM, along with challenges that exist in applying the approach due to the inherent complexity of the material.

Biomass

Biomass is any form of organic matter that can be found on earth, one property that is common for all of its forms is that it is or had to be a living organism in one point of its existence (Morgan Jr et al., 2017).

From: Bioresource Technology, 2018

Biomass

R.A. Houghton, in Encyclopedia of Ecology, 2008

DEFINITION

Biomass refers to the mass of living organisms, including plants, animals, and microorganisms, or, from a biochemical perspective, cellulose, lignin, sugars, fats, and proteins. Biomass includes both the above- and belowground tissues of plants, for example, leaves, twigs, branches, boles, as well as roots of trees and rhizomes of grasses. Biomass is often reported as a mass per unit area (g m^{-2} or Mg ha^{-1}) and usually as dry weight (water removed by drying). Unless otherwise specified, biomass usually includes only living material. For example, neither deadwood nor the organic matter of soils is considered biomass, although soils do contain biomass in the form of bacteria, fungi, and meiofauna. Generally, the biomass of soils (living and dead microbes) is <5% of soil organic matter.

This article deals almost exclusively with terrestrial biomass and particularly with the biomass of plants. Forests account for 70–90% of terrestrial biomass, most of this biomass in trees. The distribution of terrestrial biomass among producers, consumers, and microbes is c. 0.90%, 0.001%, and 0.10%, globally, with considerable variation among ecosystems. Producers and microbes, for example, may account for similar fractions of biomass in some nonforest ecosystems. The estimates given here refer to the biomass of plants, or producers, only.

Vulnerability of Energy to Climate

B.M. Fekete, in Climate Vulnerability, 2013

ABSTRACT

Biomass has been used as a fuel source ever since humanity learned to make fire and served as the primary source of energy before fossil fuels became common in the twentieth century. Biomass is still the dominant source of energy for one billion of the poorest people. Biofuels are attractive for a number of reasons - plants act as 'solar panels', capture carbon, and store energy. Their large-scale adaptation as energy source for modern industrial societies hinges on the solar utilization efficiency of plants. Plants appear to have similar efficiencies in capturing solar radiation as the most efficient solar panels that can be deployed at large scale, but the plants' own metabolism combined with the 'metabolism' of the infrastructure to produce biofuel from biomass yields a very low solar utilization. The climate vulnerability of biomass as renewable energy source is largely similar to food crops. Slight differences might be expected for different biofuel types. First generation biofuels might be more vulnerable due to constraints on deploying often energy intensive agricultural practices that can offset adverse climate impacts. Second generation biofuels are likely to be more resilient than food crops since their feedstock comes from marginal lands that are more close to natural vegetation.

Engineering Perspectives in Biotechnology

A. Vijaya Bhaskar Reddy, ... M. Goto, in Comprehensive Biotechnology (Third Edition), 2019

2.16.3.1 BIOMASS LOADING

Biomass loading largely depends on the solubility of biomass in a particular IL at the operating temperature and the biomass dissolution rate, which influences the pretreatment time. Because the time requirement can be excessively long, the thermodynamic solubility limit may not be reached during the given pretreatment time. Thus, the IL-to-biomass mass ratio should be substantially higher than the solubility limit. A smaller biomass particle size typically means a faster biomass dissolution rate. Typically, researchers use a nominal biomass loading ratio of 20:1 to 30:1 (g ionic liquid:g biomass) for IL pretreatment of various types of biomass under different conditions of temperature and time. In comparison, a ratio of 10:1 (g ionic liquid:g biomass) is common for aqueous ammonia, acid hydrolysis, supercritical CO₂, and hydrothermal pretreatment methods. It should be noted that if the biomass concentration reaches 10% (w/w), the IL solution is almost always very viscous, which makes it difficult to process. Thus, the viscosity could be a limiting factor rather than the biomass solubility in a practical pretreatment process.

The ratio of biomass to IL (% biomass loading) is an important aspect to improve the process economy, recyclability, dissolution, and regeneration efficiency. Studies have reported that chemical equilibrium of a reaction might have shifted to favor more cellulose dissolution only at the appropriate biomass loading and temperature. In one study, higher dissolution rates were obtained at 12 wt% rather than 8 wt% of biomass loading because of more frequent contact or collision between the IL and biomass particles, which inadvertently accelerated dissolution. Conversely, a reduced dissolution rate was reported as the biomass loading increased from 4 to 10 wt%, whereas the optimal biomass loading was 5.0 wt%. Similarly, a reduction in the dissolution rate from 35% to 26% was observed in another study when the biomass loading increased from 1.0 to 5.0 wt%.

A higher dissolution rate at a lower biomass loading may be attributed to efficient dispersion and diffusion of the IL inside the pores of the biomass sample. The existing literature shows that the biomass loading is an important processing parameter, whereby researchers selected 5.0–8.0 wt% of biomass loading. However, the biomass loading may depend on the particle size and biomass type.

Biomass and Biofuel Production

G. Evans, C. Smith, in *Comprehensive Renewable Energy*, 2012

ABSTRACT

Biomass to liquids (BtL) is a thermochemical process, currently moving from pilot scale to demonstration scale worldwide, that can convert a range of biomass types to a range of fuels and chemicals. BtL is based on established coal-to-liquids and gas-to-liquids technologies, but the scale and technologies used are not necessarily appropriate for BtL. Recently, there has been considerable interest in developing smaller scale BtL and in using waste as a feedstock. Uptake of BtL can help decarbonize the transport fuel sector, and is of considerable interest worldwide as policy increasingly focuses on the environmental implications of biofuel use.

Functioning of Ecosystems at the Land–Ocean Interface

J. Carstensen, ... D. Krause-Jensen, in *Treatise on Estuarine and Coastal Science*, 2011

7.08.6.1.1 Models of biomass and secondary production

Biomass, that is, the tissue weight of all individuals, is an expression of the stored energy in the system, and biomass increase reflects secondary production. In the early phase of eutrophication, before limiting factors like oxygen deficiency are effective, biomass is expected to increase linearly with increasing organic input. When limiting factors take effect, biomass is expected to decrease and eventually vanish. Several empirical models of biomass and secondary production have been proposed where biomass as such and the biomass of the individual are important determinants of secondary production (Rasmussen and Kalff (1987), in lakes; Tumbiolo and Downing (1994) and Brey (1999, 2001) for marine invertebrates). Herman et al. (1999) examined benthic biomass in several estuaries worldwide and presented a regression model where biomass could be predicted from primary production. Similar to nutrient concentrations in water bodies like lakes, benthic biomass in fjords may be described by a Vollenweider type of model (Vollenweider, 1969) where the important parameters are nutrient load and the flushing of the fjords (Josefson and Rasmussen, 2000; Josefson, unpublished data; Figure 9).

Figure 9. An empirical model of benthic biomass in Danish estuaries. Major determinants of nitrogen content in macrofauna (biomass N, BN) are annual area-specific N-load (TN) and residence time (T, days) of the estuaries. Model predictions were based on data from 1989 to 1995 (12 estuaries) and verified with measured data from a later period (1998 to 2004). Smoothed curves were obtained using LOWESS regression.

From Josefson, A.B., Rasmussen, B., 2000. Nutrient retention by benthic macrofaunal biomass of Danish estuaries: importance of nutrient load and residence time. *Estuarine, Coastal and Shelf Science* 50, 205–216.

Biomass and Pigments of Benthic Algae

Alan D. Steinman, ... Donald G. Uzarski, in *Methods in Stream Ecology*, Volume 1 (Third Edition), 2017

ABSTRACT

Biomass is one of the most fundamental measurements made in ecology. In stream ecology, biomass is frequently used to estimate the abundance of benthic primary producers, both autotrophic and heterotrophic. In this chapter, we (1) provide a context for the study of benthic algal biomass; (2) discuss in detail some of the more commonly used approaches to measure benthic algal biomass; and (3) describe a field exercise to examine the influence of irradiance on algal biomass, whereby these approaches can be employed and compared with each other to assess their individual performance.

Peaking of World Oil Production and Its Mitigation

Robert L. Hirsch, ... Robert Wendling, in *Driving Climate Change*, 2007

BIOMASS

Biomass can be grown, collected, and converted to substitute liquid fuels by a number of processes. Currently, biomass-to-ethanol is produced on a large scale to provide a gasoline additive in the United States and Brazil, among other places. The market for ethanol derived from biomass is influenced by government requirements and facilitated by generous tax subsidies. Research holds promise of more economical ethanol production from cellulosic, or woody, biomass, but related processes are far from economic. Reducing the cost of growing, harvesting, and converting biomass crops will be necessary (Smith et al., 2004).

INTRODUCTION

Prabir Basu, in *Biomass Gasification, Pyrolysis and Torrefaction* (Third Edition), 2018

1.1.1.2 ENERGY INDUSTRIES

Biomass was probably the first on-demand source of energy that people on the earth exploited. However, less than 22% of our primary energy demand is currently met by biomass or biomass-derived fuels. The position of biomass as a primary source of energy varies widely depending on the geographical and socioeconomic conditions. For example, it constitutes 90% of the primary energy source in Nepal but only 0.1% in the Middle Eastern countries. Cooking, although highly inefficient, is one of the most extensive uses of biomass in lesser-developed countries. Fig. 1.1 shows a cooking stove still employed by millions in the rural areas using twigs or logs as fuel. A more efficient modern commercial use of biomass is in the production of steam for generation of process heat and electricity like in the facility shown in Fig. 1.2.

Heat and electricity are two major forms of energy derived from biomass. The use of biomass for efficient energy production is presently on the rise in developed countries because of its carbon-neutral feature, while its use for cooking is declining because of a shortage of biomass in lesser-developed countries. Substitution of fossil fuel with biomass in existing plants is made simpler with the developments of the torrefaction process (Chapter 4).

STRUCTURE AND PRODUCTIVITY OF AQUATIC ECOSYSTEMS

ROBERT G. WETZEL, in *Limnology* (Third Edition), 2001

C. PRODUCTION/BIOMASS (P/B) RATIOS

Biomass (B) is a measurement of mass for a population present at one point in time in units of mass per unit area (e.g., g m^{-2}) or volume and is therefore a temporary storage of mass or energy. Production (P) is a flow or flux of mass (or energy) per area per time (e.g., $\text{g m}^{-2} \text{yr}^{-1}$). The ratio (P/B) of production (P) divided by mean biomass (B) is a rate with units of inverse time (e.g., 1/year). P/B is essentially a weighted mean value of biomass growth rates of all individuals in a population (Benke, 1993). The P/B ratios can be used to estimate the turnover rate of organisms and for an entire trophic level to give a general index of the rate of energy flow relative to the biomass. Determination of P/B values is useful in making comparisons among different trophic levels, as well as among similar trophic levels under different environmental conditions.

Average annual P/B ratios generally decrease with increasing trophic level (Table 8-3) and range over 2 orders of magnitude (Brylinsky, 1980; Benke, 1993). As would be expected, (a) annual production is higher in short-lived species than in long-lived species, and (b) annual production of a species decreases proportionally as its biomass increases. Therefore, smaller organisms tend to have greater P/B values, and P/B ratios decrease with increasing organism size and biomass. Production per unit biomass generally increases with decreasing latitude of the aquatic ecosystem since the active growing season is longer, which allows increased numbers of generations per growing season at lower latitudes. Organisms of oligotrophic lakes tend to have lower P/B values than those in eutrophic lakes (Brylinsky, 1980; Saunders et al., 1980).

TABLE 8-3. Mean and Range of P/B Ratios among Trophic Groups of Freshwater Ecosystems^a

	Mean	Range
Bacteria	141.0	73–237
Phytoplankton	113.0	9–359
Herbivorous Zooplankton	15.9	0.5–44.0
Carnivorous Zooplankton	11.6	1.5–30.4
Herbivorous Benthic Invertebrates	3.7	0.6–200
Carnivorous Benthic Invertebrates	4.8	1.0–80

^aAfter data of Saunders et al. (1980), Brylinsky (1980), and Benke (1993).

Polycyclic Aromatic Hydrocarbon

PAHs are organic substances made up of carbon and hydrogen atoms grouped into at least two condensed or fused aromatic ring structures (CCME, 2010).

From: Environment International, 2013

Polycyclic Aromatic Hydrocarbons (PAHs)

Paul D. Boehm, in *Environmental Forensics*, 1964

PUBLISHER SUMMARY

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Anthropogenic inputs of PAH arise from the release into the environment of petrogenic PAHs through accidental acute

petroleum spillages and through chronic non-point source and point-source inputs such as urban (storm water) runoff and municipal waste treatment plant discharges. The most common and ubiquitous sources of anthropogenic PAHs, however, are those associated with pyrogenic inputs.

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Hazards and Diseases

M. Huang, T.M. Penning, in *Encyclopedia of Food Safety*, 2014

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of diverse organic compounds that contain two or more fused aromatic rings ranging from the two-ring naphthalene and naphthalene derivatives to complex ring structures containing up to 10 rings. PAHs with up to six fused aromatic rings are often known as 'small' PAHs, whereas those containing more than six aromatic rings are called 'large' PAHs. PAHs have also been classified into alternant and nonalternant compounds. Alternant PAHs are those compounds composed solely of fused six-member benzene rings, whereas nonalternant PAHs contain both six-member benzene and five-member carbon rings. Common structural features of PAH compounds are illustrated in Figure 1. Differences in the configuration of rings may lead to differences in properties. In their purest form, PAHs are solids with low volatility at room temperature and range in appearance from colorless to white or pale yellow–green. They are relatively insoluble in water and most can be photooxidized and degraded to simpler substances.

Figure 1. Common structural features of PAH compounds.

PAHs are formed by condensation of smaller organic compounds by pyrolysis or pyrosynthesis. Smaller organic compounds are pyrolyzed at a high temperature and the free radicals produced join together as aggregate large PAH molecules (pyrosynthesis). Diels–Alder-type rearrangements are commonly involved in the formation of the PAHs. Temperature is an important factor to affect both the structure and diversity of the PAHs formed. Large PAHs are formed at lower levels than small PAHs due to the kinetic limitation in their production through addition of successive rings. In addition, with many more isomers possible for larger PAHs, the occurrence of specific structures is much lower.

