

# We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

5,000

Open access books available

124,000

International authors and editors

140M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index  
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?  
Contact [book.department@intechopen.com](mailto:book.department@intechopen.com)

Numbers displayed above are based on latest data collected.  
For more information visit [www.intechopen.com](http://www.intechopen.com)



# Introductory Chapter: Pyrolysis

*Hassan Al-Haj Ibrahim*

## 1. Introduction

Pyrolysis, or thermolysis, is in essence an irreversible thermochemical treatment process of complex solid or fluid chemical substances at elevated temperatures in an inert or oxygen-free atmosphere, where the rate of pyrolysis is temperature-dependent and it increases with temperature. During pyrolysis the molecules are subjected to very high temperatures leading to very high molecular vibrations at which the molecules are stretched and shaken to such an extent that they start breaking down into smaller molecules. Pyrolysis also is always the first step in other processes such as gasification and combustion where partial or total oxidation of the treated material occurs. Thermochemical treatment processes are generally classified according to their equivalence ratio (ER), which is defined as the amount of air added relative to the amount of air required for stoichiometric combustion. The equivalence ratio for pyrolysis is 0 ( $ER = 0$ ), whereas the equivalence ratio for combustion is equal to or greater than 1 ( $ER \geq 1$ ), and the equivalence ratio for gasification varies between 0.25 and 0.50 ( $Er = 0.25 - 0.50$ ).

The word “pyrolysis” is coined from two Ancient Greek words pyro (πυρο) meaning fire and lysis (λύσις) meaning separating (or solution), so pyrolysis means separation by fire or heat. In photolysis, by contrast, the chemical substances are treated with light rather than heat.

The simplest example of pyrolysis is food cooking. When food is cooked, the temperature of food increases leading to higher molecular vibrations and break-down of larger complex molecules into smaller and simpler molecules which are easier to digest. Another example of pyrolysis is the pyrolysis of tobacco, paper and additives, in cigarettes and other products, which generates many volatile products including nicotine, carbon monoxide and tar that are responsible for the aroma and the hazardous health effects of smoking.

A process similar to the pyrolysis process takes place to some extent in nature, where organic substances of biological origin are buried and transformed into fossil fuels and coals of progressively higher carbon content under the action of temperature, pressure and chemical agents [1].

Pyrolysis is basically a thermal decomposition process where a raw material of high molecular weight is decomposed or cracked to produce primary volatiles. The primary thermal decomposition and dehydrogenation reactions are accompanied in general with secondary polymerization and isomerization reactions of the primary volatiles. The extent of the secondary reactions depends on the pyrolysis conditions as well as on the type of the pyrolysis reactor used. Secondary reactions are generally favored by high residence times and high temperatures. As it is practically impossible to achieve a completely oxygen-free atmosphere, there will be a small amount of oxidation reactions as well. The yields of the pyrolysis products are due to both the primary decomposition reactions of the raw material and the subsequent secondary reactions of the primary volatiles.

The end products of pyrolysis include solid residual coproducts and ash, noncondensable gases and condensable liquids known variously as pyrolysis oil, pyrolytic oil, bio-oil or tar. The type and yields of the pyrolysis products depend for the most part on the type of material treated. The pyrolysis end products can also be controlled by optimizing pyrolysis parameters such as temperature, heating rate, residence time, pressure, feed particle size and type of reactor. For example, the production of bio-oil through pyrolysis, which is a thermodynamically nonequilibrium process, requires only a short residence time in a high-temperature zone followed by rapid thermal quenching. In some pyrolysis processes, a product that is up to 80% liquid by weight can be produced.

Pyrolysis is mostly applied to organic materials. It is basically a carbonization process where an organic material of high molecular weight is decomposed or cracked to produce a solid residue with high (or higher) carbon content and some volatile products. As is well-known, any organic matter can be carbonized or made to lose progressively its atoms other than carbon to become an artificial carbon material or “carbon”. In addition to organic materials, pyrolysis can be applied in certain cases to inorganic materials and to water and aqueous solutions.

Pyrolysis is an endothermic process. Determination of the overall energy balance and the thermal efficiency of the process is a fundamental step in designing an efficient pyrolysis reactor. The use of renewable energy or solar-thermal power to drive pyrolysis could make the process more economical and carbon neutral [2, 3].

Pyrolysis reactions typically occur at temperatures between 400 and 800°C. As the temperature changes, the product distribution can be altered. Lower pyrolysis temperatures usually produce more liquid and solid products, while higher temperatures favor the production of more gases as a result of more powerful thermal cracking reactions. The pyrolysis temperature has also a significant effect on the properties of the pyrolysis products. The calorific value of the pyrolytic oil, for example, increases mostly with increasing temperature.

