Methods for Producing Biochar and Advanced Biofuels in Washington State

Part 1: Literature Review of Pyrolysis Reactors

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This report is available on the Department of Ecology's website at: www.ecy.wa.gov/beyondwaste/organics. Some figures and photos can be seen in color in the online file. Additional project reports supported by Organic Wastes to Fuel Technology sponsored by Ecology are also available on this web site. This report is also available at the Washington State University Extension Energy Program library of bioenergy information at www.pacificbiomass.org.

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Beyond Waste Objectives:
Turning organic waste into resources, such as compost, biofuels, recovery of stable carbon and nutrients and other products promotes economic vitality in growing industries, and protects the environment. This creates robust markets and sustainable jobs in all sectors of the economy, and facilitates closed-loop materials management where by-product from one process becomes feedstock for another with no waste generated.

Disclaimer:

It is our objective to investigate previous technologies in order to create extremely clean, non-polluting thermochemical processes for producing energy, fuels and valuable by-products. The Department of Ecology and Washington State University provide this publication as a review of ancient and existing methods of reduction of cellulosic materials to gases, liquids and char. This does not represent an endorsement of these processes.

The historical development of pyrolysis related industries is one of the most interesting in the annals of industrial chemistry. Very often the by-products of today become the main products of tomorrow.

James Withrow, 1915

Since the chemical industry today can produce by-products obtained from the pyrolysis of wood, with the exception of biochar, more cheaply than the pyrolysis process the main emphasis in the latter is on the production of biochar. For this reason simple carbonization methods, similar to the original biochar piles but in improved form are likely to be more economical than more complicated plants that place emphasis on the isolation and processing of by-products.

Herman F.J. Wenzl, 1970

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SUMMARY

About 16.4 million tons of underutilized organic waste is produced in Washington State annually (Frear et al., 2005; Liao et al., 2007). Agricultural wastes generated in eastern and southern Washington, residues generated by the forest and paper industries in western and northern Washington, along with woody debris (construction wastes) from the Puget Sound and Spokane metropolitan regions are potential resources that may stimulate economic activity in the state. However, the utilization of these diverse waste materials requires development of suitable strategies and technologies.

The potential to convert lignocellulosic materials into biochar and bio-oil is generating renewed interest in pyrolysis (Bridgwater and Peacocke 2000; Granatstein et al., 2009; Huber 2008; Mason et al., 2009). Biochar has the capacity to increase soil fertility and sequester carbon (Granatstein et al., 2009; Lehman et al., 2004), while bio-oil is currently being studied as a new bio-crude to produce second-generation transportation fuels (Jones et al., 2009; Garcia-Perez et al., 2009). However, the growth of this industry has been limited by the lack of viable bio-oil refinement technologies and by clean technologies for biochar production. Recent breakthroughs in thermochemical sciences have proven the feasibility of converting bio-oil into ethanol, green gasoline, and green diesel. As a result, we can expect to see the operation of pyrolysis units and rural bio-oil refineries able to produce bio-oils that are compatible with existing refineries within the next ten years (Garcia-Perez et al., 2009; Jones et al., 2009).

On the other hand, billions of people use biochar for cooking in developing nations (Kammen et al., 2005). Despite the cooking advantages of biochar, its large-scale production in developing nations is seriously harmful to the environment (Kammen et al., 2005). Nonetheless, biochar is likely to remain the fuel of choice in many poor countries as long as the feedstock supply and demand from impoverished people in the world exist (Kammen et al., 2005). New and less polluting pyrolysis technologies to produce biochar and heat are needed across the globe to reduce the environmental impact of biochar production practices.

Despite the growing interest to produce biochar and bio-oil, the lack of historic and current information hinders those interested in developing this industry. This inadequate flow of information for potential users forces the design of a pyrolysis unit to remain an art (Emrich, 1985). Still, the potential for biochar and bio-oil production has enticed many entrepreneurs to develop their own businesses, but lack of technical skills frequently results in highly polluting and inefficient systems, as those shown in Figures 1 and 2.

Those interested in commercializing biochar and bio-oil technology and developing production facilities are often unaware of available designs and existing regulations that exist. The diversity of situations in which pyrolysis can be applied (different feedstock, scale, capacity, use of mobile or stationary units) as well as the diversity of products that can be obtained from this technology is vast. This makes it very difficult to find an exclusive design that is sustainable across all the potential applications. *Thus, the main purpose of this report is to raise awareness of available designs to those involved in the development of pyrolysis projects and to show how a clear understanding of the specific conditions under which the technology is utilized (a clear purpose) helps to identify suitable technologies. This report is also important to guide our state agencies and researchers in the development of pyrolysis technology for producing biochar and second generation bio-fuels in Washington State.*

Five main factors prevent the development of a biomass pyrolysis industry: (1) technologies are being developed by researchers and engineers with a limited understanding of the conditions for which these technologies are to be used; (2) technologies are being developed that are not tailored to specific materials and locations; (3) the knowledge base of state of the art and science of pyrolysis technologies is insufficient; (4) we lack rural refineries to convert pyrolysis oils into a stabilized product that then can be refined in existing petroleum refineries; (5) technologies without bio-oil or heat recovery are harmful to the environment - clean technologies to produce bio-char and heat are imperative.

Figure 1. Although biochar production is has been around for centuries, old practices are still used today. Source: http://www.treehugger.com/files/2008/12/betting-on-biochar-to-break-the-co2-imbalance.php (Photo: By Ecksunderscore @ flickr).

Figure 2. Environmental impact of carbonization units without recovery of volatile products (Courtesy of the Washington State Department of Ecology).

This report has been written with the final users in mind. We have avoided discussions at the phenomenological level since our intent is to make this report valuable for engineers, the business community, policy makers, and the general public interested in developing a sustainable biomass economy in our state.

1. INTRODUCTION

Washington States consumes 405 thousand barrels of petroleum every day (approximately 20 million tons per year), of which 44 % is converted into motor gasoline, 21 % into diesel fuel and another 14% into jet fuel (US Energy Information Administration, 2010). Meanwhile, the state generates 16.4 million tons of underutilized biomass (dry equivalent) every year (Frear et al., 2005, Liao et al., 2007). The majority of this is forest residues which accounts for 49% of the organic waste generated in the state. Other important sources include municipal waste (24%), field residues (14%), and animal waste (11%).

Pyrolysis, a thermal conversion process, is unquestionably one of the most promising technologies for the sequestration of carbon and the production of a bio-oil as feedstock for producing second-generation transportation fuels (Bridgwater and Peacocke, 2000; Granatstein et al., 2009; Huber 2008; Mason et al., 2009; Woolf et al., 2010). This report is intended to help identify pyrolysis facility design and scale for biochar production, and intermediate fuel and chemical recovery that are viable at a local level.