PAHs are ubiquitous environmental pollutants. They are not only found naturally in the environment but they can also be man made. PAHs are formed as a result of incomplete combustion of carbon-containing materials, such as wood, coal, oil, gas, or biomass. They are also created in car and diesel exhaust, smoked or charbroiled food, and are present in cigarette smoke condensate, and tobacco products. According to their origins, PAHs are classified into pyrogenic PAHs (Figure 2) arising from fossil fuel combustion and petrogenic PAHs (Figure 3) that are unique to crude oil and contaminate water after an oil spill. Petrogenic PAHs differ in structure to pyrogenic PAHs in that they are either extensively alkylated or oxygenated to yield PAH quinones.

Figure 2. The 16 priority pyrogenic PAHs listed by the United States Environmental Protection Agency (US EPA).

Figure 3. Representative petrogenic PAHs.

PAHs are complex mixtures of hundreds of chemicals, including derivatives of PAHs, such as nitro- and hydroxy-PAHs, as well as heterocyclic PAHs. In the 1970s, the United States Environmental Protection Agency (US EPA) listed 16 PAHs as priority pollutants. These priority PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene (B[a]P), indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and dibenz[a,h]anthracene (Figure 2). Among these priority PAHs, B[a]P, a known human carcinogen, is commonly used as an indicator for PAH exposure.

PAHs are present in air, soil, water, and food, and routes of exposure include inhalation, dermal contact, and ingestion. Some exposures may involve more than one route simultaneously affecting the total absorbed dose (such as dermal and inhalation exposures from contaminated air). Occupational sources of exposure mainly involve workers in coal gasification plants, municipal incinerators, smoke houses, and aluminum production facilities. Nonoccupational sources of exposure mainly involve diet, smoking, and burning of coal and wood. In most cases, intake of food is the major involuntary exposure route of PAHs. Therefore, this article will only discuss the occurrence of PAHs in food, health concerns, analysis, mitigation and biomonitoring, and guidelines to reduce PAHs in food.

POLYCYCLIC AROMATIC HYDROCARBONS | Environmental Applications

A.N. Gachanja, in *Encyclopedia of Analytical Science* (Second Edition), 2005

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) from anthropogenic sources are discharged into the atmosphere either in the gaseous state or adsorbed onto particulates. These PAHs are subject to removal mechanisms such as oxidative and photolytic reactions and wet and dry deposition. Air currents and prevailing winds disperse and transport the PAHs over long distances and deposit them on soil and in water. PAHs on soil are carried during storms by water runoff to rivers and seas. In the aquatic

environment, the PAHs enter marine plants, fish, and sedentary organisms. PAHs are thus ubiquitous pollutants that have been detected even in remote parts of the earth, e.g., the average atmospheric concentration of the sum of 11 PAHs at Barrow, Alaska, was reported to be 1.2 and 0.16 ng m⁻³ for Mar. and Aug. 1979, respectively, and PAH concentrations in sediments have ranged from undetectable in the Amazon river to greater than 10000 µg l⁻¹ in the Charles river, Boston, USA. This article briefly reviews the analysis of PAHs in the atmosphere, water, food, and biological samples.

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Volume 2

Z. Fan, L. Lin, in *Encyclopedia of Environmental Health (Second Edition)*, 2011

PAHs

PAHs, which contain two or more fused aromatic rings, constitute a broad family of compounds, many of which are mutagens and carcinogens. More than 100 different PAHs have been identified in environmental samples and 16 PAHs (Table 2) are generally measured in most exposure and environmental air pollution studies. PAHs are introduced into the environment via natural emissions, for example, volcanic eruptions and forest–prairie fires, but largely from the incomplete burning of some organic substances during anthropogenic combustion processes, such as vehicular emissions, wood smoke, coke and asphalt production, waste incineration, and ETS in indoor environments. Among all sources, vehicular exhaust is the major and common source for PAH air pollution in most urban areas. The loading of PAHs in aquatic and terrestrial systems has a component that is atmospheric in origin. Since PAHs are semivolatile compounds, they distribute in both gas and particulate phase under ambient conditions, leading to different biologically effective pathways through inhalation. In the atmosphere, PAHs are not stable and can undergo photodecomposition under sunlight and react with other pollutants such as ozone and nitrogen oxides to form oxygenated and nitro/dinitro-PAHs. These processes lead to more complex and toxic mixtures because many nitro- and oxygenated PAHs often pose higher toxicities than their parent compounds.

PAHs exposures may occur in all routes, that is, inhalation, ingestion, and dermal contact. Occupational exposure studies have showed a variety of adverse health effects resulting from exposure to elevated PAHs, including cancer. However, limited exposure data are available for PAHs and their substituted pollutants in the community setting because these pollutants often are present at trace levels in the environment and are difficult to detect. Also, current methods for the measurement of PAHs and nitro-PAHs are very time consuming and expensive. Thus, innovative, sensitive, and cost-effective sampling and analytic techniques are needed to accurately quantify exposure to PAHs and their derivatives in future exposure studies.

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HUMAN HEALTH HAZARDS OF WASTEWATER

Bing Wu PhD, in *High-Risk Pollutants in Wastewater*, 2020

6.1.3.2 POLYCYCLIC AROMATIC HYDROCARBONS

PAHs are mainly derived from incomplete combustion of coal and oil, and wastewater discharge is one of the main channels for PAHs to enter the environment. Long-term irrigation with industrial effluent mixed with municipal wastewater (Cai et al., 2007; Villar et al., 2006) has resulted in the excessive accumulation of PAHs in agricultural soil. In addition, part of PAHs in the air could directly enter the soil by atmospheric deposition. The exposure pathways are illustrated in Fig. 6.3. PAHs in the soils have brought a potential risk to human health along the food chain. Ingestion is considered as the major source of PAHs (McGrath et al., 2007). Vegetables cultivated on the wastewater-contaminated soils may take up these pollutants in sufficient quantities. Numerous studies have demonstrated that vegetables accumulated high concentrations of PAHs that were grown in PAH-contaminated soils (Samsoe-Petersen et al., 2002; Wennrich et al., 2002). Additionally, other pathways, including inhalation and dermal contact, also contribute to the human exposure to environmental carcinogenic PAHs (Chen, Liao, 2006).

Figure 6.3. Exposure pathways of PAHs from wastewater.

PAHs intake could interfere with the cellular membrane functions and enzyme systems associated with the membrane. The major concern of PAHs is about the epoxides and dihydrodiols that can bind with the cellular proteins and DNA leading to biochemical disruptions, cell damage, mutations, developmental malformations, tumors, and cancer. To quantify the carcinogenicity of the selected PAHs, toxic equivalency factor compared to benzo(a)pyrene was applied.

HYDRAULIC FRACTURING

Tarek Saba, in *Introduction to Environmental Forensics (Third Edition)*, 2015

14.5.2.4 Polycyclic Aromatic Hydrocarbons (PAHs): Analysis of Fingerprints

PAHs are a group of organic compounds consisting of two or more fused aromatic rings. Naphthalene, consisting of two fused benzene rings, is the simplest PAH compound. PAHs are found in crude oil, petroleum products such as diesel, and organic seams in subsurface soils. PAHs are also formed during rapid, high-temperature (>500 °C), incomplete or inefficient (i.e.,

oxygen-starved) combustion of organic biomass (i.e., pyrogenic) (Boehm, 2006). Example pyrogenic sources that contain PAHs include soot, creosote, and waste oils, among other sources. See Figure 14.6 for example PAHs in creosote and diesel oil.

FIGURE 14.6. PAH compound distribution in example petrogenic and pyrogenic sources.

In claims of groundwater contamination, PAH compounds (e.g., benzo(a)pyrene) may be found in a water well, and chemical fingerprinting analysis is an available method for tracing the PAH source. For example, the ratio of two of the PAH compounds (fluoranthene/pyrene [FL/PY]) can provide information on the source of the PAHs, whether a petroleum-based source (i.e., petrogenic) or a pyrogenic source (e.g., Brenner et al., 2002). A fluoranthene/pyrene ratio greater than 1.0 indicates that the PAHs originated, at least in part, from a pyrogenic source such as soot (which could originate from household activities such as chimney cleaning) or road runoff.

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Mycoremediation of polycyclic aromatic hydrocarbons

Shalini Gupta, Bhawana Pathak, in *Abatement of Environmental Pollutants*, 2020

1.2 EFFECT OF PAHS EXPOSURE ON ENVIRONMENT AND HUMAN HEALTH

PAHs are ubiquitously present in the environment mainly evaporated into the atmosphere. PAHs undergo photolysis in presence of sunlight, mainly when adsorbed to dust particles. Oxidation of PAHs can break down the complex compound structure in days or week (Santodonato, 1981). PAH compounds are hydrophobic, immiscible in water and adsorbed on dust, and precipitate in sediments of aquatic water bodies, else they are miscible in any hydrophobic matter which may contaminate aquatic body. Microbes inhabited in terrestrial and water system possess adaptability to degrade and mineralize PAHs over longer or shorter time duration (ATSDR, 2010).

The PAH metabolites are usually more toxic in the existence of UV light. PAHs in soil are improbable to employ toxicity influence on terrestrial invertebrates (Peter, 2003). PAHs get absorbed to plants from roots from soils and translocate contaminant to rest of the plant parts. Mobility of these contaminants is commonly ruled by dose, solubility, and other physicochemical properties such as nature of soil. Some plant species contains constituents which may guard against toxic consequence of PAHs; however, some plants could synthesize PAHs and perform as growth hormones (ATSDR, 2010; Beyer et al., 2010). PAH bioaccumulation has been observed in terrestrial invertebrates because of persistence and longer half-life shellfish expected to consist much higher concentration of PAH than in the environment. Nevertheless, metabolism of PAHs is sufficient to prevent biomagnifications (Tudoran and Putz, 2012; Inomata et al., 2012; Abdel-Shafy and Mansour, 2016; Borosky, 1999). Organisms are adversely affected because of tumors, reproduction, growth development, and immunity. PAH absorption occurs in mammals by inhalation, dermal contact, and ingestion (Dong et al., 2012; Veltman et al., 2012; Beyer et al., 2010).

The interactions of microplastics and chemical pollutants

Christopher Blair Crawford, Brian Quinn, in *Microplastic Pollutants*, 2017

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are class of chemicals that can exist in more than 100 different combinations and are among the most ubiquitous pollutants in the natural environment. Many PAHs are considerably toxic to aquatic species, such as pyrene, which exhibits considerable toxicity even at low levels of exposure.³²² Furthermore, some are even carcinogenic, such as benzo[a]pyrene. Consequently, 16 PAH compounds have been listed by the United States Environmental Protection Agency as pollutants of concern and consequently a value of 200 ng/l has been set as the maximum allowable limit in drinking water¹²³ (Fig. 6.9).

Figure 6.9. Ovalene, a PAH compound.

PAHs are readily produced as a consequence of incomplete combustion of wood, tobacco and other fuel sources composed of carbon compounds.³³⁰ Consequently, it is recognised that some PAHs in the environment can originate from natural sources, such as forest fires and volcano eruptions.¹¹¹ However, their presence in the environment is mainly due to anthropogenic activities, such as coal burning power plants, shipping activities⁴⁴² and refuse dumping sites.⁴⁴¹ Furthermore, some PAHs are used in industry to produce plastics, pesticides and dyes.

Ocean-based industrial oil-extraction platforms regularly emit PAHs into the atmosphere as part of their manufacturing process,³⁶³ while PAH by-products from combustion can be washed into marine habitats via rainfall and watercourses or settle from the atmosphere onto ocean surface waters.⁴⁴⁴ Moreover, it has been determined that the burning of plastic refuse emits PAHs, with polystyrene producing the highest quantities.⁴⁵⁰ Additionally, the manufacture of polystyrene can produce PAHs as an undesired consequence of incomplete polymerisation during processing in which the toxic PAH precursors, benzene and styrene, can become incorporated into the polymer matrix.³⁵⁸

The marine environment can also be directly polluted with PAHs due to the unintentional release of oil into seawater.⁴⁴⁴ Interestingly, when analysing marine samples, the ratio between parent PAHs and alkylated PAHs can be used to

determine whether the source of PAH contamination was of combusive origin or from petroleum-based fuels.³⁶³ Accordingly, high levels of parent PAHs would equate to combusive emissions, such as the burning of oil and gas, while high levels of alkylated PAHs would represent contamination from petroleum products, such as fuel leakage during vessel activities in the region or from accidental spillages.

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Human health hazards of wastewater

Bing Wu PhD, in High-Risk Pollutants in Wastewater, 2020

6.1.3.2 POLYCYCLIC AROMATIC HYDROCARBONS

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Hydraulic Fracturing

Tarek Saba, in *Introduction to Environmental Forensics (Third Edition)*, 2015

14.5.2.4 Polycyclic Aromatic Hydrocarbons (PAHs): Analysis of Fingerprints

PAHs are a group of organic compounds consisting of two or more fused aromatic rings. Naphthalene, consisting of two fused benzene rings, is the simplest PAH compound. PAHs are found in crude oil, petroleum products such as diesel, and organic seams in subsurface soils. PAHs are also formed during rapid, high-temperature (>500 °C), incomplete or inefficient (i.e., oxygen-starved) combustion of organic biomass (i.e., pyrogenic) (Boehm, 2006). Example pyrogenic sources that contain PAHs include soot, creosote, and waste oils, among other sources. See Figure 14.6 for example PAHs in creosote and diesel oil.

FIGURE 14.6. PAH compound distribution in example petrogenic and pyrogenic sources.

In claims of groundwater contamination, PAH compounds (e.g., benzo(a)pyrene) may be found in a water well, and chemical fingerprinting analysis is an available method for tracing the PAH source. For example, the ratio of two of the PAH compounds (fluoranthene/pyrene [FL/PY]) can provide information on the source of the PAHs, whether a petroleum-based source (i.e., petrogenic) or a pyrogenic source (e.g., Brenner et al., 2002). A fluoranthene/pyrene ratio greater than 1.0 indicates that the PAHs originated, at least in part, from a pyrogenic source such as soot (which could originate from household activities such as chimney cleaning) or road runoff.

