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Chapter

Pyrolysis: A Convenient Route for Production of Eco-Friendly Fuels and Precursors for Chemical and Allied Industries

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Abstract

Thermochemical decomposition of post harvest agro-wastes (biomass) to solid carbonaceous material called as bio-char, condensible vapors (bio-oils and bio-tars) and non-condensable vapors (bio-gas or syn-gas) is referred as pyrolysis. The yield of these products from biomass pyrolysis depends on temperature and other conditions (such as vapor retention time and heating rate) of thermal decomposition in air or oxygen excluded reactor. Bio-char is often used as adsorbent in treatment of water contaminated with dye effluent from textile industry and/or emerging contaminants from other industries. It is also used in production of supercapacitor for energy storage, fertilizer composite and soil amendment for slow release of nutrients for plants and stabilizing pH, enhances water holding and ion exchange capacity of soil. Bio-oils are used for transportation fuels, soaps and other cosmetics production. Bio-tars are also used for transportation fuels but with high heating values and also as organic solvents in chemical, biological and biochemical laboratories. Non-condensable vapors are mostly used as bio-fuels. Products of biomass pyrolysis are potential alternative eco-friendly precursors for chemical and allied industries.

Keywords: bio-char, bio-fuel, bio-gas, bio-oil, bio-tar

1. Introduction

Post harvest agricultural wastes are promising materials for generating renewable and eco-friendly energy source and raw materials for chemical and allied industries. Agricultural wastes serving as a potential alternative source of energy and starting renewable materials for industrial productions will definitely bring about reduction in demand for non-renewable petrochemical feed stocks often used by most chemical industries today. Other benefits are efficient carbon cycle and reduction in carbon(iv) oxide (CO$_2$) emissions [1]. Among the agro-wastes, plant-based (lignocellulose) materials are most abundant and disposed indiscriminately, where by constituting nuisance to the environment. Plant-based agricultural wastes are called lignocellulosic materials because their compositions are majorly of lignin and cellulose. Others are hemicellulose, pectin, wax, oil and inorganic matters [2]. These compositions of plant vary from one plant to another. Other factors that
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Contribute to the variation in compositions are age of the plant, processing methods, geological and climatic factor [3, 4]. The plant-based agro-wastes worked on by researchers as energy source and feed stocks for chemical and allied industries are sugarcane bagasse, cola nut pod, cocoa pod, moringa seed pod, oil palm empty fruit bunch, almond leaf, *Bridelia ferruginea* bark, elephant grass etc. [5–9]. Conversion of these agro-wastes to energy source and starting materials for chemical and allied industries will bring a turn around to high dependence on ever depleting and price fluctuating petrochemicals. This will in turn generate wealth from wastes; creating jobs for teeming unemployed youths and keep our environments clean [3].

Several technologies deployed for converting agro-wastes to energy source and precursors for chemical and allied industries are hot acid carbonization by dehydration and anaerobic digestion. Others that are thermally based are torrefaction, pyrolysis, combustion, gasification and hydrothermal process. Among these technologies, pyrolysis is most preferred, because the products which are solid, liquid and gas can easily be stored, transported and handled [10]. Figure 1 shows summary of various biomass conversion techniques and products obtained. Pyrolysis is a composition of two Greek words, split able into ‘pyro’ meaning fire and ‘lysis’ means degradation into many parts. Therefore, pyrolysis can be defined as thermochemical degradation of biomass into biochar (solid carbonaceous material), bio-tar, bio-oil (condensable vapor) and non condensable gases (syngas) in absence or very limited supply of oxidizing agents [10, 11]. Depending on degradation temperature, heating rate and vapor retention time, pyrolysis can be classified as slow, fast or flash pyrolysis. The choice of any of the pyrolysis techniques depends on desired or targeted products [10].

2. Biomass

Biomass waste stream can be categorized into proteineous (animal-based), lignocellulosic (plant-based), municipal solid (biogenic and non biogenic),

![Figure 1. Various forms of biomass conversion techniques.](image-url)
industrial (sewage sludge) and other wastes. They are referred to as feedstock in bio-refinery. Biomass based on animal and plant residues (briefly described in subsections 2.1–2.2) is an area where researchers are currently exploiting for possibility of obtaining sustainable and environmental friendly alternative to fossil fuels/precursors for chemical and allied industries. The use of biomass for these aforementioned purposes reduces demand for fossil fuels, their derivatives and makes our environment greener [1].