Although it is economically inefficient to transport low energy density biomass beyond 96 km (60 miles), pyrolysis units can be operated close to biomass resources avoiding the need for long hauling. Once pyrolysis has converted the original biomass into crude bio-oil (with an energy density of about 26,800 $MJ/m^{3)}$ it can then be transported economically up to 500 km from the biomass sources to rural bio-oil refineries where it is converted into high value products and a stabilized bio-oil that can be further refined to produce fuel and chemicals in existing refineries. Biochar can be applied to soils in the vicinity to sequester carbon and enhance soil fertility. According to Woolf et al. (2010) production of bio-char and its storage in soils can contribute to a reduction of up to 12% of current anthropogenic CO_2 emissions. Ecology's goal for this study is to support development of renewable fuels, while emphasizing reduction of fuel use, conservation, and replacement. Ecology is also interested in moderating fuel uses with locally available fuel sources and higher value product.

The growth of the pyrolysis industry is severely hindered by current technological limitations to refine bio-oils. Yet, recent progress in this area suggests that development of the pyrolysis industry is viable within the next ten years (Garcia-Perez et al., 2009; Jones et al., 2009). Development of bio-oil refineries is a critical element in implementing a biomass economy based on locating pyrolysis units close to biomass resources, and bio-oil refineries near consumption centers to process materials into transportation fuels and chemicals.

In 2005, the world production of biochar was more than 44 million tons (http://www.nationmaster.com/graph/ene_cha_pro_fro_cha_pla-energy-biochar-production-from-plants, date accessed: August 24, 2010). Because current biochar production yields a mere 20% of the original biomass, it can be estimated that more than 220 million tons of biomass is processed to produce the world's supply of biochar annually (Baker, 1985). By tapping into the vast waste reserves of the world, enhanced biochar technology with high-grade energy recovery systems can find a new application; and the biochar industry can make one of the most important contributions to mankind by helping to provide for the energy needs of the future while helping to sequester carbon (Levine, 2010).

Brazil is by far the largest biochar producer in the world producing 9.9 million tons /year. Other important biochar producing countries are: Thailand (3.9 million tons/year), Ethiopia (3.2 million tons/year), Tanzania (2.5 million tons/year), India (1.7 million tons/year) and the Democratic Republic of Congo (1.7 million tons/year). Despite being the 10th largest biochar producer in the world (at 0.9 million tons/year), most of the biochar consumed in the United States is imported from other countries. Pyrolysis is the only technology available to produce biochar. Yet, a lack of investment to improve its environmental performance of pyrolysis units has resulted in few production options in the United States. Many existing technologies produce excessive air pollution and do not comply with current U.S. environmental regulations. Nor do they meet the "Beyond Waste" goals or the Hanover Principles for process design.

However, due to the ability of biochar to increase soil fertility and sequester carbon, it is being studied intensively (Lehman et al., 2004). Results from studies of Amazonian soils and investigations of the genesis of soils on the Illinois Plain show that soils amended with biochar produce a significant improvement in soil quality (Krug et al., 2003). This and the promise biochar presents for carbon sequestration (due to its resistance to microbial breakdown) have sparked interest in its use as a soil amendment. Developing flexible designs for pyrolysis units to produce high yields of both bio-oil and biochar is a technological challenge facing the thermochemical industry.

Reactors developed and built by the wood distillation industry almost a century ago which aimed at producing bio-char and light distillable products may serve as a good source of inspiration, however, most of the literature about this industry was edited between 1900 and 1930 (Dumesny and Noyer, 1908; Klark, 1925) and new developments are not well documented. *Because of the low heating rates achieved these reactors are known as "slow pyrolysis reactors". Reactors designed to achieve high heating rates by processing very small particles, known in the literature as fast pyrolysis reactors, have been well described in excellent reviews published in the last 20 years (Bridgwater et al 1999, 2000, 2001, Czernik et al 2004).* This report is one of the first attempts since Walter Emrich's comprehensive work in 1985 to present the available information for slow and fast pyrolysis into a single document. Our hope is that the knowledge generated by these two methods (slow and fast pyrolysis) can be integrated into new designs.

The pyrolysis industry must be well planned to ensure that long-term goals are satisfied (Emrich, 1985). State and federal agency involvement during project planning is crucial to ensure a supply of raw materials at the regional and national levels. Interconnection with other industries and energy consumers as well as with a state or national household supply program is critical for success.

This report emphasizes advantages and disadvantages of producing fuel and fixing carbon, and will provide enough background information to create a decision tree for pyrolysis technologies that support better use of organic wastes. The information provided should allow for the creation of a sound, technical, economic, and environmental based methodology in order to identify the best alternative (production of fuel, stable carbon, or a combination of both) for utilizing organic wastes available in Washington. We identify and recommend actions that Washington State can take to effectively utilize available new technologies. With Dynamotive, Ensyn, and UOP leading the way as commercial developers, Washington State University is pursuing designs that are more flexible, more sustainable, and intended to establish a better balance between stable carbon and bio-fuel production in order to meet the goals of "Beyond Waste."

This study identifies opportunities and obstacles for producing fuels and stable carbon from organic wastes generated in Washington, while focusing on methods that are compatible with both fast and slow pyrolysis. The information collected in this review is intended to inspire experts to develop new models to utilize these resources, and new designs of pyrolysis units that are well suited for the conditions in Washington.

2. EVOLUTION OF PYROLYSIS TECHNOLOGIES

2.1 History of Pyrolysis Technologies

For as long as human history has been recorded, heating or carbonizing wood for the purpose of manufacturing biochar has been practiced (Emrich, 1985; Klark, 1925). Carbonization is as old as civilization itself (Brown, 1917). In ancient times, the production of biochar was not the only intention. It appears that ancient peoples were also well acquainted with the method of liquid product recovery. This can be seen in the remains of the ancient Egyptian societies that indicate they used liquid products like fluid wood-tar and pyroligneous acid to embalm their dead. The preserving agent in this ancient tradition was a watery condensate collected from the charring process (Emrich, 1985). According to the writings of Theophrastus, the Macedonians obtained wood tar from burning biochar in pits (Klark 1925). Wood tar had many applications such as house paints, caulking for sealing wood barrels, and use in shipbuilding. Dating as far back as 6,000 years, evidence shows that wood tar was used to attach arrowheads to spear shafts (Emrich, 1985; Klark, 1925).