Mycoremediation of polycyclic aromatic hydrocarbons

Shalini Gupta, Bhawana Pathak, in *Abatement of Environmental Pollutants*, 2020

1.2 EFFECT OF PAHS EXPOSURE ON ENVIRONMENT AND HUMAN HEALTH

PAHs are ubiquitously present in the environment mainly evaporated into the atmosphere. PAHs undergo photolysis in presence of sunlight, mainly when adsorbed to dust particles. Oxidation of PAHs can break down the complex compound structure in days or week (Santodonato, 1981). PAH compounds are hydrophobic, immiscible in water and adsorbed on dust, and precipitate in sediments of aquatic water bodies, else they are miscible in any hydrophobic matter which may contaminate aquatic body. Microbes inhabited in terrestrial and water system possess adaptability to degrade and mineralize PAHs over longer or shorter time duration (ATSDR, 2010).

The PAH metabolites are usually more toxic in the existence of UV light. PAHs in soil are improbable to employ toxicity influence on terrestrial invertebrates (Peter, 2003). PAHs get absorbed to plants from roots from soils and translocate contaminant to rest of the plant parts. Mobility of these contaminants is commonly ruled by dose, solubility, and other physicochemical properties such as nature of soil. Some plant species contains constituents which may guard against toxic consequence of PAHs; however, some plants could synthesize PAHs and perform as growth hormones (ATSDR, 2010; Beyer et al., 2010). PAH bioaccumulation has been observed in terrestrial invertebrates because of persistence and longer half-life shellfish expected to consist much higher concentration of PAH than in the environment. Nevertheless, metabolism of PAHs is sufficient to prevent biomagnifications (Tudoran and Putz, 2012; Inomata et al., 2012; Abdel-Shafy and Mansour, 2016; Borosky, 1999). Organisms are adversely affected because of tumors, reproduction, growth development, and immunity. PAH absorption occurs in mammals by inhalation, dermal contact, and ingestion (Dong et al., 2012; Veltman et al., 2012; Beyer et al., 2010).

The interactions of microplastics and chemical pollutants

Christopher Blair Crawford, Brian Quinn, in *Microplastic Pollutants*, 2017

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are class of chemicals that can exist in more than 100 different combinations and are among the most ubiquitous pollutants in the natural environment. Many PAHs are considerably toxic to aquatic species, such as pyrene, which exhibits considerable toxicity even at low levels of exposure.³²² Furthermore, some are even carcinogenic, such as benzo[a]pyrene. Consequently, 16 PAH compounds have been listed by the United States Environmental Protection Agency as pollutants of concern and consequently a value of 200 ng/l has been set as the maximum allowable limit in drinking water¹²³ (Fig. 6.9).

Figure 6.9. Ovalene, a PAH compound.

PAHs are readily produced as a consequence of incomplete combustion of wood, tobacco and other fuel sources composed of carbon compounds.³³⁰ Consequently, it is recognised that some PAHs in the environment can originate from natural sources, such as forest fires and volcano eruptions.¹¹¹ However, their presence in the environment is mainly due to anthropogenic activities, such as coal burning power plants, shipping activities⁴⁴² and refuse dumping sites.⁴⁴¹ Furthermore, some PAHs are used in industry to produce plastics, pesticides and dyes.

Ocean-based industrial oil-extraction platforms regularly emit PAHs into the atmosphere as part of their manufacturing process,³⁶³ while PAH by-products from combustion can be washed into marine habitats via rainfall and watercourses or settle from the atmosphere onto ocean surface waters.⁴⁴⁴ Moreover, it has been determined that the burning of plastic refuse emits PAHs, with polystyrene producing the highest quantities.⁴⁵⁰ Additionally, the manufacture of polystyrene can produce PAHs as an undesired consequence of incomplete polymerisation during processing in which the toxic PAH precursors, benzene and styrene, can become incorporated into the polymer matrix.³⁵⁸

The marine environment can also be directly polluted with PAHs due to the unintentional release of oil into seawater.⁴⁴⁴ Interestingly, when analysing marine samples, the ratio between parent PAHs and alkylated PAHs can be used to determinewhether the source of PAH contamination was of combustive origin or from petroleum-based fuels.³⁶³ Accordingly, high levels of parent PAHs would equate to combustive emissions, such as the burning of oil and gas, while high levels of alkylated PAHs would represent contamination from petroleum products, such as fuel leakage during vessel activities in the region or from accidental spillages.

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Polycyclic Aromatic Hydrocarbon

PAHs are organic substances made up of carbon and hydrogen atoms grouped into at least two condensed or fused aromatic ring structures (CCME, 2010).

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Polycyclic Aromatic Hydrocarbons (PAHs)

Paul D. Boehm, in Environmental Forensics, 1964

PUBLISHER SUMMARY

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Anthropogenic inputs of PAH arise from the release into the environment of petrogenic PAHs through accidental acute petroleum spillages and through chronic non-point source and point-source inputs such as urban (storm water) runoff and

municipal waste treatment plant discharges. The most common and ubiquitous sources of anthropogenic PAHs, however, are those associated with pyrogenic inputs.

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Hazards and Diseases

M. Huang, T.M. Penning, in *Encyclopedia of Food Safety*, 2014

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of diverse organic compounds that contain two or more fused aromatic rings ranging from the two-ring naphthalene and naphthalene derivatives to complex ring structures containing up to 10 rings. PAHs with up to six fused aromatic rings are often known as 'small' PAHs, whereas those containing more than six aromatic rings are called 'large' PAHs. PAHs have also been classified into alternant and nonalternant compounds. Alternant PAHs are those compounds composed solely of fused six-member benzene rings, whereas nonalternant PAHs contain both six-member benzene and five-member carbon rings. Common structural features of PAH compounds are illustrated in Figure 1. Differences in the configuration of rings may lead to differences in properties. In their purest form, PAHs are solids with low volatility at room temperature and range in appearance from colorless to white or pale yellow–green. They are relatively insoluble in water and most can be photooxidized and degraded to simpler substances.

Figure 1. Common structural features of PAH compounds.

PAHs are formed by condensation of smaller organic compounds by pyrolysis or pyrosynthesis. Smaller organic compounds are pyrolyzed at a high temperature and the free radicals produced join together as aggregate large PAH molecules (pyrosynthesis). Diels–Alder-type rearrangements are commonly involved in the formation of the PAHs. Temperature is an important factor to affect both the structure and diversity of the PAHs formed. Large PAHs are formed at lower levels than small PAHs due to the kinetic limitation in their production through addition of successive rings. In addition, with many more isomers possible for larger PAHs, the occurrence of specific structures is much lower.

PAHs are ubiquitous environmental pollutants. They are not only found naturally in the environment but they can also be man made. PAHs are formed as a result of incomplete combustion of carbon-containing materials, such as wood, coal, oil, gas, or biomass. They are also created in car and diesel exhaust, smoked or charbroiled food, and are present in cigarette smoke condensate, and tobacco products. According to their origins, PAHs are classified into pyrogenic PAHs (Figure 2) arising from fossil fuel combustion and petrogenic PAHs (Figure 3) that are unique to crude oil and contaminate water after an oil spill. Petrogenic PAHs differ in structure to pyrogenic PAHs in that they are either extensively alkylated or oxygenated to yield PAH quinones.

Figure 3. Representative petrogenic PAHs.

PAHs are complex mixtures of hundreds of chemicals, including derivatives of PAHs, such as nitro- and hydroxy-PAHs, as well as heterocyclic PAHs. In the 1970s, the United States Environmental Protection Agency (US EPA) listed 16 PAHs as priority pollutants. These priority PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene (B[a]P), indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and dibenz[a,h]anthracene (Figure 2). Among these priority PAHs, B[a]P, a known human carcinogen, is commonly used as an indicator for PAH exposure.

PAHs are present in air, soil, water, and food, and routes of exposure include inhalation, dermal contact, and ingestion. Some exposures may involve more than one route simultaneously affecting the total absorbed dose (such as dermal and inhalation exposures from contaminated air). Occupational sources of exposure mainly involve workers in coal gasification plants, municipal incinerators, smoke houses, and aluminum production facilities. Nonoccupational sources of exposure mainly involve diet, smoking, and burning of coal and wood. In most cases, intake of food is the major involuntary exposure route of PAHs. Therefore, this article will only discuss the occurrence of PAHs in food, health concerns, analysis, mitigation and biomonitoring, and guidelines to reduce PAHs in food.

POLYCYCLIC AROMATIC HYDROCARBONS | Environmental Applications

A.N. Gachanja, in *Encyclopedia of Analytical Science (Second Edition)*, 2005

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) from anthropogenic sources are discharged into the atmosphere either in the gaseous state or adsorbed onto particulates. These PAHs are subject to removal mechanisms such as oxidative and photolytic reactions and wet and dry deposition. Air currents and prevailing winds disperse and transport the PAHs over long distances and deposit them on soil and in water. PAHs on soil are carried during storms by water runoff to rivers and seas. In the aquatic environment, the PAHs enter marine plants, fish, and sedentary organisms. PAHs are thus ubiquitous pollutants that have been detected even in remote parts of the earth, e.g., the average atmospheric concentration of the sum of 11 PAHs at Barrow,

Alaska, was reported to be 1.2 and 0.16 ng m⁻³ for Mar. and Aug. 1979, respectively, and PAH concentrations in sediments have ranged from undetectable in the Amazon river to greater than 10000 µg l⁻¹ in the Charles river, Boston, USA. This article briefly reviews the analysis of PAHs in the atmosphere, water, food, and biological samples.

Z. Fan, L. Lin, in *Encyclopedia of Environmental Health (Second Edition)*, 2011

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PAHs, which contain two or more fused aromatic rings, constitute a broad family of compounds, many of which are mutagens and carcinogens. More than 100 different PAHs have been identified in environmental samples and 16 PAHs (Table 2) are generally measured in most exposure and environmental air pollution studies. PAHs are introduced into the environment via natural emissions, for example, volcanic eruptions and forest–prairie fires, but largely from the incomplete burning of some organic substances during anthropogenic combustion processes, such as vehicular emissions, wood smoke, coke and asphalt production, waste incineration, and ETS in indoor environments. Among all sources, vehicular exhaust is the major and common source for PAH air pollution in most urban areas. The loading of PAHs in aquatic and terrestrial systems has a component that is atmospheric in origin. Since PAHs are semivolatile compounds, they distribute in both gas and particulate phase under ambient conditions, leading to different biologically effective pathways through inhalation. In the atmosphere, PAHs are not stable and can undergo photodecomposition under sunlight and react with other pollutants such as ozone and nitrogen oxides to form oxygenated and nitro/dinitro-PAHs. These processes lead to more complex and toxic mixtures because many nitro- and oxygenated PAHs often pose higher toxicities than their parent compounds.

PAHs exposures may occur in all routes, that is, inhalation, ingestion, and dermal contact. Occupational exposure studies have showed a variety of adverse health effects resulting from exposure to elevated PAHs, including cancer. However, limited exposure data are available for PAHs and their substituted pollutants in the community setting because these pollutants often are present at trace levels in the environment and are difficult to detect. Also, current methods for the measurement of PAHs and nitro-PAHs are very time consuming and expensive. Thus, innovative, sensitive, and cost-effective sampling and analytic techniques are needed to accurately quantify exposure to PAHs and their derivatives in future exposure studies.

Human health hazards of wastewater

Bing Wu PhD, in *High-Risk Pollutants in Wastewater*, 2020

6.1.3.2 POLYCYCLIC AROMATIC HYDROCARBONS

PAHs are mainly derived from incomplete combustion of coal and oil, and wastewater discharge is one of the main channels for PAHs to enter the environment. Long-term irrigation with industrial effluent mixed with municipal wastewater (Cai et al., 2007; Villar et al., 2006) has resulted in the excessive accumulation of PAHs in agricultural soil. In addition, part of PAHs in the air could directly enter the soil by atmospheric deposition. The exposure pathways are illustrated in Fig. 6.3. PAHs in the soils have brought a potential risk to human health along the food chain. Ingestion is considered as the major source of PAHs (McGrath et al., 2007). Vegetables cultivated on the wastewater-contaminated soils may take up these pollutants in sufficient quantities. Numerous studies have demonstrated that vegetables accumulated high concentrations of PAHs that were grown in PAH-contaminated soils (Samsoe-Petersen et al., 2002; Wennrich et al., 2002). Additionally, other pathways, including inhalation and dermal contact, also contribute to the human exposure to environmental carcinogenic PAHs (Chen, Liao, 2006). Figure 6.3. Exposure pathways of PAHs from wastewater.

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Shalini Gupta, Bhawana Pathak, in *Abatement of Environmental Pollutants*, 2020

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Human health hazards of wastewater

Bing Wu PhD, in High-Risk Pollutants in Wastewater, 2020

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Hydraulic Fracturing

Tarek Saba, in Introduction to Environmental Forensics (Third Edition), 2015

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Mycoremediation of polycyclic aromatic hydrocarbons

Shalini Gupta, Bhawana Pathak, in Abatement of Environmental Pollutants, 2020

1.2 Effect of PAHs exposure on environment and human health

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The PAH metabolites are usually more toxic in the existence of UV light. PAHs in soil are improbable to employ toxicity influence on terrestrial invertebrates (Peter, 2003). PAHs get absorbed to plants from roots from soils and translocate contaminant to rest of the plant parts. Mobility of these contaminants is commonly ruled by dose, solubility, and other physicochemical properties such as nature of soil. Some plant species contains constituents which may guard against toxic consequence of PAHs; however, some plants could synthesize PAHs and perform as growth hormones (ATSDR, 2010; Beyer et al., 2010). PAH bioaccumulation has been observed in terrestrial invertebrates because of persistence and longer half-life shellfish expected to consist much higher concentration of PAH than in the environment. Nevertheless, metabolism of PAHs is sufficient to prevent biomagnifications (Tudoran and Putz, 2012; Inomata et al., 2012; Abdel-Shafy and Mansour, 2016; Borosky, 1999). Organisms are adversely affected because of tumors, reproduction, growth development, and immunity. PAH

absorption occurs in mammals by inhalation, dermal contact, and ingestion (Dong et al., 2012; Veltman et al., 2012; Beyer et al., 2010).