The rate of heat transfer also influences the product distribution. In fast pyrolysis at lower temperatures, higher heating rates and small residence times favor liquid yield as the cracking of larger molecules to produce gaseous products is hindered. Liquid yield is also favored by immediate and rapid quenching which is often used to maximize the production of liquid products by condensing the vapors and gaseous molecules. Intermediate pyrolysis in screw reactors with longer residence time (minutes vs. seconds) can also be used for bio-oil production. In this process, two condensates are usually obtained, an aqueous phase and an organic phase defined as bio-oil. Although the yield of bio-oil is lower compared to fast pyrolysis, the bio-oils produced from intermediate pyrolysis are more stable, contain less oxygen, and have lower molecular weight substances, and the process is easier to control [4]. Slow pyrolysis, on the other hand, can be used to maximize the yield of solid char. This process requires slow pyrolytic decomposition at low temperatures.

Pyrolysis may be carried out at atmospheric or higher pressure or in vacuum where uncontrolled combustion is avoided. In practice, however, pyrolysis is mostly carried out at atmospheric pressure as creating a vacuum or high pressure drastically increases the cost of process equipment. Operation under high pressures results generally in greater yields of biochar and gases, while lower pressure or vacuum results in increased production of liquid products.

While feed particle size may not greatly affect pyrolysis product distribution, larger particle size tends in general to increase the liquid yield at a higher temperature range. Smaller particle sizes on the other hand favor the internal heat transfer within the particles. In fluidized bed reactors, the particles must be greater than a minimum, in order to avoid entrainment of fines, particularly where the material has a low density [5].

Reactor type is crucial for the efficient production of pyrolysis oil. Reactor types include packed or fixed-bed reactors, rotary kiln reactors and fluidized bed reactors. Fluidized bed reactors in particular, such as the auger, bubbling fluidized bed reactor and the circulating fluidized bed reactor, are highly efficient for the large commercial-scale production of pyrolysis oil [6].

Fluidized and fixed-bed reactors are mostly exterior-heating pyrolysis reactors where heat is transmitted from the exterior surface to the interior of the material. In fluidized bed reactors, fluidization increases mixing and interaction leading to efficient heat transfer, uniform temperatures, improved reaction rates and higher yield of bio-oil. On the other hand, interior heating is utilized in microwave-assisted pyrolysis with high energy effectiveness and the production of uniform products. Unlike traditional heating, microwave heating provides quick quenching of the pyrolysis vapors, which avoids secondary decomposition reactions of the primary products.

A catalyst may be used in catalytic pyrolysis processes to improve the yield and lower the temperature and/or time of reaction. Aromatic hydrocarbons such as benzene, toluene and xylenes may be directly produced by catalytic pyrolysis of biomass [7, 8].

A pyrolysis-based process has several advantages over other treatment processes:

1. The technology is relatively simple and can be made compact and lightweight. Applications of pyrolysis processes range from large-scale industrial applications where high temperatures are used to smaller-scale operations, even portable biomass conversion units, where the temperatures may be much lower. Mobile pyrolysis units for the production of liquid and solid fuels have been designed for the treatment of timber and lumber mill and other agricultural wastes. The pyrolysis units are built on trailers and consist of four basic groups: feed preparation machinery, a fluidized bed pyrolysis vessel, product separation equipment and an onboard gas turbine electrical generation system [9].
2. Pyrolysis, furthermore, can be conducted as a batch, low-pressure process, with minimal requirements for feedstock preprocessing.
3. Pyrolysis can also be used for all types of solid and liquid products and can be easily adapted to changes in feedstock composition.
4. The pyrolysis technology can be designed to produce minimal amounts of unusable byproducts.
5. In comparison with other treatment processes such as gasification, pyrolysis produces in general fewer air emissions, lower emission of nitrogen and sulfur oxides, less CO<sub>2</sub> generation, less dust emission and no emission of dioxin inside the pyrolyzer due to the pyrolysis with deoxidized hydrocarbon gas.

## 2. Industrial applications of pyrolysis

Pyrolysis is a proven and energetically efficient chemical technology that is used heavily in the chemical industry. Pyrolysis may be used in biorefineries for making a wide range of products and materials on which a future sustainable society may be based including many forms of carbon, fuels and other potentially valuable chemicals and chemical feedstocks.



