

Historical Developments of Pyrolysis Reactors: A Review

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ABSTRACT: This paper provides a review of pyrolysis technologies, focusing on reactor designs and companies commercializing these technologies. The renewed interest in pyrolysis is driven by the potential to convert lignocellulosic materials into bio-oil and biochar and the use of these intermediates for the production of biofuels, biochemicals, and engineered biochars for environmental services. This review presents slow, intermediate, fast, and microwave pyrolysis as complementary technologies that share some commonalities in their designs. While slow pyrolysis technologies (traditional carbonization kilns) use wood trunks to produce char chunks for cooking, fast pyrolysis systems process small particles to maximize bio-oil yield. The realization of the environmental issues associated with the use of carbonization technologies and the technical difficulties of operating fast pyrolysis reactors using sand as the heating medium and large volumes of carrier gas, as well as the problems with refining the resulting highly oxygenated oils, are forcing the thermochemical conversion community to rethink the design and use of these reactors. Intermediate pyrolysis reactors (also known as converters) offer opportunities for the large-scale balanced production of char and bio-oil. The capacity of these reactors to process forest and agricultural wastes without much preprocessing is a clear advantage. Microwave pyrolysis is an option for modular small autonomous devices for solid waste management. Herein, the evolution of pyrolysis technology is presented from a historical perspective; thus, old and new innovative designs are discussed together.

1. INTRODUCTION

The practice of carbonizing wood to manufacture char has existed for as long as human history has been recorded.^{1–5} Initially, producing char was the sole objective of wood carbonization.^{2,4,5} In fact, char is the first synthetic material produced by humankind.^{6,7} However, new byproducts (tars, acetic acid, methanol, acetone) were obtained from wood as civilization progressed and new reactors and bio-oil recovery systems were designed. The ancient Egyptians used pyrolytic liquid products such as fluid wood tar and pyrolytic acid to embalm their dead.⁵ According to the writings of Theophrastus, the Macedonians obtained wood tar from burning biomass in pits.⁴ At the end of the 18th century, technologies to recover and utilize condensable pyrolysis products were relatively well developed.^{3,4,8} This resulted in brick kilns to recover the condensable gases that were normally lost in the pits. Iron retorts (vessels) followed brick kilns. In the 19th century the “acid-wood industry”, also known as the “wood distillation industry”, was established⁹ to produce charcoal and liquid byproducts (e.g., acetic acid, methanol, and acetone). The historical development of carbonization industry is one of the most fascinating in the annals of industrial chemistry.^{1,4} The hardwood distillation industry is frequently considered to be the precursor of the modern petrochemical industry.¹⁰ The rise of the petroleum industry at the beginning of the

20th century, with cheaper products, caused the decline of the pyrolysis industry. However, the oil crisis during the 1970s forced a reconsideration of biomass pyrolysis as a technology that could contribute to reducing our dependence on fossil oil. “Fast” pyrolysis reactors were introduced at that time, aiming at maximizing liquid products.^{11–19} Recent advances in bio-oil hydrotreatment,^{20,21} bio-oil fractionation,^{22–25} and new bio-oil derived products (e.g., transportation fuels, phenol formaldehyde resins, carbon fibers) are catalyzing the development of bio-oil refineries. Figure 1 shows important developmental milestones of pyrolysis technology.

The social and economic impact of wood carbonization in today's world is significant.²⁶ The wood used as fuel wood and charcoal constitutes about half of the wood extracted from forest, generating income for 40 million people worldwide.²⁶ The world's top producers of charcoal are (in descending order) Brazil, Nigeria, Ethiopia, India, the Democratic Republic of Congo, Ghana, Tanzania, China, Madagascar, and Thailand.²⁶ Today this industry contributes an estimated \$650 million to Tanzania's economy (300 000 people involved in production and trade).²⁶ The Food and Agriculture Organization of the

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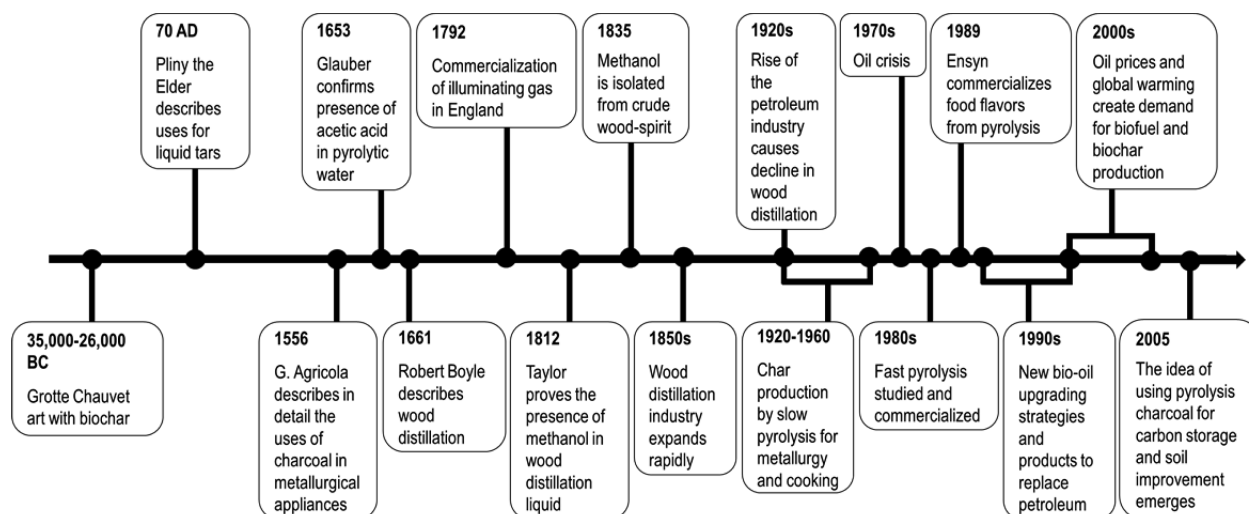


Figure 1. Some important milestones in the development and use of pyrolysis (adapted from refs 2, 4, and 5).

United Nations (FAO) estimated that 2.4 billion people in developing nations use charcoal as domestic fuel.^{26–31} Approximately 3 billion people still lack access to clean fuels and technologies for cooking.²⁶ According to the FAO,³² more than 52 million tons (Mt) of charcoal were produced worldwide in 2015 (Africa, 62%; Americas, 19.6%; Asia, 17%),²⁶ showing an increase of close to 20% since 2005. Since current char yields a mere 20 wt % of the original biomass, it can be estimated that more than 260 Mt of wood are currently processed worldwide to produce charcoal. Between 1 and 2.4 gigatons of CO₂ equivalent (Gt CO_{2eq}) of greenhouse gases are emitted annually in the production and use of fuel wood and charcoal, which represents 2–7% of global anthropogenic emissions.^{26,33} Producing charcoal using sustainable managed resources and improved pyrolysis technologies has the potential to reduce emissions by 80%.²⁶ Therefore, there are huge opportunities to improve the environmental performance of current carbonization units.^{34–36} The potential use of char as a means to fight global warming is also attracting renewed interest in pyrolysis.³⁷ Char has the capacity to increase soil fertility and sequester carbon.^{38–41} Sustainable char technology could offset up to 130 Gt CO_{2eq} of emissions during the first century of adoption.³⁹ Greening the pyrolysis value supply chain (with sustainable sourcing, production, transport, and distribution) is critical to supporting livelihoods and providing energy security in developing nations.²⁶ The International Energy Agency forecasted that by 2030 charcoal will become a \$12 billion industry.²⁷

According to Scopus, the numbers of research papers with the keywords “carbonization reactors (CR)” and “fast pyrolysis reactors (FP)” have been steadily growing: 1980–1990 (CR, 59 papers; FP, 63 papers), 1990–2000 (CR, 86 papers; FP, 88 papers), 2000–2010 (CR, 306 papers; FP, 371 papers), 2010–2017 (CR, 340 papers; FP, 840 papers). Despite the growing interest in producing bio-oil and char, the disperse information on pyrolysis technologies and manufacturers hinders the development of this industry. A vast diversity of factors affect the pyrolysis process (different feedstocks, scale, capacity, use of mobile or stationary units), which makes it very difficult to find an exclusive design that is sustainable across all of the potential feedstocks and applications.

Although there are excellent reviews of fast pyrolysis technologies,^{13–19,42} conventional carbonization reactors,^{5,6,41,43}

and microwave pyrolysis,^{44,45} there are only few reviews of converters and retorts.^{1,4,9,46} Lynch and Joseph⁴⁷ published guidelines for the development and testing of pyrolysis plants for char production. Interestingly, some companies are reproducing old concepts to design new pyrolysis reactors. Thus, the main goal of this paper is to provide a comprehensive overview of pyrolysis reactors. Herein we describe designs, operating conditions, scales, and yields to help those involved in the development of pyrolysis projects identify robust flexible designs for their business models. This work is an attempt to present all pyrolysis reactors in a single document within a historical perspective, intending that the knowledge and experience generated through centuries could serve as an inspiration for the development of new designs.

2. FUNDAMENTALS OF BIOMASS PYROLYSIS

The main factors in the operation of pyrolysis reactors that affect the yield and composition of the products are (1) the biomass pyrolysis temperature,⁴⁸ (2) the particle size,^{49–51} (3) the alkali content,^{52–54} (4) the residence time in the vapor phase,^{55–57} (5) the pressure,^{58–60} (6) the pretreatment temperature,^{61,62} and (7) the heating rate.^{55,56,63} Other factors such as feedstock composition, use of additives, and condensation conditions are outside the scope of this review.

Thermochemical depolymerization reactions are important between 250 and 600 °C.⁶³ When biomass is heated, thermal cracking of bonds in biomass constituents (cellulose, hemicellulose, and lignin) happens. These primary thermal depolymerization reactions happen in the solid. When biomass macromolecules are heated, some fractions can cross-link and form a solid product,^{63,64} and others can depolymerize into light oxygenates that can be easily evaporated⁶⁵ or into oligomeric products that can form a liquid intermediate.^{66–68} This liquid intermediate is acidic, which enhances dehydration and polycondensation reactions.⁶⁹ Most of the pyrolytic water is formed in the liquid intermediate.⁶⁹ The oligomeric molecules in the liquid intermediate may be removed from the hot reaction environment in the form of aerosols by thermal ejection.^{66,67}

The biomass particle size has a direct impact on the heating rate and release of aerosols and ultimately on the product distribution of pyrolysis. Indeed, the evacuation of the aerosols formed during the pyrolysis reaction can proceed in two distinct ways depending on the particle size. When very small

particles (mostly formed by cell walls) are used, aerosols formed in the pyrolysis reaction can be easily ejected, and pyrolysis vapors can be removed without traveling inside the cell cavities.^{50,51} Mass transfer limitations increase with particle size. The second regime involves aerosol formation inside cell walls. An important part of these aerosols is retained from escaping through the cell walls and eventually contributes to the formation of extra char through secondary reactions. Volatile pyrolysis products are also formed inside the particles and will react on their way out of the biomass particle and the reactor.^{49,50} Secondary reactions are typically called intra- and extraparticle homogeneous and heterogeneous reactions.^{49,57,70,71}

The temperature and hydrodynamics of the gaseous reaction environment, the presence of a secondary heating medium (e.g., sand, steel balls, reactor walls, heating tubes), and the size of the biomass particle determine the total conversion time by controlling the internal particle heat transfer and reaction kinetics.⁷² External heat transfer is determined by the reactor type and its heating method. These factors together define the traditional distinction between slow and fast pyrolysis reactors. The heat transfer in carbonization units operating with logs is controlled by the heat transfer rate inside the wood pile (bed) and inside the logs (typically low heating rates are

achieved: less than 100 °C/min). Fast pyrolysis reactors typically operate with very small particles to achieve high heating rates (>1000 °C/s) inside the particles and high bio-oil yields.

Although there are few studies on the effect of these parameters for all of the reactors covered in this review, a discussion of the specific case of fluidized bed reactors is instructive to gain insights into their potential impact in other reactors. Fluidized beds are designed to maximize bio-oil yields, and thus, in order to obtain adequate gas–solid heat transfer for this purpose, the biomass particles should be very small. This is due to the poor thermal conductivity of biomass (typically around 0.1 W m⁻¹ K⁻¹ along the grain and around 0.05 W m⁻¹ K⁻¹ across the grain). A thin reaction layer may achieve a temperature increase of 10 000 °C/s, but the low thermal conductivity of wood will prevent this heating rate from occurring throughout the entire particle. As the size of the particle increases, secondary reactions within the particle become increasingly significant, leading to a reduction in the liquid yield.¹¹

Figure 2 shows the effect of some operational parameters on the yields of pyrolysis products in fluidized beds. These studies clearly show that to achieve high bio-oil yields, (i) the pyrolysis temperature should be between 450 and 550 °C, (ii) very small

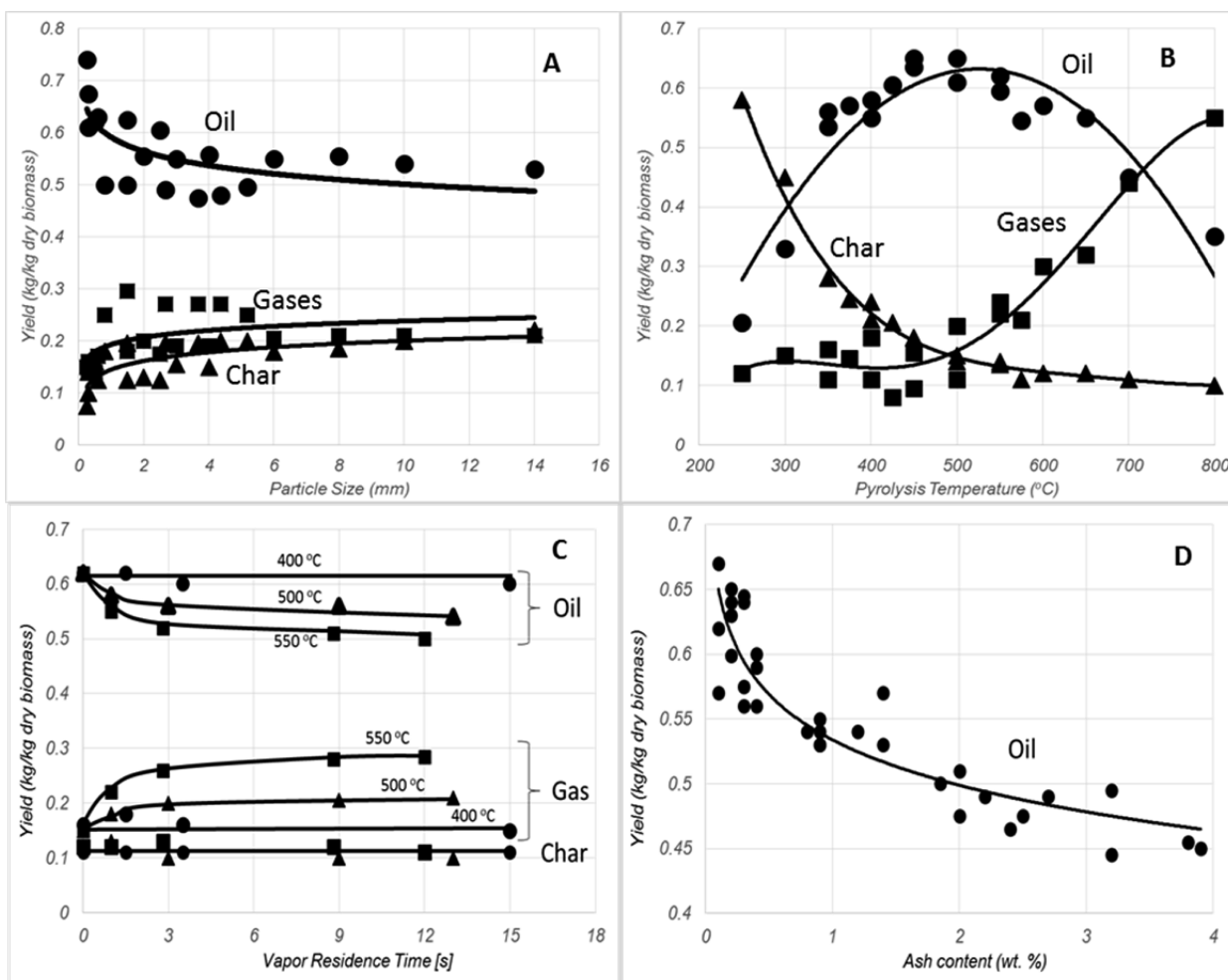


Figure 2. Effect of operational parameters on the yield of products during fast pyrolysis. (A) Effect of particle size (adapted from refs 49 and 50). Feedstocks: mallee wood,⁴⁹ beech wood.⁵⁰ (B) Effect of pyrolysis temperature (adapted from refs 48 and 74). Feedstocks: pine, beech, bamboo, and demolition wood⁴⁸ and mallee wood.⁷⁴ (C) Effect of vapor residence time (adapted from ref 55). Feedstock: pine wood.⁵⁵ (D) Effect of ash content (Adapted from ref 54).

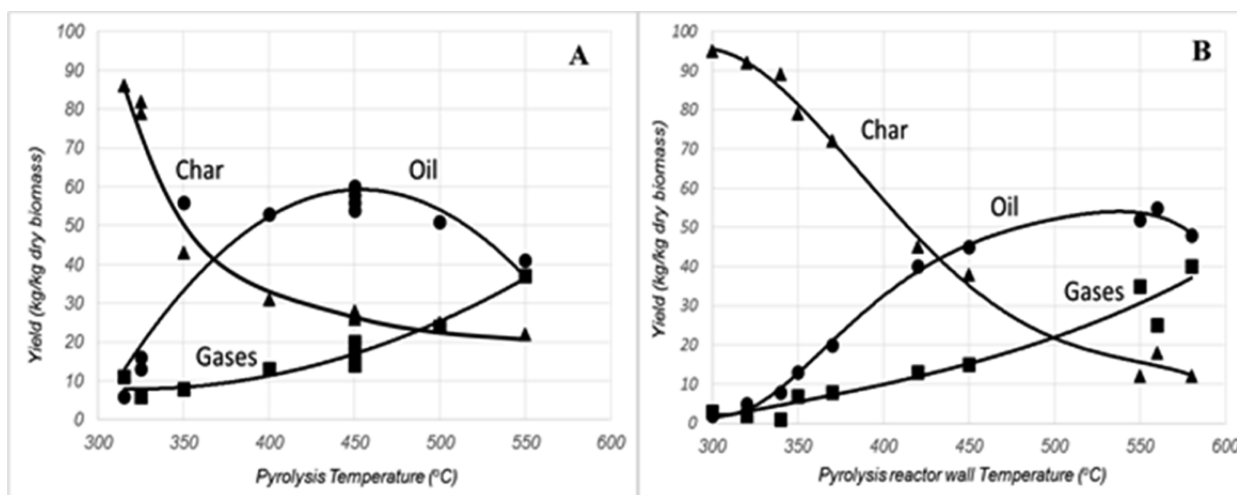


Figure 3. Yields of products in (A) a rotary drum pyrolysis reactor (feedstock: arbor pellet⁷⁶) and (B) an auger pyrolysis reactor (feedstock: Douglas fir wood⁷⁷).

particle sizes should be used, (iii) the residence time of pyrolysis vapors inside the reactor should be minimized, and (iv) the alkaline content in the biomass should be low.^{48–50,54,55,73,74} Data from this figure also suggest that (a) the type of reactor is only one of several factors controlling the product yields and (b) careful control of the operating conditions (temperature, particle size, ash content) of systems that are not traditionally considered fast pyrolysis reactors could dramatically improve the yield of desirable products. This is especially relevant since most of the literature on fast pyrolysis from the 1980s and 1990s focused on identifying the very stringent operational conditions that maximize bio-oil yields, while assuming that char should be combusted to provide the energy needed for the process. Instead, currently there is a growing research interest in the design and use of simpler systems for combined production of bio-oil and char, both or which are presently regarded as valuable products.^{20,75} The design of reactors resulting in oils with lower oxygen content and higher yields of gases by taking advantage of secondary homogeneous reactions in the gas phase warrants further investigation.