The interactions of microplastics and chemical pollutants

Christopher Blair Crawford, Brian Quinn, in *Microplastic Pollutants*, 2017

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are class of chemicals that can exist in more than 100 different combinations and are among the most ubiquitous pollutants in the natural environment. Many PAHs are considerably toxic to aquatic species, such as pyrene, which exhibits considerable toxicity even at low levels of exposure.³²² Furthermore, some are even carcinogenic, such as benzo[a]pyrene. Consequently, 16 PAH compounds have been listed by the United States Environmental Protection Agency as pollutants of concern and consequently a value of 200 ng/l has been set as the maximum allowable limit in drinking water¹²³ (Fig. 6.9).

FIGURE 6.9. OVALENE, A PAH COMPOUND.

PAHs are readily produced as a consequence of incomplete combustion of wood, tobacco and other fuel sources composed of carbon compounds.³³⁰ Consequently, it is recognised that some PAHs in the environment can originate from natural sources, such as forest fires and volcano eruptions.¹¹¹ However, their presence in the environment is mainly due to anthropogenic activities, such as coal burning power plants, shipping activities⁴⁴² and refuse dumping sites.⁴⁴¹ Furthermore, some PAHs are used in industry to produce plastics, pesticides and dyes.

Ocean-based industrial oil-extraction platforms regularly emit PAHs into the atmosphere as part of their manufacturing process,³⁶³ while PAH by-products from combustion can be washed into marine habitats via rainfall and watercourses or settle from the atmosphere onto ocean surface waters.⁴⁴⁴ Moreover, it has been determined that the burning of plastic refuse emits PAHs, with polystyrene producing the highest quantities.⁴⁵⁰ Additionally, the manufacture of polystyrene can produce PAHs as an undesired consequence of incomplete polymerisation during processing in which the toxic PAH precursors, benzene and styrene, can become incorporated into the polymer matrix.³⁵⁸

The marine environment can also be directly polluted with PAHs due to the unintentional release of oil into seawater.⁴⁴⁴ Interestingly, when analysing marine samples, the ratio between parent PAHs and alkylated PAHs can be used to determinewhether the source of PAH contamination was of combustive origin or from petroleum-based fuels.³⁶³ Accordingly, high levels of parent PAHs would equate to combustive emissions, such as the burning of oil and gas, while high levels of alkylated PAHs would represent contamination from petroleum products, such as fuel leakage during vessel activities in the region or from accidental spillages.

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Polycyclic Aromatic Hydrocarbon

PAHs are organic substances made up of carbon and hydrogen atoms grouped into at least two condensed or fused aromatic ring structures (CCME, 2010).

From: *Environment International*, 2013

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- IV. [Pyrene](#)
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- VII. [Phenanthrene](#)
- VIII. [DNA](#)
- IX. [Enzyme](#)
- X. [Petroleum](#)

Polycyclic Aromatic Hydrocarbons (PAHs)

Paul D. Boehm, in *Environmental Forensics*, 1964

PUBLISHER SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) are sometimes referred to as polynuclear aromatic hydrocarbons (PNAs), condensed ring aromatics, or fused ring aromatics. They are a class of organic compounds consisting of two or more fused aromatic rings. Polycyclic aromatic hydrocarbons most commonly encountered in the environment contain two (naphthalene) to seven (coronene) fused benzene rings, though PAHs with greater number of rings are also found. Natural sources of petrogenic PAHs

arise from oil seepages and erosion of petroliferous shales, while natural sources of PAHs from combustion or pyrolysis include PAHs from incomplete combustion of wood and biomass via forest and grass fires. Anthropogenic (pollution) related PAHs inputs can result in similar, but not identical, PAH compounds and assemblages of PAHs to those of natural origin.

Anthropogenic inputs of PAH arise from the release into the environment of petrogenic PAHs through accidental acute petroleum spillages and through chronic non-point source and point-source inputs such as urban (storm water) runoff and municipal waste treatment plant discharges. The most common and ubiquitous sources of anthropogenic PAHs, however, are those associated with pyrogenic inputs.

HAZARDS AND DISEASES

M. Huang, T.M. Penning, in Encyclopedia of Food Safety, 2014

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of diverse organic compounds that contain two or more fused aromatic rings ranging from the two-ring naphthalene and naphthalene derivatives to complex ring structures containing up to 10 rings. PAHs with up to six fused aromatic rings are often known as 'small' PAHs, whereas those containing more than six aromatic rings are called 'large' PAHs. PAHs have also been classified into alternant and nonalternant compounds. Alternant PAHs are those compounds composed solely of fused six-member benzene rings, whereas nonalternant PAHs contain both six-member benzene and five-member carbon rings. Common structural features of PAH compounds are illustrated in Figure 1. Differences in the configuration of rings may lead to differences in properties. In their purest form, PAHs are solids with low volatility at room temperature and range in appearance from colorless to white or pale yellow–green. They are relatively insoluble in water and most can be photooxidized and degraded to simpler substances.

Figure 1. Common structural features of PAH compounds.

PAHs are formed by condensation of smaller organic compounds by pyrolysis or pyrosynthesis. Smaller organic compounds are pyrolyzed at a high temperature and the free radicals produced join together as aggregate large PAH molecules (pyrosynthesis). Diels–Alder-type rearrangements are commonly involved in the formation of the PAHs. Temperature is an important factor to affect both the structure and diversity of the PAHs formed. Large PAHs are formed at lower levels than small PAHs due to the kinetic limitation in their production through addition of successive rings. In addition, with many more isomers possible for larger PAHs, the occurrence of specific structures is much lower.

PAHs are ubiquitous environmental pollutants. They are not only found naturally in the environment but they can also be man made. PAHs are formed as a result of incomplete combustion of carbon-containing materials, such as wood, coal, oil, gas, or biomass. They are also created in car and diesel exhaust, smoked or charbroiled food, and are present in cigarette smoke condensate, and tobacco products. According to their origins, PAHs are classified into pyrogenic PAHs (Figure 2) arising from fossil fuel combustion and petrogenic PAHs (Figure 3) that are unique to crude oil and contaminate water after an oil spill. Petrogenic PAHs differ in structure to pyrogenic PAHs in that they are either extensively alkylated or oxygenated to yield PAH quinones.

Figure 2. The 16 priority pyrogenic PAHs listed by the United States Environmental Protection Agency (US EPA).

Figure 3. Representative petrogenic PAHs.

PAHs are complex mixtures of hundreds of chemicals, including derivatives of PAHs, such as nitro- and hydroxy-PAHs, as well as heterocyclic PAHs. In the 1970s, the United States Environmental Protection Agency (US EPA) listed 16 PAHs as priority pollutants. These priority PAHs include naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, chrysene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene (B[a]P), indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, and dibenz[a,h]anthracene (Figure 2). Among these priority PAHs, B[a]P, a known human carcinogen, is commonly used as an indicator for PAH exposure.

PAHs are present in air, soil, water, and food, and routes of exposure include inhalation, dermal contact, and ingestion. Some exposures may involve more than one route simultaneously affecting the total absorbed dose (such as dermal and inhalation exposures from contaminated air). Occupational sources of exposure mainly involve workers in coal gasification plants, municipal incinerators, smoke houses, and aluminum production facilities. Nonoccupational sources of exposure mainly involve diet, smoking, and burning of coal and wood. In most cases, intake of food is the major involuntary exposure route of PAHs. Therefore, this article will only discuss the occurrence of PAHs in food, health concerns, analysis, mitigation and biomonitoring, and guidelines to reduce PAHs in food.

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POLYCYCLIC AROMATIC HYDROCARBONS | Environmental Applications

A.N. Gachanja, in Encyclopedia of Analytical Science (Second Edition), 2005

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) from anthropogenic sources are discharged into the atmosphere either in the gaseous state or adsorbed onto particulates. These PAHs are subject to removal mechanisms such as oxidative and photolytic reactions and wet and dry deposition. Air currents and prevailing winds disperse and transport the PAHs over long distances and deposit them on soil and in water. PAHs on soil are carried during storms by water runoff to rivers and seas. In the aquatic environment, the PAHs enter marine plants, fish, and sedentary organisms. PAHs are thus ubiquitous pollutants that have been detected even in remote parts of the earth, e.g., the average atmospheric concentration of the sum of 11 PAHs at Barrow, Alaska, was reported to be 1.2 and 0.16 ng m⁻³ for Mar. and Aug. 1979, respectively, and PAH concentrations in sediments have ranged from undetectable in the Amazon river to greater than 10000 µg l⁻¹ in the Charles river, Boston, USA. This article briefly reviews the analysis of PAHs in the atmosphere, water, food, and biological samples.

PAHs

PAHs, which contain two or more fused aromatic rings, constitute a broad family of compounds, many of which are mutagens and carcinogens. More than 100 different PAHs have been identified in environmental samples and 16 PAHs (Table 2) are generally measured in most exposure and environmental air pollution studies. PAHs are introduced into the environment via natural emissions, for example, volcanic eruptions and forest–prairie fires, but largely from the incomplete burning of some organic substances during anthropogenic combustion processes, such as vehicular emissions, wood smoke, coke and asphalt production, waste incineration, and ETS in indoor environments. Among all sources, vehicular exhaust is the major and common source for PAH air pollution in most urban areas. The loading of PAHs in aquatic and terrestrial systems has a component that is atmospheric in origin. Since PAHs are semivolatile compounds, they distribute in both gas and particulate phase under ambient conditions, leading to different biologically effective pathways through inhalation. In the atmosphere, PAHs are not stable and can undergo photodecomposition under sunlight and react with other pollutants such as ozone and nitrogen oxides to form oxygenated and nitro/dinitro-PAHs. These processes lead to more complex and toxic mixtures because many nitro- and oxygenated PAHs often pose higher toxicities than their parent compounds.

PAHs exposures may occur in all routes, that is, inhalation, ingestion, and dermal contact. Occupational exposure studies have showed a variety of adverse health effects resulting from exposure to elevated PAHs, including cancer. However, limited exposure data are available for PAHs and their substituted pollutants in the community setting because these pollutants often are present at trace levels in the environment and are difficult to detect. Also, current methods for the measurement of PAHs and nitro-PAHs are very time consuming and expensive. Thus, innovative, sensitive, and cost-effective sampling and analytic techniques are needed to accurately quantify exposure to PAHs and their derivatives in future exposure studies.

Human health hazards of wastewater

Bing Wu PhD, in High-Risk Pollutants in Wastewater, 2020

6.1.3.2 Polycyclic aromatic hydrocarbons

PAHs are mainly derived from incomplete combustion of coal and oil, and wastewater discharge is one of the main channels for PAHs to enter the environment. Long-term irrigation with industrial effluent mixed with municipal wastewater (Cai et al., 2007; Villar et al., 2006) has resulted in the excessive accumulation of PAHs in agricultural soil. In addition, part of PAHs in the air could directly enter the soil by atmospheric deposition. The exposure pathways are illustrated in Fig. 6.3. PAHs in the soils have brought a potential risk to human health along the food chain. Ingestion is considered as the major source of PAHs (McGrath et al., 2007). Vegetables cultivated on the wastewater-contaminated soils may take up these pollutants in sufficient quantities. Numerous studies have demonstrated that vegetables accumulated high concentrations of PAHs that were grown in PAH-contaminated soils (Samsoe-Petersen et al., 2002; Wennrich et al., 2002). Additionally, other pathways, including inhalation and dermal contact, also contribute to the human exposure to environmental carcinogenic PAHs (Chen, Liao, 2006). Figure 6.3. Exposure pathways of PAHs from wastewater.

PAHs intake could interfere with the cellular membrane functions and enzyme systems associated with the membrane. The major concern of PAHs is about the epoxides and dihydrodiols that can bind with the cellular proteins and DNA leading to biochemical disruptions, cell damage, mutations, developmental malformations, tumors, and cancer. To quantify the carcinogenicity of the selected PAHs, toxic equivalency factor compared to benzo(a)pyrene was applied.

HYDRAULIC FRACTURING

Tarek Saba, in Introduction to Environmental Forensics (Third Edition), 2015

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Mycoremediation of polycyclic aromatic hydrocarbons

Shalini Gupta, Bhawana Pathak, in *Abatement of Environmental Pollutants*, 2020

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The interactions of microplastics and chemical pollutants

Christopher Blair Crawford, Brian Quinn, in *Microplastic Pollutants*, 2017

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Figure 6.9. Ovalene, a PAH compound.

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POLYCYCLIC AROMATIC HYDROCARBON

PAHs are organic substances made up of carbon and hydrogen atoms grouped into at least two condensed or fused aromatic ring structures (CCME, 2010).

From: Environment International, 2013

Polycyclic Aromatic Hydrocarbons (PAHs)

Paul D. Boehm, in Environmental Forensics, 1964

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Hazards and Diseases

M. Huang, T.M. Penning, in Encyclopedia of Food Safety, 2014

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PAHs are present in air, soil, water, and food, and routes of exposure include inhalation, dermal contact, and ingestion. Some exposures may involve more than one route simultaneously affecting the total absorbed dose (such as dermal and inhalation exposures from contaminated air). Occupational sources of exposure mainly involve workers in coal gasification plants, municipal incinerators, smoke houses, and aluminum production facilities. Nonoccupational sources of exposure mainly involve diet, smoking, and burning of coal and wood. In most cases, intake of food is the major involuntary exposure route of PAHs. Therefore, this article will only discuss the occurrence of PAHs in food, health concerns, analysis, mitigation and biomonitoring, and guidelines to reduce PAHs in food.

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POLYCYCLIC AROMATIC HYDROCARBONS | Environmental Applications

A.N. Gachanja, in *Encyclopedia of Analytical Science (Second Edition)*, 2005

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Volume 2

Z. Fan, L. Lin, in *Encyclopedia of Environmental Health (Second Edition)*, 2011

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Human health hazards of wastewater

Bing Wu PhD, in *High-Risk Pollutants in Wastewater*, 2020

6.1.3.2 POLYCYCLIC AROMATIC HYDROCARBONS

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Figure 6.3. Exposure pathways of PAHs from wastewater.