There are a great many pyrolysis processes used in the production of fuels and chemicals. Such processes differ in the type of process, the use of catalysts, the substances treated and the end products. Pyrolysis processes include catalytic and noncatalytic pyrolysis, hydrous pyrolysis, vacuum pyrolysis, slow pyrolysis, torrefaction, fast pyrolysis, fluidized bed pyrolysis, flash pyrolysis, microwave-induced pyrolysis, plasma pyrolysis, empty tube pyrolysis, on-line pyrolysis and ultrasonic spray pyrolysis (USP). Other pyrolysis processes include also thermal decomposition, destructive and dry distillation, charring, tyre recycling and pyrolysis, liquefaction, high- and low-temperature carbonization, coking and thermal and catalytic cracking.

Common pyrolysis methods are frequently associated with many disadvantages including low gas yield, reducing the total energy value of the gas, and high content of tar in the gas, causing corrosion problems in the gas collection equipment and increasing the need for further treatment of the gas produced [6, 10, 11]. The disadvantages of the traditional pyrolysis methods may be overcome by radio-frequency plasma pyrolysis technology or by adding catalysts and steam.

Compared with noncatalytic pyrolysis, catalytic pyrolysis increases the pyrolytic gas and char yields but decreases the amount of oil [12]. The hydrogen concentration of the pyrolytic gas can also be considerably increased by the use of some catalysts [13]. The effect of the use of catalysts on the pyrolytic gas yield was investigated by Chen et al. It was found that some catalysts, particularly chromium oxide, have a strong positive influence on the pyrolytic gas, while other catalysts such as CuO even inhibits the pyrolytic gas yield [14]. Catalytic pyrolysis affects also the chemical composition and characteristics of the bio-oil produced. With catalytic biomass pyrolysis, the need for costly condensation and re-evaporation procedures prior to bio-oil upgrading is essentially eliminated [15, 16]. The effect of the catalysts on the yields and structure of products, however, becomes less significant with increasing temperature [17, 18].

Hydrogen may also be used in the pyrolysis process to enhance the chemical reduction and suppress oxidation by the elemental oxygen in the feedstock. The use of hydrogen can also change the pyrolysis products distribution.

Different catalysts may be used in different catalytic processes including Pt–Rh alloy, nickel-based catalysts, chromium oxide, Co/Mo/Al<sub>2</sub>O<sub>3</sub>, solid phosphoric acid and zeolite [19]. In a study conducted on biomass pyrolysis in a fixed-bed reactor, chromium oxide was used leading to gas yield improvement [14]. Oxygenated products can be reduced by utilizing zeolite-type catalysts [20]. Because of their high surface area and regular pore structures, mesoporous zeolites tend to inhibit repolymerization reactions [21, 22]. Zeolite catalyst was used in a catalytic pyrolysis process for the production of bio-oil from rice straw in a fluidized bed reactor. The water content in the bio-oil increased due to deoxygenation, and the aromatic compounds and the calorific value were also increased [12].

In hydrous or steam pyrolysis, organic materials are decomposed in the presence of superheated water or steam. The use of water as a pyrolyzing media also allows the feedstock to be introduced into the reactor in an aqueous form. The use of steam allows pyrolysis to occur at lower temperatures and higher pressures. In general, hydrous pyrolysis gives cleaner carbon with better properties and a relatively high surface area and porosity that are similar in nature to activated charcoal. The oil produced, however, contains high sulfur content and should normally be desulphurized. The C/H ratio of the pyrolytic oil is somewhat higher than that found for petroleum-derived fuels. This ratio indicates that such oil is a mixture of aliphatic and aromatic compounds. There is evidence to indicate that increasing the steam ratio (kg of steam/kg of biomass) leads to an almost linear increase of the calorific value of the biogas and an equally linear decrease in the calorific value of the biochar.

Bio-oils and fuels can be produced by hydrous pyrolysis of rice straw and other biomass materials. Steam cracking of petroleum oils can be used for the production of different cracking chemicals such as ethylene, which is a compound used for the production of many polymers and antifreeze (ethylene glycol).

According to Tu et al., radio-frequency plasma pyrolysis technology can overcome the disadvantages of common pyrolysis methods [23]. This is a capacitive dielectric heating method which employs an alternating current with high frequency and voltage to build up an electromagnetic field that produces plasma to induce the target material resulting in vigorous colliding, rubbing and thus self-heating. As the material is heated under a suitable degree of vacuum, pyrolysis occurs. The many advantages of this method include high heating rate, short heating time to reach the setting temperature, low heat loss, high concentration of syngas and low residual tar [5, 9, 24–27]. The high heating rate can efficiently decompose the combustible solid to gas products of  $H_2$ , CO,  $CH_4$  and low carbon hydrocarbons such as  $C_2$ – $C_5$  [23]. The low concentration of tar in the gas phase, mostly below  $10\text{ mg/Nm}^3$ , can be achieved because high-energy species, such as electrons, ions, atoms and free radicals, produced from the radio-frequency plasma can enhance the decomposition of tar [27].