The interest in reactors capable of producing both char and bio-oil has resulted in a growing number of designs for the balanced production of these two products.^{76,77} Figure 3 shows the effect of the temperature on the yields of products obtained when pellets and small particles are processed in a rotary drum and an auger pyrolysis reactor, respectively.^{76,77} Although the bio-oil yields in the auger and rotary drum reactors were lower than for fluidized beds (see Figure 2), these reactors are easier to operate (use less carrier gas and do not use sand) and do not consume the charcoal for their energy needs. The higher gas yields could help to satisfy an important fraction of the energy needs of these systems. Moreover, pyrolysis gas produced in auger and rotary drums is less diluted in the carrier gas than in bubbling or circulating fluidized beds, making its combustion in conventional boilers and gas engines more plausible.

3. TYPES OF PYROLYSIS REACTORS

There are hundreds of pyrolysis reactor designs.⁷⁸ Reviewing all of them is beyond the scope of this paper. Therefore, in this review we will focus on the reactors most commonly employed. Bridgwater¹⁶ classified pyrolysis reactors on the basis of the

vapor residence time (VRT) inside the reactor and the time the biomass particle takes to reach the final temperature (or the heating rate) as follows: fast (final temperature, 500 °C; particle diameter <2 mm; VRT, 1 s), intermediate (final temperature, 500 °C; small particles; VRT, 1 s), and slow (final temperature, 500 °C; logs or chips; VRT, days). The term *fast pyrolysis reactor* refers to reactors that are designed to maximize the yield of bio-oil and typically use powdery biomass as the feedstock. Emrich⁵ subclassified the slow pyrolysis (carbonization) reactors as kilns, retorts, and converters. The term *kiln* is used to describe traditional char-making equipment, solely employed to produce char from wood logs. Industrial reactors capable of recovering char and products from volatile fractions (liquid condensates and syngas) are herein called *retorts* and *converters*. A retort is a reactor that is able to pyrolyze pile wood or wood logs over 30 cm long and over 18 cm in diameter.⁵ A converter produces char by carbonizing small particles of biomass such as chipped or pelletized wood. Converters using small particles operate at conditions comparable to the intermediate pyrolysis reactors described by Bridgwater.¹⁶ In this review we use the heating mechanism to group pyrolysis reactors as follows: slow (kilns, retorts), intermediate (converters), fast, and microwave.^{5,16,44,45} Classification of reactors can also be based on (1) the final products targeted (oil, char, heat, electricity, gases), (2) the reactor's mode of operation (batch or continuous), (3) the manner in which it is heated (direct or indirect heating, autothermal, microwave), (4) the heat source used (electric, gas heater, biomass combustion), (5) the method used to load the reactor (by hand, mechanical), (6) the pressure at which the unit operates (vacuum, atmospheric, pressurized), (7) the material used for the construction of the reactor (soil, brick, concrete, steel), (8) reactor portability (stationary, mobile), and (9) the reactor's position. More information on the classification of pyrolysis reactors can be found elsewhere.⁷⁹

Although the type of pyrolysis reactor and its operating conditions greatly determine the quality of the final targeted products, there is limited information in the open literature linking the reactor type, operating conditions, and product quality. For charcoal, proximate analysis gives a good indication of its quality. According to Antal and Gronli,⁶ the fixed carbon content of charcoal for domestic cooking should have volatile

matter content less than 30%, whereas that of metallurgical charcoal should be less than 15%. The ash content should be between 0.5 and 5%. These values correspond to calorific values between 28 and 33 MJ/kg. For the use of charcoal as biochar (soil amendment), the International Biochar Initiative provides a standardized definition of its characteristics.⁸⁰ A common issue in carbonization reactors, especially in batch systems, is the inhomogeneous quality of charcoal due to temperature gradients inside the reactor, uneven gas circulation, partial combustion, and heterogeneous wood particle sizes. Thus, in terms of product quality, good temperature control is a key factor for well-designed retorts or converters.⁵ The type of reactor is also one of the factors that define bio-oil quality, together with biomass feedstock composition, particle size, and condensation system.⁸¹ The desired bio-oil characteristics will differ depending on the targeted final use (i.e., as a fuel, for further upgrading, or as a product source). From the point of view of bio-oil as a fuel, the multiphase nature of bio-oil is a critical issue.⁸¹ The bio-oil obtained by fast pyrolysis of relatively dry materials is a homogeneous single-phase oil. The liquid obtained from intermediate, slow, and microwave pyrolysis processes typically consists of a decanted oil and an aqueous phase.¹⁶ The formation of separated phases depends on the relative quantities of the polar compounds (water, sugars, pyrolytic humins), nonpolar compounds (pyrolytic lignin), and solvents (organic compounds of low molecular weight, such as methanol, hydroxyacetaldehyde, and acetol).^{54,81} Most of the research on bio-oil properties has focused on fast pyrolysis. Thus, more studies are needed to understand how the type of intermediate or slow pyrolysis reactor and its operational conditions affect the bio-oil composition^{81–85} and multiphase behavior.^{54,81,86}

4. KILNS (CARBONIZATION METHODS)

This section covers examples of the main groups of kilns: earth (pit or mound) and brick/concrete/metal (Brazilian, Argentine, Missouri, TPI) (Figure 4). There are excellent reviews and books covering these reactors.^{5,31,87} Therefore, this section will focus on the generalities and recent publications related to these reactors. Since, the number of recent publications on these reactors is limited, the information herein reported relates mostly to the operating conditions of reactors in real settings.

Earth Kilns. Earth kilns (pit or mound) have been used for centuries and are still very popular in some developing countries.⁴¹ Soil is used as a barrier for oxygen attack to prevent high levels of oxidation. The liquids (condensates) released to the soil during

carbonization and the vapors released to the atmosphere are important sources of pollution. Two types of earth kilns are distinguished: pit kilns and mound kilns (sometimes termed earth-mound kilns) (Figure 4).

When the soil is well-drained, deep, and easy to excavate, *pit kilns* are preferred.⁸⁸ The main advantage of these kilns is their low capital investment. However, the circulation of air is difficult to control, and pit kilns are harmful to the environment because of the emission of vapors to the atmosphere and condensation of oils in soils.⁸⁸

Mound kilns can be classified into three types: vertical mound kilns, horizontal mound kilns, and improved mound kiln designs (the Casamance mound kiln).⁸⁹ Casamance-type kilns, which use oil drums as chimneys, are the result of improvements made during the 1970s and 1980s. A Casamance kiln can typically produce up to 1.7 times more charcoal than a traditional earth kiln (i.e., reaching efficiencies up to 34 wt %, compared with 20 wt % in pit kilns).^{27,29,89,90} A number of factors, such as the location of the kiln, the conditions and type of wood, and the qualifications of the operator, greatly affect the carbonization efficiency of mound kilns. This explains why some publications present different yields for similar types of kilns operating in different places. For example, Mangue²⁸ reports efficiencies of 12–16% in Mozambique. Schenkel et al.⁸⁹ show tables comparing efficiencies of similar kilns operated in other latitudes, with efficiencies varying from 12 to 34%. Kammen and Lew²⁹ show the charcoal energy yield as a function of the kiln size for traditional and Casamance kilns, noticing a better efficiency of the latter. The average energy efficiency is around 18% for the traditional kiln and 32% for the Casamance kiln.²⁹ Menemencioglu⁹¹ reported data on wood charcoal production in Turkey. The author collected data from 44 kilns with volumes ranging from 25 to 45 m³, which were built by 23 adults. Typically, 1 kg of charcoal was obtained from every 5–6 kg of biomass, using 1350 tons of oak and having 255 tons of charcoal. The average productivity was 11 tons of charcoal per adult for the 7 month production season. The wholesale price was \$0.7 kg⁻¹, resulting in an average income of \$7,761 per season (7 months).⁹¹

The main advantage of mound kilns is that they are simple and made of earth and can be built in the same area that the biomass is available. This technology is well-suited to operate with logs. Its final product (charcoal chunks) can be easily commercialized as domestic fuel in some developing nations. No special equipment is required, and the initial investment is low (\$27 ton⁻¹).⁸⁷ This type of kiln is easy to operate and very flexible with regard to capacity.⁸⁸ Its main disadvantages are high labor demand, dirtiness of the char as a result of the covering, sensitiveness to weather conditions, very poor control of carbonization, low efficiency, difficulty of carbonizing small-size agricultural wastes, and the release of very large quantities of organic pollutants.⁸⁸ Detailed descriptions of the construction and operation of earth kilns can be found elsewhere.^{10,31,88} Some of the main characteristics of these kilns are presented in Table 1.

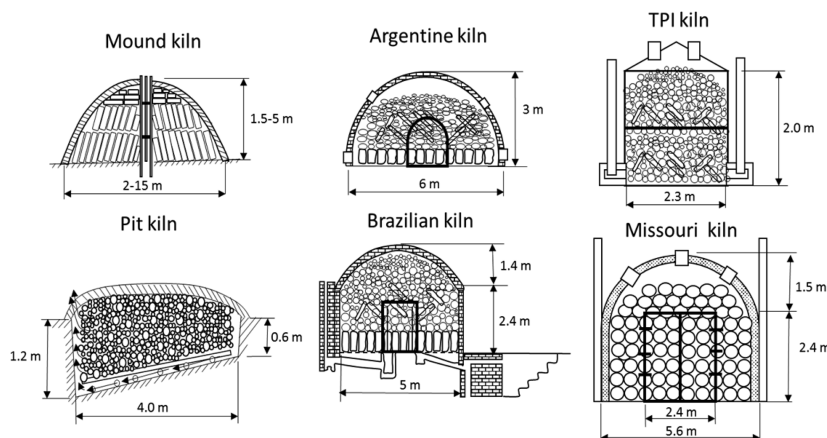


Figure 4. Schematic representation of typical kilns. Dimensions are presented for reference only. (Adapted from refs 5, 31, and 88.)

Table 1. Characteristics of Kilns for Charcoal Production

	earth kilns	cinder block, brick, and metal kilns
types/ representative kilns	pit kilns and mound kilns	Brazilian beehive and half orange kiln, Argentine beehive kiln, Adam retort, TPI kiln, New Hampshire kiln, Connecticut kiln, Missouri kiln
construction materials	earth	cinder block/brick/concrete/iron bands ⁴⁴
portability	built in place	stationary
carbonization duration	1–5 weeks ⁸⁸	10–30 days ^{43,88}
capacity	mound: 50–32000 kg (3–330 m ³) ⁹² Casamance: 50–1000 kg ⁸⁷	Brazilian: 20 tons ⁸⁷ Argentine: 30 tons ⁸⁷ Missouri: 80 tons ⁸⁷
charcoal yields reported	Pit kiln: 12–30 wt %; ²⁹ 12–16 wt % ²⁸ Mound: 2–42 wt % ²⁹ Casamance: 30 wt % ⁸⁷	Brick: 12–33 wt % ²⁹ Portable Steel (TPI): 19–31 wt % ²⁹ Missouri: 33% ²⁹
loading and discharge methods	manual	manual/mechanical
reactor dimensions	pit kiln: depth, 0.6–1.2; length, 4.0 m; capacity, 1–30 m ³ mound kiln: diameter, 2–15 m; height, 1–5 m (volume, 8–156 m ³)	Brazilian/Argentine: diameter, 5–7 m; height, 2–3 m Missouri kiln: width, 7 m; length, 11–13 m; height, 3.5–4 m TPI kiln: diameter, 2.3 m; height, 2 m
reactor capital cost	mound: \$27/ton of charcoal ⁸⁷ Casamance: \$200 ⁸⁷	Brazilian: \$150–1,500 ⁸⁷ Missouri: \$15,000 ⁸⁷
charge ignition method	small kindled wood at midpoint	small kindled wood/burning oil/gas-fired torch
process control	observing color of produced vapors	observing color of produced vapors or temperature measurements
raw material used	cordwood	
final product targeted	char	
heat transfer rate achieved	slow pyrolysis	
mode of operation	batch operation	
heating method	partial combustion of foliage (autothermal process)	
pressure	atmospheric	

Brick/Concrete/Metal. The four main kilns reviewed in this section are Brazilian, Argentine, Missouri, and TPI kilns (Figure 4). In the United States, during the 19th century, earth kilns were replaced by the so-called “beehive kilns”.^{8,93} The basic difference between earth kilns and cinder block and brick kilns is the construction material (Table 1). These kilns have a long lifespan, and several types have proved their economic viability. Cinder block and brick kilns can be differentiated by their shapes: hangar kilns, with rectangular or square shapes, and round brick kilns.⁵ The main advantages of brick kilns are the use of local materials, higher yields than mound and pit kilns, good-quality charcoal, good thermal isolation, easy operation, lifespans of 6–10 years, and insensitivity to climate conditions.⁸⁸ These kilns can operate with logs, and the final products (charcoal chunks) can be easily commercialized as domestic fuel. The main disadvantages of brick kilns are associated with the need of skilled workers for their construction and their fixed location, long production cycle (on average 15 days, as the cooling process is slow), and higher construction and operating costs than mound and pit kilns. These kilns are also responsible for important air pollution.⁵ The most commonly used round brick kilns are the Argentine half-orange kiln and the Brazilian beehive kiln (see Figure 4). The most commonly used hangar kiln is the Missouri kiln (see Figure 4). All of these kilns are autothermal and operate by burning part of the charge within the kiln.

The *Brazilian brick* kiln is an internally heated, fixed, batch-type kiln that is widely operated in Brazil, especially in the state of Minas Gerais and in the Amazonian region, with a typical capacity of 45 m³.⁴³ Thousands of them are used to produce charcoal for the Brazilian iron and steel industry.^{5,94} Detailed descriptions of the methods used to build and operate these kilns can be found elsewhere.^{31,95} A typical operational cycle consists of 8 h for loading/discharging, 80 h for

carbonization, and 70 h for cooling.⁴³ Some of the most advanced modifications to the Brazilian kilns are the attachment of an external heating chamber and the reduction of the number of smokestacks.⁵ Branches, brushwood, and other residual materials, which are not suitable for charcoal production and would be otherwise wasted, are used to heat the kiln. The raw material used for carbonization is typically cordwood, obtained from dedicated plantations or forest clear-cutting.^{5,95} These kilns can be modified to recover pyrolytic water and decanted oil. Only a few research papers describe the operation and yields of products from Brazilian kilns.⁹⁶

The *Argentine kiln* is also generally called the “half-orange-kiln” because of its hemispherical shape. This kiln, like many others, can be built in various sizes. Unlike the Brazilian kiln, Argentine kilns are built completely out of bricks with no iron parts.⁵ A detailed description of how to build and operate a half-orange kiln can be found elsewhere.³¹

Missouri-type kilns are sometimes called concrete kilns³⁸ or batch-type charcoal kilns.⁹⁷ They can be built with volumes of up to 350 m³ (typically between 150 and 200 m³),^{27,31,43,97} thus requiring mechanized loading and unloading.^{10,31} The operational cycle consists of 4 days of loading/discharging, 6 days of carbonization, and 20 days of cooling.⁴³ The Missouri charcoal kiln, which was developed in the early 1950s by V. Wulff in Ozark County, Missouri,²⁷ is a well-proven kiln.^{5,10,38,98} Missouri-type kilns are still used in Missouri^{41,97,98} and are responsible for an important fraction of the charcoal produced in the United States.^{97,99,100} Several improvements have been made to the original design. For instance, using thermocouples within the kiln contributes to the identification of cold spots and control of airflow.³⁸ Additionally, the environmental impact of these kilns can be reduced by using afterburners.^{78,97,99,101} More information on the design and operation of this type of kiln can be found elsewhere.^{5,10,31}

The *TPI kiln* is a small-sized kiln developed by the Tropical Products Institute (TPI) (Figure 4). This kiln is built with two interlocking cylindrical sections and a conical cover with ports to release vapors.^{31,38} Eight channels located at the perimeter of the base section support the kiln and serve as air inlets or smokestacks. Compared with earth kilns, air inlet and gas outlet are easy to control and require less supervision. All of the carbon produced can be recovered. These reactors can be transported to the place the feedstock is collected. They produce high charcoal yields with relatively short carbonization times (around 3 days). These kilns can be easily operated in high-rainfall regions. However, they have important air pollution issues.^{31,38} Other disadvantages include higher capital costs compared with earth kilns, the need to cut and split biomass to fit inside the kiln, difficult transportation in hilly terrain, and a relatively short lifespan (only 2–3 years).⁸⁸

The emission of gases and particulates from charcoal production in rural areas using medium-sized traditional and improved kilns has been studied by Sparrevik et al.¹⁰² They reported the following average emission levels: 1950 g of CO₂/kg of charcoal, 157 g of CO/kg of charcoal, 6.1 g of non-methane organic volatile compounds/kg of charcoal, 24 g of CH₄/kg of charcoal, 24 g of solid particles/kg of charcoal, and 1.8 g of NO_x/kg of charcoal.¹⁰²

Other important kilns reported in the literature that have not been discussed in this section include the New Hampshire kiln,^{103,104} the Connecticut kiln,^{10,103,105,106} The Black Rock Forest kiln,^{5,10,105,106} the Rima contained kiln (RCK),⁹² the Adam retort,^{102,107,108} and the European Schwartz kiln.⁵

5. RETORTS

While kilns are typically closed containers that release gas and vapor to the atmosphere, retorts condense the vapors and make good use of the energy content of gases.^{88,109} The main reactors discussed in this section are the wagon reactor, the Lambiotte French SIFIC (http://www.lambiotte.com/), the Lurgi process,¹¹⁰ and the Carbo twin retort¹¹¹ (Figure 5). All of these systems operate with logs. Their main characteristics are listed in Table 2. The main advantages of these systems are the high charcoal yield and high charcoal quality. Additionally, the byproducts from the vapors can be recovered. The main disadvantages are the high capital cost, attrition problems, the need for external sources of energy, and the fact that most of these systems are not portable and require a concentrated supply of raw materials.⁸⁸

A *wagon retort* consists of the following components: (a) a steel horizontal carbonizing chamber fitted with either a fixed

cover at one end and a door at the other or doors at both ends,⁴ one or two vapor outlets provided at the side, top, or one end of the chamber, and a rail track for running retort cars through; (b) a furnace for the heating process; (c) a condenser connected to the retort; (d) a steel chamber with a door at each end for cooling char placed in front of the retort and fitted with a similar rail track; (e) a section of rail that connects the retort with the char cooler, which can be moved as needed; (f) mechanical equipment for moving the cars; and (g) retort cars. A length of 8–9 m and a diameter of up to 2.5 m are standard for retorts.¹¹² Retorts usually require gradual cooling of the carbonization products, generally by heat release to the surroundings at room temperature.² Compared with other methods, the wagon retort required a substantial amount of manpower.^{5,113} This retort commonly used raw material made up of round wood and split round wood with an average length between 1.0 and 1.2 m. A limited quantity of shorter pieces was also charged.^{5,113} These reactors were able to produce charcoal with efficiencies of up to 36%, tar and oils with efficiencies varying from 5 to 20%, crude pyrolytic water varying from 30 to 50%, and noncondensable gases varying from 20 to 30%, depending on the composition of the wood.^{4,8} According to Klar,⁴ these units were able to obtain between 2.3 and 10.5 wt % acetate of lime (80% purity), between 0.6 and 2.5 wt % crude naphtha, between 5 and 20 wt % tars, and between 0.4 and 8 wt % pine oil. Charcoal was mainly used in the iron industry. Burning of gases and tar in boilers was a common practice.⁸

A wagon retort system was recently being operated by the Italian company Impianti Trattamento Biomasse. In 2010, this company had plants in Milazzo and Mortera (Italy) producing up to 6000 tons of charcoal/year.⁴¹ The process was called O.E.T. Calusco (formerly Carbolisi), but it does not seem in operation currently.⁴¹ Alterna Biocarbon, a company with head office in Prince George, BC, Canada, recently commercialized an upgraded design of the wagon retort⁸⁷ (the company is not currently in operation). The main products targeted by this company were energy pellets, activated carbon, products for mercury recovery, and chars for soil applications.