In the early development of pyrolysis, producing biochar was the sole objective of wood carbonization. Throughout history the process has evolved from using wasteful biochar pits to modern, fast pyrolysis reactors and bio-oil refineries. At the end of the eighteenth century, new technologies were developed to recover and utilize the volatile compounds produced from pyrolysis (Klark, 1925). This resulted in a crude process using brick kilns to recover the condensable gases that were normally lost in biochar pits. Following brick kilns was the use of iron retorts (vessels) placed in "batteries" of two each in long bricked up rows. By the end of the nineteenth century, labor and time saving steel ovens were developed, contributing significantly to the success of the wood distillation industry. In the 1970's the fast pyrolysis reactor was introduced, influencing progress in bio-oil refining. *The maturity of pyrolysis and bio-oil refining technologies now has the potential to support a new biomass economy capable of competing with the prevailing petroleum-based economy.*

A delicate balance between scientific discoveries, development of new products, technological improvements, and market forces has made the long, painful, and chaotic evolution of pyrolysis possible. Below are a number of important developmental milestones of pyrolysis technology worldwide.

1658	Johann Rudolf Glauber confirmed that the acid contained in pyroligneous water was the same acid contained in vinegar (Emrich, 1985; Klark, 1925).
1661	The separation of a spirituous liquid from volatile products of wood distillation was described by Robert Boyle (Klark, 1925).
1792	England commercialized luminating gas manufactured from wood (Klark, 1925).
1812	Taylor showed that methyl alcohol was present in the liquid obtained from the distillation of pyroligneous water (Klark, 1925).
1819	The first pyrolysis oven to transfer heat through its metal walls was designed by Carl Reichenbach (Klark, 1925).
1835	Methyl alcohol, an isolated product of crude wood spirit, was discovered by Jean Baptiste Andre Dumas and Eugene Peligot which confirmed Taylor's ideas on the nature of pyroligneous acid (Klark, 1925).

1850	Horizontal retorts (1 meter diameter, and 3 meters long) were used mainly by Germany, England, and Austria, while the French were becoming more inclined to the use of vertical retorts made portable by Robiquete (Klark, 1925).
1856	An increase in demand for methyl alcohol was a result of Sr. William H. Perkin's patent on aniline purple (Klark, 1925).
1864	The discovery of iodine increased the demand for wood spirits (Klark, 1925).
1870	Early investigations performed by Tobias Lowitz resulted in a new, chemically pure acetic acid (Klark, 1925).
1870	The rise of the celluloid industry and the manufacture of smokeless powder increased the demand for acetone (Klark, 1925).
1850	The wood distillation industry began to expand (Klark, 1925).
1920-1950	The rise of the petroleum industry caused a decline in wood distillation (Klark, 1925).
1970	Oil Crisis gave rise to the need for alternative liquid fuels.
1970-90s	Development of new pyrolysis reactors occurred side by side with the understanding of the fundamentals of biomass pyrolysis reactions (Boroson et al., Bridgwater et al., 1994; 1989 a, b; Evans et al., 1987 a, b; Mottocks, 1981, Piskortz et al., 1988a, b; Scott et al., 1984, 1988).
1980-90s	New techniques and approaches to characterize bio-oil were proposed (Moses, 1994, Nicolaides, 1984; Oasmaa, et al., 1997; Oasmaa and Czernick, 1999; Radlein et al., 1987).
1980-90s	Several fast Pyrolysis Technologies (Fast, Flash, Vacuum and Ablative) reach commercial or near commercial status (Bridgwater et al. 2001b; Freel et al 1990; 1996, Roy et al., 1985; Roy et al., 1997; Yang et al., 1995).
1980-90s	Bio-oils derived from fast pyrolysis reactions were successfully combusted at atmospheric pressure in flame tunnels and boilers (Banks et al., 1992; Barbucci et al., 1995; Gust, 1997; Huffman et al., 1996, 1997; Lee, 1993; Moses, 1994, Rossi et al., 1993; Shihadeh et al., 1994; van de Kamp et al., 1991, 1993).
1980-90s	An understanding of the bio-oil combustion phenomena resulted in its use in gas turbines and diesel engines (Andrews et al., 1997; D'Alessio et al., 1998; Frigo et

	al., 1998; Gross, 1995; Jay et al., 1995; Kasper et al., 1983; Leech et al., 1997; Solantausta et al., 1993, 1994; Wormat et al., 1994).
1990s	Bio-oil fuel specifications were first proposed (Diebold et al., 1999; Fagernas, 1995; Meier et al., 1997; Oasmaa et al., 1997; Oasmaa and Czernick, 1999; Sipila et al., 1998).
1990s	Bio-oil upgrading strategies and separation strategies (bio-oil micro-emulsions, hot vapor filtration, use of additives, hydrotreatment) began to be developed (Baglioni et al., 2001; Elliott and Baker, 1987; Fagernas, 1995; Ikura et al., 1998; Maggi and Elliott, 1997; Oasmaa et al., 1997; Salantausta et al., 2000; Suppes et al., 1996).
1990s	New crude bio-oil based products (e.g. bio-lime, slow release fertilizers, road de-icers, wood preservatives, glues, sealing materials, bio-pitches, hydrogen, browning agents, hydroxyacetaldehyde, phenol-formaldehyde resins) were developed (Chum and Kreibich, 1993; Freel and Graham, 2002; Oehr, 1993; Radlein, 1999; Roy et al., 2000; Underwood and Graham, 1991; Underwood, 1990).
2000s	Progress in the understanding of bio-oil physio-chemical structure (Fratini et al., 2006; Garcia-Perez et al., 2006).
2000s	New bio-oil based refinery concepts are proposed (Bridgwater, 2005; Czernik et al., 2002; Elliott, 2007; Helle et al., 2007; Huber and Dumesic, 2006, Jones et al., 2009; Mahfud et al., 2007; van Rosuum et al., 2007).

2.2 History of Pyrolysis Technologies in the United States

The ups and downs of biochar production in the United States are shown in Figure 3. A high demand for bio-char by the metallurgical industry and the birth of the wood distillation industry caused a peak in production around 1882 (Baker, 1985). Despite technological achievements resulting in better quality char production dropped because the metallurgy and the steel industry began fueling their blast furnaces with new resources like refined bituminous coal, coke, and lignite. The 1882 peak in biochar production was surpassed only 125 years later. The increase in charcoal production after 1945 is mainly attributed to the production of briquettes for domestic consumption (Baker, 1985).

Today, southeastern Missouri produces approximately three-quarters of all the barbecue charcoal used in the United States. Sawmill wastes are the main feedstock used for charcoal production in Missouri (Yronwode 2000). Although, the Missouri Air Conservation act in 1972, attempted to control charcoal kiln smoke, the charcoal industry was able to obtain three important exemptions on the limit on particle matter (soot), the limit on odors and the limit on opacity. By 1980 all the other states had implemented controls on air emissions, resulting in a migration and concentration of charcoal production in Missouri. Until 1998, the production of biochar in Missouri was a major source of air pollution. In March 1998, the Missouri Air Conservation Commission adopted regulations to phase in controls of charcoal kiln smoke by introducing afterburners. Due to the agreement between the Missouri Department of Natural Resources, EPA and the charcoal industry, by July 2005 the dense smoke was completely eliminated (Yronwode 2000).