In vacuum pyrolysis, the organic material is heated in vacuum to reduce its boiling point and also to avoid adverse chemical reactions.

In slow, or conventional, pyrolysis, the feedstock is heated slowly at a low heating rate ( $0.1$  to  $2^\circ\text{C}$  per second) to low temperatures ( $<400^\circ\text{C}$ ) for a long period of time. During slow pyrolysis of biomass, the biomass is slowly devolatilized leading to the production of tar and char as the main products. The gas produced consists mainly of methane along with minor amounts of hydrogen, propane, ethylene, CO and  $CO_2$ .

Torrefaction, also known as mild pyrolysis, is an example of a slow pyrolysis process. Torrefaction of biomass is a mild form of pyrolysis carried out under atmospheric conditions and at temperatures typically ranging between  $200$  and  $320^\circ\text{C}$ , where the onset of primary pyrolysis occurs at  $200^\circ\text{C}$ . For the low temperatures applied in torrefaction, the warm-up period is relatively short, even for the low heating rates commonly applied in torrefaction.

Torrefaction serves to improve the properties of biomass in relation to thermochemical processing techniques for energy generation such as combustion, co-combustion with coal or gasification. Torrefaction also eliminates all biological activity reducing the risk of fire and stopping biological decomposition. About 10% of the energy content in the biomass is lost as a result of the torrefaction process, but this energy of the volatiles can be used as a heating fuel for the process itself. During torrefaction, moisture and low-weight organic volatile components are removed, and the biomass loses typically 20% of its mass (dry bone basis). In addition, torrefaction partly depolymerizes the biopolymers (cellulose, hemicellulose and lignin) and the long polysaccharide chains, producing a hydrophobic, dry, blackened solid product as “torrefied biomass” or “bio-coal” with an increased energy density (on a mass basis) and greatly increased grindability. As a result, significantly lower energy is required to process the torrefied fuel, and it no longer requires separate handling facilities when co-fired with coal in existing power stations [20]. Torrefied or so-called roasted wood has found applications as a barbecue fuel and firelighter [28]. Finally, it has been suggested that torrefied biomass is a suitable feedstock for systems previously not considered feasible for raw biomass solid fuels such as entrained flow gasification. This is because torrefied biomass forms more spherical-shaped particles during grinding or milling [29].

In fast pyrolysis, on the other hand, the organic materials are rapidly heated at  $450$ – $600^\circ\text{C}$  in the absence of air in which fast heat transfer ( $100$ – $1000^\circ\text{C/s}$ ) is

applied. Achieving very high heating and heat transfer rates during pyrolysis usually requires a finely ground biomass feed. Fast pyrolysis is a well-known technique for the production of high-volatile products. Due to the short vapor residence times, products are high-quality ethylene-rich gases which can be used subsequently to produce alcohols or gasoline. The production of char and tar is considerably less in this process [30, 31].

The fast pyrolysis process has been progressively designed and optimized for producing bio-oils from biomass. A number of essential features are required for the production of bio-oil by fast pyrolysis. These include very high heating rates ( $1000^{\circ}\text{C/s}$ ), high heat transfer rates ( $600\text{--}1000\text{ W/cm}^2$ ), short vapor residence times (typically less than 2 seconds), lower process temperatures and efficient and rapid quenching of the condensable vapors in order to prevent their cracking and hence maximize oil production [6, 32]. In experiments conducted by Lee et al., the optimum reaction temperature range for the production of bio-oil by fast pyrolysis was found to be  $410\text{--}510^{\circ}\text{C}$  [33]. The bio-oil produced by such a process may contain large molecules derived from lignin which adversely affects the bio-oil properties [34, 35].

Catalytic fast pyrolysis can be used to produce aromatics using a range of different lignocellulosic feedstocks. Catalytic fast pyrolysis has several advantages over other biomass conversion processes where pyrolysis reactions can occur in a single reactor using inexpensive aluminosilicate catalysts [36].

With the application of induction heating, a fast pyrolysis process was used for producing valuable products from rice straw, sugarcane bagasse and coconut shell in an externally heated fixed-bed reactor [37]. In one process, the straw is pulverized, dried at  $150^{\circ}\text{C}$ , mixed with other raw materials, press formed at  $200^{\circ}\text{C}$  and finally carbonized at  $300\text{--}350^{\circ}\text{C}$  [38]. In another process, the biomass mixture, after pulverization and extrusion, is oven dried and carbonized at  $600\text{--}800^{\circ}\text{C}$  [39].