PAHs intake could interfere with the cellular membrane functions and enzyme systems associated with the membrane. The major concern of PAHs is about the epoxides and dihydrodiols that can bind with the cellular proteins and DNA leading to biochemical disruptions, cell damage, mutations, developmental malformations, tumors, and cancer. To quantify the carcinogenicity of the selected PAHs, toxic equivalency factor compared to benzo(a)pyrene was applied.

HYDRAULIC FRACTURING

Tarek Saba, in *Introduction to Environmental Forensics* (Third Edition), 2015

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PAHs are a group of organic compounds consisting of two or more fused aromatic rings. Naphthalene, consisting of two fused benzene rings, is the simplest PAH compound. PAHs are found in crude oil, petroleum products such as diesel, and organic seams in subsurface soils. PAHs are also formed during rapid, high-temperature (>500 °C), incomplete or inefficient (i.e., oxygen-starved) combustion of organic biomass (i.e., pyrogenic) (Boehm, 2006). Example pyrogenic sources that contain PAHs include soot, creosote, and waste oils, among other sources. See Figure 14.6 for example PAHs in creosote and diesel oil.

FIGURE 14.6. PAH compound distribution in example petrogenic and pyrogenic sources.

In claims of groundwater contamination, PAH compounds (e.g., benzo(a)pyrene) may be found in a water well, and chemical fingerprinting analysis is an available method for tracing the PAH source. For example, the ratio of two of the PAH compounds (fluoranthene/pyrene [FL/PY]) can provide information on the source of the PAHs, whether a petroleum-based source (i.e., petrogenic) or a pyrogenic source (e.g., Brenner et al., 2002). A fluoranthene/pyrene ratio greater than 1.0 indicates that the PAHs originated, at least in part, from a pyrogenic source such as soot (which could originate from household activities such as chimney cleaning) or road runoff.

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Mycoremediation of polycyclic aromatic hydrocarbons

Shalini Gupta, Bhawana Pathak, in *Abatement of Environmental Pollutants*, 2020

1.2 Effect of PAHs exposure on environment and human health

PAHs are ubiquitously present in the environment mainly evaporated into the atmosphere. PAHs undergo photolysis in presence of sunlight, mainly when adsorbed to dust particles. Oxidation of PAHs can break down the complex compound structure in days or week (Santodonato, 1981). PAH compounds are hydrophobic, immiscible in water and adsorbed on dust, and precipitate in sediments of aquatic water bodies, else they are miscible in any hydrophobic matter which may contaminate aquatic body. Microbes inhabited in terrestrial and water system possess adaptability to degrade and mineralize PAHs over longer or shorter time duration (ATSDR, 2010).

The PAH metabolites are usually more toxic in the existence of UV light. PAHs in soil are improbable to employ toxicity influence on terrestrial invertebrates (Peter, 2003). PAHs get absorbed to plants from roots from soils and translocate contaminant to rest of the plant parts. Mobility of these contaminants is commonly ruled by dose, solubility, and other physicochemical properties such as nature of soil. Some plant species contains constituents which may guard against toxic consequence of PAHs; however, some plants could synthesize PAHs and perform as growth hormones (ATSDR, 2010; Beyer et al., 2010). PAH bioaccumulation has been observed in terrestrial invertebrates because of persistence and longer half-life shellfish expected to consist much higher concentration of PAH than in the environment. Nevertheless, metabolism of PAHs is sufficient to prevent biomagnifications (Tudoran and Putz, 2012; Inomata et al., 2012; Abdel-Shafy and Mansour, 2016; Borosky, 1999). Organisms are adversely affected because of tumors, reproduction, growth development, and immunity. PAH absorption occurs in mammals by inhalation, dermal contact, and ingestion (Dong et al., 2012; Veltman et al., 2012; Beyer et al., 2010).

The interactions of microplastics and chemical pollutants

Christopher Blair Crawford, Brian Quinn, in *Microplastic Pollutants*, 2017

POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Polycyclic aromatic hydrocarbons (PAHs) are class of chemicals that can exist in more than 100 different combinations and are among the most ubiquitous pollutants in the natural environment. Many PAHs are considerably toxic to aquatic species, such as pyrene, which exhibits considerable toxicity even at low levels of exposure.³²² Furthermore, some are even carcinogenic, such as benzo[a]pyrene. Consequently, 16 PAH compounds have been listed by the United States Environmental Protection Agency as pollutants of concern and consequently a value of 200 ng/l has been set as the maximum allowable limit in drinking water¹²³ (Fig. 6.9).

Figure 6.9. Ovalene, a PAH compound.

PAHs are readily produced as a consequence of incomplete combustion of wood, tobacco and other fuel sources composed of carbon compounds.³³⁰ Consequently, it is recognised that some PAHs in the environment can originate from natural sources, such as forest fires and volcano eruptions.¹¹¹ However, their presence in the environment is mainly due to anthropogenic activities, such as coal burning power plants, shipping activities⁴⁴² and refuse dumping sites.⁴⁴¹ Furthermore, some PAHs are used in industry to produce plastics, pesticides and dyes.

Ocean-based industrial oil-extraction platforms regularly emit PAHs into the atmosphere as part of their manufacturing process,³⁶³ while PAH by-products from combustion can be washed into marine habitats via rainfall and watercourses or settle from the atmosphere onto ocean surface waters.⁴⁴⁴ Moreover, it has been determined that the burning of plastic refuse emits PAHs, with polystyrene producing the highest quantities.⁴⁵⁰ Additionally, the manufacture of polystyrene can produce PAHs as an undesired consequence of incomplete polymerisation during processing in which the toxic PAH precursors, benzene and styrene, can become incorporated into the polymer matrix.³⁵⁸

The marine environment can also be directly polluted with PAHs due to the unintentional release of oil into seawater.⁴⁴⁴ Interestingly, when analysing marine samples, the ratio between parent PAHs and alkylated PAHs can be used to determinewhether the source of PAH contamination was of combustive origin or from petroleum-based fuels.³⁶³ Accordingly, high levels of parent PAHs would equate to combustive emissions, such as the burning of oil and gas, while high levels of alkylated PAHs would represent contamination from petroleum products, such as fuel leakage during vessel activities in the region or from accidental spillages.

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What does PFAS do to your body?

A growing body of science has found that there are potential adverse health impacts associated with PFAS exposure,

- I. including liver damage,
- II. thyroid disease,
- III. decreased fertility,
- IV. high cholesterol,
- V. obesity,
- VI. hormone suppression
- VII. and cancer.
- VIII. low infant birth weights,
- IX. effects on the immune system,
- X. cancer (for PFOA), and
- XI. thyroid hormone disruption (for PFOS).
- XII. Increase cholesterol levels
- XIII. Affect the immune system
- XIV. Increase the risk of cancer

These chemicals can easily migrate into the air, dust, food, soil and water.^{Feb 14, 2019}

Some scientific studies suggest that certain PFAS may affect different systems in the body. Although more research is needed, some studies in people have shown that certain PFAS may:

- I. Affect growth, learning and behavior of babies and older children
- II. Lower a woman's chance of getting pregnant
- III. Interfere with the body's natural hormones
- IV. Increase cholesterol levels
- V. Affect the immune system
- VI. Increase the risk of cancer

Water filtration units that use granular activated carbon (GAC, also called charcoal filters) or reverse osmosis (RO) can both be effective in removing the PFAS compounds that commercial labs typically analyze.

PERFLUOROALKYL AND POLYFLUOROALKYL SUBSTANCES (PFAS) IN DRINKING WATER

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) in Drinking Water

Perfluoroalkyl and polyfluoroalkyl substances (PFAS) are a large group of human-made chemicals that have been used in industry and consumer products worldwide since the 1950s. These chemicals are used to make household and commercial products that resist heat and chemical reactions and repel oil, stains, grease and water. PFAS chemicals include PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonic acid).

PFAS are found in people, wildlife and fish all over the world. Some PFAS do not break down easily and therefore stay in the environment for a very long time, especially in water.

PFAS CAN BE FOUND IN:

Food packaged in PFAS-containing materials, processed with equipment that used PFAS, or grown in PFAS-contaminated soil or water.

Commercial household products, including stain- and water-repellent fabrics, nonstick products (e.g., Teflon), polishes, waxes, paints, cleaning products, and fire-fighting foams (a major source of groundwater contamination at airports and military bases where firefighting training occurs).

Workplace, including production facilities or industries (e.g., chrome plating, electronics manufacturing or oil recovery) that use PFAS.

Drinking water, typically localized and associated with a specific facility (e.g., manufacturer, landfill, wastewater treatment plant, firefighter training facility).

Living organisms, including fish, animals and humans, where PFAS have the ability to build up and persist over time.

PFAS CAN BE FOUND IN:

Food packaged in PFAS-containing materials, processed with equipment that used PFAS, or grown in PFAS-contaminated soil or water.

Commercial household products, including stain- and water-repellent fabrics, nonstick products (e.g., Teflon), polishes, waxes, paints, cleaning products, and fire-fighting foams (a major source of groundwater contamination at airports and military bases where firefighting training occurs).

Workplace, including production facilities or industries (e.g., chrome plating, electronics manufacturing or oil recovery) that use PFAS.

Drinking water, typically localized and associated with a specific facility (e.g., manufacturer, landfill, wastewater treatment plant, firefighter training facility).

Living organisms, including fish, animals and humans, where PFAS have the ability to build up and persist over time.

Certain PFAS chemicals are no longer manufactured in the United States as a result of phase outs including the PFOA Stewardship Program in which eight major chemical manufacturers agreed to eliminate the use of PFOA and PFOA-related chemicals in their products and as emissions from their facilities. Although PFOA and PFOS are no longer manufactured in the United States, they are still produced internationally and can be imported into the United States in consumer goods such as carpet, leather and apparel, textiles, paper and packaging, coatings, rubber and plastics.

PFAS are found in a wide range of consumer products that people use daily such as cookware, pizza boxes and stain repellants. Most people have been exposed to PFAS. Certain PFAS can accumulate and stay in the human body for long periods of time.

There is evidence that exposure to PFAS can lead to adverse health outcomes in humans. The most-studied PFAS chemicals are PFOA and PFOS. Studies indicate that PFOA and PFOS can cause reproductive and developmental, liver and kidney, and immunological effects in laboratory animals. Both chemicals have caused tumors in animals. The most consistent findings are increased cholesterol levels among exposed populations, with more limited findings related to:

- I. low infant birth weights,
- II. effects on the immune system,
- III. cancer (for PFOA), and
- IV. thyroid hormone disruption (for PFOS).

What is the difference between PFOA, PFOS and GenX and other replacement PFAS?

Per- and polyfluoroalkyl substances (PFAS) are a group of man-made chemicals that have been in use since the 1940s, and are (or have been) found in many consumer products like cookware, food packaging, and stain repellants. PFAS manufacturing and processing facilities, airports, and military installations that use firefighting foams are some of the main sources of PFAS. PFAS may be released into the air, soil, and water, including sources of drinking water. PFOA and PFOS are the most studied PFAS chemicals and have been voluntarily phased out by industry, though they are still persistent in the environment. There are many other PFAS, including GenX chemicals and PFBS in use throughout our economy.

GenX is a trade name for a technology that is used to make high performance fluoropolymers (e.g., some nonstick coatings) without the use of perfluorooctanoic acid (PFOA). HFPO dimer acid and its ammonium salt are the major chemicals associated with the GenX technology. GenX chemicals have been found in surface water, groundwater, finished drinking water, rainwater,

and air emissions in some areas. As part of EPA's draft toxicity assessment, EPA has developed draft oral reference doses (RfDs) for GenX chemicals.

Perfluorobutane sulfonic acid (PFBS) has been used as a replacement chemical for PFOS. PFBS has been identified in environmental media and consumer products, including surface water, wastewater, drinking water, dust, carpeting and carpet cleaners, and floor wax. EPA has developed RfDs for PFBS as part of EPA's efforts to increase the amount of research and information that is publicly available on chemicals in the PFAS family.

PPCP

Pharmaceuticals and personal care products (PPCPs) are a unique group of emerging environmental contaminants, due to their inherent ability to induce physiological effects in human at low doses.

From: Emerging Contaminants, 2017

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Emerging Contaminant Contaminant Adsorption Antibiotic Sorption Waste Water Treatment Plant Effluent

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Removal of pharmaceutical and personal care products from wastewater using advanced materials

Amruta Morone, ... Sanjay P. Kamble, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019

8.3 Environmental fate and behavior of pharmaceuticals and personal care products

PPCPs enter the environment through various routes like absorption of PPCP by the body during therapeutic use followed by excretion and discharge into sewage systems. Another important route for entry of PPCPs into environment is through the discharge of effluent directly into river bodies by the manufacturing plant facility which subsequently enters the surface water/groundwater after leaching through the soil. The topical PCPs are usually washed off as shower waste, bathing waste, and through washing sinks. PPCPs are usually transported via aqueous streams or by sludge samples through adsorption (Fick et al., 2009). These PPCPs then undergo biodegradation, photolysis, etc. depending upon the nature of contaminant. The sources, fate, and transport of PPCPs are depicted in Fig. 8.1.

Figure 8.1. Sources, environmental fate and transport of PPCPs. PPCPs, Pharmaceuticals and personal care products.

Nanotechnology applications for the removal of environmental contaminants from pharmaceuticals and personal care products

Ryan Rienzie, ... Nadeesh M. Adassooriya, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019

ABSTRACT

Pharmaceuticals and personal care products (PPCPs) and pharmaceutically active compounds (PhACs) are important as environmental contaminants, and most of them are indebted in causing detrimental effects to aquatic lives even under minute concentrations and potential risks upon drinking by the higher animals. PPCPs/PhACs belonging to a number of therapeutic classes are not completely assimilated upon the intake by higher animals and are removed as original compounds or as metabolites from the body, ultimately reaching the water reserves. The complete removal of PPCPs/PhACs is challenging during conventional wastewater treatment (WWT) and none of the drinking or WWT plants are specifically designed to remove PPCPs/PhACs. Nanotechnology has provided a greater space in removing the PPCPs/PhACs with higher efficiencies of such technologies compared to the conventional WWT mechanisms. This chapter discusses a number of available methods of nanoenhanced techniques for purifying the contaminated water with PPCPs/PhACs such as nanomaterials for PhACs adsorption, nanoenhanced photocatalysis, and nanofiltration and their future implications.

