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## Petroleum Hydrocarbons: Energy and Pollution in the Environment

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**Abstract** Over the year's nature has favoured the formation of hydrocarbon sources of energy for human and its development. However, the formation of these hydrocarbons involves the absorption of solar energy by the sunlight gatherers (autotrophs) to the transformation process of organic materials through the process of diagenesis, catagenesis and metagenesis. The materials become readily available as petroleum oil or crude oil. Critical observations revealed the variations in colour, odour, flowed properties, different molecular weight and other trace elements and heavy metals. With the increasing demand for petroleum products around the world, this has become a global concern and a challenge. Because the spillage of the hydrocarbons to the environment may modify the natural conditions that sustain life forms on earth. Spilt hydrocarbon such as diesel in the ecosystem could bind aquatic sediment and soil thereby leading to contaminations of land and underground water. Plant-assisted remediation by encouraging large numbers of microorganisms around the plant root zones can bioremediate polycyclic aromatic hydrocarbon (PAH) compounds found in diesel contaminated land.

**Keywords** Petroleum, polycyclic aromatic hydrocarbon and phytoremediation

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### Introduction

The evolution of human society and their culture has been linked with the progressive development of energy sources alongside the associated conversion technologies [1]. In the pre-industrial era and early stage of industrialization, energy source was major generated by the physical strength of humans, animals, tide-power, and wind-power technologies. Major [2] reported how machines are been drive by the muscle power of both humans and animals in 780-330 BC. Hall *et al.* [1] also mentioned the principal sources of energy in the ancient times as humans and animals muscle power, wood, the wind and flowing water. But in the middle of the industrial revolution, energy sources were replaced by fossil hydrocarbons: coal in the nineteenth century, oil since the twentieth century and now, increasingly natural gas [1].

### Petroleum hydrocarbons

Most of the developed and developing nations of the world depend on hydrocarbons as sources of energy to maintain, increase, and to further develop their economic activities. This strong relationship between energy and economic activity for industrialised [3] and developing economies [4] is as old as the journey in the industrial revolution.

### Petroleum

Over the years nature has favoured the formation of hydrocarbon sources of energy in the chemical bond that linked hydrogen and carbon atoms in the organic matters [1]. Even though the formation of this type of hydrocarbons involves complex step-wise biochemical processes, the important basic knowledge is the absorption of solar energy by the sunlight gatherers (autotrophs) leading to the formation of hydrocarbon sources of energy in organic matters.



However, the change process is complex and is not well understood. It is known that organic matters derived from plants and algae are best conserved in the fine-grained sediments deposited in the absence of oxygen [5]. The transformation process of organic materials to hydrocarbons can be divided into three stages: diagenesis, catagenesis and metagenesis. At the early stage of hydrocarbon generations, the low- temperature chemical and biological reactions of the organic matter bring about the formation of mostly larger molecules called kerogens [5]. At the organic diagenesis stage, as a result of increased temperature, the kerogens were decomposed to smaller molecules forming the precursors of petroleum called bitumen [5]. Then smaller gas molecules were formed at the final change stage. Once formed, oil and gas molecules can be ejected from the source rock into more porous carrier beds or channels [5]. These materials may become readily available as petroleum oil or crude oil.

### Petroleum Composition and Properties

Petroleum (often called crude oil) is a word derived from the Latin *petra* and *oleum*, meaning rock oil [6]. It is an extremely complex mixture of hydrocarbon compounds that occur naturally in the sedimentary rocks in the form of gasses, liquids, semisolids, or solids that contains nitrogen-, oxygen-, and sulphur-containing compounds as well as traces of metals [7-9]. Critical observations revealed the dramatic variations in colour, odour and flowed properties of the rich fluid that reflect the diversity of its origin [10]. Further investigations have also shown variation in the molecular types present in the petroleum including compounds of nitrogen, oxygen, sulfur, heavy metals as well as other trace elements [11]. These differences in compositions and properties of crude oils may be the source of variation in the petroleum types that originated from different oil fields in the world. Cockerham and Shane [12] described the unique variations in compositional properties of petroleum concerning the individual reservoir and also different depth.