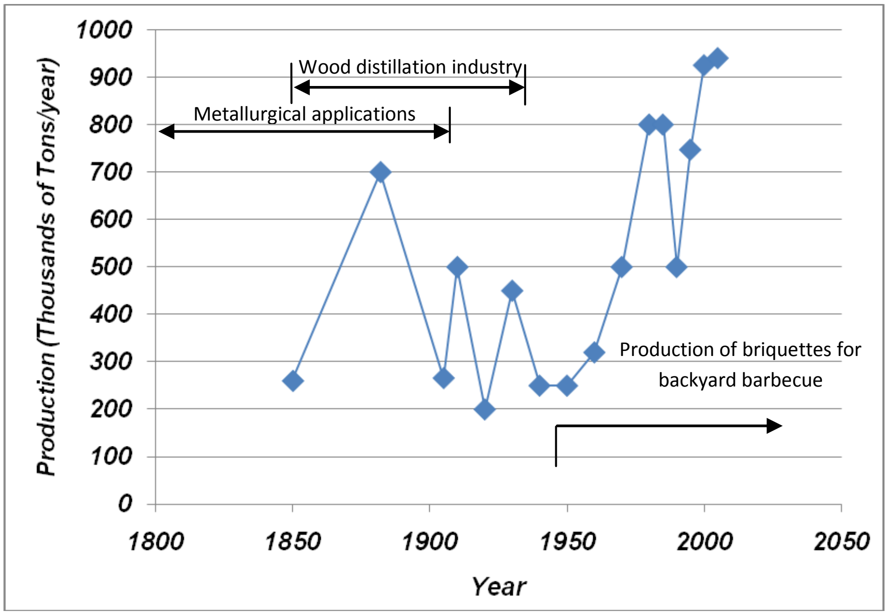

Figure 3. Production of biochar in the United States (Baker,1985).

Milestones in the development of pyrolysis technologies in the United States are as follows:

1600-1770	Carbon required for iron smelting came from wood carbonization in earthen kilns or pits (Baker, 1985; Toole et al., 1961).
1620	The construction of a furnace at Falling Creek outside Jamestown, VA began the biochar industry in the United States (Baker, 1985; Toole et al., 1961).
1645-1675	Construction and operation of a furnace for charcoal production near Saugus, MA (Baker, 1985; Toole et al., 1961).
1790	After the Revolutionary War colonists began to move westward and the iron-making industry expanded rapidly resulting in the construction of the first blast furnace west of the Alleghany Mountains (Baker, 1985; Toole et al., 1961).
1796	The construction of a furnace in Pittsburgh, PA started the great iron and steel center (Baker, 1985; Toole et al., 1961).
1830	James Ward began to manufacture pyroligneous acid at North Adams, MA (Baker, 1985; Toole et al., 1961).
1832	Most of the wood biochar produced in United States was used to produce pig iron (Baker, 1985; Toole et al., 1961).
1850	Around 563,000 tons per year of biochar was produced by 377 furnaces operational in the United States (Baker, 1985; Toole et al., 1961).
1850	In the State of New York, John H. Turnbull constructed the first successful wood distillation plant. This plant used cast iron retorts of about half a cord[1]. The chief product at this time was acetate of lime. Biochar was used largely as fuel for the plant, while the market for crude wood alcohol had decreased (Baker, 1985; Bates, 1922; Toole et al., 1961).

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[1] This is the official measurement of firewood. The concept of a cord or wood emerged in the 17th century, when stacks of wood were literally measured with a cord. A full cord is a large amount of wood. It measure 4 feet high by 4 feet wide by eight feet long (4’x4’x8’) and has a volume of 128 cubic feet. A cord of wood weighs about 5600 pounds (**2.54 tons**).

1880	Beehive type furnaces replaced the pit kiln (Toole et al., 1961) and biochar production increased to about 800,000 tons/year producing 14% of the pig iron generated in the US (Baker, 1985).
1882	Technological changes in blast furnaces made them larger, reducing the share of biochar-based pig iron by 5%. Biochar did not have adequate strength to support these large furnaces (Baker, 1985).
1890-1920	Construction of large wood distillation plants were used to recover biochar, which was at least as important as methanol, acetic acid, and various other chemicals that were produced (Toole et al., 1961). Retorts began to replace beehive type furnaces, which were becoming larger; further stimulating the expansion of the industry. The importance of the production of acid for textile manufacturing resulted in facilities for producing biochar and recovering chemical byproducts becoming more elaborate and expensive. The condensation of distillation volatiles produced a crude liquor which was refined in highly specialized equipment to yield mostly methanol and pure acetic acid (Toole et al., 1961).
1910-1940	Economic pressure, high investment costs, and the loss of chemicals to cheap synthetics resulted in the decline of the wood distillation industry. Manufacturing metals and chemicals was done using carbon materials that replaced biochar, which resulted in the abandonment of many of these distillation plants (Toole et al., 1961).
1950	Plants remaining in business downsized their operations and began to produce biochar as a cooking fuel for backyard home barbecues (Toole et al., 1961). An increase in demand for biochar by restaurants and home cooks benefited these remaining businesses.
1955	New biochar sources were needed as most of the large wood distillation plants ceased operation. Biochar needed for cooking as briquettes, ferrosilicon production, filtration processes, and horticultural uses came from small kilns constructed in rural areas designed to utilize low-grade logs from woodlots, as well as slabs and endings from sawmills (Baker, 1985).

1956	The most popular type of kiln was a concrete or masonry block kiln comprising 600 of the existing 1,500 operating units in 1956. Among the remaining types of kilns were only a few earth kilns, brick kilns, beehive kilns, and sheet metal kilns, which were the least common (Toole et al., 1961).
1961	Of the 1,977 biochar converting units in the United States, 262 were brick kilns, 805 were concrete masonry block kilns, 430 were sheet steel kilns, and 480 comprised of other types of kilns like retorts and ovens (Baker, 1985). A substantial amount of biochar was also produced by several newly developed methods such as vertical batch carbonization and continuous carbonization which utilizes both slab and round wood (Toole et al., 1961).
1972	Charcoal kilns were exempted from Missouri air regulations (Yronwode 2000).
1994	Citizens petitioned EPA for ambient monitoring of charcoal kiln air pollution (Yronwode 2000).
1995	First test on charcoal air pollutant emissions (Yronwode 2000).
1996	Missouri DNR/EPA began monitoring charcoal kiln air pollution (Yronwode 2000).
1997	Air pollution limits for Missouri charcoal kilns negotiated (Yronwode 2000).
1998	Missouri charcoal kiln regulations became effective (Yronwode 2000).
2005	Deadline for complete control of Missouri charcoal kilns emissions (Yronwode 2000).