Chemical HRP in wastewater

Gang Wu, ... Jinju Geng PhD, in *High-Risk Pollutants in Wastewater*, 2020

2.3.3 Migration and transformation of PPCPs in wastewater

PPCPs can be removed or be retained in WWTPs after entering the wastewater. Generally, biodegradation, adsorption, volatilization, hydrolyzation, and photolysis are the likely transformation routes in wastewater treatment process (Li and Zhang, 2010). For most of PPCPs, removal caused by volatilization is insignificant attributed to the relatively greater molecular weight (Yang et al., 2017a). Similarly, photolysis generally cannot account for a mentionable proportion of removal for PPCPs in WWTPs. This can be explained by the turbidity in WWTPs that is unbeneficial to phototransformation. Biodegradation generally plays a crucial role in degrading PPCPs. For example, biodegradation of diclofenac accounted for about 80% for the total removal volume in activated sludge (Wu et al., 2019). For other PPCPs such as antibiotic, the removal attributed to adsorption, hydrolyzation, volatilization, and biodegradation process has been explored by Li and Zhang (2010) and the results demonstrated that other than biodegradation, other removal routes played a limited role (less 20%) for the removal of antibiotic in wastewater. It is noted that PPCPs generally cannot be eliminated completely by biological treatment methods

(Tran et al. 2017). Some advanced treatment methods such as advanced oxidation processes (Zhang et al., 2016b; Fu et al., 2019a) and disinfection (Zhang et al., 2015b) are promising approaches to effectively remove PPCPs in wastewater effluents. Due to PPCPs cannot be metabolized completely in wastewater treatment system, some intermediate products are generated in wastewater treatment process (Gulde et al., 2016; Helbling et al., 2010). With the development of technology in identifying transformation products, microbial mediated transformation products of PPCPs have increasingly received attention. Some transformation products have been detected and quantified in WWTPs concurrent with parent PPCPs (Beretsou et al., 2016). In addition, some transformation products have been found to be more toxicant than parent compounds (Gao et al., 2018; Escher and Fenner, 2011). Therefore, transformation products and parent compounds should receive equivalent attention.

Health effects of pharmaceuticals and personal care products

Kaiser Jamil, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019

5.3 Classification of pharmaceuticals and personal care products

PPCPs are generally classified into many categories as shown in Table 5.1. Among these, antibiotics are commonly researched subgroup of PPCPs (Liu and Wong, 2013), including hormones and analgesics.

Table 5.1. Pharmaceutical and personal care products (PPCPs)

S. NO. PPCPS CATEGORY SUBCATEGORY

1. Pharmaceuticals Antibiotics (Sui et al., 2015), analgesics (Oliveira et al., 2015), antimalarial drugs (Tella et al., 2018), antiseptics (Peng et al., 2014), hormones (Peng et al., 2014), steroid and endocrine-disrupting products (Yu et al., 2011), antiinflammatory (Guerra et al., 2014), antifungal (Guerra et al., 2014), antiepileptic and antianxiety drugs (Kathleen, 2010.), cytotoxic drugs (Al-Farsi et al., 2017), anticancer drugs (Xie, 2012), cytostatic drugs (Prasanna et al., 2015), beta-blockers, estrogen, lipid regulators (Zheng and Li, 2013), anticonvulsants (Cizmas et al., 2015)
2. Personal care products Moisturizers, hair colors, deodorants, toothpastes (Boxall et al., 2012), sunscreen, detergents (Juliano and Magrini, 2017), disinfectants (Zhang et al., 2014), preservatives (Archer et al., 2017), fragrances and perfumes (Zheng and Li, 2013)

A few methods from our study and from other standard sources are illustrated below to draw focus on the vast procedural details which help us to decide the limit or the threshold for commercial exploitation of these PPCPs that are active at very low concentrations. Overall, a platform of evaluation techniques will be shown that would effectively serve to understand the nanobiointeractions, and dose dependence, cell type dependence, and so on, of these interactions, which aid in defining the biological inertness/safety of the nanomaterials.

Pharmaceuticals and personal care product (PPCP) contamination—a global discharge inventory

Saptarshi Dey, ... Anushree Malik, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019

ABSTRACT

Pharmaceuticals and personal care products (PPCPs) form a source for a diverse group of bioactive ingredients such as analgesics, antibiotics, cytostatic hormones, disinfectants, and antiseptics whose steady occurrence in urban wastewater has raised concern on their potential toxicity and ecological implication. The European Union Water Framework Directive updates its database of identified emerging contaminants every 4 years that includes several PPCP originating chemicals. Increasing trends in urbanization and commercial activity are likely to facilitate increased threats from PPCP-based water pollutants globally. Chronic effects on aquatic organisms, tolerance to biodegradation, and conventional water treatment methods allow them to infiltrate the water cycle and food web, thus, reaching humans. Today, China, Brazil, the United States, and European countries are regularly monitoring and assessing the environmental risk of over a hundred identified PPCPs from their wastewater treatment plants and developing treatment technologies such as bioadsorbents, membrane separation, advanced oxidation processes, biological treatment, and electrochemical processes.

FOREWORD

Majeti Narasimha Vara Prasad, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019

Pharmaceutical and personal care products contamination routes

PPCPs enter the environment (both aquatic and soil) due to a combination of activities, actions, and behavior of industries and individuals. PPCPs are released all over the world from either a point or diffused sources, including effluent, treated sewage sludge, landfill leachate, industrial effluent, combined sewer overflows, aquaculture, and animal feedlots (Acar and Alshawabkeh, 1993; Daughton and Ternes, 1999; Beretta et al., 2014). The speed of the passage and impact severity of PPCPs depend on the quality of water treatment (in WWTPs), compounds physicochemical properties, compound concentration

(quantity), species affected and the fate they take once in the ecosystem, concomitantly, depending on the characteristics of the receiving environment/species (Jjemba, 2008). According to the regulatory exposure modeling based on European and North American systems, the main pathways to environment are, primarily, WWTP effluent (to waterways) and, secondarily, terrestrial run-off (to soil) (Daughton and Ternes, 1999).

Human used PPCPs are generally excreted, entering the sewage system. Wastewater treatment processes were not directly designed to remove PPCPs from the water. The processes that remove PPCP concentration from WWTP to some extent are activated sludge process, tertiary treatment with nutrients removal, membrane bioreactors, and advanced oxidation processes (Miao et al., 2005; Ternes et al., 2007; Tsang et al., 2007; Reyes-Contreras et al., 2011; Zhao et al., 2014; Ávila and García 2015). But even with additional tertiary or complementary treatment steps, such as ozonation and/or powdered activated carbon adsorption to improve water quality, several PPCPs (and other compounds) may not be significantly removed (Reemtsma et al., 2006). The amount of PPCPs that passes the WWTP barrier may reach the environment, making their way up to the food chain (Fig. 2).

Figure 2. PPCPs and their complex interactions with biota (plant, animals, human, and microbes) and physical environment (soil, water, and air). PPCPs with long-term persistence induce resistance to microbial strains. PPCPs, Pharmaceutical and personal care products.

Sorptive removal of pharmaceutical and personal care products from water and wastewater

Anushka Upamali Rajapaksha, ... Meththika Vithanage, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019

9.1 INTRODUCTION

Pharmaceutical and personal care products (PPCPs) comprise a diverse group of organic chemicals including therapeutic drugs, veterinary drugs, fragrances, cosmetics, diagnostic agents, surfactants, and nutraceuticals. Pharmaceuticals are used to prevent or treat human and animal diseases, while personal care products are used for personal hygiene to improve the quality of daily life. PPCPs are bioactive complex molecules as they can exist as neutral, anionic, cationic, or zwitterionic molecules depending on the environmental conditions and octanol/water partition coefficient (K_{ow}) values (Kümmerer, 2008). Also, their specific properties, such as solubility, polarity, acid dissociation constants (pK_a values), hydrophobicity and hydrophilicity, K_{ow} , and the distribution coefficient (K_D), are all pH dependent. These PPCPs and their bioactive metabolites have recently been recognized as emerging contaminants and are continually introduced into the environment mainly through untreated/treated sewage, livestock industries, human excretion, leeching from landfill, drain water, wastewater and sewage treatment plants, etc. (Daughton and Ternes, 1999).

In most of the countries, PPCPs are found in the environment due to the discharge of treated wastewater from wastewater treatment plants (WWTPs). Since the conventional wastewater treatment processes are not designed to remove PPCPs, those are found in subsequent discharge to surface waters including rivers, lakes, and coastal waters. It has been reported that more than 100 PPCPs have been reported in environmental waters (Ebele et al., 2017; Archer et al., 2017; Petrie et al., 2015). High concentrations of analgesic tramadol have been observed in river water in the United Kingdom reaching the highest of 7731 ng/L (Kasprzyk-Hordern et al., 2009). The mostly reported PPCPs are nonsteroidal antiinflammatory drugs (NSAIDs), β -blockers, antidepressants, and the antiepileptic carbamazepine (Petrie et al., 2015). Those have been categorized as highly prescribed (>1000 kg per annum) drugs and hence ubiquitous to influent wastewaters. At the same time, antimicrobials, sunscreen agents, and preservatives are also considered as high usage PPCPs (Petrie et al., 2015). As an example, the sunscreen agent 4-benzophenone has been observed at concentrations as high as 5800 ng/L (Kasprzyk-Hordern et al., 2009).

The presence of high levels of diclofenac, ibuprofen, ketoprofen, sulfamethoxazole (SMX), and bezafibrate was observed in South African surface waters (Agunbiade and Moodley, 2016). A most recent publication from South Africa further reveals the presence of antibiotics, NSAIDs, lipid regulators, antihistamines, X-ray contrast media, beta blockers, stimulants, antidepressants, medications to hypertension, antiepileptic, diabetes, and analgesics in the downstream treated wastewaters in high concentrations (Archer et al., 2017). A clear view of the concentrations of different classes of PPCPs in the freshwater aquatic environment was well reported from each continent in the study by Ebele et al. (2017). Based on country-wise data the highest concentrations of NSAIDs were reported from Nigeria and India, respectively (Ebele et al., 2017). Other than waters, soil can be also one of the sinks for PPCPs. The presence of PPCPs in environmental matrices may adversely influence the biota due to their persistence, bioaccumulation, and toxicity. The effects have been listed well in different studies (Archer et al., 2017; Ebele et al., 2017).

Recently, numerous biological, chemical, and physical approaches have been studied for the remediation of PPCP contaminated sites. Among other techniques available such as membrane/electrochemical separation technologies, bioremediation, ozonation, coagulation, volatilization, and sedimentation, sorption-based techniques have been recently

recognized as a friendly approach to remove PPCPs from aqueous solutions (Xu et al., 2017). The activated sludge system is the most common conventional biological treatment process adopted in the WWTPs. It has the capacity to remove the PPCPs from the wastewater; however, the removal efficiency changed greatly and varied with the physiochemical properties of compounds as well as environmental conditions and operational parameters (Wang and Wang, 2016). Removal efficiencies have been well listed with different treatment processes of the WWTPs indicated the diversity of PPCPs removal based on the types (Wang and Wang, 2016). Other than conventional processes of WWTPs, Fenton oxidation, ultra violet (UV) treatment, ozone degradation, microbial degradation, adsorption, irradiation, and integrated techniques, are used for the removal of PPCPs from environmental waters. The development of cheaper and effective sorbents is essential for the removal of PPCPs; however, it is still a challenge due to their complex chemical nature. In order to enhance the sorptive removal capacity for PPCPs, different adsorbents have been researched and modified for the removal of PPCPs from aqueous media. This chapter provides a comprehensive overview of sorptive removal techniques of PPCPs and the mechanism of interactions.

Sustainable sludge management by removing emerging contaminants from urban wastewater using carbon nanotubes
Binoy Sarkar, ... Yong Sik Ok, in *Industrial and Municipal Sludge*, 2019

4.2 Removal of PPCPs

PPCPs have been discovered in surface water, groundwater, raw sewage, and treated effluents globally. Even in trace concentrations, some of these contaminants can be linked to significant ecological effects (Benotti et al., 2009; Chang and Wilton, 2009). For example, ibuprofen and triclosan, which are the commonly used PPCPs in nonsteroidal antiinflammatory drugs and commercial disinfectants, are the typical PPCPs found in aquatic environments. However, conventional drinking-water treatment plants relying on coagulation could remove only a small portion of PPCPs from aqueous solution (Westerhoff et al., 2005; Jung et al., 2015). On the other hand, CNTs showed significant improvement in the removal of these compounds from aqueous solution owing to the large surface area and O-containing functional groups of the adsorbent material (Cho et al., 2011). Operating parameters, such as pH, temperature, ionic strength, initial solution concentration, and contact time, significantly influence the adsorption rate of PPCPs onto CNTs (Jung et al., 2015). Of the various types of CNTs, SWCNTs showed a greater capacity for adsorption of ibuprofen than MWCNTs due to their larger surface area (1020 vs 283 m²/g) and thin layer structure (Cho et al., 2011).

Usually, wastewater samples contain a mixture of pollutants, including humic acids, carbohydrates, proteins, and other biological building blocks, and the interaction of these pollutants may enhance or deteriorate the adsorption capacity of CNTs. For example, all these compounds compete with diclofenac for binding sites on the MWCNTs, while the adsorption capacity of diclofenac alone was significantly greater than the mixed wastewater sample (Sotelo et al., 2012). Contaminant properties like hydrophobicity also could affect their affinity for CNTs. For example, disinfectant triclosan showed a noticeably stronger affinity for SWCNTs and MWCNTs than ibuprofen due to the difference in hydrophobicity (i.e., log K_{ow} = 4.76 and 3.97 for triclosan and ibuprofen, respectively) (Cho et al., 2011). In addition to hydrophobicity, the presence of specific functional groups (e.g., OH groups) on the surface of PPCPs could enhance their adsorption on CNTs. The OH groups in the PPCP molecules may create an attraction between the adsorbed molecules and molecules in aqueous solution, and additional hydrogen bonding may develop between the adsorbate's OH groups and the adsorbent's O-containing functional groups (Lin and Xing, 2008).