Physical and chemical properties have been used in categorising petroleum oils and their products into various classes. Physical properties such as boiling point and density (gravity) have been used to describe crude oil as light or heavy oil, while the odour is used to differentiate between low and high sulfur oils [10,13]. On the other hand, chemical properties such as molecular composition are used to categorise the petroleum oils into three classes of compounds: saturates, aromatics and compounds bearing heteroatoms (nitrogen, oxygen, sulfur, and metals) [10]. The saturates alkanes with straight, branched and cyclic hydrocarbons, while aromatic are compounds that contain one or more aromatic benzene rings. In petroleum, alkynes are not present, but alkenes can be found at lower proportions [14]. However, in the aromatic group, alkylated compounds dominate [15].

It is also important to describe petroleum into three convenient subdivisions with their related materials [13]: materials that are of natural origin, materials that are manufactured, and materials that are integral fractions derived from the natural or manufactured products (Table 1) [13, 16-18]. However, in some classes of petroleum such as conventional (light, sweet) petroleum, the percentage of pure hydrocarbons content is high: for example, 80% w/w for paraffin and less than 50% w/w for heavy crude oil and much lower for tar sand bitumen [10]. Even though carbon and hydrogen contents are nearly the same from crude oil to crude oil, the carbon content of the various petroleum is usually between 83 % and 87 % by weight, and the hydrogen is in the range of 11-14 % by weight [10].

Table 1: Subdivision of fossil fuel into various subgroups adapted after Speight 2015 [10]

Natural Material	Derived Materials	Manufactured Materials
Natural gas		
Petroleum	Saturates	Synthetic crude oil
Heavy oil	Aromatics	Distillates
Bitumen*	Resins	Lubricating oils
Asphaltite	Asphaltenes	Wax
Asphaltoid	Carbenes'	Residuuum
Ozocerite	Carboids'	Asphalt
(natural gas)		Coke
Kerogen		
Coal		

\*Bitumen from tar sand deposits.



### Products of petroleum processing

However, in petroleum or heavy oil, the ratio of the hydrogen to carbon atom increases from the low- to the high-molecular-weight fractions due to an increase in the volume of polynuclear aromatics and multi-ring cycloparaffins contents that are molecular constituents of the higher -boiling petroleum oils (Speight, 2015). These properties of petroleum oil are chemical characteristics and are useful as a guide in the choice of the appropriate exploration technology.

### Petroleum Products

Petroleum oil or crude oil is used in many different forms known as petroleum products. In its raw form, it is hardly used because of its complex composition and molecular weight hydrocarbons [13, 16-20]. This complexity in molecular weight compounds results in two extremes boiling temperatures ranging from -160°C to 1100 °C [16-18, 21]. However, to separate hydrocarbon components into groups of the same molecular weight with the same boiling temperature, then the refinery process is inevitable.

Different physical and chemical techniques are used in petroleum refining processes including heating, pressuring, catalysing and the use of chemicals during reactions to convert crude oil and other hydrocarbons into petroleum products [16]. The operation of the refining processes are grouped into five basic stages: distillation, conversion (decomposition, unification and reforming), treatment, blending and other refining operations [16]. These step-wise stages in refinery operations will lead to the production of petroleum products.

The refined products belong to three classes: light distillates (liquefied petroleum gas, naphtha and gasoline), middle distillates (kerosene and diesel), and heavy distillates (fuel oil, lubricating oil, waxes and tar) [16]. Each of these classes has a specified boiling point temperature and density during the fractional distillation process. However, the boiling range of petroleum products are stated (Table 2) [18, 22]. Because the products formed are groups of hydrocarbons each with its own standard boiling temperature with a tendency of influencing the adjacent hydrocarbons [18].

**Table 2:** General boiling ranges of petroleum fractions by Speight and Ozum [18]

Fraction	Boiling	Range <sup>a</sup>
	°C	°F
Light naphtha	-1-150	30-300
Gasoline	-1-180	30-355
Heavy naphtha	150-205	300-400
Kerosene	205-260	400-500
Stove oil	205-290	400-550
Light gas oil	260-315	400-600
Heavy gas oil	315-425	600-800
Lubricating oil	> 400	> 750
Vacuum gas oil	425-600	800-1000
Residuum	> 600	> 1000

<sup>a</sup> For convenience, boiling ranges are interconverted to nearest 5°.