The *Lambiotte retort* has proven to be a successful technology for the production of char. As a result of several attempts to simplify the SIFIC process, the CISR Lambiotte retort was developed (see Figure 5).⁴³ The predried wood enters by the

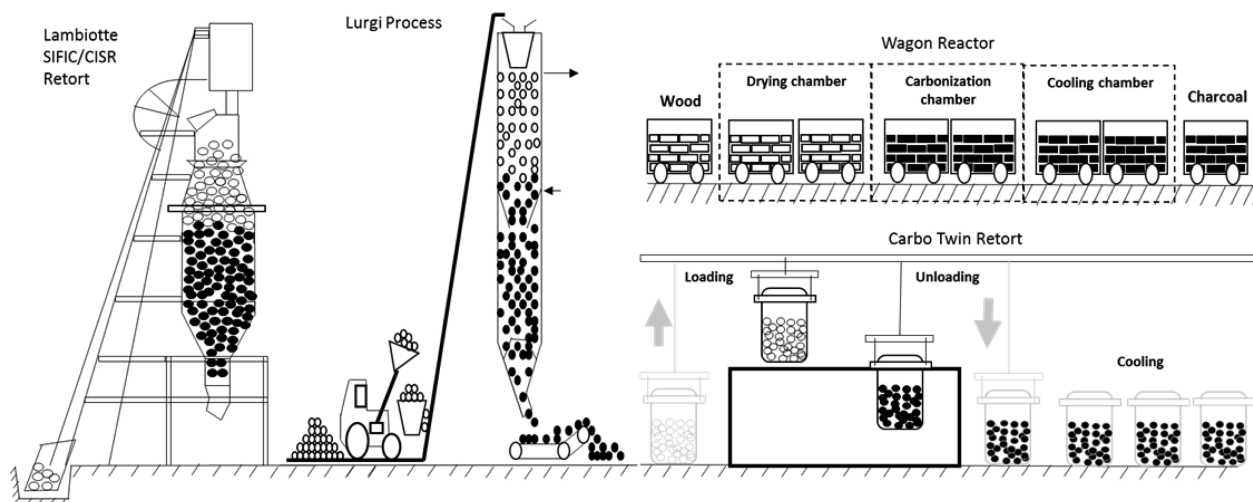


Figure 5. Schematics of retorts (adapted from refs 31 and 109–111).

Table 2. Characteristics and Operational Details of Some Retorts Operating with Logs

	Lurgi	Lambiotte French SIFIC	wagon retort	Carbo twin retort
final product targeted			char	
heat transfer rate achieved			slow pyrolysis	
capacity	6.2 tons of wood/h (per unit) ¹¹⁰ 13000 tons of charcoal/year (per unit)	2000–6000 ton/year (per unit) ⁸⁷	6000 ton/year ⁸⁷	900 ton/year (per furnace) ¹¹¹
production rate (ton year ⁻¹ m ⁻³)	10	16		70
carbonization time	n/a	n/a	25–35 h	8 h (carbonization), 24–48 h (cooling)
heating method	contact with heat gases		external heat and volatile combustion; an oil burner (or LPG) is used to provide heat for the initial startup	
dimensions	height: 27 m diameter: 3 m wood feed size: 150 mm × 150 mm × 250 mm	height: 16.3–18 m ¹⁰⁹ diameter: 3–4.3 m ⁴³ volume: 600 m ³ ¹⁰⁹	trolleys: 12 m ³ length: 8–16 m diameter: 2.5 m tunnel capacity: 35–60 m ³ length: 45 m	volume: 5 m ³ /vessel (six vessels are needed to keep the system running)
construction materials			steel	
portability			stationary	
reactor position	vertical	vertical	horizontal	vertical
raw material used	cordwood	cordwood	cordwood	
loading and discharge methods	mechanical	mechanical	use of wagons	
process control	direct measurement of temperature			
mode of operation		continuous		semicontinuous
pressure			atmospheric	
efficiency	30–40%	35%		30%
pretreatment needed			predried	
capital cost	\$10 million (1989)	\$0.5–2 million		€480,000 ¹¹¹ (char sales price: €250/ton ¹¹¹)
operating cost	€320/ton of charcoal	€360/ton of charcoal		€380/ton of charcoal
reported yields		char: 30–35 wt %	char: 30–33 wt % pyrolygneous acid: 20–25%	char: 33 wt % ¹¹¹

top of the retort through a lock controlled electronically to keep the retort always full. The retort has four zones (cooling, carbonization, drying, and torch).¹⁰⁹ The carbonization section is where the wood decomposes into char, vapors, and gases. Carbonization usually proceeds over a narrow temperature range (547–560 °C). The gases released from this section are drawn upward by a fan. The energy needed for carbonization is provided by the hot flue gases coming from the combustion of part of the pyrolysis vapors in an external chamber.^{5,92} Once the char is discharged, it is loaded on the converter plenum and carried away for storage. Since the lower segment of the retort acts as the first step in the cooling process, there is no need to separate char in the cooler.⁵ The surplus combustible vapors can easily be used for steam or electricity generation (Table 2). These plants have been running commercially for several years. Balt Carbon Ltd. is the supplier of Lambiotte retorts for Russia and other Eastern European and Central Asian countries. The company has built a unit producing 2000 tons of charcoal/year in Kaplava (in eastern Latvia) and one producing 8000 tons of charcoal/year in Ugale (in western Latvia).²⁷ Biochar Solutions Inc. (<http://www.biocharsolutions.com/>), based in Carbondale, CO, USA, has built a reactor using similar principles (continuous-downdraft pyrolysis reactor) but employing chips or pellets. This system is a mobile downdraft autothermal gasifier that can convert up to 225 kg of biomass/h into synthesis gas and char. The main advantages of the Lambiotte system compared with other retorts are (1) high labor efficiency

due to the high level of automation, (2) higher charcoal yields, (3) good product quality, and (4) the ability to use the vapors produced for cogeneration.²⁷ A disadvantage of the system is its sensitivity to the biomass moisture content. Biomass with high moisture content reduces the capacity and in some cases may require burning of auxiliary (oil) fuel. Attrition with the consequent production of fines happens as a result of the vertical movement of the load. These retorts are also prone to corrosion by acetic acid.²⁷

The operation of the *Lurgi reactor* is similar to that of the Lambiotte reactor. The *Lurgi reactor* (Figure 5) also has an upper carbonization zone and a lower cooling zone, each with its own recycling gases.^{43,110} The reactor has an air-lock hopper fed with a skip hoist that elevates dry wood blocks to the top of the reactor.¹¹⁰ The combustion of pyrolytic vapors and gases in a staged external incinerator provides the heat for carbonization. In the first stage, the retort gas is burned under near-stoichiometric conditions. In the second stage, more air is added to ensure complete combustion before release to the atmosphere. Up to 6000 Nm³ of gas per hour at 600 °C is used for heating the retort.¹¹⁰ The largest *Lurgi charcoal plant* forms part of the Silicon Metal Complex (SIMCOA, <http://simcoa.com.au>) in Bunbury, Western Australia, and produces 27 000 tons of charcoal every year in two retorts from local hardwood.^{43,110}

The *Carbo twin retort* was initially developed in the 1990s in The Netherlands. The twin system is formed by two retorts placed in an insulated oven, with a monorail and overhead

crane that enables the placement of retort vessels into and out of the carbonization unit. The pyrolysis vapors released by the pyrolysis reactions taking place inside the vessel are combusted outside to provide the heat supply needed to heat up the system.¹¹¹ The system is equipped with an internal afterburner furnace with an excess of air to burn all of the organic compounds.²⁷ One of the main advantages of this system is the low labor requirements: one worker per shift can operate (load and discharge) and supervise a battery of 10 twin retorts.²⁷ Other advantages of this system are high energy efficiency, high char yield, superior product quality, straightforward operation, easy scale-up with modular designs, low emissions, flexible operation and control, and continuous operation.¹¹¹ Carbo twin retorts have been installed in Almelo, The Netherlands; Parnu, Estonia; Manso Amenfi, Ghana; and Hailin, China.²⁷ Similar twin reactor concepts have also been developed in The Netherlands by VMR Systems,⁴³ Charbon Engineering, and Clean Fuels BV and in Portugal by Ibero Massa Florestal.

Other important retorts that have not been reviewed in detail in this section are the Reichert converter,^{5,113} the Rima container kiln (RCK),⁹² and the CML France batteries.^{43,92} Although not commercialized, the innovative concept of the flash carbonization process developed by Antal⁷ (in situ partial burning of the pyrolysis vapors inside the reactor with air at high pressure) is worth mentioning.

6. CONVERTERS (INTERMEDIARY PYROLYSIS REACTORS)

The carbonization techniques described in the previous section are used for logs and are not suitable for the small particles and chips found in agricultural and forest logging residues. If one of the large kilns is charged with small waste particles such as sawdust, the particles will tend to pack much more tightly, thus promoting insufficient penetration of gases unless the cargo is continuously rotated or moved.^{4,5} This section reviews reactors that can handle chips and pellets as well as deliberately crushed or chopped material such as sugar cane bagasse, bark, twiglets, olive stones, and coconut shells. The reactors herein reviewed are Herreshoff furnaces, rotary drums, auger reactors, paddle pyrolysis kilns, and moving beds (Figure 6). The main operational features of these reactors are shown in Table 3.

The *Herreshoff multiple* hearth furnace was patented in 1921 by R. D. Pike. It consists of four to 10 circular hearths or plates located one above another inside a refractory-lined steel shell.²⁷ A vertical rotating (1–2 rpm) shaft with radial arms located in

the center of the shell moves the feed from the top of the hearth to the bottom using a spiral of teeth across each hearth. This converter was designed for conversion of raw materials in the form of sawdust, shavings, or milled wood and bark into charcoal. The system is typically heated to 500–600 °C using external gas or oil burners.²⁷ The yield of dry char for this process is about 25 wt %. Automatic oxygen monitoring is used to minimize power draw and fuel demand. The first carbonization Herreshoff furnace was used in 1984, and by 1985 there were about 16 Herreshoff furnaces in use in the southern United States, producing over half of the total char obtained from wood and bark.²⁷ This type of reactor has also been used under vacuum conditions.^{115,116} Currently, a mobile Herreshoff pyrolysis reactor is commercialized by Big Char, a company with headquarters in Queensland, Australia. This company is commercializing a patented mobile multiple-hearth furnace that can produce char and heat with capacities of up to 1 ton of biomass/h. The char produced is available in briquetted form (<http://www.bigchar.com.au>). The major advantage of a Herreshoff furnace is its ability to efficiently and flexibly use fine-grained materials of little economic value. One disadvantage is the need for briquetting of the charcoal powder before it can be commercialized. The capital cost is high.

The *rotary drum* reactor is a very reliable system for carbonizing biomass. Figure 6 presents the two main types of rotary drum designs (directly heated and indirectly heated). The residence time of the biomass particles in these systems is controlled by the angle of the drum and the rotation speed. A converter of this type consists of an internal concentric steel tube and a cylindrical internally insulated mantle that makes up the rotary part. A sequence of radial steel fins is supported by the mantle, which has a solid connection to the steel tube. The solid and gaseous products are charged and discharged by two fixed parts at the end of the rotary part. This furnace provides the heat required for the carbonization process by burning gases and pyrolysis vapors. Table 4 shows the yields of liquid, char, and gases reported for tests with rotary drums. This type of reactor is able to achieve a good balance between oil (37–62 wt % liquid product) and char yield (19–38 wt %).

The European Union¹¹⁷ and Japan¹¹⁸ have extensively used these reactors for tires, sewage sludge, municipal solid waste, and plastics. Examples of these systems are a 2.2 MW pyrolysis plant operating since 1983 in Burgau-Unterknöringen, Germany, a 100 000 ton/year pyrolysis plant at the VEW Energie AG

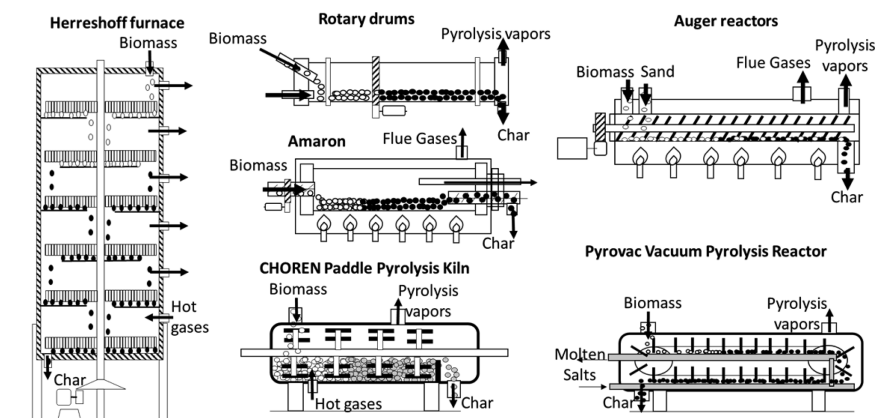


Figure 6. Schematics of common converters for processing of wood chips and other small biomass particles (adapted from refs 5, 31, 76, and 114).

Table 3. Characteristics of Converters for Processing of Wood Chips

	Herreshoff furnace	rotary drum	auger reactor	moving agitated bed	paddle pyrolysis kiln
final product targeted			char/bio-oil/heat		
heat transfer rate achieved		commonly slow to medium, depending on the particle size			
mode of operation			continuous		
capacity (ton/day)	up to 96	up to 288	up to 50 ⁴²	84 ¹⁶	–
heating method	direct contact with hot gases	direct contact with hot gases or indirect heating	direct contact with hot gases/use of a hot heat carrier/indirect heating		indirect heating
construction material			metal		
portability	stationary	stationary/portable	stationary/portable		stationary
reactor position	vertical		horizontal		
raw material used	chips/shells/fine particles				
loading and discharge methods			mechanical		
size of the reactor	large	large/medium/small	small/medium	medium/large	small/medium
charge ignition method	combustion of pyrolysis gases and/or of auxiliary fuels	combustion of auxiliary fuels and direct or indirect contact of combustion gases	external oven heating a hot sand heat carrier	external heater	
process control			direct measurement of temperature		
pressure			atmospheric/vacuum		
yield of carbon	25–30 wt % ⁸⁷	–	–	–	–
pretreatment needed			ground in chips/fine particles		

Table 4. Yields of Products Obtained from Rotary Kilns

biomass species	capacity (ton/h)	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
olive stones		500	26	38	35	121
pinon-juniper wood	0.5	500	30	59	11	120
black liquor	0.5	500	38	37	25	120
fir pellets	0.5	500	23	62	16	120
fir fines	0.5	500	19	59	22	120
lemna	0.5	500	28	44	28	120
shredded pine	0.5	500	30	58	12	120
pine bark	0.5	500	34	36	30	120
aspen	0.5	500	28	43	29	120

(VEW) Westfalen power station in Hamm-Uentrop, Germany, and other systems that combine gasification with pyrolysis or pyrolysis with combustion.¹¹⁷ Specific concepts of interest are the ConTherm technology by RWE Energie AG (RWE), the Serpac technology, the EDDITH process, The PYROPLEQ process, the Gibros PEC Process or PKA technology, the SIEMENS Schwel-Brenn technology, and the THERMOSE-LECT process.¹¹⁷ Most of those reactors could be easily adapted to work with biomass.

In 2009 Amaron Energy designed, constructed, and began testing a unique indirectly heated rotary kiln for pyrolysis of biomass to produce bio-oil and char.^{119,120} Amaron has achieved char and bio oil yields close to those from fast pyrolysis fluid beds (Figure 6). The Amaron rotary reactor consists of (1) a cylindrical reaction section heated by multiple high-intensity gas-fueled burners located and controlled to optimize heat transfer into the materials being heated, (2) a feed section with an auger arrangement that suppresses heating

of the material until the particles reach the area where optimized heat transfer begins, (3) a withdrawal section with a char outlet below the end of the rotating reaction section, and (4) a stationary end closure supporting a withdrawal pipe for vapors and gases. The vapors are condensed in multiple units designed to operate without problems caused by condensation of tars in the interconnecting piping.

The *auger reactor* is typically fed at one end through a hopper or a feeding screw.^{114,122} A screw then gradually carries the biomass to the hot zone of the reactor, where it is carbonized, and the gases and vapors are extracted and led to a condenser.⁴⁶ The residence time of the hot vapors in these reactors can vary, averaging from 5 to 30 s.¹⁶ These reactors can be operated with and without using hot sand, steel, or ceramic balls as heat carriers.^{122,42} The char and heat carriers are discharged by gravity.⁹³ Table 5 shows the yields of products obtained under different operational conditions using auger pyrolysis reactors. Experimental studies with woody biomass show char yields of 17–30 wt % and oil yields of 48–62 wt %.⁴² The bio-oil yield is slightly lower than that of fluidized bed reactors and contains more water (30–55%).⁴² As expected, the oil yield of agricultural residues was much lower because of the high ash content of this feedstock. Although difficult to compare, it seems that the yields obtained with sand as the heat carrier are slightly higher than those obtained without. ABRI-Tech in Canada has sold several 1 ton/day units.⁴² Auburn University (Auburn, AL, USA), KIT (FZK) (Germany), Mississippi State University (Starkville, MS, USA), Michigan State University (East Lansing, MI, USA), Texas A&M University (College Station, TX, USA), and Washington State University (Pullman, WA, USA)⁶¹ have active research programs on this technology.¹⁶

Table 5. Auger Pyrolysis Results

biomass species	capacity (kg/h)	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
Without Heat Carrier						
oak	1	450	18–20	50–56		123
pinewood sawdust	1	450	18–20	49–55		123
pinewood chips	1.5	500	30	58	12	61
pinewood chips	15	500	20	57	25	124
miscanthus	7	425		60		125
pinewood sawdust	7	450	19	54		126
Douglas fir wood	1	400	12	48	40	77
corn stover	7	450		35		128
switchgrass	7	450		33		128
cassava stalk		450		32		128
peanut shell		450		33		128
rice husk				35		128
rice straw	60	500	45	26	13	129
With Heat Carrier						
<i>Eucalyptus grandis</i>	10	500		60.3		127
wheat straw (twin screw, Biolq)	500	500	23–28	50–55	22	130
wheat straw (twin screw, Biolq)	10	500	24	51	24	131
wheat bran (twin screw, Biolq)	10	500	18	60	22	131
softwood (twin screw, Biolq)	10	500	15	69	16	131
hardwood (twin screw, Biolq)	10	500	15	66	18	131

In *moving agitated bed* reactors, biomass is conveyed by patented mixers over a horizontal surface heated by molten salts. These reactors have been used under vacuum conditions.^{132,133} The molten salt used is a mixture of potassium nitrate, sodium nitrate, and sodium nitrite.¹³⁴ The size (height)

of an industrial moving bed (a few cm) is comparable to the height of the fixed bed in most of the laboratory tests (also a few cm). In fact, the scale-up of this reactor is typically conducted with the aid of fixed bed reactors operating in vacuum. In this section, we report results obtained with a fixed bed on a laboratory scale (Table 6). Bio-oil yields over 50 wt % are obtained with woody biomass in most vacuum tests.