Infrared radiation is an efficient technique for fast heating processes since the energy from the infrared radiation is directly transferred to the process material. Infrared radiation is used as the heating source for many applications such as food processing, surface heating, solid decomposition and fast pyrolysis of oil shale [40]. In a study by Siramard et al. on the pyrolysis of shale oil in a fixed-bed reactor with infrared heating, it was found that shale oil production is affected by the direction of the infrared beam with higher yield achieved by the cross-current in comparison with the co-current heating. This is to be explained by the fact that the residence time of the volatiles was shorter in the case of the cross-current which led to the reduction of secondary cracking reactions of the volatiles. Reduced pyrolysis pressure was also found to be beneficial to the release of volatiles and the reduction of secondary cracking reactions [40].

Fluidized bed pyrolysis is carried out in a fluidized bed created by passing an upwardly moving carrier gas stream through a bed of the solid particulate substance under appropriate conditions to cause the solid/fluid mixture to behave as a fluid. The use of a carrier gas for fluidization results in a lower calorific value of the biogas produced. A fluidized bed reactor operating at atmospheric pressure at  $500^{\circ}\text{C}$  was used to produce bio-oils from wood feedstocks and rice straw [41]. A circulating fluidized bed reactor with sand used as bed material was used at a gauge pressure of about  $5\text{--}15\text{ kPa}$  for the production of pyrolysis oil from napier grass (*Pennisetum purpureum*) with a calorific value of  $19.79\text{ MJ/kg}$ . The maximum pyrolysis oil production was 37 wt% at  $480^{\circ}\text{C}$  of bed temperature. The oil produced is applicable to steam engines and gas turbine engines but not to diesel engines [42].

Higher efficiency is sometimes achieved by flash pyrolysis, also called anhydrous pyrolysis. In this process, the starting material is finely divided or crushed and quickly heated to between  $350$  and  $500^{\circ}\text{C}$  for less than 2 seconds, generally in



vacuum in order to decrease the boiling point of the byproducts and avoid adverse chemical reactions. In this process, the insulating char layer that forms at the surface of the reacting particles is continuously removed. This process is used, for example, in organic synthesis.

A flash pyrolysis process was developed by Longanbach and Bauer to produce liquid fuels, chars and gases from bituminous and subbituminous coal, municipal refuse, grass straw and other biomass materials. In this process, the biomass material is heated by contact with hot recycle char and carried in gas stream through a reactor where pyrolysis occurs at very short residence times and heat-up rates [43]. A flash pyrolysis process was also developed to convert municipal, industrial and agricultural wastes into pyrolytic oil at near ambient pressure with no need for chemicals or catalysts. At the same time, inorganics were recovered [44].

Microwave heating is an electromagnetic irradiation in the range of wavelengths from 0.01 to 1 m and the equivalent frequency range of 0.3–300 GHz. Normally, the microwave reactors for chemical synthesis and all domestic microwave ovens operate at 2.45 GHz frequency, which corresponds to a wavelength of 12.25 cm. The material which absorbs microwave irradiation is known as microwave dielectrics, and microwave heating is thus referred to sometimes as dielectric heating [45, 46].

Microwave heating has been widely used in many areas of thermochemical treatment of waste materials such as biomass, waste cooking oil and scrap tyres. This is mainly due to its high heating efficiency and easy operation. Microwave heating is an inside heating process that is carried out within the heated sample as a whole. It requires in general less energy input than conventional heating and has in addition other advantages including heating uniformity and shorter heating time [47]. In microwave-induced pyrolysis, focussed heating by microwaves makes the resulting pyrolysis different from the traditional pyrolysis. Microwave-induced pyrolysis does not require in general agitation, fluidization or a high degree of grinding, and, furthermore, it can be used for the treatment of mixed feedstocks such as municipal solid wastes [48].

According to Huang et al., higher microwave power levels contribute to higher heating rates and reaction temperatures and can therefore produce a torrefied biomass with higher calorific value and lower H/C and O/C ratios [49]. The suitable microwave power levels proposed by Wang et al. are to be set between 250 and 300 W for the torrefaction of rice husk and sugarcane residues [50]. In a study by Ahmad et al., torrefied palm kernel shell had the highest calorific value at the microwave power level of 450 W. However, when the microwave power level increased from 450 to 600 W, the calorific value of the torrefied mass decreased [45].