3. CRITERIA TO SELECT PYROLYSIS REACTORS

This section discusses criteria for selecting the heart of the pyrolysis plant, “the reactor.” A strong regional and global biomass economy requires development of more selective, controlled, multi-product, flexible, and integrated pyrolysis units (Pelaez-Samaniego et al., 2008). An in-depth understanding of the socioeconomic context of pyrolysis must govern specific choices of pyrolysis technologies. Pyrolysis units should be designed with a clear business model in mind; even if a set formula has produced good results in other contexts, it should be applied cautiously (Girard, 2002). Achieving the highest energy yield from the raw material under consideration is one of the most important criteria however; this project seeks a means for balanced recovery of fuel with stable carbon (biochar) for improving soil productivity and sequestering atmospheric carbon.

Hanover Principles for sustainable design: An important goal of this report is to encourage the design of pyrolysis technologies meeting several essential design elements provided by the Hannover Principles of Sustainability (McDonough, 2000) which are embedded in the Ecology Waste to Resources Program. Several guiding ideas for the design of environmentally friendly pyrolysis reactors are as follows:

(1) Pyrolysis units should be net exporters of energy and only operate on renewable energy without reliance on fossil fuels or any sort of remote energy generation.
(2) The heating process must be efficiently incorporated into the design and be generated from renewable resources.
(3) The entire design process must use water carefully and conservatively.
(4) Beneficial consideration of rainwater and surface water runoff shall be incorporated into the design.
(5) Short- and long-term environmental impacts must be considered during the design process.
(7) Designs must be flexible enough to accommodate several different production needs.
(8) The evaluation of the design shall consider the necessary air, land, water, and solids to eliminate pollutant releases.

One of the main aims of this report is to collect enough background information to support the development of advanced pyrolysis concepts to produce both biochar and bio-fuels from wastes generated in the state of Washington. This literature review and technological assessment identify potential holistic designs for pyrolysis reactors and ancillary equipment in order to produce biochar for carbon sequestration and bio-oil for the production of green fuels and chemicals. We identify weaknesses of existing technologies and discuss possible alternative concepts addressing these weaknesses.

To differentiate between the different pyrolysis reactors, we employ the nomenclature recommended by Emrich (1985).

Kiln – Kilns are used in traditional biochar making, solely to produce biochar.
Retorts and converters – Industrial reactors that are capable of recovering and refining not only the biochar but also products from volatile fractions (liquid condensates and syngases) are referred to as **retorts or converters**.
Retort – The term **retort** refers to a reactor that has the ability to pyrolyze pile-wood, or wood logs over 30 cm long and over 18 cm in diameter (Emrich, 1985).
Converters produce biochar by carbonizing small particles of biomass such as chipped or pelletized wood.
Slow pyrolysis refers to a process in which large biomass particles are heated slowly in the absence oxygen to produce bio-char.
Fast pyrolysis refers to reactors designed to maximize the yields of bio-oil and typically use powdery biomass as feedstock.

A vast number of existing pyrolysis technologies make it difficult to identify which type of reactor is better suited for a targeted application. Classification of reactors varies according to several factors (listed in Table 1). A thorough analysis of the advantages and disadvantages of each existing design will improve selection of an appropriate design for a given application. Sections 3.1 – 3.14 describe general features of the design criteria for pyrolysis technology.

Table 1. Key criteria for selecting appropriate pyrolysis technology (these and additional criteria are described in Sections 3.1 – 3.14).

Reactor type	Final Products	Heat Transfer Rate	Particle size (Pretreatment)	Mode of Operation	Heating Method	Construction Materials	Portability	Reactor Position	Loading Mode
Fixed bed Fluidized bed Circulating bed Ablative Auger Rotary drums Moving beds Auger Reactors	Bio-oil Syn-Gas Bio-char Hydrogen Heat Electricity	Slow Fast	Logs; large particles Chips Fine Particles	For Intermittent operation For nearly continuous operation For continuous operation	Heating by direct admission of air to the wood (autothermal) Heating by direct contact of the biomass with furnace gases on the wood Indirect heating Internal radiators Heating through the walls	Earth pits Brickwork Steel	Stationary Semi-portable Portable	Vertical Horizontal	Manual Mechanical loading With cars

3.1. Final Products

The first criteria to consider are the targeted final products: (1) biochar and heat, (2) biochar, bio-oil and gases, (3) biochar, carbon black, and syngas (gas mixtures that contains varying amounts of CO and H), and (4) syngas (Pelaez-Samaniego et al., 2008). The following sections describe each of these concepts in greater detail.

3.1.1. Biochar and Heat

The first possible combination is the production of biochar and the recovery of the heat resulting from the combustion of pyrolysis vapors (Figures 4 and 5) (Pelaez-Samaniego et al., 2008). Plants that operate pyrolysis reactors coupled with boilers or incinerators produce biochar and the heat recovered from the combustion of pyrolysis vapors is used to produce steam, which may generate electricity in steam turbines (Pelaez-Samaniego et al., 2008).

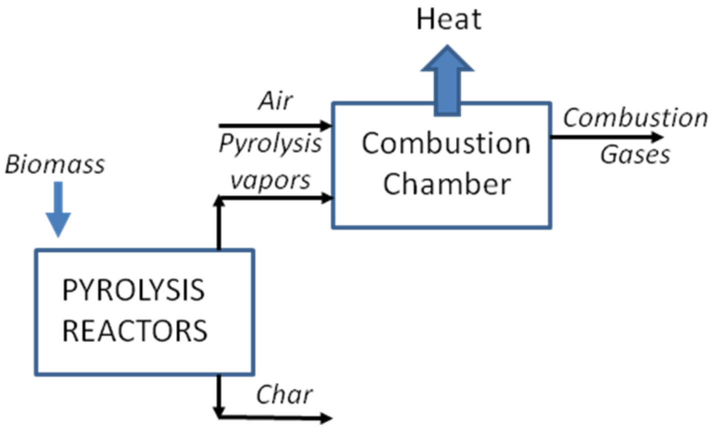

Figure 4. Pyrolysis scheme for the production of biochar and heat (Pelaez-Samaniego et al 2008)

Using pyrolysis vapors as a fuel for boilers or incinerators is an exceptionally promising alternative because it eliminates the use of natural gas or other liquid fuels without any major modification to the combustion chamber (Pelaez-Samaniego et al., 2008). Success of similar co-combustion schemes has been demonstrated using gasification in Lahti (Finland) and Amer (Holland) (Czernik and Bridgwater, 2004; van Loo and Koppjan, 2002). Mitsui Engineering & Shipbuilding Co., Ltd. has also employed this scheme in their recycling process creating heat and biochar from solid municipal wastes. International Tech Corporation (Figure 5), Agri-Tech Producers, and Choren are three examples of companies commercializing continuous pyrolysis reactors coupled to an incinerator to produce heat.