### Toxicity of Petroleum Hydrocarbons

At every stage of petroleum production and consumption, humans, animals and plants are exposed to the toxic components of petroleum hydrocarbons at different concentrations. With the increasing demand for petroleum products around the world, this has become a global concern and a challenge. However, it has been reported that the toxicity levels in hydrocarbons increase as their molecular weight decreases [23-24]. In the case of diesel oil, a middle distillates product with more aromatics proved to be more toxic than other products of petroleum [25]. This was further explained by the amount of polycyclic aromatic hydrocarbons or polynuclear aromatic hydrocarbons (PAHs) discovered in diesel spills and they are quite persistent in the ecosystem [26]. The existence, persistence, and disposition of PAHs in the ecosystem is of toxicological concern [27]. Some hundred different groups of PAHs exist, but about 28 compounds were currently listed as priority contaminants in January 2008 by the U.S. Environmental Protection Agency (US EPA) [28].



One of the main characteristics of these toxic compounds is that they are highly hydrophobic. So it will be easier for PAHs to be adsorbed onto the organic material of solid particles, creating persistent micropollutants in the ecosystem [29]. Different ecosystem types act as sinks for PAHs, however, a preliminary record of PAHs in the United Kingdom (UK) environment displayed that soil was the main source [30]. The presence of these compounds in the environment has been associated with mutagenicity and carcinogenicity [31-32]. Therefore, PAHs in the environment present potential threats to human and ecological health [29].

To have a good understanding of the toxic component of hydrocarbon products, the toxicity assessment of biological indicators is important. Hentati *et al* [33] described the significance of eco-toxicity analysis that comprises of various techniques to use soil-inhabiting organism and plants as testing devices. Earthworm in soil has been extensively used as an indicator of toxic potential in infiltrated soil [34]. Avoidance reaction from both earthworms and collembolans can serve as a signal for early screening [33]. While in plants, toxicity assessment includes the study of root elongation, seed germination and plant growth as a standard technique by ISO11269-1 (1993) and Organisation for Economic Co-operation and Development [35]. Most of the reports show a relative sensitivity of plants in response to contaminants [36]. There were also reports on the use of *Microtox* to evaluate total petroleum hydrocarbon (TPH) toxicity [37]. It seems that the relative sensitivity shown by biological indicators to toxicity is useful.

### **Impact of Petroleum Hydrocarbon Contamination**

Petroleum hydrocarbons are a source of energy that has been driving industrial and societal development since the last century but pollution also results and revealing the fragility of our environment [1, 38-39]. A statistical report from International Tanker Owners Pollution Federal confirmed that about 5.74 million tonnes of oil was spilt accidentally between 1970 – 2014 [40]. Molina-Barahona *et al* [41] reported that a significant portion of the land and water resources on earth are adversely polluted by diesel, a petroleum hydrocarbons fuel. Toxic waste in ecosystems is commonly linked to petroleum products, resulting from cracks in storage facilities, conduit seeps, and tanker collisions [42].

This may imply that without proper containment methods of petroleum products, pollution levels would continue to increase in ecosystems. Environmental pollutions of complex origin may modify the natural conditions that sustain life forms on earth. Therefore, any element or chemical compound that pollutes ecosystems can alter the structural features of humus which in turn disrupts soil-plant relationship [43]. However, a decrease in biological productivity on land is mostly caused by the presence of contaminants, which pose a negative impact on the environment [44]. Therefore, whether these contaminants are simple or complex, they will likely interfere with the physicochemical properties of soils and the resultant effects may impact adversely on ecosystems.

### **Effect of Diesel on Plants**

Pollution problems related to diesel fuel may likely have been caused by different combinations of elements or compounds that may be present in the diesel fuel contaminant. It has been reported that diesel fuels are universal pollutants with a combination of low molecular weight alkanes and volatile alkanes [26]. It was also confirmed that diesel contains higher concentrations of persistent polycyclic aromatic hydrocarbons (PAHs), paraffin's and total aromatic hydrocarbon than other distillate oils [45-46]. Studies revealed that spilt diesel oil in the ecosystem could bind aquatic sediment and soil thereby leading to land and groundwater contamination [45]. Therefore, the presence of this kind of pollutants in ecosystems may elevate the level of trace metals and PAHs in the soil.