A work by Zhu et al. has shown that microwave heating can change the super-molecular structure of lignocellulosic materials [51]. In a study by Huang et al., it was suggested that a hydrogen-rich fuel gas (51–55% H<sub>2</sub>) can be produced from rice straw using microwave-induced pyrolysis. The major components in the gaseous product were H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub>. Alkanes, polars and low-ringed polycyclic aromatic hydrocarbons were the three primary kinds of compounds in the liquid product. From the viewpoint of energy consumption, close to 60% of the input energy could be derived and utilized as bioenergy [52].

Bio-oils of viscosities lower than the viscosity of light and heavy fuel oil and therefore easier to handle and process were obtained by microwave-assisted pyrolysis of aspen, canola and corncob feedstocks [41].

Microwave heating was also used for the treatment of waste tyres. Experiments were run in a batch laboratory scale with an oven operating at a frequency of 2.45 GHz with a variable energy output up to 6 kW. Short pyrolysis time and manageable product properties were achieved. Typical products were a solid residue



containing up to 92% of carbon, a low-viscosity oil with a high calorific value and a gas containing light hydrocarbons, hydrogen and only traces of  $N_2$  [53].

In empty tube pyrolysis, a heated alumina or nickel tube is used in which the samples are injected. This method was developed simultaneously by two groups working at the Scottish Crop Research Institute and at Indiana University.

In ultrasonic spray pyrolysis (USP), an ultrasonic nozzle is utilized for fine chemical synthesis such as the synthesis of nanoparticles, zirconia and oxides.

Liquefaction is the thermochemical conversion of an organic solid into a liquid composed of heavy molecular compounds with characteristics similar to petroleum-based liquids such as fuel oils. Liquefaction may also involve the production of a liquid from a pyrolytic gas stream.

The materials treated by pyrolysis include:

- Solid materials such as oil shale, coal, wood, woody and herbaceous biomass and organic, agricultural and municipal solid waste materials including straw, animal dung and human fecal waste, waste plastics and even waste printed circuit boards. Rice straw in particular has several characteristics that make it an attractive lignocellulosic material for bioethanol production, such as high cellulose and hemicellulose content that can be readily hydrolysed into fermentable sugars. The high ash and silica content of rice straw, however, makes the selection of an appropriate pretreatment technique a major challenge in developing an economically viable technology for bioethanol production [54].
- Liquid materials such as petroleum fractions.

### **3. Other applications of pyrolysis**

In addition to being a production process of chemicals and fuels, pyrolysis can be used for other purposes such as carbon-14 dating, thermal decomposition, thermal cleaning and removing of contaminants and for analysis and identification purposes as well. Pyrolysis can also be used as a pretreatment for more conventional techniques, such as incineration, gasification or steam reforming. Thermal decomposition reactions are the basis of reforming processes in the oil refining industry used to improve the combustion characteristics of gasoline and increase its octane number. In the petrochemical industry, reforming is used mainly to produce aromatic compounds which are used as feedstocks. In the treatment of plastic waste, a dual process of pyrolysis followed by steam reforming of the pyrolytic products is used for the production of gaseous fuels and hydrogen. Pyrolysis may also be used to coat a preformed substrate with a layer of pyrolytic carbon. This is typically done in a fluidized bed reactor heated to 1000–2000°C. Pyrolytic carbon coatings are used in many applications, including artificial heart valves.

A common process of thermal cleaning that is of particular interest in the oil and petrochemical industry is thermal desulphurization. Thermal desulphurization is the process where the substance to be treated is heated under atmospheric pressure in an inert atmosphere to a specified temperature and then kept at that temperature for a specified period of time. Most organic sulfur compounds undergo thermal decomposition at elevated temperatures, but some sulfur compounds decompose at lower temperatures such as many mercaptans which decompose at about 600 K and some sulphides which decompose at 530–670 K [26]. This process was found to be the most practical process for the desulphurization of petcoke and can be the only one possible when other techniques prove to be difficult or inefficient as was found in at least one case with Syrian petcoke [55].

IntechOpen

IntechOpen

### **Author details**

Hassan Al-Haj Ibrahim  
Arab University for Science and Technology, Hamah, Syria

\*Address all correspondence to: [sanjim84@yahoo.com](mailto:sanjim84@yahoo.com); [hasahi123@hotmail.com](mailto:hasahi123@hotmail.com)