2.1 Animal-based biomass

Animal wastes, such as blood, bones, crab shells, hairs, horns, dung, etc. are by-products of livestock rearing. Often seen livestock that generate these wastes are cattle, sheep, chickens, goats, crabs and pigs (Table 1). They have been used in raw or pyrolyzed form as source of energy and raw materials for industrial productions by several researchers. Adetuyi and Jabar [9] are among the researchers that have used carbonized animal bone for treatment of wastewater. Table 1 shows list and applications of some animal-based biomass.

| Animal | Residue | Application | Ref. |
|--------|---------|-------------|------|
| Cattle | Bone    | Char for production shoe sole, breakable plate, soil enhancement | [9] |
| Horn   |         | Char for soil enhancement, bio-oil for fuel and cosmetic industry | |
| Crab   | Shell   | For wastewater treatment | |
| Sheep  | Hair    | Textile fiber production | |
| Born   | Char for wastewater treatment, supercapacitor production | |
| Camel  | Bone    | Char for production shoe sole, breakable plate, soil enhancement | |
| Horn   |         | Char for soil enhancement, bio-oil for fuel and cosmetic industry | |

Table 1.
Animal-based biomass and applications.
waste management approach in the forest. Consequently, this conversion of wastes to wealth will reduce rate of deforestation for fuels and industrial precursors [18].

2.2.2 Herbaceous biomass

Herbaceous is non-woody biomass called annual crops. They include rice, wheat, sorghum, maize, millet, groundnut, soyabean etc. After harvesting, their residues do not constitute much treat to the environment, as they are grown and their residues decay within a year. Alternatively, their residues can be utilized for production of bio-gas, bio-oil and bio-char as bio-fuels and bio-chemical raw materials for chemical and allied industries [19].

2.2.3 Aquatic biomass

Approximately, one-third of the world is water body. Weeds grow exceptionally on water bodies when compared to terrestrial, whereby enhancing aquatic pollution index. The aquatic biomass includes algae (micro and macro), water hyacinth, kelp, water lily, seaweed etc. These so called aquatic weeds are underutilized; they can be made to serve as raw materials for bio-fuels and bio-chemicals for industrial productions through pyrolysis [20].

3. Pyrolysis

Pyrolysis is the thermochemical decomposition of biomass or other feedstock into biochar, bio-tar, bio-oil, bio-gas and other related products in absence or very limited supply of oxidizing agents [10, 11, 21]. This process can be broadly classified as fast, slow and flash, depending on degradation temperature, heating rate and vapor retention time as stated earlier. Other factors that affect pyrolysis are nature and moisture content of the chosen biomass [22]. Figure 2 presents possible products of pyrolysis of biomass, while Figure 3 illustrates pyrolysis mechanism. Incipient pyrolysis products are solid bio-char and condensable vapor. The later breaks down into char, liquid and non-condensable gases through gas-solid and

| Lignocellulose | Compositions | Ref. |
|----------------|--------------|------|
|                | Hemicellulose| Lignin| Cellulose| Extractives | Pectin and others |
| Coir fiber     | 9.0          | 47.7  | 40.8     | 2.5         | [12]               |
| Oil palm fiber | 13.7         | 21.6  | 61.6     | 3.0         | [12]               |
| Palm kernel fiber | 14.0   | 30.0  | 51.8     | 4.1         | [12]               |
| Sorghum        | 23.4         | 17.9  | 31.4     | 23.7        | [13]               |
| Switchgrass    | 21.5         | 21.1  | 35.8     | 16.9        | [13]               |
| Alfalfa        | 19.0         | 13.0  | 25.0     | 20.0        | [14]               |
| Pine           | 21.0         | 26.0  | 42.0     | 2.7         | [14]               |
| Kenaf fiber    | 38.0         | 19.0  | 49.0     | 4.7         | [15]               |
| Oak            | 22.0         | 24.0  | 46.0     | 6.0         | [16]               |

Table 2. Chemical composition of some selected lignocellulose.
gas phase heterogeneous and homogeneous reaction respectively at high temperature. In homogeneous gas phase reaction, condensable vapor cracks into small molecules of non-condensable gases (CO, CO$_2$, H$_2$O, H$_2$, N$_2$ and CH$_4$). In gas-solid phase heterogeneous reaction, high molecular weight hydrocarbons are broken into low molecular weight hydrocarbons (such as CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_6$H$_6$ etc.). Several reactors called pyrolyzers have been used by many researchers to obtain two or more of these products from biomass. Some of these pyrolyzers are bed, vacuum, microwave and solar reactor [11].