The *paddle pyrolysis reactor* (see Figure 6)¹⁴³ is characterized by the use of internal mechanisms to move and mix the biomass and thus to increase heat transfer. This kind of reactor has been used by companies such as BEST Energies, currently part of Pacific Pyrolysis Inc. (<http://pacificpyrolysis.com/technology.html>), and was also part of the design of Choren.¹⁴⁴

Other important reactors in this category that have not been included in this review are shelf reactors^{4,46} and the Stafford–Badger retort.¹⁰ Converters are reactors with more potential for the balanced production of char and oil. However, more research is needed to understand the potential of these reactors.

7. FAST PYROLYSIS REACTORS FOR HIGH YIELDS OF BIO-OIL PRODUCTION

This section reviews the most common fast pyrolysis reactors that have been developed to optimize the yields of bio-oil (rotating cone, ablative, conical spouted bed, bubbling fluidized bed, and circulating bed; Figure 7). There are very good literature reviews of fast pyrolysis reactors.^{15,16,19,134,145} Thus, this section will focus only on recent developments. The main characteristics of the reactors studied in this section are summarized in Table 7.

Bubbling fluidized bed reactors use a mixture of convection and conduction to transfer heat from a heat source (hot sand) to the biomass particles. Although most of the literature suggests that fast pyrolysis should be performed with particles having diameters of 2–3 mm¹⁶ to obtain high liquid yields (over 65%), the particles must be smaller (typically

Table 6. Fixed Bed Reactor Results

biomass species (reactor)	capacity	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
rice husk (fixed bed)	180 g	100–500 °C/min	42–48	28–35		135
switch grass (100 psi, fixed bed)			42	27	10	136
pine chips	1.4 kg	500	31	50	18	60
hardwood rich in fiber [aspen poplar, white birch] (vacuum, fixed bed)	4.2 kg (15 dm ³ reactor)	500	26	54	20	60
softwood bark residue [white spruce, balsam fir, larch] (vacuum, moving bed)	15 kg/h (total of 1050 kg pyrolyzed)	500	28	45	27	60
sugar cane bagasse (vacuum pyrolysis)	pilot (20 kg) laboratory (80 g)	530 500	26 19	51 62	22 18	59
rape straw (vacuum reactor)		500		43		137
palm oil decanter cake (vacuum reactor)		500	39	41	20	138
rice husk (vacuum reactor)	10 g	500	38	49	13	139
rice straw (vacuum reactor)	10 g	500	35	47	18	139
empty fruit bunch (vacuum reactor)	10 g	500	26	54	20	139
Douglas fir (fixed bed)	800 mg	500	22	66	8	140
pine (vacuum)	500 g	500		52	25	141
pine sawdust (vacuum reactor)		500	20	50	30	141
red oak	800 mg	500	24	67	8	140
camphorwood sawdust (vacuum)		474	20	50	30	142
eucalyptus (vacuum)	10 g	500	26	62	17	142
teng wood (vacuum)	10 g	500	30	58	12	142
rubberwood (vacuum)	10 g	500	30	51	19	142

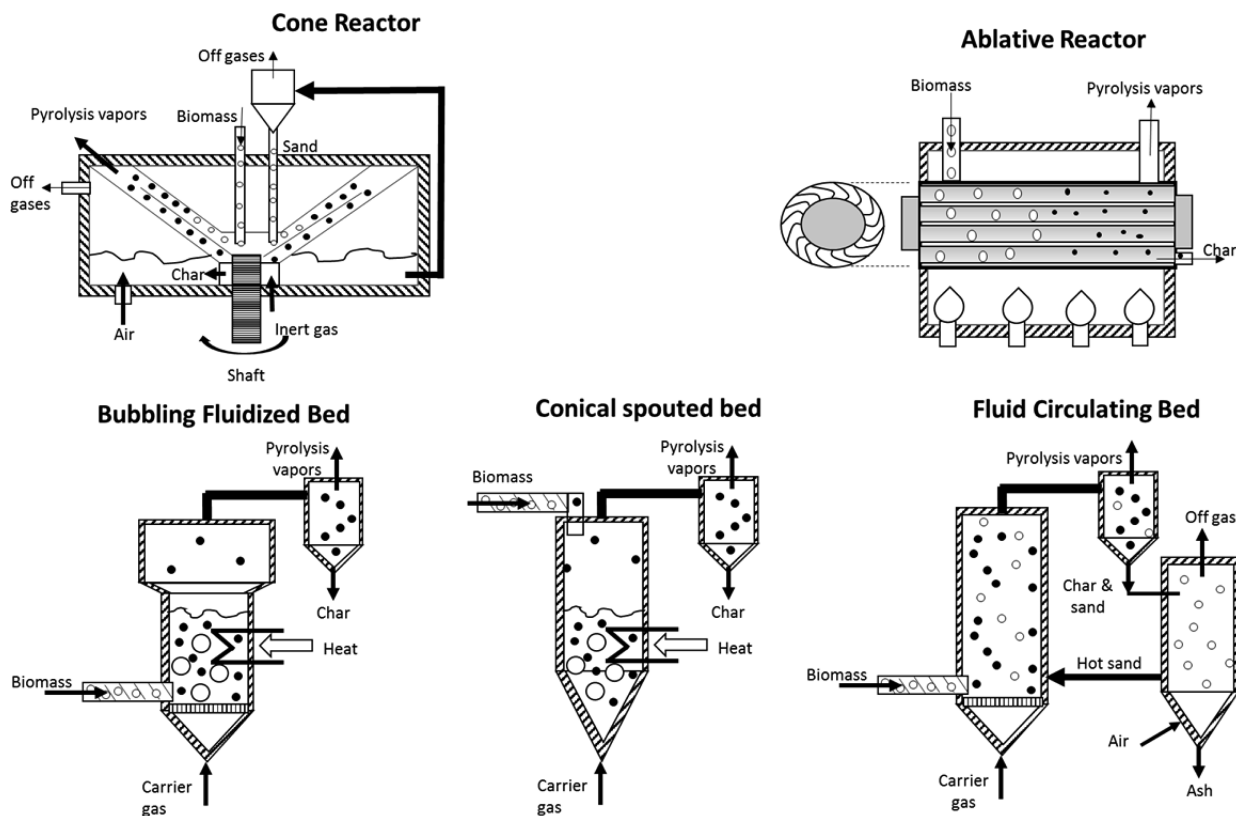


Figure 7. Schematics of fast pyrolysis reactors (adapted from ref 134).

Table 7. Characteristics of Some Fast Pyrolysis Reactors

	bubbling fluidized bed	circulating bed	ablative pyrolysis	rotating cone
final product targeted	bio-oil		bio-oil/char	bio-oil
heat transfer rate achieved		fast		
mode of operation		continuous		
heating method	direct and indirect heat/sand		indirect heating	direct and indirect heating
construction materials		metal		
portability		stationary		
reactor position	vertical		horizontal	vertical
raw material used	fine particles (<2 mm)		chips	fine particles
Loading and discharge methods		mechanical		
Ind. reactor capacity built (ton/day)	0.5–200 ¹⁶	9.6–96 ¹⁶	6 ¹⁶	50 ¹⁶
charge ignition method		external combustion chamber to heat the carrier gases		
process control complexity	medium	direct measurement of temperature		
status	demonstration	commercial	high pilot	high demonstration
industrial companies	Agritherm Canada; ¹⁶ Biomass Engineering Ltd., U.K.; ¹⁶ Dynamotive, Canada; ¹⁶ RTI, Canada; ¹⁶ Avello Bioenergy, USA	Ensyn, Canada; ¹⁶ Metso/UPM, Finland ¹⁶	PyTec, Germany ¹⁶	BTG, The Netherlands ¹⁶
pressure		atmospheric		
pretreatment needed	particle milling and predrying		none	particle milling
reported yields		up to 70 wt % bio-oil ¹⁴⁵		

below 0.5 mm)^{49,50} to avoid the retention of aerosols inside the particles and to achieve high heat transfer rates. One of the best-known examples of using a fluidized bed reactor was

Dynamotive, a company that resulted from the pioneering job conducted by the University of Waterloo.^{11,12,146} In the design of most fluidized bed reactors in operation, the char is entrained

by carefully control of the differences between the sizes and densities of biomass particles and the sand. Char particles obtained from the pyrolysis of raw materials with very high ash content, such as sewage sludge, usually abandon the bubbling fluidized beds by overflow. The heat used in bubbling fluidized beds is generated from the combustion of pyrolysis gases and chars and is typically transferred to the fluidized bed by heating coils and heating of the carrier gas (under industrial conditions typically a recirculated pyrolytic gas). Because of the low rates of heat transfer between the combustion gases and the bed ($100\text{--}200\text{ W m}^{-2}\text{ K}^{-1}$), a surface area of at least $10\text{--}20\text{ m}^2$ is required to transfer the heat required to pyrolyze 1 ton of biomass per hour. These heat transfer surfaces are very susceptible to attrition from the sand.¹³⁴ Several main features of this type of reactor are the ability to accurately control the temperature, the use of entrainment for the separation of the char, the use of cyclone separation, easy scaling, the well-known and understood technology, the requirement of small particles, and the need for large scale heat transfer to the bed. Dynamotive developed bench-scale plants, a 15 ton/day pilot plant, a 130 ton/day plant in West Lorne, and a 200 ton/day plant in Guelph, ON, Canada¹⁴⁷ that are currently not operating. Tables 8–10 show the yields of products obtained from the pyrolysis of grass and agricultural residues, softwood, and hardwood species in fluidized beds. With grasses and other agricultural wastes, the conversion yields to liquid bio-oil, solid char, and noncondensable gases are in the ranges of 35–68.7, 12.9–45.7, and 3–25.7 wt %, respectively, on an as-fed basis (Table 8). This broad range of values is mostly due to the wide range of ash contents in these materials. Softwoods result in 59–78.1 wt % bio-oil, 10–15.7 wt % char, and 7.8–28 wt % noncondensable gases. Comparable yields were also obtained for hardwood species (9.8–20.7 wt % char, 59–77 wt % bio-oil, and 9.3–24.6 wt % gases). Lower oil yields (35–73 wt %) and higher char yields (13.4–45.7 wt %) are obtained with some grasses, likely as a result of higher ash content in some of these materials.

A 10 ton/day mobile pyrolysis unit with a fluidized bed reactor has been developed by Agritherm at the University of Western Ontario (<http://agri-therm.com>).^{16,42} An important feature of the design proposed by this company is its compactness, as the pyrolysis reactor is built using an annulus with a burner at the core to providing the energy needed for the pyrolysis process. Avello Bioenergy (Ames, IA, USA) is another company commercializing fast pyrolysis technologies (<http://www.avellobioenergy.com>). This company specializes in the development of fractionation strategies to obtain different products from bio-oils. Bioware is a Brazilian company commercializing autothermal fluidized bed reactors¹⁷⁰ to produce bio-oil, char, and phenolic resins (<https://www.bioware.com.br>). Nettenergy BV is a private company from The Netherlands (<http://www.nettenergy.com/index.php/en/>) that built a 100 kg/h mobile unit with a unique multistage compact separation design.⁴²

The *circulating fluidized bed reactor* originated from research performed by the University of Western Ontario in the late 1970s and early 1980s, which spawned the Rapid Thermal Processing (RTP) technology commercialized and developed by Ensyn. Before being fed into this system's reactor, the biomass is comminuted to approximately 6 mm and then dried to a moisture content of 10% or less. The hot recirculated biomass and sand enter in an upflowing transported bed reactor. Once the products have passed through two cyclones

Table 8. Pyrolysis of Grasses and Agricultural Residues Using Fluidized Bed Reactors

biomass species	capacity	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
corn stover	100 g/h	450	46	35	11	12
corn stover	100 g/h	550	34	50	14	12
corn stover	100 g/h	600	28	50	13	12
rice husk	120 kg/h	475	–	50		148
rice husk	<150 kg/h	450	30	50	20	149
rice husk	7.32 kg/h	450	29	56	15	150
rice husk	60 g/h	500		55		151
rice straw	300 g/h	500	27	43	23	129
rice straw	60 g/h	500	31	53	15	151
corn cob	60 g/h	500	20	62	17	151
sugar cane bagasse	60 g/h	500		67		151
sugar cane bagasse	2–5.3 kg/h	500	23	73	4	152
sugar cane bagasse	100 g/h	510	19	69	12	146
barley straw	1 kg/h	525		54		153
timothy	1 kg/h	525		61		153
switchgrass	1 kg/h	510	19	60	16	154
switchgrass	2.5 kg/h	480	13	61	11	155
switchgrass			20	58		156
miscanthus	1 kg/h	505	29	51	12	154
wheat straw	1 kg/h	525	27	38	26	154
wheat straw	1.5 kg/h	525	22	61	17	156
wheat straw	100 g/h	550	24	54	24	146
wheat chaff	100 g/h	515	18	67	16	146
sorghum bagasse	100 g/h	510	13	69	12	146
sunflower hulls	100 g/h	500	23	57	20	146

that separate both solids from the produced vapors, they experience rapid cooling and quenching in multiple stages.¹⁴ The residence times of the solids and vapors in these reactors are almost the same.¹⁶ The recirculation of gases from secondary char combustion is the main heat source.¹⁶ RTP is the only pyrolysis technology in the world that has operated on a long-term commercial basis (<http://www.ensyn.com>, <https://www.envergenttech.com>). Larger-scale units include the ENEL plant built by Ensyn in Italy (15.6 ton/day), several 40 ton/day units operated by Red Arrow (Manitowoc, WI, USA) operating for the production of smoke aromas, and the Ensyn 50 ton/day unit at their R&D center in Renfrew, ON, Canada.¹⁶ Some features of the transported bed reactor include precise temperature control within the reactor, the ability to use large-sized particles, suitability for very large throughputs, and well-understood technology.¹⁶ Some of the main disadvantages of these technologies are (1) the use of large volumes of inert carrier gases, which causes a dilution of the pyrolytic gases, making bio-oil recovery very difficult; (2) the use of sand as a heat carrier in many fast pyrolysis reactors; (3) complex hydrodynamics; (4) the need for high velocities, which lead to higher levels of attrition, and the separation of the char and the sand from the vapors with a “cyclone”; (5) the need for careful control of the closely integrated combustion and for large-scale heat transfer to the bed; and (6) char and sand attrition. Table 11 shows the yields of bio-oil reported in the literature for different feedstocks. Bio-oil yields between 54 and 71 wt % have been reported.

A similar technology that uses catalysts instead of inert sand is being developed by Inaeris Technologies (formerly KIOR) (<http://www.inaeristech.com/>), a company located in Houston,

Table 9. Pyrolysis of Softwood Species Using Fluidized Bed Reactors

biomass species	capacity	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
pine wood chips and pellets	1 kg/h	530	10	59	28	157
pitch pine (debarked, dp < 5 mm)	noncont. feed	500	16	64	21	158
pine sawdust	1 kg/h	525		67–71		153
Douglas fir	220 g/h	500		52		159
Douglas fir	3–5 kg/h	480	12	64	24	160
spruce	300 g/h	465–470	14	61	27	161
Japanese cedar (debarked, dp < 0.5 mm)	noncont. feed	500	13	66	22	158
pine sawdust	1 kg/h	525		67–71		153
spruce sawdust	100 g/h	500	12	78	8	146

Table 10. Pyrolysis of Hardwood Species Using Fluidized Bed Reactors

biomass species	capacity	T (°C)	yields (wt %)			ref(s)
			char	bio-oil	gas	
red oak	6 kg/h	400	21	67	13	162
red oak	6 kg/h	500	19	63	18	162
red oak	1.5 kg/h	450–500	25	62	13	163
<i>Eucalyptus grandis</i>	700 g/h	500		69		164
<i>Eucalyptus grandis</i>	0.1 kg/h	500		69		127
<i>Eucalyptus grandis</i> woodchips	1 kg/h	500		62		127
eucalyptus (debarked)	0.85 kg/h	500		62		165
<i>Eucalyptus loxophleba</i> wood	0.15 kg/h	500	14	61	25	158
<i>Eucalyptus loxophleba</i> wood	2 kg/h	500	14	62	12	49
eucalyptus wood	1 kg/h	450	17	64		166
<i>Eucalyptus grandis</i> woodchips	1 kg/h	500	18	59	23	167
<i>Eucalyptus loxophleba</i> wood	0.1 kg/h	450	14	71	14	168
beech	1 kg/h	510	13	72	9	169
beech	1 kg/h	512	13	67	12	154
beech	300 g/h	465–470	10	70	23	161
beech	1 kg/h	500	10	71	15	50, 62
poplar sawdust	100 g/h	504	12	77	11	146

TX, USA. The company uses a proprietary catalyst system to produce a deoxygenated bio-oil in a fluid catalytic cracking (FCC) reactor. Metso, UPM, and Fortum constructed and since 2013 have operated a 400 kg/h circulating bed pyrolysis reactor coupled with a condensation system in Joensuu, Finland. The bio-oil produced is combusted in a fluidized bed power boiler.¹⁶ CPERI (Thermi, Greece), Guangzhou Institute of Energy Conversion (Guangzhou, China), the Universities of Birmingham and Nottingham in the U.K., and VTT (Espoo, Finland) have active research programs on this technology.¹⁶

The *rotating cone* technology was developed by the University of Twente and is commercialized by Biomass Technology Group—Biomass to Liquid (BTG-BTL) (Enschede, The Netherlands) (<http://www.btgworld.com/en/>).¹⁶ The hot sand and biomass are transported up in a conical bed by the centrifugal force created by rotation of the cone.¹⁶ The centrifugal force effectively develops a transported bed without the need for large volumes of carrier gas.¹⁶ This process has been successfully applied in Malaysia for the conversion of empty fruit

Table 11. Pyrolysis of Biomass Using Circulating Fluidized Bed Reactors

biomass species	capacity (kg/h)	T (°C)	bio-oil yield (wt %)	ref
timothy	20	520	54	153
rapeseed straw	20	520	60	153
pine saw dust	20	520	74	153
green forest residue (86% spruce, 9% pine, 5% birch)	20	520	64	153
brown forest residue (80% spruce, 10% pine, 10% birch)	20	520	58	153
eucalyptus chips	20	520	71	153

bunches from palm oil trees in a demonstration plant with a 50 ton/day capacity.¹⁶³ This technology has been also used by Empyro for the construction of a plant that has operated since 2015 in Hengelo, The Netherlands. This plant converts 5 tons of wood residues per hour into pyrolysis oil, process steam, and electricity. In both plants, gas and char are burned to heat the sand, which is recycled back to the pyrolysis reactor.¹⁶