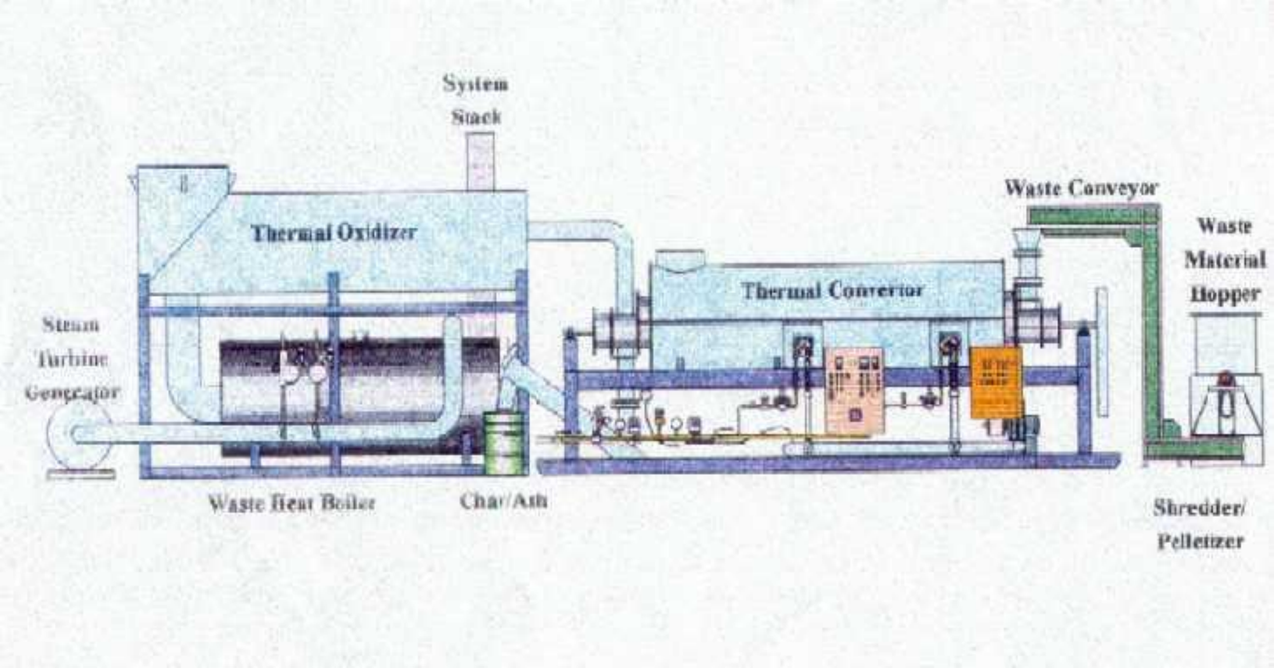

Figure 5. Pyrolysis unit with heat recovery **(**International Tech Corporation) (http://www.internationaltechcorp.org/IT-info.htm, date accessed: Nov. 13, 2010).

Recovering heat from pyrolysis vapors generated in batch rectors is much more difficult because the flow rate of pyrolysis gases is continuously changing. The CML Process developed by CIRAD and Innov-energies addresses the problem of heat recovery and gas cleaning from batch systems through combusting the pyrolysis vapors produced by several batch reactors in a centralized incinerator. A typical production plan is formed by 12 charcoal production kilns (CIRAD and Innov-energies, 2007) and a central anti-pollution incinerator (Figures 6 and 7).

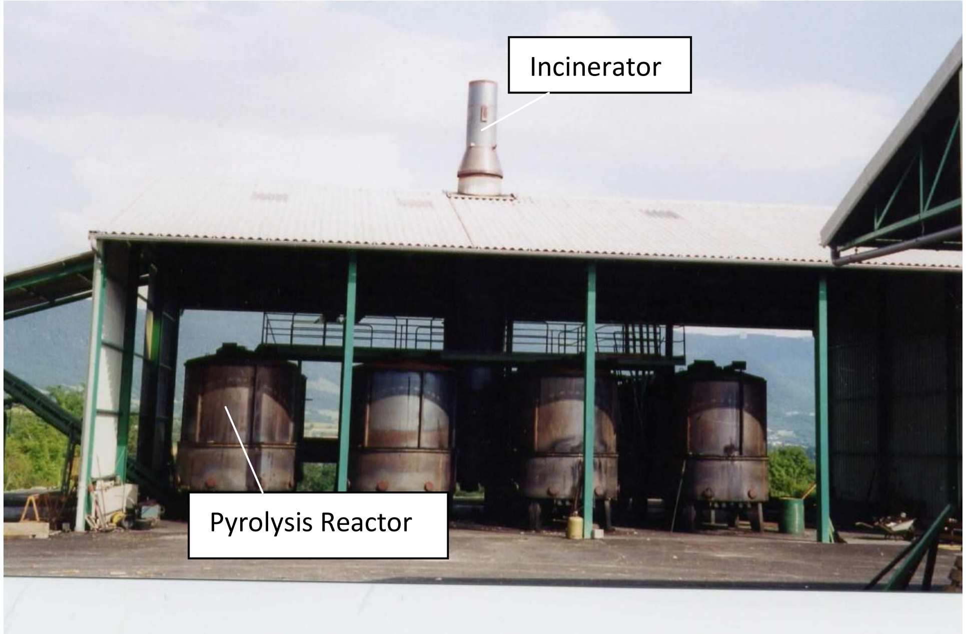

Figure 6. CML process for heat recovery in batch systems (CIRAD and Innov-energies, 2007).

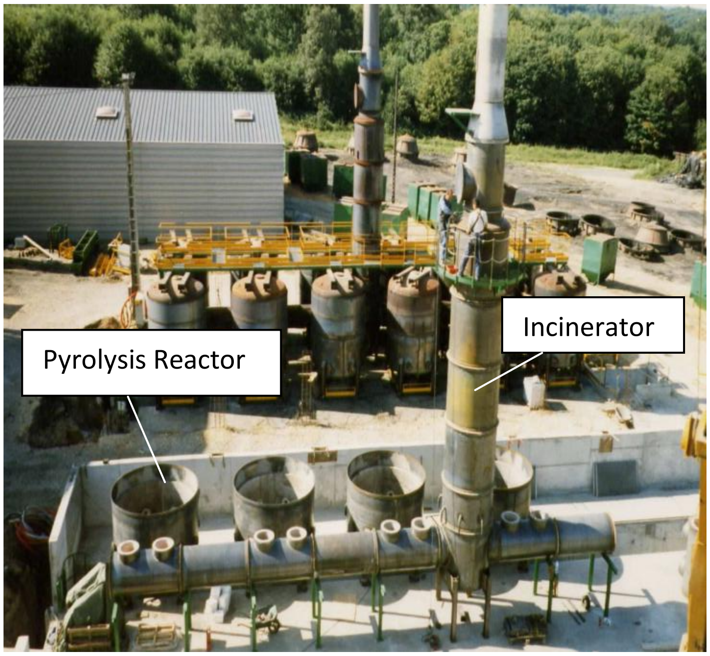

Figure 7. A CML Process under construction (CIRAD and Innov-energies, 2007).