Natural trace elements take part in vital biological functions as indispensable micro-elements but can also be as environmental pollutants [47]. Micro-concentrations of trace metals support plant growth and development but the high bioavailability of excess metal ions in soil could affect plant development [48]. PAHs can undergo biotransformation and could alter root morphology resulting in alterations that could affect the influx of water and mineral elements needed for normal plant development [49]. Metabolic pathway redirection and cellular structural changes are some of the changes that result from elevated concentrations of PAHs and trace elements [50]. However, their mechanisms of action are not well understood [50]. Doran [51], reported that plant-assisted



remediation is limited by the knowledge of different enzymes involved and their metabolic pathways. This was also shown by the inadequate understanding of the molecular processes of plants in response to stress agents *in vitro* [52].

The report by Zeng *et al* [53] further confirmed that morphological and physiological changes due to contaminant toxicity in plants are not well understood at the molecular levels. Some plant root cultures have been shown to be useful in the study of xenobiotic decontamination through identifying metabolic pathways without the possible complications in interpretation of findings resulting from microbial associations [54-57]. The *in vitro* synergistic strategy of using two different ornamental plants together was successful in the treatment of simulated textile dyes through their activated enzymes machinery [58].

A biological remediation is an alternative approach that is offering the opportunity to degrade or at least reduce the environmental pollutants to less toxic materials using natural biological processes [59] that include the use of microbes, plants, and animals [60]. It is commonly considered a non-toxic, cost-efficient method [61] and is frequently carried out on site. As such, it has attracted a lot of attention from all over the world. The concept behind the use of microbes, plants, and animals for environmental clean-up can be based on certain biological principles and activities. However, the use of microbes and plants for the clean-up of PAH-contaminated sites has been experimentally tested with varying degrees of success [62].

Microbial remediation is a type of degradation that involves the use of microorganisms with their associated enzymes to dissipate most organic contaminants under controlled situations to a harmless state [63]. This technology depends upon many factors, including the concentrations of organic contaminants, mobility of the contaminants, access by the microbes to other nutrients, presence of activated enzymes (e.g. laccase (E.C.1.10.3.2) [64] manganese peroxidase [65]), and the ability to stimulate the numbers of microflora or microbial groups native to the contaminated sites that are capable of performing the required activities [66-67].

In this method, microorganisms use the pollutants as a source of nutrients or energy [66, 68-69]. These abilities to change and utilise the contaminant as a source of energy can increase their numbers in the contaminated site and so improve their effectiveness. Microorganisms have been described as having developed various mechanisms of reacting to different types of environmental contaminants through transport across the cell membrane, biosorption to cell walls, entrapment in extracellular capsules, precipitation, complexation and oxidation-reduction reaction [22, 70-75]. Among the many reported challenges of microbial remediation is the inability to create uniform spatial distribution on a polluted medium such as soil [76]. Also, it may take a long time to reduce the level of contaminants, which may not always be acceptable [59]. Moreover, the application of microbes can only be operational if the ecological conditions are optimal for their development and activity [63].

Bioremediation treatment includes land farming, biostimulation, bioaugmentation, and bioreactors. There are various limitations associated with these different bioremediation treatment options [77-78]. For instance, in the biostimulation treatment, additives are used to stimulate the functioning of microorganisms to speed up the remediation process [76]. This may affect other organisms present in the habitat [59]. Israr *et al* [63] described possible concerns with the use of microbes, particularly if genetically modified microorganisms are released into a contaminated site during bioaugmentation treatment for remediation purposes.

Plant-assisted bioremediation (phytoremediation), however, is the *in-situ* clean-up of PAH-contaminated sites on a large scale by encouraging large numbers of microorganisms around the plant root zones [79]. It is also defined as an environmental clean-up by plants and their related microbes [80-82].

In the different studies of phytoremediation of PAHs, it was reported that plants could accumulate/sequester/chemically transform and localise toxic contaminants in different environmental media [29, 83-84]. It was also found that plants release enzymes that can act as a surfactant to increase the bioavailability of the contaminants and enhance the nutrient status of the soil [29, 83].