The *ablative pyrolysis* process entails a heated surface on which wood is pressed and moved rapidly, leaving an oily film that then evaporates.¹⁶ Larger particles of wood can be used for this process, and the limiting factor is typically the rate of heat supplied to the reactor. These reactors can process large amounts of biomass in a little volume, are compact, and do not require carrier gases or recirculation.^{70,71} The rate of reaction is proportional to the force exerted on the biomass in contact with the wall and the available heat transfer surface.¹⁶ An important feature of ablative heat transfer is that when the biomass contacts the hot solid, ablation occurs and subsequently exposes new fresh biomass to the hot surface. In theory, this allows for no limitations on particle size. The U.S. National Renewable Energy Laboratory (Golden, CO, USA) and CNRS laboratories (France) conducted most of the pioneering studies on ablative reactors.¹⁶ In the 1990s, BBC from Canada built and operated an ablative reactor with a capacity between 10 and 25 kg/h¹³⁴ (this company is not in operation today). The University of Hamburg built three plants using ablative reactors. The first plant was conceived for research and has a capacity of 20 kg/h; the second one is a 250 kg/h pilot plant, and the third is a demonstration unit with capacity of 2 ton/h.^{16,134} Reed and Cowdery constructed an ablative pyrolysis reactor testing bone dry wood at a feeding rate of 0.2 kg/h.¹⁴ The biomass-to-oil (BTO) process was developed by PYTEC (Hamburg, Germany). The process is based on the ablative pyrolysis principle. Biomass wood (including chips with dimensions of 60 mm × 40 mm × 5 mm) is put into

Table 12. Results on Biomass Fast Pyrolysis Using Ablative Pyrolysis Reactors

biomass species	capacity	T (°C)	yields (wt %)			
			char	bio-oil	gas	ref
barley or wheat straw	10 kg/h	549	32	50	12	174
wheat straw	lab-scale pyrolysis centrifuge reactor	525	23–32	40–47	27–30	175
wood	250 kg/h	650	6	60	34	172

direct contact with a rotating hot metal surface that melts the wood and produces oil.¹⁷¹ The crude bio-oil produced is combusted in a CHP unit running on a 300 MW_e diesel engine.¹⁷¹ Compared with fluidized beds, the main advantages of ablative reactors are (1) no need for biomass milling efforts, (2) compact design because of ideal heat transfer with high heating rates at relatively small contact surfaces, (3) energy and cost efficiency because no heating and cooling of the fluidized bed is required, and (4) the ability to use condensation units with small volume, requiring less space and lower cost.¹⁷² The main downsides are that these reactors require a heated surface area control system and operate with moving parts at high temperatures, which increases their complexity and induces inevitable wear and tear on the moving components.¹⁷³ Table 12 reports the yields obtained in ablative reactors using wood and wheat straw. The yields of char, oil, and gases are comparable to those obtained with similar feedstocks using fluidized bed reactors. Aston University (Birmingham, UK), the Institute of Engineering Thermophysics (Kyiv, Ukraine), the Latvian State Institute of Wood Chemistry (Riga, Latvia) and the Technical University of Denmark have active programs on this technology.^{16,42}

The viability of the *spouted fluid bed reactor* technology for pyrolysis was studied by the Chemical Engineering Department of the University of the Basque Country (San Sebastian, Spain). A pilot plant at the Ikerlan-IK4 facility with the capacity to process up to 25 kg of biomass per hour is now operational.^{16,176} The yields of products shown in Table 13 are

Table 13. Biomass Pyrolysis Results Using a Conical Spouted Bed Reactor

biomass species	capacity	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
rice husk	60 g/h	450	26	70	4	177
50% <i>Cytisus multiflorus</i> and 50% <i>Spartium junceum</i>	200 g/h	500	17	80	4	178
<i>Pterospartum tridentatum</i>	200 g/h	500	20	75	5	178
miscanthus	lab scale	500	38	40	20	179
pine saw dust	200 g/h	500	17	75	8	180
pine saw dust	5 kg/h	480	14	73	13	181
<i>Acacia dealbata</i> (silver wattle)	200 g/h	500	23	72	5	178
eucalyptus	200 g/h	500	18	75	6	182

comparable to and even higher than those reported for fluidized bed reactors for similar feedstocks. The Anhui University of Science & Technology is also developing this technology.¹⁶

8. MICROWAVE PYROLYSIS

There are excellent reviews on microwave pyrolysis.^{44,45,183,184} Von Hippel developed the basic understanding of macroscopic microwave–matter interactions.⁴⁴ Microwave wavelengths fall between the infrared and radio regions (from 0.3 to 300 GHz).^{44,45} Heating is due to molecular friction during

rotation of dipolar molecules induced by the electromagnetic radiation. Conversely to conventional heating, microwave heating is a volumetric heating technique, so an opposite temperature gradient is established.⁴⁴ Tech-En Ltd. (Hainault, UK) developed microwave pyrolysis in the mid-1990s.^{183,185,186} In this process, the feedstock is thoroughly mixed with a highly microwave-adsorbent material (often char), which absorbs enough microwave energy (typically at 915 MHz or 2.45 GHz).¹⁸³ Although microwave penetration is typically 1–2 cm, the penetration depth varies depending on the properties of the materials and the radiation frequency (oil palm fiber, 10.2 cm at 5.8 GHz; oil palm shell, 5.5 cm at 5.8 GHz; biochar, 8.5 cm at 5.8 GHz; paper and cardboard, 20–60 cm at 2.54 GHz; wood, 8–350 cm at 2.54 GHz).⁴⁴ While microwave heating favors solid-phase reactions (or heterogeneous reactions), conventional heating has a stronger effect on gas-phase reactions.⁴⁴ Table 14 shows product yields obtained with these reactors.

The main advantages of microwave pyrolysis compared with conventional technologies are that (1) it provides rapid heating;¹⁸³ (2) it is much cleaner and easier to control;¹⁹³ (3) it can be easily modularized for small applications (these processes can be developed for on-site processing, reducing transportation cost); (4) heat is generated within the material (the particles are heated from the center), allowing the surface of the reactor to operate at lower temperatures; (5) high energy-to-heat conversion efficiencies (80–85%) are obtained; and (6) higher power densities are used.¹⁸³ The main challenges and barriers for microwave pyrolysis are that (1) limited information is available on the microwave-relevant properties of waste materials;¹⁸³ (2) uneven heating can lead to poor product quality control; (3) electricity is expensive and often produced from fossil fuels by Rankine cycles (with efficiencies typically between 20 and 30%); (4) electrical hazards exist, requiring containment with an appropriate Faraday cage; (5) the presence of metals may generate arcing that could damage the equipment; and (6) microwave heating systems are more expensive than traditional heating systems.¹⁸³

Some of the institutions with active programs in microwave pyrolysis are the Chinese Academy of Sciences, the National Institute of Advanced Industrial Science and Technology of Japan, Shandong University (Jinan, China), the Technical University of Vienna (Vienna, Austria), the Universiti Malaysia Sarawak (Sarawak, Malaysia), the University of Minnesota (Minneapolis, MN, USA), Washington State University Tri-Cities (Richland, WA, USA), the University of Mississippi (Oxford, MS, USA), the University of Nottingham (Nottingham, UK), the University of York (York, UK), and the Ecole Polytechnique de Montreal (Montreal, QC, Canada).^{16,42}

9. DESIGN AND SCALE-UP OF PYROLYSIS UNITS

Business Models. There are very few reports with information on the development of business models, technical design, and techno-economic evaluation of pyrolysis units.^{47,200,201} The technical design of the pyrolysis unit will depend on the business model selected.²⁰¹ The International Biochar Initiative

Table 14. Results of Biomass Microwave Pyrolysis

biomass species	reactor	T (°C)	yields (wt %)			ref
			char	bio-oil	gas	
wheat straw	mass: 5–30 g; N ₂ : 3 L/min; power: 3 kW at 2.45 GHz	400–600			17–22	187
larch (<i>Larix leptolepis</i> GORDON) cylindrical blocks (diameter: 60–300 mm; weight: 80–12000 g)	power: 1.5–3 kW at 2.45 GHz; exposure time: 3–12.5 min		18–50	15–30		188
microalgae (<i>Chlorella vulgaris</i>), particle size <200 μm	mass: 30 g; power: 0.75–2.25 kW at 2.45 GHz; N ₂ : 300 mL/min; catalysts: activated carbon, CaO, SiC	200	90	0	10	189
		600	30	36	34	
		775	25	22	52	
Douglas fir sawdust pellets (diameter: 6 mm; length: 10 mm)	mass: 400 g; power: 0.7 kW; reaction time: 10–20 min	350–450	31–61	31–54	8–15	190
sewage sludge	mass: 100 g, 25 g of graphite (1 mm × 1 mm) as microwave absorber; N ₂ : 100 mL/min; power: 0.4–0.6 kW at 2.45 GHz	490–570	39–40	48–50	11–12	191
rice straw	mass: 3–5 g; N ₂ : 50 mL/min; power: 0.2–0.5 kW	280–500			<70	192
oil palm fiber (OPF) (0.3–0.6 mm) and oil palm shell (OPS) (0.001 to 0.1 m)	sample:microwave absorber ratio: 1:0.25, 1:0.5, 1:1; power: 0.45 kW at 2.45 GHz; exposure time: 25 min	400–1300	OPS: 45–70 OPF: 50–80	OPS: 10–20 OPF: 5–25	OPS: 20–30 OPF: 10–28	193
microalgae (<i>Chlorella</i> sp.)	mass: 30 g, 6 g of char as microwave absorber; N ₂ : 500 mL/min; power: 0.5–1.25 kW at 2.45 GHz; exposure time: 20 min	460–630	25–28	oil: 18–28 water: 20–22	24–35	194
sewage sludge	mass: 3.5 kg; N ₂ : 5–20 L/min; power: 6.4–8.0 kW at 2.45 GHz; exposure time: 120 min	350–500		30.4% of organic fraction		195
rice straw (0.425–0.850 mm)	mass: 3–5 g; N ₂ : 50 mL/min; power: 0.2–0.5 kW	400	28	23	49	196
OPS (<0.850 mm)	mass: 150 g; sample:microwave absorber ratio: 1:0.25, 1:0.5, 1:1; power 0.45 kW at 2.45 GHz; exposure time: 25 min	450–925	40–65	10–17	25–47	197
corn stover	mass: 50 g; power: 0.3–0.9 kW at 2.45 GHz			30 (0.9 kW)	47 (0.9 kW)	198
rice husk (RH) (0.149–0.297 mm, 0.149–0.074 mm, and <0.074 mm) and sugar cane residue (SCR)	mass: 7–10 g; power: 0.15–0.4 kW at 2.45 GHz; exposure time: 4–30 min	280–600	RH: 33–50 SCR: 25–67			199

Table 15. Summary of the Technology Status of Pyrolysis Reactors

type of reactor	companies/institutions	technology status	remarks	refs
earth kiln, traditional methods	Kilns Using Trunks of Cordwood or Logs families for household income, farmers, communities	commercial	widely used in developing nations	41, 215
cinder block, brick, and metal kilns (Brazilian, Brazilian beehive, half-orange, TPI, New Hampshire, Connecticut, and Missouri kilns)	families for household income, farmers, communities, multiple small companies	commercial	widely used in developing nations	41, 87
small metal kilns and retorts	Applied Gaia Corporation (US), Carbon Compost Co. Ltd. (UK), Pressvess (UK), CarbonZero, (Switzerland), Ithaka Institut (Switzerland)	commercial	multiple designs, some can include liquid recovery	http://appliedgaia.com http://www.pressvess.co.uk http://www.carbonzero.ch http://www.ithaka-institut.org/en/kon-tiki
Adam retort	Adam + Partner (Ethiopia)	commercial	no operating units	107, 108
wagon retorts	O.E.T. Calusco (Imperatori Trattamento Biomass), Alterna Bio-carbon	commercial		4, 5, 41, 43
Reichert converter	Evonik (formerly Degussa) (Germany)	commercial		5, 216
French SIFIC process (CISR Lambiotte retort)	Lambiotte (France), Balt Carbon (Latvia)	commercial		http://www.lambiotte.com , 41, 43
Lurgi carbonization retort (Lurgi Umwelt GmbH)	Simcoa (Australia), Lurgi LR (Germany)	commercial		http://www.simcoa.com.au , 43, 16
twin-type retorts	Charbon Engineering (Carbon-Twin) (The Netherlands), Clean Fuels (The Netherlands), VMR Systems (The Netherlands), CG2000 Carboniser Ibero Massa Florestal (Portugal)	commercial	some designs can include liquid recovery	http://www.charbon-engineering.eu , http://www.cleanfuels.nl , http://www.vmrsystems.com , http://www.imflorestal.com , 41, 43, 111, 217
flash carbonization	University of Hawai'i	pilot plant		6, 43
Herreshoff multiple hearth furnaces	Pyrocal Pty Ltd. (BigChar) (Australia), CSE Hankin Environmental Systems (USA)	commercial		http://www.bigchar.com.au , http://hankines.com , 41, 117
autogenous pyrolysis reactor	CSIRO (Australia)	pilot plant		218
auger reactors	BioGreen Spirajoule (France), Genesis Industries (USA), Bio-MaCon GmbH (Germany), Karr Group (USA), Polvax (Ukraine), Pro-Natura (France)	commercial	multiple designs and companies offering auger reactors	http://www.biogreen-energy.com , http://egenindustries.com , http://www.biomacon.com , http://karrgroupco.com , http://www.pyrolys.net , http://www.pronatura.org/?page_id=521&lang=en , 41
	Biolog, Karlsruhe Institute für Technologie (Germany), Energy Farmers (Australia), ABRITech (Canada), Renewable Oil International LLC (USA)	demonstration		http://www.energyfarmers.com.au , http://www.abritechinc.com , http://demoplants2.bioenergy2020.eu/projects/displaymap/twHWWt , www.renewableoil.com , 219, 16
indirectly heated rotary kilns	Thermo-catalytic reforming (Fraunhofer UMSICHT and Susteen Technologies, Germany), Alternative Energy Solutions Ltd. (New Zealand), Renewable Oil Int. (USA)	pilot plant		http://www.susteen-tech.com , 16, 220
	Anatron Energy (USA), Mitsubishi Heavy Industries (Japan), Anzac Energy Ltd. (Australia), 3R Environmental Technology Group (Hungary), Mitsui R21 ITC (USA)	commercial	multiple plants for waste treatment (MSW, sludge) are adaptable to biomass pyrolysis	http://www.amaronenergy.com , http://www.mhic.co.jp/en/products/water/sludge/contents/sludge_carbonization_facility.html , 220
moving agitated bed	University of Perugia (Italy)	pilot plant		221
shelf reactors	Pyrovac	demonstration		132, 133
paddle pyrolysis kiln	BEST	commercial	no operating units	4, 46
ablative pyrolysis	Pytec (Germany)	demonstration		BEST Web site not working
rotating cone	BTG-BTL (The Netherlands)	demonstration	Web site is not working	16
		commercial		http://www.empyproject.eu , http://www.bigworld.com/en/ , 16

Table 15. continued

type of reactor	companies/institutions	technology status	remarks	refs
bubbling fluidized bed reactors	East Pyrolysis Using Fine Particles (Catalytic and Noncatalytic Processes) Anellotech (USA), Valmet-Fortum (Finland), Agritherm (Canada), RTI (USA), Avello Bioenergy (USA), Bioware (Brazil), Biomass Engineering Ltd. (BEL), Netteenergy BV (The Netherlands)	commercial/ demonstration	static/mobile	http://anellotech.com , http://www.fortum.com , http://agri-therm.com , http://www.rti.org/energy , http://www.avellobioenergy.com , https://www.bioware.com.br , http://www.nettenenergy.com/index.php/en/ , 16, 42
circulating bed reactors	Rapid Thermal Processing: Ensyn (USA), Emergent Technologies (USA), Metso (Finland), Inaeris Technologies (formerly KIOR) (USA)	commercial/ demonstration		http://www.ensyn.com , https://www.emergenttech.com , http://www.inaeristech.com/ , 147, 16
spouted bed	Ikerlan (Spain)	pilot plant		16, 176
microwave pyrolysis	Carbonescape (New Zealand), Beijing Sino-Green Technology Co., Ltd. (China), Bioenergy 2020+ GmbH (Austria)	Microwave Pyrolysis pilot plant		http://carbonescape.com , 184, 16

(IBI) (<http://www.biochar-international.org/commercialization>) has identified a number of business models for biochar production, including the characteristics of the feedstock, sustainability issues, associated production technology, potential coproducts, and economic and social challenges. The main business models discussed by the IBI and the associated technologies are (1) restoration site (e.g., forest, wetland) (mobile pyrolysis, charring piles in situ), (2) managed forest (mobile pyrolysis, hog fuel for cogeneration, feedstock for pellets and briquettes), (3) forest product processing waste (cogeneration, pyrolysis, or gasification, feedstock for pellet or briquettes), (4) biomass plantation (cogeneration, pyrolysis, or gasification, feedstock for pellets or briquettes), (5) urban forestry and landscaping (biochar, process heat, electricity, home heat), (6) agricultural waste–industrial (mobile pyrolysis, cogeneration, pyrolysis, or gasification), (7) agricultural waste subsistence (stoves, kilns, feedstock for briquettes), and (8) municipal solid waste (MSW) (cogeneration, pyrolysis, or gasification).²⁰¹

Reactor Sizing. Although companies designing and building pyrolysis reactors may have developed scale-up criteria and methodologies for sizing these systems, we were not able to find systematic methodologies for the design of pyrolysis reactors in the open literature. Therefore, the design of pyrolysis reactors is still an art. For this reason, in this section we will briefly present a strategy based on our own experience. The design of pyrolysis reactors can be conducted following these steps: (1) Select the throughput capacity. (2) Determine the biomass particle size to be used. (3) In the case of fluidized bed reactors, select the appropriate sand:biomass particle size ratio. (4) Select and quantify the carrier gas to be used (for fluidized bed reactors 2.75 kg of carrier gas/kg of dry biomass is recommended²⁰²). (5) Specify the reaction temperature (typically 500 °C in the case of fast pyrolysis) and conduct pyrolysis tests at lab or pilot facilities. (6) Conduct a mass balance with the yields of products obtained experimentally (see the information in Tables 5, 6, 7, 8, and 10). (7) Conduct energy balances to calculate how much heat has to be removed or supplied to the reactor. Thermodynamic information for the overall energy balance of pyrolysis reactors can be found elsewhere.^{203–206} (8) Calculate the residence time of the biomass particle to achieve the targeted conversion. Information on experimental and modeling strategies (single-particle models) to calculate conversion as a function of residence time can be found elsewhere.^{72,75,207–209} (9) Calculate the solid holdup in the reactor. The residence time of the solid in the reactor depends on the hydrodynamic and mechanical design of these reactors. In the case of rotary drums, it depends on the slope of the reactor, the kiln rotational speed, and the length and diameter of the reactor.²¹⁰ For fluidized beds, the retention of the solid is controlled by the terminal velocity of the converted biomass particle in the free board.²¹¹ (10) In the case of fluidized bed reactors, calculate or determine experimentally the minimum fluidization velocity (typically use 2–3 times the minimum fluidization velocity).^{211,212} (11) Calculate the cross-sectional area and diameter of the reactor.²¹¹ (12) In the case of fluidized bed reactors, calculate the volume of the expanded fluidized bed (sand and char particles).^{211,213} (13) If designing a fluidized bed reactor, calculate the length and the of the free board.²¹¹ (14) Select the heating or cooling method to be used (e.g., indirect, direct, or microwave heating) and calculate the heat transfer area needed to supply or remove the heat calculated in the

energy balances.²¹¹ (15) In the case of fluidized bed reactors, determine the size of the distribution grate.²¹¹

10. CHALLENGES FOR THE IMPLEMENTATION OF PYROLYSIS

The development of pyrolysis technologies must overcome two major hurdles: the lack of markets for pyrolysis oils and the lack of biochar-derived products with well-defined performance characteristics. Consequently, it is imperative to accelerate the development and deployment of bio-oil refineries and the development and commercialization of engineered biochar for environmental services. Developing flexible designs for pyrolysis units to produce high yields of both bio-oil and char is a technological challenge facing the thermochemical community.