3.1.2. Biochar, Bio-oil, and Gases

This combination also includes biochar, heat, and gases in addition to a liquid product (bio-oil) that results from the condensation of pyrolysis vapors (Figure 8). These bio-oils can be used as fuel for the production of electricity, to produce syngas through gasification, to produce transportation fuels through hydrotreatment, or to obtain an array of valuable co-products through advanced bio-oil refinement (Pelaez-Samaniego et al., 2008). Pyrolysis units can stand alone or can be incorporated into bio-refineries, depending on the capacity of the plant.

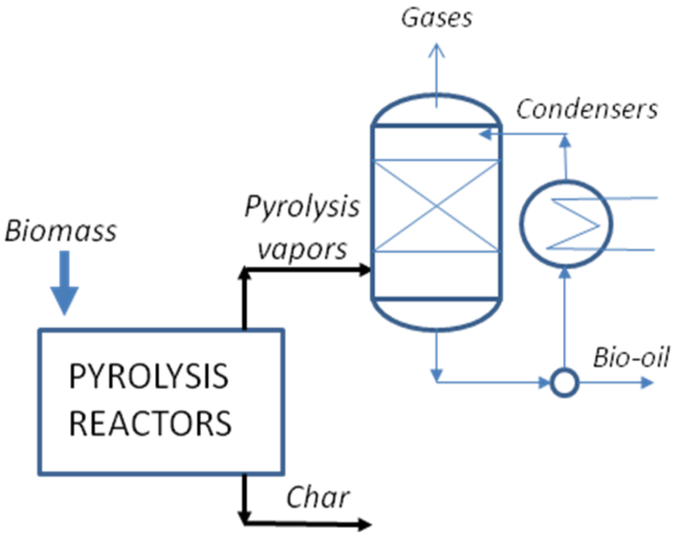

Figure 8. Pyrolysis scheme for the production of biochar, bio-oil, and gases (Pelaez-Samaniego et al., 2008).

Pyrolysis units intended to collect bio-oil are slightly more complex than those producing heat. Figure 9 shows a configuration of a pyrolysis unit with bio-oil recovery. One or more condensation steps can be used. While slow pyrolysis results in the production of a liquid formed by two phases called “pyroligneous water” and “decanted oil;” fast pyrolysis results in the formation of a single liquid phase called “bio-oil.” The wood distillation industry produced acetic acid and methanol from the “pyroligneous water” resulting from slow pyrolysis reactors.

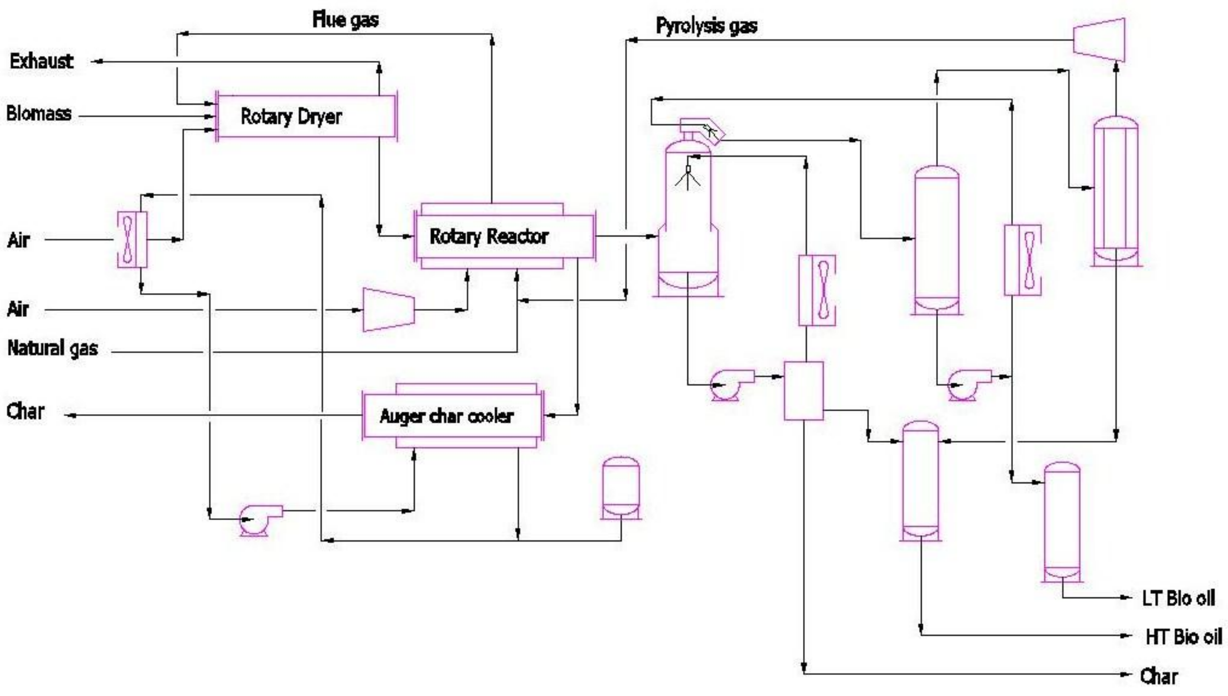

Figure 9. Rotary reactor process flow diagram (Courtesy of Coates Engineering, http://www.coatesengineering.com).

Although producing bio-oil is a relatively mature technology, bio-oil commercialization will not be viable until rural bio-oil refineries are developed that are able to convert these oils into stabilized bio-oils compatible with existing petroleum industry. The development of high-value products from bio-oils and biochar will improve the economic viability of this technology. Figure 10 shows a concept of biomass economy, which includes pyrolysis units, rural bio-oil refineries and modified petroleum refineries, for producing high-value products from bio-oil and biochar.