### **IntechOpen**

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

## References

- [1] Figueiredo, Mouljin, editors. Carbon and Coal Gasification. Dordrecht: Martinus Nijhoff Publishers; 1986
- [2] Yacob TW et al. Pyrolysis of human feces: Gas yield analysis and kinetic modelling. *Waste Management*. 2018;**79**:214-222
- [3] Lichty P. Rapid high temperature solar thermal biomass gasification in a prototype cavity reactor. *Journal of Solar Energy Engineering*. 2010;**132**:11-12
- [4] Boscagli C et al. Influence of feedstock, catalyst, pyrolysis and hydrotreatment temperature on the composition of upgraded oils from intermediate pyrolysis. *Biomass and Bioenergy*. 2018;**116**:236-248
- [5] Conesa JA et al. Pyrolysis of polyethylene in a fluidized bed reactor. *Energy & Fuels*. 1994;**8**:1238-1246
- [6] Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal*. 2003;**91**:87-102
- [7] Jae J et al. Depolymerization of lignocellulosic biomass to fuel precursors: Maximizing carbon efficiency by combining hydrolysis with pyrolysis. *Energy & Environmental Science*. 2010;**3**:358-365
- [8] Thring RW et al. The production of gasoline range hydrocarbons from Alcell lignin using HZSM-5 catalyst. *Fuel Processing Technology*. 2000;**62**:17-30
- [9] Wiens J. Mobile pyrolysis system for on-site biomass conversion to liquid and solid fuels. *Symposium Papers: Energy from Biomass and Wastes*. 1980;**4**:713-720
- [10] Chen G et al. Biomass pyrolysis/gasification for product gas production: The overall investigation of parametric effects. *Energy Conversion and Management*. 2003;**44**:1875-1884
- [11] Caldeira MIK et al. Advanced technology paths to global climate stability: Energy for a greenhouse planet. *Science*. 2002;**298**:981-987
- [12] Choi JC et al. Bio-oil production from rice straw by the catalytic pyrolysis over zeolites. *Hwahak Konghak*. 2006;**44**(4):382-386
- [13] Chen G et al. Catalytic pyrolysis of biomass for hydrogen rich fuel gas production. *Energy Conversion and Management*. 2003;**44**(14):2289-2296
- [14] Chen G et al. Catalytic application to biomass pyrolysis in a fixed bed reactor. *Energy Sources*. 2003;**25**(3):223-228
- [15] Lu Q et al. On-line catalytic upgrading of biomass fast pyrolysis products. *Chinese Science Bulletin*. 2009;**54**:1941-1948
- [16] Samolada MC. Catalyst evaluation for catalytic biomass pyrolysis. *Energy & Fuels*. 2000;**14**:1161-1167
- [17] Panda AK et al. Thermolysis of waste plastics to liquid fuel, a suitable method for plastic waste management and manufacture of value added products—A world prospective. *Renewable and Sustainable Energy Reviews*. 2010;**14**:233-248
- [18] Miskolczi N et al. Thermal and thermo-catalytic degradation of high-density polyethylene waste. *Journal of Analytical and Applied Pyrolysis*. 2004;**72**(2):235-242
- [19] Morris M. Production of bio-oils via catalytic pyrolysis. In: *Handbook of Biofuels Production*. Elsevier: Woodhead Publishing Series in Energy; 2011. pp. 349-389

- [20] Yaman S. Pyrolysis of biomass to produce fuels and chemical feed stocks. *Energy Conversion and Management*. 2004;**45**:651-671
- [21] Zhu Y et al. Monodispersed mesoporous SBA-15 with novel morphologies: Controllable synthesis and morphology dependence of humidity sensing. *CrystEngComm*. 2011;**13**:402-405
- [22] Zhu Y et al. Amine-functionalized SBA-15 with uniform morphology and well-defined mesostructure for highly sensitive chemosensors to detect formaldehyde vapor. *Langmuir*. 2012;**28**:7843-7850
- [23] Tu W et al. Products and bioenergy from the pyrolysis of rice straw via radio frequency plasma and its kinetics. *Bioresource Technology*. 2009;**100**:2052-2061
- [24] Zhao ZL et al. Biomass pyrolysis in an argon/hydrogen plasma reactor. *Chemical Engineering and Technology*. 2001;**24**:197-199
- [25] Merida W et al. Enhanced hydrogen production from indirectly heated, gasified biomass, and removal of carbon gas emissions using a novel biological gas reformer. *International Journal of Hydrogen Energy*. 2004;**29**:283-290
- [26] Shie JL et al. Major products obtained from plasma torch pyrolysis of sunflower-oil cake. *Energy and Fuels*. 2008;**22**:75-82
- [27] Hlina M et al. Plasma gasification of wood and production of gas with low content of tar. *Czechoslovak Journal of Physics*. 2006;**56**:B1179-B1184
- [28] Girard P, Shah N. Recent developments on torrefied wood, an alternative to charcoal for reducing deforestation. *REUR Technical series*. 1991;**20**:101-114
- [29] Bridgeman TG et al. Torrefaction of Reed Canary Grass, Wheat Straw and Willow to enhance solid fuel qualities and combustion properties. *Fuel*. 2008;**87**(6): 844-856. Available at: [www.bioenergysite.com](http://www.bioenergysite.com)
- [30] Meyers RA. Coal desulphurization. New York: Marcel Dekker; 1977
- [31] Gibbins-Matham J, Kandiyoti R. Coal pyrolysis yields from fast and slow heating in a wire-mesh apparatus with a gas sweep. *Energy & Fuels*. 1988;**2**:505-511
- [32] Bayerbach R, Meier D. *Journal of Analytical and Applied Pyrolysis*. 2009;**85**:98-107
- [33] Lee K et al. Influence of reaction temperature, pretreatment, and a char removal system on the production of bio-oil from Rice straw by fast pyrolysis, using a fluidized bed. *Energy & Fuels*. 2005;**19**(5):2179-2184
- [34] Lédé J et al. Properties of bio-oils produced by biomass fast pyrolysis in a cyclone reactor. *Fuel*. 2007;**86**(11-12):1800-1810
- [35] Oasmaa A, Kuoppala E. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energy Fuel*. 2003;**17**:1075-1084
- [36] Fosteret AJ et al. optimizing the aromatic yield and distribution from catalytic fast pyrolysis of biomass over ZSM-5. *Applied Catalysis A: General*. 2012;**423**:154-161
- [37] Tsai WT et al. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. *Journal of Analytical and Applied Pyrolysis*. 2006;**76**(1-2):230-237
- [38] Zhang L, Wang G. Method for preparation of solid fuel briquets from straw. China Patent No. CN 1699525; 2004