The selection of pyrolysis technologies, their operational conditions, and the feedstocks to be used will depend mostly on economic trade-offs.²¹⁴ The results presented in this review clearly show that there are multiple operational conditions and designs to obtain a wide range of product yields. Most of the fast pyrolysis reactors reviewed are operated under conditions (500 °C, small particles (<2 mm), use of a heat carrier (sand), and vapor residence times of <2 s (use of a carrier gas)) that maximize the bio-oil yield with little regard for the quality of the product. The use of high volumes of carrier gas and the heat carrier reduces the energy efficiency of these processes, creates important sand attrition problems, and makes it very difficult to condense the diluted vapors, requiring very large surface areas and considerable cooling power. Most fast pyrolysis designs combust the char to satisfy the energy needs of the process. The difficulty of refining fast pyrolysis oils with high oxygen content is the main reason for the growing interest in catalytic pyrolysis for the production of bio-oils with lower oxygen content. The catalytic cracking strategies to reduce bio-oil oxygen content typically result in an increase in gas yield and coke formation. The converters reviewed are flexible enough to operate under conditions where bio-oil and biochar production is possible. More studies are needed to explore designs that take advantage of homogeneous secondary reactions in the gas phase for oxygen removal from pyrolysis oils.

There is a vast diversity of situations in which pyrolysis can be applied (different feedstocks, scales, and capacities as well as the use of mobile or stationary units) and a diversity of products that can be obtained. This makes it very difficult to find an exclusive design that is sustainable across all potential applications. Table 15 is an attempt to summarize the types of reactors suitable for specific cases. A balanced investment in the creation of new knowledge (i.e., science) in the design, testing, and scale-up of new technologies for pyrolysis reactors and rural bio-oil refineries (i.e., technology) and in the development of new products from bio-oil and char (i.e., market) in order to build a shared vision that takes advantage of existing infrastructure and is achievable in small steps is critical for the deployment of a viable biomass-based economy involving pyrolysis technologies.

11. CONCLUSIONS

The number of publications on slow and fast pyrolysis reactors has been growing steadily in the last 30 years. The community interested in these reactors is formed by researchers interested in char production and those interested in bio-oil production. This paper has reviewed slow, intermediate, fast, and

microwave pyrolysis, intending that companies and academic institutions that are researching, designing, and commercializing pyrolysis/carbonization reactors can take advantage of the technological solutions shown. Very little progress has been made in the last century in the design of *kilns*. The release of large quantities of pyrolysis vapors to the atmosphere and/or their condensation in soils are major sources of pollution that need to be urgently addressed. Several of the *retorts* used today were developed and commercialized by the “wood distillation industry”. These units were designed for the carbonization of logs. However, deforestation issues and the limited availability of logs for carbonization are major hurdles for their widespread deployment in today’s world. *Converters* are receiving growing attention for their capacity to convert forest and agricultural residues in the form of chips and shredded materials into bio-oil and charcoal. These systems do not require the use of large volumes of carrier gas or a heat carrier (sand). Nevertheless, the lack of commercial interest in fine chars produced by these systems has been a major hurdle for the commercialization of this technology. The growing interest in using char for soil amendment and the development of technologies for the production of char pellets and briquettes from these fines are catalyzing new companies that are commercializing these designs. The current design and operation of *fast pyrolysis reactors* are based on conditions maximizing the bio-oil yield with little regard for the quality of the bio-oil produced. High bio-oil yield is achieved at 500 °C using small particles (<1 mm), a heat carrier (sand), and high volumes of carrier gas to reduce the residence time of vapors to less than 2 s. The energy need of these reactors is typically satisfied by char combustion. Consequently, most of these processes do not commercialize char as one of their products. The lack of commercial bio-oil refineries is the main barrier for the commercialization of these reactors. Problems with refining of fast pyrolysis oil are catalyzing interest in strategies to produce oils with lower oxygen content. Most of these strategies result in high gas yields, which is an opportunity to explore the use of the gases to supply part of the energy needed for the system without sacrificing char production. Microwave pyrolysis is a promising technology for the development of small convenient systems for waste management.

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■ REFERENCES

(1) Withrow, J. The Chemical Engineering of the Hardwood Distillation Industry. *J. Ind. Eng. Chem.* **1915**, 7 (II), 912.

- (2) Brown, N. C. *The Hardwood Distillation Industry in New York*; The New York State College of Forestry at Syracuse University: Syracuse, NY, 1917.
- (3) Bunbury, H. M. *The Destructive Distillation of Wood*; Benn Brothers: London, 1923.
- (4) Klar, M.; Rule, A. *The Technology of Wood Distillation*; Chapman & Hall: London, 1925.
- (5) Emrich, W. *Handbook of Charcoal Making: The Traditional and Industrial Methods*; D. Reidel: Dordrecht, The Netherlands, 1985.
- (6) Antal, M. J.; Gronli, M. The Art, Science, and Technology of Charcoal Production. *Ind. Eng. Chem. Res.* **2003**, *42*, 1619–1640.
- (7) Antal, M. J., Jr.; Mochidzuki, K.; Paredes, L. S. Flash Carbonization of Biomass. *Ind. Eng. Chem. Res.* **2003**, *42* (16), 3690–3699.
- (8) Veitch, F. P. *Chemical Methods for Utilizing Wood, Including Destructive Distillation, Recovery of Turpentine, Rosin, and Pulp, and the Preparation of Alcohols and Oxalic Acid*; USDA: Washington, DC, 1907.
- (9) Canham, H. O. The Wood Chemical Industry in the Northeast: An Old Industry with New Possibilities. *Northern Woodlands*, Feb 8, 2010. <http://www.faqs.org/photo-dict/phrase/10393/kilns.html> (accessed March 2, 2017).
- (10) Massengale, R. *Black Gold: A History of Charcoal in Missouri*; Author House: Bloomington, IN, 2006.
- (11) Scott, D. S.; Piskorz, J. The Continuous Flash Pyrolysis of Biomass. *Can. J. Chem. Eng.* **1984**, *62* (3), 404–412.
- (12) Scott, D. S.; Piskorz, J.; Radlein, D. Liquid products from the continuous flash pyrolysis of biomass. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 581–588.
- (13) Bridgwater, A. V.; Czernik, S.; Piskorz, J. The Status of Biomass Fast Pyrolysis. In *Fast Pyrolysis of Biomass: A Handbook*; Bridgwater, A. V., Ed.; CPL Press: Newbury, U.K., 2002; Vol. 2, pp 1–22.
- (14) Bridgwater, A. V.; Peacocke, G. V. C. Fast Pyrolysis Processes for Biomass. *Renewable Sustainable Energy Rev.* **2000**, *4*, 1–73.
- (15) Czernik, S.; Bridgwater, A. V. Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy Fuels* **2004**, *18* (2), 590–598.
- (16) Bridgwater, A. V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94.
- (17) Diebold, J. P.; Bridgwater, A. V. Overview of Fast Pyrolysis of Biomass for the Production of Liquid Fuels. In *Fast Pyrolysis of Biomass: A Handbook*; Bridgwater, A. V., Ed.; CPL Press: Newbury, U.K., 1999; pp 14–32.
- (18) Kersten, S. R. A.; Wang, X.; Prins, W.; van Swaaij, W. P. M. Biomass pyrolysis in a fluidized bed reactor. Part I: literature review and model simulations. *Ind. Eng. Chem. Res.* **2005**, *44*, 8773–85.
- (19) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. Pyrolysis of Wood/Biomass: A Critical Review. *Energy Fuels* **2006**, *20* (3), 848–889.
- (20) Elliott, D. C. Historical developments in hydroprocessing bio-oils. *Energy Fuels* **2007**, *21*, 1792–1815.
- (21) Elliott, D. Advancement of Bio-oil Utilization for Refinery Feedstock. Presented at the Washington Bioenergy Research Symposium, Seattle, WA, Nov 8, 2010; [http://www.pacificbiomass.org/documents/Elliott%20\(C1\).pdf](http://www.pacificbiomass.org/documents/Elliott%20(C1).pdf) (accessed March 2, 2017).
- (22) Kumar, S.; Lange, J.-P.; Van Rossum, G.; Kersten, S. R. A. Bio-oil fractionation by temperature-swing extraction: Principle and Application. *Biomass Bioenergy* **2015**, *83*, 96–104.
- (23) Ijmker, H. M.; Gramblicka, M.; Kersten, S. R. A.; van der Ham, A. G. J.; Schuur, B. Acetic Acid extraction from aqueous solutions using fatty acids. *Sep. Purif. Technol.* **2014**, *125*, 256–263.
- (24) Li, X.; Luque-Moreno, L. C.; Oudenhoven, S. R. C.; Rehmann, L.; Kersten, S. R. A.; Schuur, B. Aromatics extraction from pyrolytic sugars using ionic liquid to enhance sugar fermentability. *Bioresour. Technol.* **2016**, *216*, 12–18.
- (25) Li, X.; Kersten, S. R. A.; Schuur, B. Extraction of acetic acid, glycoaldehyde and acetol from aqueous solutions mimicking pyrolysis oil cuts using ionic liquid. *Sep. Purif. Technol.* **2017**, *175*, 498–505.
- (26) van Dam, J. *The Charcoal Transition: Greening the Charcoal Value Chain To Mitigate Climate Change and Improve Local Livelihoods*; Food and Agriculture Organization of the United Nations: Rome, 2017; <http://www.fao.org/3/a-i6935e.pdf> (accessed March 2, 2017).
- (27) Stassen, H. E.: Current Issues in Charcoal Production and Use. In *Biomass Power for the World*; van Swaaij, W. P. M., Kersten, S. R. A., Palz, W., Eds.; CRC Press: Boca Raton, FL, 2015; Chapter 14.
- (28) Mangué, P. D. Review of the existing studies related to fuelwood and/or charcoal in Mozambique, Project GCP/INT/679/EC, EC-FAO Partnership Programme, 2000.
- (29) Kammen, D. M.; Lew, D. J. *Review of Technologies for the Production and Use of Charcoal*; Renewable & Appropriate Energy Laboratory: Berkeley, CA, 2005.
- (30) Seidel, A. *Charcoal in Africa: Importance, Problems and Possible Solution Strategies*; Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH: Eschborn, Germany, 2008.
- (31) *Simple Technologies for Charcoal Making*; FAO Forestry Paper 41; Food and Agriculture Organization of the United Nations: Rome, 1983; <http://www.fao.org/docrep/X5328e/X5328e00.htm> (accessed March 2, 2017).
- (32) Food and Agriculture Organization of the United Nations. FAOSTAT, Forestry Production and Trade. <http://www.fao.org/faostat/en/#data/FO> (accessed Feb 17, 2017).
- (33) Chidumayo, E. N.; Gumbo, D. J. The environmental impacts of charcoal production in tropical ecosystems of the world: A synthesis. *Energy Sustainable Dev.* **2013**, *17* (2), 86–94.
- (34) Bailis, R.; Rujanavech, C.; Dwivedi, P.; de Oliveira Vilela, A.; Chang, H.; Carneiro de Miranda, R. Innovation in charcoal production: A comparative life-cycle assessment of two kiln technologies in Brazil. *Energy Sustainable Dev.* **2013**, *17* (2), 189–200.
- (35) Kituyi, E. Towards sustainable production and use of charcoal in Kenya: exploring the potential in life cycle management approach. *J. Cleaner Prod.* **2004**, *12*, 1047–1057.
- (36) Norgate, T.; Langberg, D. Environmental and Economic Aspects of Charcoal Use in Steelmaking. *ISIJ Int.* **2009**, *49* (4), 587–595.
- (37) Amonette, J. Biochar and Bioenergy: What Can They Do To Help Mitigate Climate Change. Presented at the Washington Bioenergy Research Symposium, Seattle, WA, Nov 8, 2010; [http://www.pacificbiomass.org/documents/Amonette%20\(C1\).pdf](http://www.pacificbiomass.org/documents/Amonette%20(C1).pdf) (accessed March 2, 2017).
- (38) Lehmann, J.; Joseph, S. Biochar for Environmental Management: An Introduction. In *Biochar for Environmental Management: Science and Technology*; Lehmann, J., Joseph, S., Eds.; Earthscan Publishers: London, 2009.
- (39) Woolf, D.; Amonette, J. E.; Street-Perrott, F. A.; Lehmann, J.; Joseph, S. Sustainable biochar to mitigate global change. *Nat. Commun.* **2010**, *1*, 56.
- (40) Ogawa, M.; Okimori, Y. Pioneering works in biochar research, Japan. *Aust. J. Soil Res.* **2010**, *48*, 489–500.
- (41) Siemons, R. *Industrial Charcoal Production*; FAO Project TCP/CRO/3101 (A) Development of a Sustainable Charcoal Industry; North-West Croatia Regional Energy Agency: Zagreb, Croatia, 2008.
- (42) Meier, D.; van de Beld, B.; Bridgwater, A. V.; Elliott, D.; Oasmaa, A.; Preto, F. State of the art of fast pyrolysis in IEA bioenergy member countries. *Renewable Sustainable Energy Rev.* **2013**, *20*, 619–641.
- (43) Gronli, M. Pyrolysis and Charcoal. <http://www.bioforsk.no/ikbViewer/Content/71499/Biokarbonseminar%20%20C5s%2011-03-2010%20Morten%20Gr%20F8nli.pdf> (accessed Feb 26, 2017).
- (44) Motasemi, F.; Afzal, M. T. A review on the microwave-assisted pyrolysis technique. *Renewable Sustainable Energy Rev.* **2013**, *28*, 317–330.
- (45) Mushtaq, F.; Mat, R.; Ani, F. N. A review on microwave assisted pyrolysis of coal and biomass for fuel production. *Renewable Sustainable Energy Rev.* **2014**, *39*, 555–574.
- (46) Dumesny, P.; Noyer, J. *Wood Products: Distillates and Extracts. Part I. The Chemical Products of Wood Distillation. Part II. Dyeing and Tanning Extracts from Wood*; Scott, Greenwood & Son: London, 1908.
- (47) Lynch, J.; Joseph, S. *Guidelines for the Development and Testing of Pyrolysis Plants To Produce Char*. International Biochar Initiative:

Logan, UT, 2010; http://www.biochar-international.org/sites/default/files/IBI_Pyrolysis_Plant_Guidelines.pdf (accessed Feb 26, 2017).

(48) Wang, X.; Kersten, S. R. A.; Prins, W.; van Swaaij, W. P. M. Biomass Pyrolysis in a Fluidized bed reactor. Part 2: Experimental Validation of Model results. *Ind. Eng. Chem. Res.* **2005**, *44*, 8786–8795.

(49) Shen, J.; Wang, X.-S.; Garcia-Perez, M.; Mourant, D.; Rhodes, M. J.; Li, C.-Z. Effects of particle size on the fast pyrolysis of oil mallee woody biomass. *Fuel* **2009**, *88*, 1810–1817.

(50) Westerhof, R. J. M.; Nygard, H. S.; van Swaaij, W. P. M.; Kersten, S. R. A.; Brilman, D. W. F. Brilman DWF. Effect of Particle Geometry and Microstructure on Fast Pyrolysis of Beech Wood. *Energy Fuels* **2012**, *26* (4), 2274.

(51) Zhou, S.; Garcia-Perez, M.; Pecha, B.; McDonald, A. G.; Westerhof, R. J. M. Effect of particle size on the composition of lignin derived oligomers obtained by the fast pyrolysis of beech wood. *Fuel* **2014**, *125*, 15–19.

(52) Patwardhan, P. R.; Satrio, J.; Brown, R. C.; Shanks, B. H. Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresour. Technol.* **2010**, *101*, 4646–4655.

(53) Mourant, D.; Wang, Z.; He, M.; Wang, X. S.; Garcia-Perez, M.; Ling, K.; Li, C.-Z. Mallee wood fast pyrolysis: Effects of alkali and alkaline earth metallic species on the yield and composition of bio-oil. *Fuel* **2011**, *90*, 2915–2922.

(54) Oasmaa, A.; Sundqvist, T.; Kuoppala, E.; Garcia-Perez, M.; Solantausta, Y.; Lindfors, C.; Paasikallio, V. Controlling Phase Stability of Biomass Fast Pyrolysis Bio-oils. *Energy Fuels* **2015**, *29* (7), 4373–4381.

(55) Hoekstra, E.; Westerhof, R. J. M.; Brilman, W.; Van Swaaij, W. P. M.; Kersten, S. R. A.; Hogendoorn, K. J. A.; Windt, M. Heterogeneous and Homogeneous Reactions of Pyrolysis Vapors from Pine Wood. *AIChE J.* **2012**, *58* (9), 2830–2842.

(56) Hoekstra, E.; Van Swaaij, W. P. M.; Kersten, S. R. A.; Hogendoorn, K. J. A. Fast Pyrolysis in a novel wire-mesh reactor: Decomposition of pine wood and model compounds. *Chem. Eng. J.* **2012**, *187*, 172–184.

(57) Zhou, S.; Garcia-Perez, M.; Pecha, B.; McDonald, A.; Kersten, S. R. A.; Westerhof, R. J. M. Secondary Vapor Phase Reactions of Lignin-Derived Oligomers Obtained by Fast Pyrolysis of Pine Wood. *Energy Fuels* **2013**, *27* (3), 1428–1438.

(58) Mok, S. W.; Antal, M. J.; Szabo, P.; Varhegyi, G.; Zelei, B. Formation of Charcoal from Biomass in a Sealed Reactor. *Ind. Eng. Chem. Res.* **1992**, *31*, 1162–1166.

(59) Garcia-Perez, M.; Chaala, A.; Roy, C. Vacuum pyrolysis of sugarcane bagasse. *J. Anal. Appl. Pyrolysis* **2002**, *65*, 111–136.

(60) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Roy, C. Vacuum pyrolysis of softwood and hardwood biomass. Comparison between product yields and bio-oil properties. *J. Anal. Appl. Pyrolysis* **2007**, *78*, 104–116.

(61) Liaw, S.-S.; Zhou, S.; Wu, H.; Garcia-Perez, M. Garcia-Perez: Effect of Pretreatment Temperature on the Yield and Properties of Bio-Oils obtained from the Auger Pyrolysis of Douglas Fir Wood. *Fuel* **2013**, *103*, 672–682.

(62) Westerhof, R. J. M.; Brilman, D. W. F.; Garcia-Perez, M.; Wang, Z.; Oudenhoven, S. R. G.; Kersten, S. R. A. Kersten SRA. Stepwise fast pyrolysis of pine wood. *Energy Fuels* **2012**, *26* (12), 7263.

(63) Montoya, J.; Pecha, B.; Roman, D.; Janna, F. C.; Garcia-Perez, M. Effect of temperature and heating rate on product distribution from the pyrolysis of sugarcane bagasse in a hot plate reactor. *J. Anal. Appl. Pyrolysis* **2017**, *123*, 347–362.

(64) Wooten, J. B.; Seeman, J. I.; Hajaligol, M. R. 2004. Observation and Characterization of Cellulose Pyrolysis Intermediates by C CPMAS NMR. A New Mechanistic Model¹³. *Energy Fuels* **2004**, *18*, 1.

(65) Westerhof, R. J. M.; Oudenhoven, S. R. G.; Marathe, P. S.; Engelen, M.; Garcia-Perez, M.; Wang, Z.; Kersten, S. R. A. The Interplay between Chemistry and Heat/Mass Transfer during Fast Pyrolysis of Cellulose. *React. Chem. Eng.* **2016**, *1*, 555.

(66) Dauenhauer, P. J.; Colby, J. L.; Balonek, C. M.; Suszynski, W. J.; Schmidt, L. D. Reactive boiling of cellulose for integrated catalysis through an intermediate liquid. *Green Chem.* **2009**, *11*, 1555–1561.