CNTs have demonstrated great potential to remove a range of PPCPs from water and wastewater due to their fibrous shape and large external surface area that are accessible to PPCP molecules (Table 2). Electrostatic attraction, partitioning effects, and π - π interactions between the aromatic molecules of PPCPs and CNT surfaces are the key mechanisms of PPCP removal by CNTs (Sarkar et al., 2018). However, the major barrier for application of CNTs in full-scale wastewater treatment plants is their high production costs. The current market price of high-quality SWCNTs and MWCNTs may reach \$300 and \$25/g, respectively (Sarkar et al., 2018), which can be prohibitive for treating thousands of gallons of wastewater in a large water treatment plant. Furthermore, it is important to understand the physicochemical properties of PPCPs and CNTs before commercialization of the materials for real-life applications in wastewater management.

Plant-based technologies for removal of pharmaceuticals and personal care products

Monika Galwa-Widera, in *Pharmaceuticals and Personal Care Products: Waste Management and Treatment Technology*, 2019
13.4 Threats caused by the presence of pharmaceuticals and personal care products in the environment

PPCPs and their metabolites present in waters can affect living organisms by acting on their bodies' endocrine system as so-called endocrine disrupting compounds (Ellis, 2006) which mimic, increase, or inhibit the action of hormones. PPCPs affect not only aquatic organisms, but also interact with naturally occurring solids such as clay, sediments, soil colloids, microorganisms, or substances added during purification, including active carbon, activated sludge, ion exchangers, and coagulants. Adsorbed

PPCPs are easier to remove from water or sewage, but adsorbent regeneration is necessary as impurities are merely transferred to another phase. Increased mobility of PPCPs in the environment is observed as a result of interaction with dissolved organic compounds (Carballa et al., 2003). Under the influence of PPCPs in bacterial organisms, genetic mutations result, for example, in the development of drug-resistant bacteria or the altered metabolism of activated sludge microorganisms in sewage treatment plants (Al-Ahmad et al., 1999). Therefore attempts have been made to assess the possibility of bioaccumulation of pharmaceutical residues in aquatic organisms (Brooks et al., 2005). It was found that the bioconcentration coefficient of diclofenac in a rainbow trout model tested in laboratory conditions (exposure time 28 days) was 10–2700 in the liver and 5–1000 in the kidneys (Schwaiger et al., 2004). In 2004 (Sanderson et al., 2004), 2986 PPCPs were identified in treated urban wastewater. Due to the fact that environmental pollution due to pharmaceuticals results from the discharge of untreated wastewater to waters and soil, measures should be taken to eliminate the primary source of pollution, in other words there is an urgent need to develop more efficient cleaning techniques. The European Union Directive 2000/60/EC identifies 33 priority substances in the aquatic environment for determination over the next 20 years, which has been extended to include PPCPs such as diclofenac, ibuprofen, triclosan, and clofibrac acid.

Ecological safety hazards of wastewater

Xiaofeng Jiang, Mei Li PhD, in High-Risk Pollutants in Wastewater, 2020

5.2.2.1 PPCPS

Most PPCPs are polar and hydrophilic, exhibiting low octanol/water partition coefficient (k_{ow}) and losses as a result of binding to the organic fraction of sludge or suspended sediments are decreased compared to other persistent organic pollutants that are capable of bioaccumulation (Yang et al., 2011). The uptake of PPCPs by plants has been well documented (Yang et al., 2011; Wu et al., 2012). However, PPCPs with strong sorption and recalcitrant to degradation remain in surface soils and have the potential to be taken up by plants (Wu et al., 2010a). Therefore, these PPCPs and several have been found to persist in the environment and exhibit bioaccumulative and endocrine disruptive activity (Clarke and Smith, 2011). Pullagurala et al. (2018) summarized the plant uptake capacity of various contaminants of emerging concern (CEC) in soil (Fig. 5.3), such as pesticides, polycyclic aromatic hydrocarbons, perfluorinated compounds, PPCPs, and engineered nanomaterials, and among which PPCPs are one of the most studied in recent years. The sorption behavior of pharmaceuticals can be very complex and difficult to assess. These compounds can absorb onto bacterial lipid structures and fat fraction of the sewage sludge through hydrophobic interaction (e.g., aliphatic and aromatic groups).

Figure 5.3. Environmental fate and transport of CEC in soil.

In recent years, researchers have investigated the distribution of PPCPs in soils and river sediments in some regions. Kinney et al. (2006) detected 19 types of PPCPs in reclaimed water-irrigated soils in Westminster region, USA. The mass ratio of carbamazepine to carbamazepine reached 549 ng/g dry weight, and some PPCPs remained in irrigated area soil for a long time. Gibson et al. (2010) studied that the highest mass ratio of Triclosan used as an antibacterial agent in the reclaimed water-irrigated soil in the Tula Valley region of Mexico is up to 16.7 ng/g dry weight; PPCPs in the soil may also contaminate groundwater by diafiltration.

Pyrolysis

Pyrolysis is the thermochemical decomposition of organic matter into noncondensable gases, condensable liquids, and a solid residual coproduct, biochar or charcoal in an inert environment (ie, in the absence of oxygen).

From: Environmental Materials and Waste, 2016

RE5.3.2 EFFECT OF PYROLYSIS TEMPERATURE

During pyrolysis, a fuel particle is heated at a defined rate from the ambient to a maximum temperature, known as the pyrolysis temperature. The fuel is held there until completion of the process. The pyrolysis temperature affects both composition and yield of the product. Fig. 5.6 is an example of how, during the pyrolysis of a biomass, the release of some product gases changes with different temperatures. We can see that the release rates vary widely for different gaseous constituents.

The amount of char produced also depends on the pyrolysis temperature. Low temperatures result in greater amount of char; high temperatures result in less. Fig. 5.7 shows how the amount of solid char produced from the pyrolysis of a biomass decreases with increasing temperature, but the heating value of the char increases with temperature. This happens because the fixed carbon, which has a higher heating value, in the char increases while the volatile content of the char decreases. The amount of noncondensable gas (CO_2 , CO , H_2 , CH_4) increases with temperature.

Figure 5.7. Char yield from pyrolysis decreases with temperature while gas yield increases.

Heating value of the solid char produced increases with temperature.

((Data for grape bagasse (0.63–1.0 mm and HHV–17.2 MJ/kg dry) replotted from Encinar, J.M., Beltran, F.J., Bernalte, A., Ramiro, A., Gonzalez, J.F., 1996. Pyrolysis of two agricultural residues: olive and grape bagasse: influence of particle size and temperature. *Biomass Bioenergy* 11(5), 397–409.)

Advances in bio-oil extraction from nonedible oil seeds and algal biomass

G. Baskar, ... I. Abarnaebenezer Selvakumari, in *Advances in Eco-Fuels for a Sustainable Environment*, 2019

7.5.1 PYROLYSIS (THERMAL CRACKING)

Pyrolysis is the process of thermal conversion of organic matter using a catalyst in the absence of oxygen. Thermal decomposition of triglycerides produces alkanes, alkenes, aldehydes, aromatics, and carboxylic acids. The liquid fractions of the thermally decomposed vegetable oils are likely to be used as diesel fuels. The pyrolyzate is observed to have a lower viscosity and flash point than diesel fuel [30]. Based on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis. Many researchers have studied the pyrolysis of nonedible vegetable oils and their cakes such as Babassu, Karanja (*Pongamia pinnata*), *Jatropha curcas*, Copra, mahua (*Madhuca indica*), and Tung. Castor oil is one of the suitable alternative and renewable fuel for internal combustion engine.

Life cycle assessment of waste-to-bioenergy processes: a review

Pooja Ghosh, ... Arunaditya Sahay, in *Bioreactors*, 2020

8.4.1.2 PYROLYSIS

Pyrolysis involves the decomposition of waste under anaerobic conditions at temperatures ranging between 300°C and 800°C. The pyrolytic products obtained include a gaseous product (syngas), a liquid (tar), and char, with ash as an undesirable residue [21]. The yields of the products depend on the composition of the waste, the pyrolysis temperature, and the heating rate. Lower pyrolysis temperatures lead to the production of more liquid products, whereas higher temperatures yield more gaseous products. The major advantage of pyrolysis is that it is a cost-effective technology and helps curb environmental pollution. However, the production of various pollutants occurs in the exhaust gas during the pyrolysis process such as hydrogen sulfide (H₂S), ammonia (NH₃), SO_x, and NO_x. So strategies for treating the exhaust gas before emission into the environment are extremely important [16].

Sustainable Waste-to-Energy Technologies: Gasification and Pyrolysis

Serpil Guran, in *Sustainable Food Waste-To-energy Systems*, 2018

PYROLYSIS

Pyrolysis of postconsumer mixed solid waste may provide a promising valorization approach to generate liquid, biochar, and gaseous coproducts. Similar to gasification, mixed food waste has its challenges because of the heterogeneous properties of the feedstock material. Several studies on mixed food waste pyrolysis concluded that food waste can be converted into useful forms of energy (Liu et al., 2014; Grycova et al., 2016a,b; Mahapatra et al., 2012). All these studies demonstrated that properties of the resulting pyrolysis products are dependent on the composition of the feedstock and reaction conditions. To understand mixed food waste thermal decomposition characteristics via pyrolysis, some studies have individually converted food waste components (carbohydrates, lipids, and proteins) and demonstrated that carbohydrates produced furan- and sugar-based products, whereas pyrolysis of proteins resulted mainly in hydrocarbon-based products in the aromatic form. The pyrolysis of lipids produced high amounts of acids and low concentrations of hydrocarbon and alkene products (Collins, 2015). The results also showed that pyrolysis oil from mixed waste is a multicomponent mixture depending on the feedstock. Substances that can serve as feedstocks for other industries can be isolated from the pyrolysis oil and recycled. Some studies showed that pyrolysis of waste cellulose from edible oil production can yield pyrolysis oil-containing substances such as capronaldehyde, valeric acid, caprylic acid, and caprolic acid that can be used in the flavors industry (Grycova et al., 2016a), and the combustible components of the product gas phase can be used for process energy (Grycova et al., 2016b). Microwave pyrolysis is also considered to be a viable technology to convert mixed food waste into upcycled products. Microwave-assisted pyrolysis of coffee hulls resulted in higher oil yields compared to conventional pyrolysis (Luque et al., 2012). Liu et al. (2014) examined the catalytic effect of metals oxides such as MgO, Fe₂O₃, and MnO₂ and chloride salts such as CuCl₂ and NaCl during microwave pyrolysis. Their results showed that the presence of metal salts negatively impacted oil yield and enhanced gas yield, whereas chloride salts provided the opposite effect.

Pyrolysis research has especially concentrated on producing biochar to be used as activated carbon, and Mahapatra et al. (2012) demonstrated that ZnCl₂ was a better activation agent for the biochar produced from pyrolysis of mixed sludge from the food industry. Pyrolysis of postconsumer fats and oils, such as waste cooking oil with animal fat content, resulted in triacylglycerols that were decomposed to fatty acids. Unsaturated fatty acids decomposed to hydrocarbons at temperatures up

to 390°C. At higher temperatures, hydrocarbons were formed by decarboxylation of ester groups. The presence of a Pd/C catalyst during the pyrolysis allowed selective decarboxylation to produce light oil fractions (Ito et al., 2012).

Paper Industry Wastes and Energy Generation From Wastes

P.M. Gopal, ... Debabrata Barik, in *Energy from Toxic Organic Waste for Heat and Power Generation*, 2019

7.4.3 PYROLYSIS

Pyrolysis involves the process of organic matter decomposition in the absolute absence of oxidizing agent that takes place in the temperatures of 280–850°C. With the difference in heating rate and residence time, reaction temperatures, and the relative yields of the solid (bio-char), gaseous (biogas) and liquid (bio-oil) products formed, this process is divided into three main types, namely slow, intermediate, and fast pyrolysis.

In similar to the gasification process, pyrolysis also necessitates the low moisture content feed material [16]. Pyrolysis is a way of thermally upgrading waste and biomass into higher calorific value fuels. Already, a pyrolysis plant which uses plastic fraction of rejects from the recycling of beverage cartons in paper and board industries as a fiber source was installed and is operational for a number of years in Spain, and it delivers the end products of pyrolysis also to clean aluminum for recycling. Conversely, pyrolysis of sludge is still under development. Numerous examples on this research can be identified in the literatures [22–25]. An approach to incorporate it into paper mill energy system would be the use of oil as fuel on-site and co-firing the gas and char for heat generation to dry the sludge and using steam for generating electricity [16]. From this use of natural gas for combusting, the sludge would thus be eliminated. Yang et al. [26] found that the pyrolysis oil derived from deinking sludge has few characteristics that could possibly restrict its application in diesel engines, but also suggest that these could be toned down by blending with biodiesel. It could also be likely transformed to other liquid fuels or chemicals, but this should first need quality enhancement like sludge pretreating [27]. The char could also find exterior uses in soil improvement or as fertilizer; for example, char obtained from deinking sludge has confirmed its environmental remediation ability on polluted soil with nickel [28]. The sludge pyrolysis also acts as a technique for separation, presenting reclaimed inorganic fillers for reuse in the paper making process [23]. Microwave pyrolysis, believed as an enhanced rapid pyrolysis method, has also been tested on paper and board industry sludge [29].