- [39] Shen X. Method for manufacturing solid fuel from cattle manure, straw, and sawdust. China Patent No. CN 101629114; 2010
- [40] Siramard S et al. Secondary cracking of volatile and its avoidance in infrared-heating pyrolysis reactor. *Carbon Resources Conversion*. 2018;**1**(3):202-208
- [41] Luo Z et al. Research on biomass fast pyrolysis for liquid fuel. *Biomass and Bioenergy*. 2004;**26**(5):455-462
- [42] Suntivarakorn R et al. Fast pyrolysis from Napier grass for pyrolysis oil production by using circulating fluidized bed reactor: Improvement of pyrolysis system and production cost. *Energy Reports*. 2018;**4**:565-575
- [43] Longanbach JR, Bauer F. *Fuels and Chemicals by Pyrolysis*, ACS Symposium Series, 1976, 32 (Ind. Lab. Pyrolyses, Symp.)1975. pp. 476-491
- [44] Pober K, Bauer H. From garbage to oil. *ChemTech*. 1977;**7**(3):164-169
- [45] Zhu SD et al. Microwave-assisted alkali pre-treatment of wheat straw and its enzymatic hydrolysis. *Biosystems Engineering*. 2006;**94**(3):437-442
- [46] Motasemi F, Afzal MT. A review on the microwave-assisted pyrolysis technique. *Renewable and Sustainable Energy Reviews*. 2013;**28**:317-330
- [47] Cheng J et al. Improvement of coal water slurry property through coal physicochemical modifications by microwave irradiation and thermal heat. *Energy & Fuels*. 2008;**22**(4):2422-2428
- [48] Karunanithy C, Muthukumarappan K. Rheological characterization of bio-oils from pilot scale microwave assisted pyrolysis, Ch. 13. In: Bernardes M, editor. *Biofuel's Engineering Process Technology*. Intech; 2011. pp. 293-316
- [49] Huang YF et al. Microwave torrefaction of rice straw and pennisetum. *Bioresource Technology*. 2012;**123**:1-7
- [50] Wang MJ et al. Microwave-induced torrefaction of rice husk and sugarcane residues. *Energy*. 2012;**37**(1):177-184
- [51] Zhu SD et al. Microwave-assisted alkali pre-treatment of wheat straw and its enzymatic hydrolysis. *Process Biochemistry*. 2005;**40**(9):3082-3086
- [52] Al-Haj Ibrahim H. Bio-energy production from rice straw. *Recent Advances in Petrochemical Science*. 2018;**5**(5):1-6
- [53] Undri A. Microwave pyrolysis of polymeric materials: Waste tires treatment and characterization of the value-added products. *Journal of Analytical and Applied Pyrolysis*. 2013;**103**:149-158
- [54] Al-Haj Ibrahim H. Pretreatment of straw for bioethanol production. *Energy Procedia*. 2012;**14**:542-551
- [55] Al-Haj Ibrahim H, Ali MM. Thermal desulphurization of Syrian petroleum coke. *Journal of King Saud University*. 2005;**17**(2):199-212