Pyrolysis of lignocellulosic biomass involves several stages of thermal decomposition. Evaporation of moisture occurs between 40 and 115°C, at this stage, biomass dries up as a result of heat absorption that evaporates free moisture and eradicates loosely bonded water [7]. The heat transfers into biomass interior through convention to wipe out all internally bonded moisture. Biomass incipient degradation occurs through decomposition of pectin and other extractives between temperatures of 115 and 180°C, generating syn-gas and organic liquids (such as carbon(ii) oxide, carbon(iv) oxide, methane, ethane, benzene, methanol, pyrogallol and ethanoic acid) [22]. Hemicellulose degrades between temperatures of 180–250°C, giving off considerable amount of carbon(ii) oxide, carbon(iv) oxide, water, hydrocarbon of low carbon content, organic liquids and minor bio-oil [23]. Temperature from 250–350°C decomposes cellulose to yield mixture of non-condensable vapor (syn-gas), condensable vapor (bio-oil and tar) and minor bio-char [24]. Proper formation of solid fraction (primary bio-char) commences from thermal decomposition of lignin from 400°C, this is the stage at which primary pyrolysis occurs. As temperature increases from 500°C upward, minor tar and bio-oil contained in the bio-char get separated and high quality bio-char obtained. Although, a low bio-char yield is obtainable...
from temperature above 700°C, but a high grade bio-char formed [25]. This is the final stage of thermochemical degradation called secondary pyrolysis. It involves cracking of condensable vapor (bio-tar and bio-oil) into non condensable gases (CO, CO$_2$, CH$_4$ etc.) and on cooling; part of the products solidifies to form char (secondary bio-char). Summary of the entire pyrolysis process is presented in Table 3.

### 3.1 Fast pyrolysis

This process involves decomposition of biomass at high heating rate (10–250°C/s), high temperature (500–1200°C) and short vapor retention time (<2 s) in the absence of oxygen. Due to high heating rate, biomass is rapidly heated to pyrolysis temperature before it is decomposed. Although, this process yield gaseous, liquid and solid fractions, but exclusively for bio-oil (liquid fuels) production, if pyrolysis temperature is less than 650°C. Quick vapor condensation enhanced formation of bio-oil, usually >50% products fraction is liquid, while gaseous formation is favored if pyrolysis temperature is up to 1000°C (about 30% yield is obtainable) and solid fraction is less 30% of pyrolysis products [26].

### 3.2 Slow pyrolysis

In contrary to fast pyrolysis, biomass is decomposed at lower heating rate (<1°C/s), lower degradation temperature (500–550°C) and longer vapor retention time (300–1800 s). This process has long been practiced and is otherwise known as conventional pyrolysis. Just like in fast pyrolysis, products of slow pyrolysis of biomass are gases, liquids and solids. Due to longer vapor retention time of condensable and non condensable gaseous fractions, the condensable volatile organic fractions react with one another to form high quantity of solid fraction (bio-char) and low quantity of bio-oil and bio-gas [27]. Therefore, one can say that this process is more desirable for bio-char production.

### 3.3 Flash pyrolysis

Flash pyrolysis can be called very fast pyrolysis, because it employs very high temperature (800–1200°C), high heating rate (>1000°C/s) and extremely low vapor retention time (below 0.5 s). The condensable and non condensable gases leave the pyrolyzer and cool rapidly to form liquid fuel called bio-oil. Some part of the poor thermally stable solid fraction (bio-char) formed degrades at high operating temperature and dissolves in the liquid fraction (bio-oil), resulting in high yield of bio-oil (>70%). The more the quantity of dissolved bio-char, the more viscose and the poorer the resulting bio-oil [28]. This process is better recommended for syn-gas production.