Characterization of NOM

Mika Sillanpää, ... Tanja Lahtinen, in *Natural Organic Matter in Water*, 2015

2.5.2.1 Pyrolysis Gas Chromatography-Mass Spectrometry

In pyrolysis, the large complex molecules in NOM are broken down into more analytically available fragments by the application of heat and under anoxic conditions. These fragments are then swept into the analytical column for gas chromatography (GC) and detected by MS. Pyrolysis combined with gas chromatography-mass spectrometry (Py-GC-MS) is a useful technique both for quantitative measurements and for producing structural information about the molecular building blocks of NOM (Bruchet et al., 1990; Schulten, 1993; Fabbri et al., 1998; Christy et al., 1999; Leenher and Croué, 2003; Templier et al., 2005; Chow et al., 2009b). The analysis of complex oxygen-containing macromolecules can be challenging. Polar pyrolysis products are poorly GC amenable and undergo undesirable thermal reactions (Templier et al., 2005). Development in the pyrolysis technique has made it possible to overcome some of these analytical limitations (Parsi et al., 2007).

Microscale sealed vessel pyrolysis is a promising new approach to NOM characterization. This technique promotes the reduction of polar NOM moieties and significantly increases the yield of GC amenable products (Greenwood et al., 2006; Berwick et al., 2007, 2010). This analytical method represents an excellent complement to conventional flash pyrolysis techniques, which may have a limited capacity for chromatographic resolution of polar biochemicals. However, the technique needs to be developed further to enable more advanced NOM characterization.

Major pyrolysis fragments, most commonly yielded from aquatic NOM pyrochromatograms, have been listed by Leenher and Croué (2003) and are summarized in Table 2.3. Besides pyrolysis-MS, the molecular-level structural information can also be obtained by chemical degradation methods such as using a reducing agent (e.g., n-butylsilane) in combination with MS (Nimmagadda and McRae, 2007).

Table 2.3. The predominant pyrolysis by-products from aquatic natural organic matter (NOM)

Type Common fragments

Polysaccharides Methylfuran, furfural, acetylfuran, methylfurfural, levoglucosenone, hydroxypropanone, cyclopentanone, methylcyclopentenone, acetic acid

Amino sugars Acetamide, N-methylacetamide, propionamide, acetic acid

Proteins Acetonitrile, benzonitrile, phenylacetone, pyridine, methylpyridine, pyrrole, methylpyrrole, indole, methylindole (from tryptophan), toluene, styrene (from phenylalanine), phenol, p-cresol (from tyrosine)

Polyphenolic compounds Phenol; o-, m-, p-cresol; methylphenols; dimethylphenols

Lignins Methoxyphenols

Tannins Catechol

DNA Furfuryl alcohol

Polyhydroxybutyrates Butenoic acid

Adapted from Leenher and Croué (2003).

Microwave-assisted fast pyrolysis of hazardous waste engine oil into green fuels

A. Santhoshkumar, R. Anand, in *Advances in Eco-Fuels for a Sustainable Environment*, 2019

5.4 FACTORS AFFECTING THE PYROLYSIS PROCESS

The pyrolysis temperature, heating rate, and residence time majorly influence the pyrolysis product and pyrolysis fuel quality. Morin et al. [33] investigated the effect of the biomass nature and the pyrolysis conditions on the reactivity of char and the physicochemical properties. Table 5.1 shows the effect of properties on the pyrolysis product.

Table 5.1. Effect of properties on the pyrolysis product

Sl. No.	Property	Effect on yield with increasing value of the property	Effect on the reactivity of char	Other comments
1	Heating rate	Decrease the char yield Increase the gas and liquid yield	Reactivity of char increased due to higher heating rate	Higher heating rate activates oxygen and hydrogen content and also increases the surface area and the availability of active sites
2	Pyrolysis temperature	Increases gas yield; decreases char yield	Decreases reactivity of char	CO ₂ concentration is decreased by increasing pyrolysis temperature; char reactivity reduces due to the enhancement in the presence of a larger aromatic ring and system structural ordering of the char by increasing the temperature of pyrolysis
3	Pyrolysis pressure	Increases the yield of char and CO ₂ ; decreases the yield of CO, CH ₄ , and H ₂		Decreases char reactivity The decrease of reactivity of the char with pyrolysis pressure is due to the rise of the char's carbonaceous structure
4	Residence time	Increases the yield of char	Decreases char reactivity	Prolonged heating reduced reactivity at the final temperature of pyrolysis, which improves the loss of active sites and structural ordering of the char
5	Biomass nature	No effect	No effect	The determining parameter is the initial biomass pertaining to the reactivity of the char as well as its properties and the structure of the char

Pyrolysis processes were divided into three subgroups based on the operating parameters. Each parameter resulted in a different product composition. These subgroups are slow pyrolysis, fast pyrolysis, and flash pyrolysis. The parameters that describe slow pyrolysis are a temperature of 400°C with a residence time of more than 30 min and a heating rate of (0.1–1°C/s). The product composition yield for slow pyrolysis as explained by the investigators is 35% biochar (solid), 30% bio-oil (liquid), and 35% syn-gas (gas) [34].

Slow pyrolysis has the lowest yield of liquid products that is the focus of most experiments. Fast pyrolysis is the second type of pyrolysis that is explained. The operating parameters that describe fast pyrolysis are a temperature of 500°C with a residence time about 10–20 s and a heating rate of (1–200°C/s). The product composition yield for fast pyrolysis is 20% biochar (solid), 50% bio-oil (liquid), and 30% syn-gas (gas) [34]. The yield for bio-oil under fast pyrolysis conditions is better than that of slow pyrolysis. The third operating parameter is flash pyrolysis, which has operating parameters that include a residence time of about 1 s, a temperature of 500°C, and a heating rate that is greater than 1000°C/s. The composition of product yield of flash pyrolysis is 13% syn-gas (gas), 2% biochar (solid), and 75% bio-oil (liquid) [35]. So, fast and flash pyrolysis is proven to be apt for max efficiency.

Miandad et al. [36] states that with pyrolysis of liquid oil from polystyrene waste at 400°C with 75 min reaction time, the char yield was 16% of the mass, the liquid oil yield was 76% of the mass, and the gas yield was 8% of the mass. Increasing the temperature to 450°C reduced the char production to 6.2%, increased the liquid oil yield to 80.8% by mass, and increased the gas production to 13% by mass. The response time and optimum temperature were found to be 75 min and 450°C. At optimum conditions, the liquid oil had an absolute viscosity of 1.77 mPa s, a pour point of –60°C, a kinematic viscosity of 1.92 cSt, a density of 0.92 g/cm³, a flash point of 30.2°C, a high heating value (HHV) of 41.6 MJ/kg, and a freezing point of –64°C; this is similar to conventional diesel.

Compared to conventional electrical pyrolysis, microwave pyrolysis has a higher heating rate and efficiency and provides uniform volumetric heating of the substances. The microwave assisted pyrolysis to increase the gas production and decrease the char formation due to hot spot formations [37]. Lam et al. [11] reported that the microwave assisted pyrolysis created an 88 wt% income of condensable pyrolysis oil with fuel assets (calorific value, density) practically identical to conventional transport fuels. Inspection of the species of the oils demonstrated that they contain light aliphatic hydrocarbon. The element of pyrolysis oils which it is shown that an excellent recovery (90%) of the quantity of energy from the surplus engine oil is restored in the pyrolysis oil and it is also free from impurities and contains few contaminants of sulphur, oxygen and dangerous mixtures of PAH. The great return of pyrolysis oil can be recognized in microwave-assisted pyrolysis with appropriate heating in

an inert atmosphere. This review amplifies current discoveries on the impacts of pyrolysis process situations on the overall yield and arrangement of the recuperated oils, by exhibiting that encouraged addition rate, stream rate of cleansing gas, and warming source impacts the focus and the atomic way of the various hydrocarbons shaped in the pyrolysis oils.

Huang et al. [38] investigated whether the corn stover, which is a standout among the most abundant rural deposits over the world, could be changed into significant biofuels and biobased items by a method of microwave pyrolysis. After the response at the microwave control level of 500 W for the processing time of 30 min, the response obtained under the N₂ environment was superior to the CO₂ environment. This might be because of the better heating absorbability of CO₂ particles to decrease the hotness of stover pyrolysis. The more significant part of the metal-oxide impetuses viably expanded the most extreme temperature and mass lessening proportion; however, they brought down the calorific estimations of massive deposits. The more CO gas was formed under the N₂ atmosphere, but higher CO₂ was formed under the CO₂ atmosphere. Catalyst expansion brought down the arrangement of polycyclic aromatic hydrocarbons and in this way, made fluid items less dangerous.

Lam et al. [39] investigated the pyrolysis of WEO using a metallic char catalyst to increase the heterogeneous reaction such as methane decomposition and attain the required temperature quickly. Moreover, the metals get converted into metal oxides and absorb the sulfur existing in the oil. The high volatile materials Cd and Cr may vaporize at the pyrolysis temperature, which is above 400°C.

Influential Aspects in Waste Management Practices

Karthik Rajendran PhD, ... Jerry D. Murphy PhD, in Sustainable Resource Recovery and Zero Waste Approaches, 2019

PYROLYSIS

Pyrolysis is a technology that breaks down organic materials in the absence of oxygen to produce liquid (bio-oil), gaseous (syngas), and solid (biochar) products, as illustrated in Fig. 5.4. Syngas comprises mainly of CO and H₂ (together 85%) with a small proportion of CO₂ and CH₄. The bio-oil produced through pyrolysis typically has a heating value of around 17 MJ/kg. The pyrolysis process can occur in the temperature range of 400–1200°C. Although the product yield depends on various operating parameters, generally low temperature and high residence time favor biochar production [27]. Pyrolysis has been investigated as an attractive alternative to incineration for waste disposal. The pyrolysis process conditions can be optimized to produce a solid char, gas, or liquid/oil product, indicating that a pyrolysis reactor can act as an effective waste-to-energy converter. When compared with the conventional incineration plant that runs in the capacity of kilotonnes (kt) per day, the scale of the pyrolysis plant is more flexible and the output of pyrolysis can be integrated with other downstream technologies for product upgrading. The existing pyrolysis technologies seldom run alone with gas, bio-oil, and biochar output as end products, most of them are combined with gasification, combustion, and smelting. The combination with gasification produces fuel gas of moderate calorific value, and this will be a competitive choice in the future. However, at the same pyrolysis-based technologies are expensive and may not be affordable compared to commercial waste treatment methods.

Gasification Technologies and Their Energy Potentials

Yaning Zhang PhD, ... Roger Ruan PhD, in Sustainable Resource Recovery and Zero Waste Approaches, 2019

PYROLYSIS

Pyrolysis is typically defined as the thermochemical decomposition of biomass feedstock at medium (300–800°C) to high temperatures (800–1300°C) in an inert atmosphere [15]. Some similar definitions are reported in other publications [5,8,9,14,16–18].

The overall reaction of biomass feedstock is

(14.3)

The products of liquid, syngas, and solid are all actually valuable fuels and are defined as biooil, biosyngas, and biochar, respectively.

The chemical reactions during the pyrolysis process include [19]

When compared with the other thermochemical technologies including liquefaction and combustion, pyrolysis generally has the following advantages: (1) the main product is biooil and the yield may be as high as 75%; (2) the biooil may have a high content of carbon; (3) the biooil may have low nitrogen and sulfur contents; (4) the HHV of biooil may be very high, e.g., 42 MJ/kg, which is comparable with those of fossil fuels; (5) the residence time is generally short, which decreases the operational cost; (6) the desired product (biooil, biosyngas, or biochar) could be produced by adjusting the operational parameters; (7) the biooil could be easily stored or transported; and (8) the biomass feedstock may not need to be processed [20].

According to the operating parameters such as heating rate, pyrolysis temperature, and residence time, conventional electric pyrolysis can be generally classified into three groups: (1) slow pyrolysis, (2) fast pyrolysis, and (3) flash pyrolysis. In some publications, catalytic pyrolysis, microwave pyrolysis, vacuum pyrolysis, and hydropyrolysis are also included [2,8,20]. For slow pyrolysis, the heating rate, pyrolysis temperature, and residence time are <1°C/s, 300–700°C, and >450 s, respectively. For fast

pyrolysis, they are 10–300°C/s, 550–1250°C, and 0.5–20 s, respectively. For flash pyrolysis, they are >1000°C/s, 800–1300°C, and <0.5 s, respectively [15,21]. These different conditions generally result in different pyrolysis results. Table 14.2 shows the pyrolysis results obtained from different pyrolysis technologies. It is observed that flash pyrolysis generally favors biooil production, followed by fast pyrolysis and slow pyrolysis.

Table 14.2. Pyrolysis Results Obtained From Different Pyrolysis Technologies [58].

Pyrolysis	Operating Conditions	Results
Slow pyrolysis	Temperature: 300–700°C Vapor residence time: 10–100 min Heating rate: 0.1–1°C/s	
	Feedstock size: 5–50 mm	Biooil: ~30 wt%
	Biochar: ~35 wt%	
	Gases: ~35 wt%	
Fast pyrolysis	Temperature: 400–800°C Vapor residence time: 0.5–5 s Heating rate: 10–200°C/s	
	Feedstock size: <3 mm	Biooil: ~50 wt%
	Biochar: ~20 wt%	
	Gases: ~30 wt%	
Flash pyrolysis	Temperature: 800–1000°C Vapor residence time: < 0.5 s Heating rate: > 1000°C/s	
	Feedstock size: <0.2 mm	Biooil: ~75 wt%
	Biochar: ~12 wt%	
	Gases: ~13 wt%	

A new pyrolysis technology, microwave-assisted pyrolysis, has been developed and widely used [22–24], and it has drawn serious attention because of its advantages over the conventional electric pyrolysis, which are shown in Table 14.3. These advantages are due to the different heat and mass transfer mechanisms. For the conventional electric pyrolysis, heat is transferred from high-temperature gas to the fuel particle surface through the convection mechanism and it is then further transferred from the outside surface to the inside core through the conduction mechanism. A temperature gradient from the outside to the inside of the feedstock particle is formed, and the released volatile diffuses from the inside core to the outside surface through a higher temperature region. For the microwave-assisted pyrolysis, microwave penetrates the feedstock particle and the microwave energy is transformed into thermal energy, which constantly accumulates inside the biomass particle and is then transferred outward. A temperature gradient from the inside to the outside of the particle is formed, and the released volatile diffuses from the inside core to the outside surface through a lower temperature region [15].