(67) Montoya, J.; Pecha, B.; Janna, F. C.; Garcia-Perez, M. Micro-explosion of liquid intermediates during the fast pyrolysis of sucrose and organosolv lignin. *J. Anal. Appl. Pyrolysis* **2016**, *122*, 106–121.

(68) Pelaez-Samaniego, M. R.; Yadama, V.; Garcia-Perez, M.; Lowell, E.; McDonald, A. G. Effect of temperature during wood torrefaction on the formation of lignin liquid intermediates. *J. Anal. Appl. Pyrolysis* **2014**, *109*, 222–233.

(69) Mamleev, V.; Bourbigot, S.; Le Bras, M.; Yvon, J. The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis: Interdependence of the steps. *J. Anal. Appl. Pyrolysis* **2009**, *84*, 1–17.

(70) Graham, R. G.; Bergougnou, M. A.; Overend, R. P. Fast Pyrolysis of Biomass. *J. Anal. Appl. Pyrolysis* **1984**, *6*, 95–135.

(71) Graham, R. G.; Bergougnou, M. A.; Freel, B. A. The kinetics of vapor phase cellulose fast pyrolysis reactions. *Biomass Bioenergy* **1994**, *7* (1–6), 33–47.

(72) Pyle, D. L.; Zaror, C. A. Heat transfer and kinetics in the low temperature pyrolysis of solids. *Chem. Eng. Sci.* **1984**, *39* (1), 147–158.

(73) Di Blasi, C.; Galgano, A.; Branca, C. Effects of Potassium Hydroxide Impregnation on Wood Pyrolysis. *Energy Fuels* **2009**, *23*, 1045–1054.

(74) Garcia-Perez, M.; Wang, X. S.; Shen, J.; Rhodes, M. J.; Tian, F.; Lee, W.-J.; Wu, H.; Li, C.-Z. Fast Pyrolysis of Oil Mallee Woody Biomass: Effect of Temperature on the Yield and Quality of Pyrolysis Products. *Ind. Eng. Chem. Res.* **2008**, *47*, 1846–1854.

(75) Kersten, S. R. A.; Garcia-Perez, M. Recent developments in fast pyrolysis of lingo-cellulosic materials. *Curr. Opin. Biotechnol.* **2013**, *24*, 414–420.

(76) Coates, R.; Gardner, T. Mobile Pyrolysis Process for Conversion of Biomass into Energy Products. Amaron Energy. Presentation at the 2014 Washington Demonstration. <http://www.pacificbiomass.org/documents/Amaron.pdf> (accessed Feb 26, 2017).

(77) Liaw, S.-S.; Wang, Z.; Ndegwa, P.; Frear, C.; Ha, S.; Li, C.-Z.; et al. Effect of pyrolysis temperature on the yield and properties of bio-oils obtained from the auger pyrolysis of Douglas Fir wood. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 52.

(78) Rousset, P. From biomass to fuel, power and chemicals: Brazilian charcoal-based pig iron. Presented at the Department of Aeronautics and Astronautics, National Cheng Kung University, Taiwan, ROC, Nov 6, 2014. <http://agritrop.cirad.fr/578836/1/taiwan%20nov%202014%20ver2%20OK.pdf> (accessed Feb 26, 2017).

(79) Boateng, A. A.; Garcia-Perez, M.; Masek, O.; Brown, R.; del Campo, B. Biochar Production Technology. In *Biochar for Environmental Management: Science, Technology and Implementation*, 2nd ed.; Lehmann, J., Joseph, S., Eds.; Routledge: New York, 2015; Chapter 4, pp 63–88.

(80) International Biochar Initiative. IBI Biochar Standards. <http://www.biochar-international.org/characterizationstandard> (accessed March 2, 2017).

(81) Oasmaa, A.; Fonts, I.; Pelaez-Samaniego, M. R.; Garcia-Perez, M. E.; Garcia-Perez, M. Pyrolysis Oil Multiphase behavior and Phase Stability: A Review. *Energy Fuels* **2016**, *30*, 6179–6200.

(82) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Roy, C. Characterization of bio-oils in Chemical families. *Biomass Bioenergy* **2007**, *31*, 222–242.

(83) Stankovikj, F.; Garcia-Perez, M. TG-FTIR Method for the Characterization of Bio-oils in Chemical Families. *Energy Fuels* **2017**, *31*, 1689–1701.

(84) Stankovikj, F.; McDonald, A.; Helms, G. L.; Olarte, M. V.; Garcia-Perez, M. Characterization of the Water Soluble Fraction of Biomass Pyrolysis Oils. *Energy Fuels* **2017**, *31*, 1650–1664.

(85) Stankovikj, F.; McDonald, A.; Helms, G. L.; Garcia-Perez, M. Quantification of Bio-oil Functional Groups and Evidence of the Presence of Pyrolytic Humins. *Energy Fuels* **2016**, *30*, 6505–6524.

(86) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Rodrigue, D.; Roy, C. Multiphase Structure of Bio-oils. *Energy Fuels* **2006**, *20* (1), 364–375.

- (87) Lohri, C. R.; Rajabu, H. M.; Sweeney, D. J.; Zurbrugg, C. Char fuel production in developing countries- A review of urban biowaste carbonization. *Renewable Sustainable Energy Rev.* **2016**, *59*, 1514–1530.
- (88) Seboka, Y. Charcoal Production: Opportunities and Barriers for Improving Efficiency and Sustainability. In *Bio-carbon Opportunities in Eastern & Southern Africa: Harnessing Carbon Finance To Promote Sustainable Forestry, Agro-Forestry and Bio-Energy*; United Nations Development Programme: New York, 2009; Chapter 6; <http://www.environmentportal.in/files/Bio-carbon%20in%20Africa.pdf#page=113> (accessed March 2, 2017).
- (89) Schenkel, Y.; Bertaux, P.; Vanwijnsberghe, S.; Carre, J. An evaluation of the mound kiln carbonization technique. *Biomass Bioenergy* **1998**, *14*, 505–516.
- (90) Nahayo, A.; Ekise, I.; Mukarugwiza, A. Comparative Study on Charcoal Yield Produced by Traditional and Improved kilns: A study of Nyaruguru and Nyamagabe Districts in Southern Province of Rwanda. *Energy Environ. Res.* **2012**, *3*, 40–48.
- (91) Menemencioglu, K. Traditional wood charcoal production labour in Turkish forestry (Cankiri sample). *J. Food Agric. Environ.* **2013**, *11* (2), 1136–1142.
- (92) De Oliveira Vilela, A.; Lora, E. S.; Quintero, Q. R.; Vicintin, R. A.; Pacceli da Silva e Souza, T. A new Technology for the combined production of charcoal and electricity through cogeneration. *Biomass Bioenergy* **2014**, *69*, 222–240.
- (93) Toole, A. W.; Lane, P. H.; Arbogast, C.; Smith, W. R.; Peter, R.; Locke, E. G.; Beglinger, E.; Erickson, E. C. O. *Char Production, Marketing, and Use*; Report no. 2213; Forest Products Laboratory: Madison, WI, 1961.
- (94) Pelaez-Samaniego, M. R.; Garcia-Perez, M.; Cortez, L. B.; Rosillo-Calle, F.; Mesa, J. Improvements of Brazilian carbonization industry as part of the creation of a global biomass economy. *Renewable Sustainable Energy Rev.* **2008**, *12*, 1063–1086.
- (95) Brito, J. O. *Princípios de produção e utilização de carvão vegetal de madeira*; Documentos florestais, no. 9; Instituto de Pesquisas e Estudos Florestais: Piracicaba, Brazil, 1990.
- (96) Bustamante-Garcia, V.; Carrillo-Parra, A.; Gonzalez-Rodriguez, H.; Ramirez-Lozano, R. G.; Corral-Rivas, J. J.; Garza-Ocanas, F. Evaluation of a charcoal production process from forest residues of *Quercus sideroxyla* hum, & Bpnpl. In a Brazilian beehive kiln. *Ind. Crops Prod.* **2013**, *42*, 169–174.
- (97) Yronwode, P. From the Hills to the Grills. In *Missouri Resources Magazine*, Spring 2000.
- (98) Lemieux, P. M. *Emissions of Air Toxics from a Simulated Charcoal Kiln Equipped with an Afterburner (Project Summary)*; U.S. Environmental Protection Agency: Washington, DC, 2001.
- (99) Braun, S. Missouri Charcoal-Makers Agree to Clean Their Kilns. *Los Angeles Times*, Aug 14, 1997; <http://articles.latimes.com/1997/aug/14/news/mn-22314> (accessed Jan 27, 2011).
- (100) Campbell, R. R. *A Revolution in the Heartland: Changes in Rural Culture, Family and Communities 1900–2000*; University of Missouri: Columbia, MO, 2004.
- (101) Fink, R. J.; Fink, R. L. *An Assessment of Biomass Feedstock Availability in Missouri*; Final Report, Contract No. SEBSRP-SSEB-2004XX-KLP-001; Southern States Energy Board: Norcross, GA, 2005.
- (102) Sparrevik, M.; Adam, C.; Martinsen, V.; Jubaedah; Cornelissen, G. Emissions of gases and particles from charcoal/biochar production in rural areas using medium-sized traditional and improved “retort” kilns. *Biomass Bioenergy* **2015**, *72*, 65–73.
- (103) Baldwin, H. I. *The New Hampshire Charcoal Kiln*; New Hampshire Forestry and Recreation Commission: Concord, NH, 1958.
- (104) Kiln design. <http://www.web3.cnre.vt.edu/frec/charcoal/documents/kiln-design.pdf> (accessed March 2, 2017).
- (105) Skok, R. A.; Beazley, R. I. *Small Kiln Charcoal Production Possibilities in Minnesota*; Minnesota Forestry Notes, April 15, 1955; School of Forestry, University of Minnesota: St. Paul, MN, 1955.
- (106) Simmons, F. C. Charcoal from portable kilns and fixed installations. *Unasylva* **1963**, *17*, 199–211. <http://www.fao.org/docrep/00950e/00950e07.htm#TopOfPage> (accessed Jan 27, 2011).
- (107) Adam + Partner: Appropriate Technology. <http://www.biocoal.org> (accessed Nov 15, 2010).
- (108) Adam, J. C. Improved and more environmentally friendly charcoal production system using a low cost retort-kiln (Eco-charcoal). *Renewable Energy* **2009**, *34*, 1923–1925.
- (109) Klavina, K.; Klavins, J.; Veidenbergs, I.; Blumberga, D. Charcoal production in a continuous operation retort. Experimental data processing. *Energy Procedia* **2016**, *95*, 208–215.
- (110) Szymkowski, C. J.; Bultitude-Paull, J. M. The Production of High-Quality Silicon Metal at Simcoa. In *Proceedings of INFACON 6, the Sixth International Ferrous Congress, Cape Town, South Africa, March 8–11, 1992*; SAIMM: Johannesburg, South Africa, 1992; Vol. 1, 185–191.
- (111) Reumerman, P. J.; Frederiks, B. Carbon Production with Reduced Emissions. Presented at the 12th European Conference on Biomass for Energy, Industry and Climate Protection, Amsterdam, 2002; [http://www.cleanfuels.nl/Sitepdfs/Charcoal%20Production%20with%20Reduced%20Emissions%20\(per\).pdf](http://www.cleanfuels.nl/Sitepdfs/Charcoal%20Production%20with%20Reduced%20Emissions%20(per).pdf) (accessed March 2, 2017).
- (112) Bates, J. S. *Distillation of Hardwoods in Canada*; Forestry Branch Bulletin no. 74; Canada Department of the Interior: Ottawa, ON, 1922.
- (113) *Industrial Charcoal Making*; FAO Forestry Paper 63; Food and Agriculture Organization of the United Nations: Rome, 1985; <http://www.fao.org/docrep/x5555e/x5555e00.htm#Contents> (accessed March 2, 2017).
- (114) Mura, E.; Debono, O.; Villot, A.; Paviet, F. Pyrolysis of biomass in a semi-industrial scale reactor: Study of the fuel-nitrogen oxidation during combustion of volatiles. *Biomass Bioenergy* **2013**, *59*, 187–194.
- (115) Pakdel, H.; Roy, C. Chemical Characterization of Wood Pyrolysis oils obtained in a Vacuum-Pyrolysis Multiple-Hearth Reactor. *ACS Symp. Ser.* **1988**, *376*, 203–219.
- (116) Lemieux, R.; Roy, C.; de Caumia, B.; Blanchette, D. Preliminary Engineering Data for Scale up of a Biomass vacuum pyrolysis reactor. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1987**, *32* (2), 12–20.
- (117) Malkow, T. Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste Manage.* **2004**, *24*, 53–79.
- (118) Fukushima, M.; Wu, B.; Ibe, H.; Wakai, K.; Sugiyama, E.; Abe, H.; Kitagawa, K.; et al. Study on dechlorination technology for municipal waste plastics containing polyvinyl chloride and polyethylene terephthalate. *J. Mater. Cycles Waste Manage.* **2010**, *12*, 108–122.
- (119) Coates, R. L.; Eddings, E. G.; Coates, B. R. Bio-oil yields from pyrolysis in a novel rotary reactor. Presented at the Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products, Iowa State University, Ames, IA, Sept 21–23, 2010.
- (120) Coates, R.; Gardner, T.; Eddings, E. Mobile Pyrolysis Process for Conversion of Biomass into Energy Products. Presented at the 2013 North American Biochar Symposium, Oct 13–16, 2013; <http://scholarworks.umass.edu/cgi/viewcontent.cgi?filename=2&article=1033&context=biochar&type=additional> (accessed March 2, 2017).
- (121) Sangines, P.; Dominguez, M. P.; Sanchez, F.; San Miguel, G. Slow pyrolysis of olive stones in a rotary kiln: Chemical and energy characterization of solid, gas, and condensable products. *J. Renewable Sustainable Energy* **2015**, *7* (4), 043103.
- (122) Brown, J. N.; Brown, R.C. Process optimization of an auger pyrolyzer with heat carrier using response surface methodology. *Bioresour. Technol.* **2012**, *103*, 405–414.
- (123) Ingram, L.; Mohan, D.; Bricka, M.; Steele, P.; Strobel, D.; Crocker, D.; et al. Pyrolysis of wood and bark in an auger reactor: Physical properties and chemical analysis of the produced bio-oils. *Energy Fuels* **2008**, *22* (1), 614–625.

- (124) Puy, N.; Murillo, R.; Navarro, M. V.; López, J. M.; Rieradevall, J.; Fowler, G.; et al. Valorisation of forestry waste by pyrolysis in an auger reactor. *Waste Manage.* **2011**, *31* (6), 1339.
- (125) Gajjala, S. K.; Mitchell, B.; Li, Q.; Hassan, E. B. M.; Steele, P. H. Production of bio-fuels from giant miscanthus. Presented at the 2011 AIChE Spring Meeting and 7th Global Congress on Process Safety, 2011.
- (126) Wang, H.; Srinivasan, R.; Yu, F.; Steele, P.; Li, Q.; Mitchell, B. Effect of acid, alkali, and steam explosion pretreatments on characteristics of bio-oil produced from pinewood. *Energy Fuels* **2011**, *25* (8), 3758.
- (127) Joubert, J. E.; Carrier, M.; Dahmen, N.; Stahl, R.; Knoetze, J. H. Inherent process variations between fast pyrolysis technologies: A case study on Eucalyptus grandis. *Fuel Process. Technol.* **2015**, *131*, 389.
- (128) Wang, H.; Srinivasan, R.; Yu, F.; Steele, P.; Li, Q.; Mitchell, B.; et al. Effect of Acid, Steam Explosion, and Size Reduction Pretreatments on Bio-oil Production from Sweetgum, Switchgrass, and Corn Stover. *Appl. Biochem. Biotechnol.* **2012**, *167* (2), 285–297.
- (129) Nam, H.; Capareda, S. C.; Ashwath, N.; Kongkasawan, J. Experimental investigation of pyrolysis of rice straw using bench-scale auger, batch and fluidized bed reactors. *Energy* **2015**, *93*, 2384–2394.
- (130) Pfitzer, C.; Dahmen, N.; Troger, N.; Weirich, F.; Sauer, J.; Gunther, A.; et al. Fast Pyrolysis of Wheat Straw in the Bioliq Pilot Plant. *Energy Fuels* **2016**, *30* (10), 8047–8054.
- (131) Henrich, E.; Dahmen, N.; Weirich, F.; Reimert, R.; Kornmayer, C. Fast pyrolysis of lignocellulosics in a twin screw mixer reactor. *Fuel Process. Technol.* **2016**, *143*, 151–161.
- (132) Roy, C.; Blanchette, D.; Korving, L.; Yang, J.; de Caumia, B. Development of a Novel Vacuum Pyrolysis Reactor with Improved Heat Transfer Potential. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Eds.; Blackie Academic and Professional: London, 1997; pp 351–367.
- (133) Roy, C.; Lemieux, S.; de Caumia, B.; Pakdel, H. Vacuum Pyrolysis of Biomass in a Multiple Heat Furnace. In *Proceedings of Biotechnology and Bioenergy Symposium No. 15, 1985*; Wiley: New York, 1986; p 107.
- (134) Venderbosch, R. H.; Prins, W. Fast Pyrolysis technology development. *Biofuels, Bioprod. Biorefin.* **2010**, *4*, 178–208.
- (135) Tsai, W. T.; Lee, M. K.; Chang, Y. M. Fast pyrolysis of rice husk: Product yields and compositions. *Bioresour. Technol.* **2007**, *98* (1), 22.
- (136) Imam, T.; Capareda, S. Characterization of bio-oil, syn-gas and char from switchgrass pyrolysis at various temperatures. *J. Anal. Appl. Pyrolysis* **2012**, *93*, 170.
- (137) Fan, Y.; Cai, Y.; Li, X.; Yin, H.; Yu, N.; Zhang, R.; et al. Rape straw as a source of bio-oil via vacuum pyrolysis: Optimization of bio-oil yield using orthogonal design method and characterization of bio-oil. *J. Anal. Appl. Pyrolysis* **2014**, *106*, 63.
- (138) Dewayanto, N.; Isha, R.; Nordin, M. R. Use of palm oil decanter cake as a new substrate for the production of bio-oil by vacuum pyrolysis. *Energy Convers. Manage.* **2014**, *86*, 226.
- (139) Fukuda, S. Pyrolysis investigation for bio-oil production from various biomass feedstocks in Thailand. *Int. J. Green Energy* **2015**, *12* (3), 215.
- (140) Le Brech, Y.; Jia, L.; Cissé, S.; Mauviel, G.; Brosse, N.; Dufour, A. Mechanisms of biomass pyrolysis studied by combining a fixed bed reactor with advanced gas analysis. *J. Anal. Appl. Pyrolysis* **2016**, *117*, 334.
- (141) Xu, Y.; Wang, T.; Ma, L.; Zhang, Q.; Chen, G. Technology of bio-oil preparation by vacuum pyrolysis of pine straw. *Trans. Chin. Soc. Agric. Eng.* **2013**, *29* (1), 196.
- (142) Fan, Y. S.; Cai, Y. X.; Li, X. H.; Yu, N.; Chen, L. Comparison of the products in vacuum pyrolysis vapors derived from non-catalytic and catalytic upgrading of camphorwood sawdust. *Chem. Ind. For. Prod.* **2015**, *35* (1), 70.
- (143) Li, R.; Deng, X. S.; Gou, J. S.; Lv, Z. L. Vacuum Paddle Fast Pyrolysis Reactor Design and Internal Heat Transfer Investigation. *Mater. Sci. Forum* **2012**, *704–705*, 468–474.
- (144) Rudloff, M. Biomass to Liquid Fuels (BtL) Presentation made by Choren. Process, Environmental Impact and Latest Developments. Automobile & Environment at Beograd Congress, May 2005.
- (145) Meier, D.; Faix, O. State of the art of applied fast pyrolysis of lignocellulosic materials—a review. *Bioresour. Technol.* **1999**, *68*, 71–77.
- (146) Scott, D.; Majerski, P.; Piskorz, J.; Radlein, D. A second look at fast pyrolysis of biomass—the RTI process. *J. Anal. Appl. Pyrolysis* **1999**, *51*, 23–37.
- (147) DynaMotive Energy Systems Corporation. BioTherm, A System for Continuous Quality, Fast Pyrolysis BioOil. Presented at the Fourth Biomass Conference of the Americas, Oakland, CA, Sept 1, 1999.
- (148) Lu, Q.; Yang, X.-I.; Zhu, X.-f. Analysis on chemical and physical properties of bio-oil pyrolyzed from rice husk. *J. Anal. Appl. Pyrolysis* **2008**, *82* (2), 191.
- (149) Heo, H. S.; Park, H. J.; Dong, J.-I.; Park, S. H.; Kim, S.; Suh, D. J.; et al. Fast pyrolysis of rice husk under different reaction conditions. *J. Ind. Eng. Chem.* **2010**, *16* (1), 27.
- (150) Ji-lu, Z. Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. *J. Anal. Appl. Pyrolysis* **2007**, *80* (1), 30.
- (151) Phan, B. M. Q.; Duong, L. T.; Nguyen, V. D.; Tran, T. B.; Nguyen, M. H. H.; Nguyen, L. H.; et al. Evaluation of the production potential of bio-oil from Vietnamese biomass resources by fast pyrolysis. *Biomass Bioenergy* **2014**, *62*, 74.
- (152) Montoya, J. L.; Valdes, C.; Chejne, F.; Gomez, C. A.; Blanco, A.; Marrugo, G.; Osorio, J.; Castillo, E.; Aristobulo, J.; Acero, J. Bio-oil production from Colombian bagasse by fast pyrolysis in a fluidized bed: An experimental study. *J. Anal. Appl. Pyrolysis* **2015**, *112*, 379–387.
- (153) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. Fast pyrolysis bio-oils from wood and agricultural residues. *Energy Fuels* **2010**, *24* (2), 1380.
- (154) Greenhalf, C. E.; Nowakowski, D. J.; Harms, A. B.; Titiloye, J. O.; Bridgwater, A. V. A comparative study of straw, perennial grasses and hardwoods in terms of fast pyrolysis products. *Fuel* **2013**, *108*, 216.
- (155) Boateng, A. A.; Daugaard, D. E.; Goldberg, N. M.; Hicks, K. B. Bench-Scale Fluidized-Bed Pyrolysis of Switchgrass for Bio-Oil Production. *Ind. Eng. Chem. Res.* **2007**, *46*, 1891–1897.
- (156) Jendoubi, N.; Broust, F.; Commandre, J. M.; Mauviel, G.; Sardin, M.; Lédé, J. Inorganics distribution in bio oils and char produced by biomass fast pyrolysis: The key role of aerosols. *J. Anal. Appl. Pyrolysis* **2011**, *92* (1), 59.
- (157) Westerhof, R. J. M.; Brillman, D. W. F.; van Swaaij, W. P. M.; Kersten, S. R. A. Effect of temperature in fluidized bed fast pyrolysis of biomass: oil quality assessment in tests units. *Ind. Eng. Chem. Res.* **2010**, *49*, 1160–1168.
- (158) Kim, K. H.; Kim, T.-S.; Lee, S.-M.; Choi, D.; Yeo, H.; Choi, I.-G.; et al. Comparison of physicochemical features of biooils and biochars produced from various woody biomasses by fast pyrolysis. *Renewable Energy* **2013**, *50*, 188.
- (159) Soysa, R.; Choi, S. K.; Jeong, Y. W.; Kim, S. J.; Choi, Y. S. Pyrolysis of Douglas fir and coffee ground and product biocrude-oil characteristics. *J. Anal. Appl. Pyrolysis* **2015**, *115*, 51.
- (160) Wu, S.-R.; Chang, C.-C.; Chang, Y.-H.; Wan, H.-P. Comparison of oil-tea shell and Douglas-fir sawdust for the production of bio-oils and chars in a fluidized-bed fast pyrolysis system. *Fuel* **2016**, *175*, 57.
- (161) Azeez, A. M.; Meier, D.; Odermatt, J.; Willner, T. Fast pyrolysis of African and European lignocellulosic biomasses using Py-GC/MS and fluidized bed reactor. *Energy Fuels* **2010**, *24* (3), 2078.
- (162) Rover, M. R.; Johnston, P. A.; Whitmer, L. E.; Smith, R. G.; Brown, R. C. The effect of pyrolysis temperature on recovery of bio-oil as distinctive stage fractions. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 262.
- (163) Mullen, C. A.; Boateng, A. A.; Goldberg, N. M. Production of deoxygenated biomass fast pyrolysis oils via product gas recycling. *Energy Fuels* **2013**, *27* (7), 3867.