| Composition | Degradation temp. (°C) | Products formed |
|-------------|------------------------|-----------------|
| Moisture    | 40–115                 | Dehydration     |
| Extractives | 115–180                | Syn-gas, organic liquids |
| Hemicellulose | 180–250              | Syn-gas, organic liquids and minor bio-oil |
| Cellulose   | 250–350                | Syn-gas, organic liquids, bio-oil and minor bio-char |
| Lignin      | >400                   | Bio-oil, bio-char and minor syngas |

Table 3.
Degradation temperature of biomass compositions and corresponding products.
4. Pyrolyzer

Pyrolyzer is a reactor where pyrolysis of biomass is done [22]. The design of pyrolyzer depends on desired pyrolysis product(s). Therefore, it is another important factor that determines products obtainable from pyrolysis [10]. Some of designed pyrolyzers are discussed in sub-sections below.

4.1 Bed pyrolyzer

This pyrolyzer can be made of firebrick, steel or concrete and is predesigned for bio-oil production. Its design contains feeding unit, non-condensing vapor collector and vapor condenser, others are filter and ash exit unit [29]. It is operated in such a way that biomass is fed downward in reactor through vertical shaft and counter current gas stream simultaneously fed-in in an upward direction. The biomass is heated by bed of hot solids (such as sand heated by external source or partial combustion of biomass) at high temperature, high heating rate and low vapor retention time in an inert environment to decompose it into non condensable gas, condensable vapor and char. The vapor is rapidly cooled to form high quality bio-oil with yield of about 70% mass of pyrolysis products [30]. Therefore, it is a simple and well designed fast pyrolyzer that gives precedence to production of bio-oil. Merits of this reactor are exemplary heat transfer system, very high relative velocity between the solid and liquid phase, good control of vapor holding time and pyrolysis reaction as a whole. Some of the existing designs are fixed bed, circulating fluidized and bubbling fluidized bed reactor [10].

4.2 Vacuum pyrolyzer

This is a slow pyrolyzer with a moderate biomass degradation temperature, very low heat transfer rate and high vapor retention time. The biomass is feed into the pyrolyzer with the aid of conveyor belt made of metal containing stirrer that agitates the biomass mechanically. The biomass is heated with attached burner for decomposition into gas, liquid and solid. It produces bio-char of yield greater than 50% and bio-oil of less than 30% yield. Therefore, it is designed for bio-char production [31].

4.3 Microwave pyrolyzer

Design of microwave pyrolyzer is done in such a way that biomass is heated to decompose into gaseous, liquid and solid products through heat generated from electrical microwave oven chamber. Inert gas is used to fashion out non oxygen environment. In this pyrolyzer, undesirable output (by-product) is not formed, there is effective heat transfer and heat process can be easily monitored. Among its merits are a very good chemical recovery, efficient control of heat transfer and heating system. This pyrolyzer is exclusively designed for syn-gas production with greater than 30% yield from feedstock biomass [32].

4.4 Solar pyrolyzer

This makes use of clean energy from sun light. It is made of quartz tube containing opaque external wall. The opaque external wall when exposed to high intensity solar radiation is capable of generating temperature higher than 700°C for decomposition of biomass into syn-gas, bio-oil and bio-char [33, 34]. In its design, there is provision for solar energy storage inform of chemical energy. Therefore, at night and during poor sun shine weather, it can still work using already stored energy for
generating heat for pyrolysis process. It is a very fast pyrolyzer with bio-oil yield greater than 50%. Although, the yield of gaseous fraction is less than 30%, but is recommended for production of syn-gas because of poor quality of bio-oil formed according to Cornelissen et al. [28].

5. Products of biomass pyrolysis

Thermochemical decomposition of biomass yields mixture of gases, liquid and solid bio-char as major products as stated earlier. The yield of any of the pyrolysis products is largely depends on pyrolysis temperature and biomass’ moisture content among others like design of pyrolyzer, vapor retention time and heating rate [22].