Organic and inorganic pollutants in solid, liquid and gaseous substrates can be phytoremediated [85]. Different types of inorganic pollutants have been phytoremediated, including macronutrients [85], trace elements [86], nonessential elements [85, 87] and radioactive isotopes [88-89]. In the case of organic contaminants such as chlorinated solvents [90], polychlorinated biphenyls (PCBs) [91] and PAHs [92], progressive achievements have been recorded using phytoremediation.



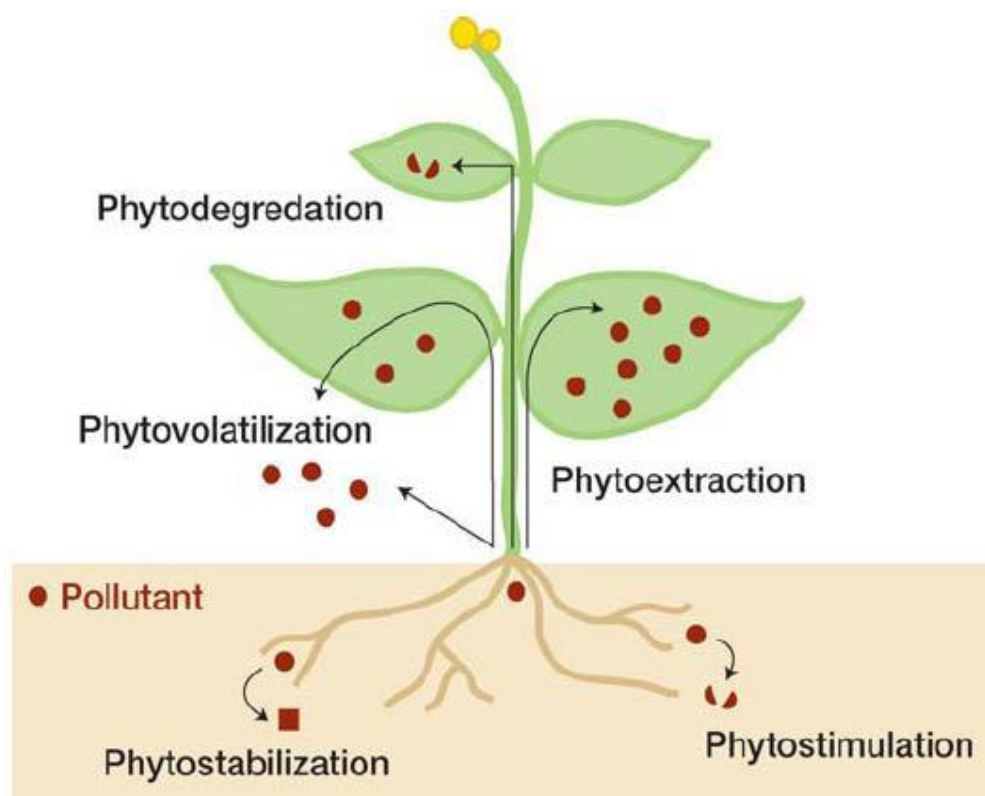


Figure 1: Schematic representation of pollutant fates during phytoremediation [93]

Pilon-Smits [93] and Flathman and Lanza [94] categorised the phytoremediation mechanisms into five different subcategories: phytodegradation, phytoextraction, phytovolatilisation, phytostabilisation and phytostimulation (Figure 1). Phytostabilisation is the use of plants to neutralise contaminants in soil [95] while phytoextraction is the ability of plants to remove and gather contaminants in their tissues [87]. However, in a process called phytostimulation, plants can also increase the rate of the biodegradation processes of organic pollutants by using microorganisms around their root zones [96]. Plants have shown the ability to allow some contaminants to escape in volatile form through their tissues and such process is called phytovolatilisation [97]. McCutcheon and Schnoor [96] described the process of phytodegradation as organic contaminants are degraded directly by plants using their enzymatic activities. These technologies are not independent in operations but rather can also occur simultaneously [98].

### Conclusion

Increasing in the global demand for energy sources especially petroleum hydrocarbons has been associated with pollution of the environment. The lack of proper containment strategies from the exploration and refining points to the transportation and down to the utilisation processes of the product has increased the chances of the hydrocarbon spillage. Plant and their associated microorganism have shown potential to decontaminate or remove of PAH contaminants in the environmental media.

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