- (164) Torri, I. D. V.; Paasikallio, V.; Faccini, C. S.; Huff, R.; Caramão, E. B.; Sacon, V.; et al. Bio-oil production of softwood and hardwood forest industry residues through fast and intermediate pyrolysis and its chromatographic characterization. *Bioresour. Technol.* **2016**, *200*, 680.
- (165) Carrier, M.; Joubert, J. E.; Danje, S.; Hugo, T.; Görgens, J.; Knoetze, J. H. Impact of the lignocellulosic material on fast pyrolysis yields and product quality. *Bioresour. Technol.* **2013**, *150*, 129.
- (166) He, M.; Mourant, D.; Gunawan, R.; Lievens, C.; Wang, X. S.; Ling, K.; et al. Yield and properties of bio-oil from the pyrolysis of mallee leaves in a fluidised-bed reactor. *Fuel* **2012**, *102*, 506.
- (167) Chang, S.; Zhao, Z.; Zheng, A.; Li, X.; Wang, X.; Huang, Z.; et al. Effect of hydrothermal pretreatment on properties of bio-oil produced from fast pyrolysis of eucalyptus wood in a fluidized bed reactor. *Bioresour. Technol.* **2013**, *138*, 321.
- (168) Heidari, A.; Stahl, R.; Younesi, H.; Rashidi, A.; Troeger, N.; Ghoreyshi, A. A. Effect of process conditions on product yield and composition of fast pyrolysis of *Eucalyptus grandis* in fluidized bed reactor. *J. Ind. Eng. Chem.* **2014**, *20* (4), 2594.
- (169) Atsonios, K.; Panopoulos, K. D.; Bridgwater, A. V.; Kakaras, E. Biomass fast pyrolysis energy balance of a 1 kg/h test rig. *International Journal of Thermodynamics* **2015**, *18* (4), 267.
- (170) Mesa-Pérez, J. M.; Cortez, L. A. B.; Marín-Mesa, H. R.; Rocha, J. D.; Pelaez-Samaniego, M. R.; Cascarosa, E. A statistical analysis of the auto thermal fast pyrolysis of elephant grass in fluidized bed reactor based on produced charcoal. *Appl. Therm. Eng.* **2014**, *65* (1–2), 322–329.
- (171) Faix, A.; Schweinle, J.; Schöll, S.; Becker, G.; Meier, D. (GTI-tcbiomass) Life-Cycle Assessment of the BTO-Process (Biomass-to-Oil) with Combined Heat and Power Generation. *Environ. Prog. Sustainable Energy* **2010**, *29*, 193–202.
- (172) Meier, D.; Schöll, S.; Klaubert, H.; Markgraf, J. Practical results from Pytec's biomass-to-oil (BTO) process with ablative pyrolyser and diesel CHP plant. Presented at Success & Visions for Bioenergy, 2007.
- (173) Bridgwater, A. V.; Meier, D.; Radlein, D. An overview of fast pyrolysis of biomass. *Org. Geochem.* **1999**, *30*, 1479–1493.
- (174) Schulzke, T.; Conrad, S.; Westermeyer, J. Fractionation of flash pyrolysis condensates by staged condensation. *Biomass Bioenergy* **2016**, *95*, 287–295.
- (175) Bech, N.; Larsen, M. B.; Jensen, P. A.; Dam-Johansen, K. Modelling solid-convective flash pyrolysis of straw and wood in the Pyrolysis Centrifuge Reactor. *Biomass Bioenergy* **2009**, *33* (6–7), 999.
- (176) Makibar, J.; Fernandez-Akarregi, A. R.; Amutio, M.; Lopez, G.; Olazar, M. Performance of a conical spouted bed pilot plant for bio-oil production by poplar flash pyrolysis. *Fuel Process. Technol.* **2015**, *137*, 283.
- (177) Alvarez, J.; Lopez, G.; Amutio, M.; Bilbao, J.; Olazar, M. Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor. *Fuel* **2014**, *128*, 162.
- (178) Amutio, M.; Lopez, G.; Alvarez, J.; Moreira, R.; Duarte, G.; Nunes, J.; et al. Flash pyrolysis of forestry residues from the Portuguese Central Inland Region within the framework of the BioREFINA-Ter project. *Bioresour. Technol.* **2013**, *129*, 512.
- (179) Du, S.; Sun, Y.; Gamliel, D. P.; Valla, J. A.; Bollas, G. M. Catalytic pyrolysis of miscanthus × giganteus in a spouted bed reactor. *Bioresour. Technol.* **2014**, *169*, 188.
- (180) Amutio, M.; Lopez, G.; Artetxe, M.; Elordi, G.; Olazar, M.; Bilbao, J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. *Resources, Conservation and Recycling* **2012**, *59*, 23.
- (181) Chen, M.; Yao, Y.; Ren, Z.; Li, T.; Guo, X.; Yan, Y. Preparation of liquid fuel through pyrolysis of biomass in a conduit-spouting fluidized reactor. In *Proceedings of the 2003 Fifth International Symposium on Coal Combustion*, 2003; p 272.
- (182) Amutio, M.; Lopez, G.; Alvarez, J.; Olazar, M.; Bilbao, J. Fast pyrolysis of eucalyptus waste in a conical spouted bed reactor. *Bioresour. Technol.* **2015**, *194*, 225.
- (183) Lam, S. S.; Chase, H. A. A review on Waste to Energy Processes using Microwave Pyrolysis. *Energies* **2012**, *5*, 4209–4232.
- (184) Li, J.; Dai, J.; Liu, G.; Zhang, H.; Gao, Z.; Fu, J.; He, Y.; Huang, Y. Biochar from microwave pyrolysis of biomass: A review. *Biomass Bioenergy* **2016**, *94*, 228–244.
- (185) Holland, K. M., Apparatus for Waste Pyrolysis, U.S. Patent 5,387,321, Feb 7, 1995.
- (186) Holland, K. M., Process for Destructive Distillation of Organic Materials. U.S. Patent 5,330,623, May 1994.
- (187) Zhao, X.; Wang, M.; Liu, H.; Li, L.; Ma, C.; Song, Z. A microwave reactor for characterization of pyrolyzed biomass. *Bioresour. Technol.* **2012**, *104*, 673–678.
- (188) Miura, M.; Kaga, H.; Sakurai, A.; Kakuchi, T.; Takahashi, K. Rapid pyrolysis of woof block by microwave heating. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 187–199.
- (189) Hu, Z.; Ma, X.; Chen, C. A study on experimental characteristic of microwave assisted pyrolysis of microalgae. *Bioresour. Technol.* **2012**, *107*, 487–493.
- (190) Ren, S.; Lei, H.; Wang, L.; Bu, Q.; Chen, S.; Wu, J.; et al. Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 163–169.
- (191) Tian, Y.; Zuo, W.; Ren, Z.; Chen, D. Estimation of a novel method to produce biooil from sewage sludge by microwave pyrolysis with the consideration of efficiency and safety. *Bioresour. Technol.* **2011**, *102*, 2053–61.
- (192) Huang, Y. F.; Kuan, W. H.; Lo, S. L.; Lin, C. F. Hydrogen-rich fuel gas from rice straw via microwave-induced pyrolysis. *Bioresour. Technol.* **2010**, *101*, 1968–73.
- (193) Salema, A. A.; Ani, F. N. Microwave induced pyrolysis of oil palm biomass. *Bioresour. Technol.* **2011**, *102*, 3388–3395.
- (194) Du, Z.; Li, Y.; Wang, X.; Wan, Y.; Chen, Q.; Wang, C.; et al. Microwave-assisted pyrolysis of microalgae for biofuel production. *Bioresour. Technol.* **2011**, *102*, 4890–4896.
- (195) Lin, Q.; Chen, G.; Liu, Y. Scale-up of microwave heating process for the production of bio-oil from sewage sludge. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 114–119.
- (196) Huang, Y. F.; Kuan, W. H.; Lo, S. L.; Lin, C. F. Total recovery of resources and energy from rice straw using microwave-induced pyrolysis. *Bioresour. Technol.* **2008**, *99*, 8252–8258.
- (197) Salema, A. A.; Ani, F. N. Microwave-assisted pyrolysis of oil palm shell biomass using an overhead stirrer. *J. Anal. Appl. Pyrolysis* **2012**, *96*, 162–72.
- (198) Yu, F.; Ruan, R.; Steele, P. Microwave pyrolysis of corn stover. *Trans. Am. Soc. Ag. Biol. Eng.* **2009**, *52*, 1595–1601.
- (199) Wang, M. J.; Huang, Y. F.; Chiueh, P. T.; Kuan, W. H.; Lo, S. L. Microwave-induced torrefaction of rice husk and sugarcane residues. *Energy* **2012**, *37*, 177–84.
- (200) Mesa-Perez, J. M.; Felfli, F. F. Technical and Marketing Criteria for the Development of Fast Pyrolysis Technologies. In *Innovative Solutions in Fluid-Particle Systems and Renewable Energy Management*; Tannous, K., Ed.; IGI Global: Hershey, PA, 2015; Chapter 9.
- (201) Garcia-Perez, M.; Garcia-Nunez, J. A.; Pelaez-Samaniego, M. R.; Kruger, C.; Fuchs, M. R.; Flora, G. Sustainability, Business Models, and Techno-Economic Analysis of Biomass Pyrolysis Technologies. In *Innovative Solutions in Fluid-Particle Systems and Renewable Energy Management*; Tannous, K., Ed.; IGI Global: Hershey, PA, 2015; Chapter 10.
- (202) Jones, S. B.; Valkenburg, C.; Walton, C.; Elliott, D. C.; Holladay, J. E.; Stevens, D. J.; Kinchin, C.; Czernik, S. *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case*; PNNL-18284, Rev. 1; Pacific Northwest National Laboratory: Richland, WA, 2009.
- (203) Daugaard, D. E.; Brown, R. C. Enthalpy of pyrolysis for several types of biomass. *Energy Fuels* **2003**, *17*, 934–939.
- (204) Catoire, L.; Yahyaoui, M.; Osmont, A.; Gokalp, I.; Brothier, M.; Lorcet, H.; Guenadou, D. Thermochemistry of Compounds Formed during Fast Pyrolysis of Lignocellulosic Biomass. *Energy Fuels* **2008**, *22*, 4265–4273.
- (205) Auber, M. Effect catalytique de certains inorganiques sur la selectivite des reactions de pyrolyse rapide de biomasses et de leurs

constituents. Ph.D. Thesis, Institut National Polytechnique de Lorraine, Nancy, France, 2009.

(206) Yang, H.; Kudo, S.; Kuo, H.-P.; Norinaga, K.; Mori, A.; Masek, O.; Hayashi, J.-I. Estimation of Enthalpy of Bio-oil Vapor and Heat Required for Pyrolysis of Biomass. *Energy Fuels* **2013**, *27*, 2675–2686.

(207) Janse, A. M. C.; Westerhout, R. W. J.; Prins, W. Modelling of flas pyrolysis of a single wood particle. *Chem. Eng. Process.* **2000**, *39*, 239–252.

(208) Wang, X.; Kersten, S. R. A.; Prins, W.; van Swaaij, W. P. M. Biomass Pyrolysis in a Fluidized Bed Reactor. Part 2: Experimental Validation of Model Results. *Ind. Eng. Chem. Res.* **2005**, *44*, 8786–8795.

(209) Thunman, H.; Leckner, B. Thermal conductivity of wood-models for different stages of combustion. *Biomass Bioenergy* **2002**, *23*, 47–54.

(210) Boateng, A. A. *Rotary Kilns: Transport Phenomena and Transport Processes*. Butterworth-Heinemann: Burlington, MA, 2008.

(211) Basu, P. *Combustion and Gasification in Fluidized Beds*; CRC Press: Boca Raton, FL, 2006.

(212) Zhong, W.; Jin, B.; Zhang, Y.; Wang, X.; Xiao, R. Fluidization of Biomass Particles in a Gas-Solid Fluid Bed. *Energy Fuels* **2008**, *22* (6), 4170–4176.

(213) Bruni, G.; Solimene, R.; Marzocchella, A.; Salatino, P.; Yates, J. G.; Lettieri, P.; Fiorentino, M. Self-segregation of high-volatile fuel particle devolatilization in a fluidized bed reactor. *Powder Technol.* **2002**, *128*, 11–21.

(214) Yoder, J.; Galinato, S.; Granatstein, D.; Garcia-Perez, M. Economic treadoff between biochar and bio-oil production via pyrolysis. *Biomass Bioenergy* **2011**, *35* (5), 1851–1862.

(215) Bailis, R. Modeling climate change mitigation from alternative methods of charcoal production in Kenya. *Biomass Bioenergy* **2009**, *33* (11), 1491–1502.

(216) Ronsse, F.; Nachenius, R. W.; Prins, W. Carbonization of Biomass. In *Recent Advances in Thermochemical Conversion of Biomass*; Pandey, A., Bashkar, T., Stocker, M., Sukumaran, R., Eds.; Elsevier: Amsterdam, 2015; pp 293–324.

(217) Siemons, R.; Baaijens, L. An Innovative Carbonisation Retort: Technology and Environmental Impact. *Termotehnika* **2012**, *38* (2), 131–138.

(218) Jahanshahi, S.; Mathieson, J. G.; Somerville, M. A.; Haque, N.; Norgate, T. E.; Deev, A.; Pan, Y.; Xie, D.; Ridgeway, P.; Zulli, P. Development of low-emission Integrated Steelmaking Process. *J. Sustainable Metall.* **2015**, *1* (1), 94–114.

(219) Dahmen, N.; Dinjus, E.; Heinrich, E. The Karlsruhe Process bioliq: Synthetic Fuels from the Biomass. In *Renewable Energy: Sustainable Energy Concepts for the Future*; Wengenmayr, R., Bührke, T., Eds.; Wiley-VCH: Weinheim, Germany, 2008.

(220) Jager, N.; Conti, R.; Neumann, J.; Apfelbacher, A.; Daschner, R.; Binder, S.; Hornung, A. Thermo-Catalytic Reforming of Wood Biomass. *Energy Fuels* **2016**, *30* (10), 7923–7929.

(221) Moriconi, N.; Laranci, P.; D'Amico, M.; Bartocci, P.; D'Alessandro, B.; Cinti, G.; Baldinelli, A.; Discepoli, G.; Bidini, G.; Desideri, U.; Cotana, F.; Fantozzi, F. Design and preliminary operation of a Gasification Plant for Micro-CHP with Internal Combustion engine and SOFC. *Energy Procedia* **2015**, *81*, 298–308.