5.1 Gas

Mixture of gases formed from primary (non condensable gases) and secondary degradation (tar and volatile organic compounds called condensable vapor) of biomass in the pyrolyzer during pyrolysis after moisture dehydration are called syn-gas. Components of syn-gas vary from one biomass specie to another. Often formed gases from primary degradation of biomass are carbon(ii) oxide, carbon(iv) oxide, hydrogen gas, gaseous water, nitrogen and hydrocarbons of lower carbon content (methane, ethane, ethylene). Additional gases are produced through secondary cracking of condensable vapor at high temperature [35]. Very high pyrolysis temperature enhances yield of these mixture of gases and reduces yield of bio-char. The increase in yield of syn-gas might be as a result of thermal decomposition of tar and hydrocarbons (condensable vapor) to produce more oxides of carbon and other gases.

Lower carbon content hydrocarbons (eg methane, ethane, ethane and butane) are often used as domestic cooking fuels. The heating value of syn-gas obtained from secondary degradation of biomass (condensable vapor) is about 82% higher than those from biomass’ primary degradation. Hydrogen can be blended with oil to upgrade it to transportation fuel [36]. Hydrogen gas and carbon(ii) oxide are mainly used as bio-fuel inform of water gas [11].

Liquefied carbon(iv) oxide is used as major component in production of fire extinguisher. It is also used as cooling agent and preservative by bottling company. Recent research work by Patel [37] claimed possibility of converting CO$_2$ to starch in the laboratory about nine times more efficient as obtainable from corn plant using combination of chemical catalysts and enzymes. During the conversion process, useful industrial chemical like methanol was obtainable. This will serve as sustainable way of feeding the ever growing world population without need of land, seed, pesticide, fertilizer and water. The approach can equally be said to be a good form of food security and reducing CO$_2$ emissions [37].

Nitrogen is utilized in production of ammonia from Haber process for preparation of fertilizer by agrochemical industry in order to enhance food production for feeding human population and livestock [38].

5.2 Liquid

Major liquid components of biomass thermochemical degradation are bio-oil (bio-crude) and black tar, others are organic solvents. Bio-oil contains mixture of heavy molecular weight hydrocarbons. High pyrolysis temperature coupled with quick vapor condensation result in high bio-oil yield (>70%) [39]. Condensed pyrolysis vapor contains more than three hundred mixture of condensable gaseous
compounds. Higher yield of bio-oil is obtainable from agricultural residues when compared with one obtainable from woody biomass. Quality of pyrolysis bio-oil is mostly affected by storage time and temperature. The higher the storage time, the more viscous and poorer quality of the bio-oil due to escape of volatile components. Decline in quality of bio-oil due to aging can be minimized through cool storage temperature. Bio-oil heating value can be maintained by monitoring its metal and water content. It is used as transportation fuel, when mixed in certain ratio with fossil fuel it minimizes greenhouse gas emission that causes major environment pollution, especially in the city. Bio-oil can serve as precursor for production of soap through saponification process in soap and detergent industry. Cosmetic industry uses bio-oil in production of shoe polish, hair and body cream [40]. Organic solvents, such as benzene is a very good precursor in production of important materials, like dyes, pigments, synthetic tyres and textile materials. Others are production of plastics, resins, rubber lubricants, detergents, drugs and pesticides. Benzene is also a good solvent used in chemical, biochemical and biological laboratories, as well as aviation bio-fuel [41]. Other organic solvents like hydroxyketones, hydroxyaldehydes, carboxylic acids, phenolic compounds, sugar and dehydrosugars are important precursors for chemical and allied industry [11].

5.3 Bio-char

The solid component of pyrolysis products is known as bio-char. It is a black amorphous carbonaceous solid matter [42]. Properties and yield of bio-char are dependents of pyrolysis temperature, heating rate, vapor retention time, inert gas flow rate and nature of biomass [43]. A coarse and high yield bio-char is obtained from woody biomass, if pyrolysis temperature between 500 and 550°C, heating rate less than 1°C/s and greater than 450 s vapor retention time are used for its thermo-chemical process under inert environment. In contrary, if a fine bio-char is a desired material, agro-residue would be required as pyrolysis feedstock using degradation temperature greater than 600°C, high heating rate between 10 and 300°C/s and vapor retention time less than 20 s [11]. Bio-char with acceptable properties contains carbon as major component; other fractions are oxygen, hydrogen, nitrogen, sulfur and ash (inorganic metals). Bio-char with a long half life has its carbon to oxygen ratio (C:O) usually greater than 3:2, but one with 1:5 (C:O) has short half life. Inorganic ash component of bio-oil is very small in comparison with fossil fuel and it has low heating value of about 32 MJ/kg, which is about 60% higher than that of lower heating value of the parent material (biomass). Bio-char has many areas of application, ranging from soil enrichment in agro-chemistry, adsorbent in wastewater treatment to energy in electrochemical capacitor (supercapacitor) and bio-fuel [10].

5.3.1 Bio-char for soil amendment

Incessant ability of agricultural activities depends largely on biological, physical and chemical properties of soil. A little change in soil organic carbon has significant impact on plant growth. Farmers mostly use synthetic fertilizers for achieving this goal, but ironically the soil fertility decreases. It is only bio-char that provides soil with organic carbon that boosts soil nutrient [22]. Environmental awareness has increased interest of global community for using bio-char as soil amendment agent. Tilling soil with bio-char stabilizes soil pH, enhances water retention capacity and available nutrients for plant growth [44]. Enhancement of soil nutrient by bio-char might be as a result of presence of potassium, magnesium, calcium, iron, zinc, phosphorous, sulfur and nitrogen in the bio-char. Equally, amendment of soil by
bio-char reduces leaching out of soil nutrient and aids slow nutrients release to the plant, where by making nutrients available for long period of time. This promotes plant growth and mitigates climate change through consumption of carbon(iv) oxide (greenhouse gas) by growing plants during photosynthesis (smart carbon cycle). Therefore, application of bio-char in soil amendment makes our environment greener and increase production of food for geometrically increasing human population [45].

5.3.2 Bio-char as adsorbent for wastewater treatment

Inadequate water supply globally has given significant attention to the production of sustainable and eco-friendly bio-char based adsorbent for treatment of wastewater containing heavy metals, emerging contaminants and dye effluent from textile industry [7]. Properties of bio-char, such as cation exchange capacity, high surface area, high carbon content, amorphous and hydrophilic nature aid its applicability. Previous research works have established bio-char as suitable material for treatment of wastewater. Jabar and Odusote [3, 6] used bio-char obtained from water lily and oil palm empty bunch fiber for treatment of water contaminated with malachite green and cibacron blue 3G-A (CB) dye respectively. Thue et al. [46] used shell of cashew of Para for treatment of wastewater containing emerging contaminants. Ozsin et al. [47] used chemically activated carbon from agricultural waste of chickpea and its application for heavy metal adsorption. Wood-based bio-char was used as adsorbent for removing toxic elements from wastewater by Shaheen et al. [48], while Gwenzi et al. [49] showed that designed water treatment plant based on biomass derived char was a prospective low cost sustainable technology for producing dirt free water.

5.3.3 Bio-char as energy and energy storage device

Use of bio-char as source of energy for heating was old as human existence. It was popularly used as energy source for blast furnace in production of iron from iron ore called hematite and in petroleum refinery plant for separation of factions using fractional distillation. Researchers are currently focusing on the use of bio-char in production of supercapacitor called electrochemical capacitor [50]. Supercapacitor is an energy storage device that stores and releases electrical energy within a few seconds [51]. It stores energy as electric charge at electrolyte porous carbon electrode interface more than ten times conventional capacitor does [52]. It has to its advantages, high power density and satisfactory energy density [53]. Properties of bio-char, such as excellent electrochemical performance, high surface area, fast electron transport and abundant functional moieties make it suitable for production of supercapacitor [54]. Several researchers have prepared and activated bio-char for production of supercapacitor in electrochemistry. One of these researchers is Vinayagam and his co-researchers [55] who prepared activated carbon from Sapindus trifoliatus nut shell for high performance symmetric supercapacitor applications.

6. Conclusion

Pyrolysis is thermochemical decomposition of biomass under inert environment. The products of this process are syn-gas, bio-oil and bio-char. These products are alternative to petrochemicals as they are good sources of renewable and eco-friendly energy and bio-chemical precursors for chemical and allied industry. Several factors including nature of biomass, biomass moisture content and design of pyrolyzer, others are vapor retention time, heating rate and degradation temperature determine quantity and quality of these pyrolysis products.
Conflict of interest

The author declares no conflict of interest.
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