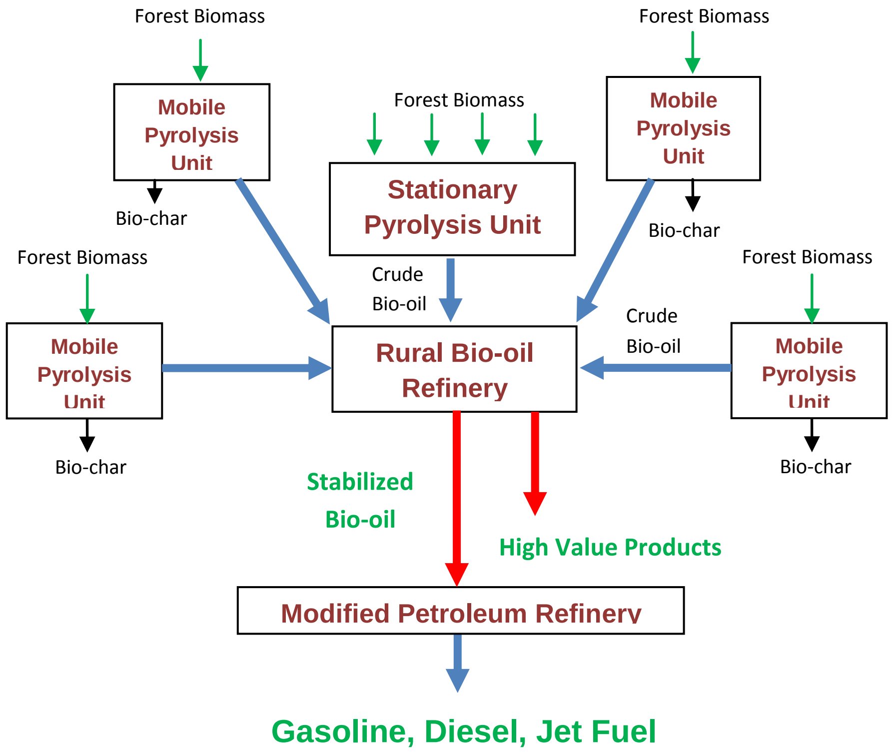

Figure 10. Biomass economy formed by mobile and stationary pyrolysis units, by rural refineries and by a modified petroleum refinery.

3.1.3. Biochar, Carbon Black, and Syngas

Producing a combination of biochar, carbon black, and syngas is a promising strategy to maximize yield of carbonaceous materials. The carbon black currently commercialized is produced from the incomplete combustion of fossil fuels. It is an amorphous material with high surface area and is typically used as pigment and reinforcement in rubber and plastics (http://en.wikipedia.org/wiki/Carbon_black, date accessed: Feb., 6, 2011). However, the production of carbon black from biomass is a poorly explored area. The technology shown in Figure 11 differs from those described in the previous sections in that immediately following the pyrolysis of the biomass there is a high temperature step in which the pyrolysis vapors are polycondensed creating soot (carbon black) and a gas rich in CO_2, CO, CH_4, and H. This technology is based on the idea that if the pyrolysis vapors are heated to temperatures up to

1200° C in a reducing atmosphere, much of the vapor will become soot, water, and syngas (Morf, 2002). Soot is the common name for carbon black which is an elementary form of carbon produced by the combustion of hydrocarbon in a limited air atmosphere. Since mineral coal and natural gas are the main raw materials used to produce carbon black, the current commercial process to produce this material generates excessive pollution.

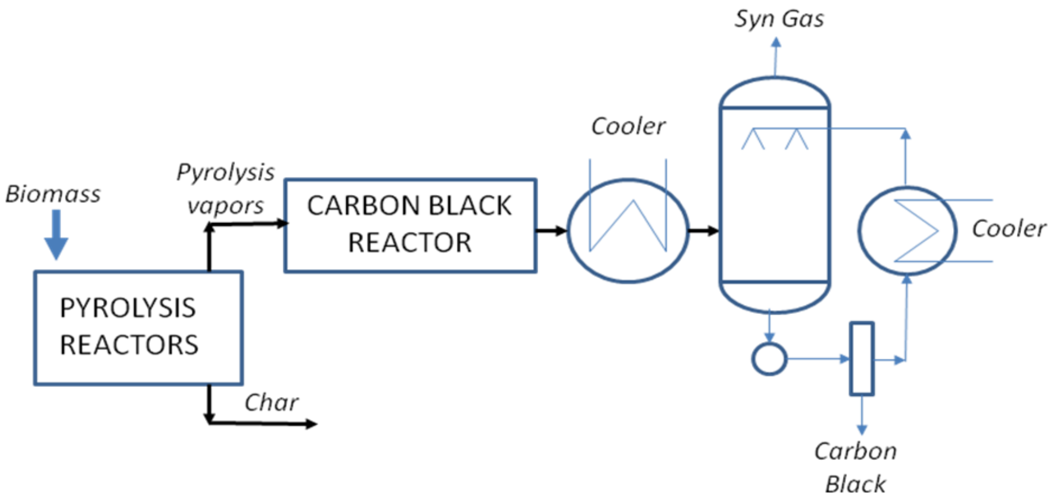

Figure 11. Pyrolysis process for the production of biochar, carbon black, and syngas (Pyrolysis reactor temperature 400-550 °C, carbon black reactor temperature over 1200 °C) (Pelaez-Samaniego et al., 2008).

Carbon black production is expected to reach 13 million metric tons by 2015. About 90% of carbon black, produced from natural gas, is currently used in the production of rubber products such as tires, as well as inks and pigments (Pira-International, 2010). Few studies document the properties of carbon black derived from biomass and its performance in rubber products.

3.1.4. Syngas

A concept called the Choren Process (Germany) (http://www.choren.com/en/, date accessed, Nov. 15, 2010), used for the production of syngas, employs a crushed and dried biomass that is pyrolyzed at temperatures of 400 to 500 °C to produce volatiles and biochar. The volatiles are then converted into carbon black by heating them to temperatures over 1400 °C. The carbon black and the remaining biochar are further gasified in a fluidized bed resulting in a synthesis gas with very low tar content (Pelaez-Samaniego et al., 2008). This concept is shown in Figures 12 and 13. This process can be modified by not gasifying the biochar, in which case the final products will be syngas and biochar.

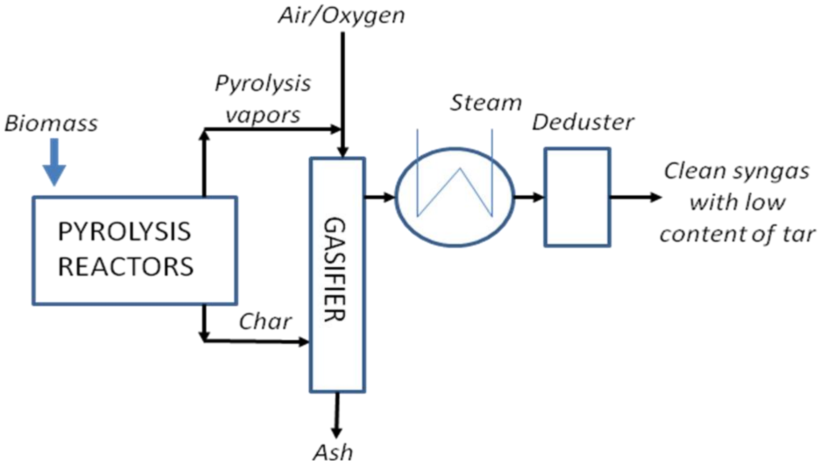

Figure 12. Process of the production of ash and syngas (Pelaez-Samaniego et al., 2008).

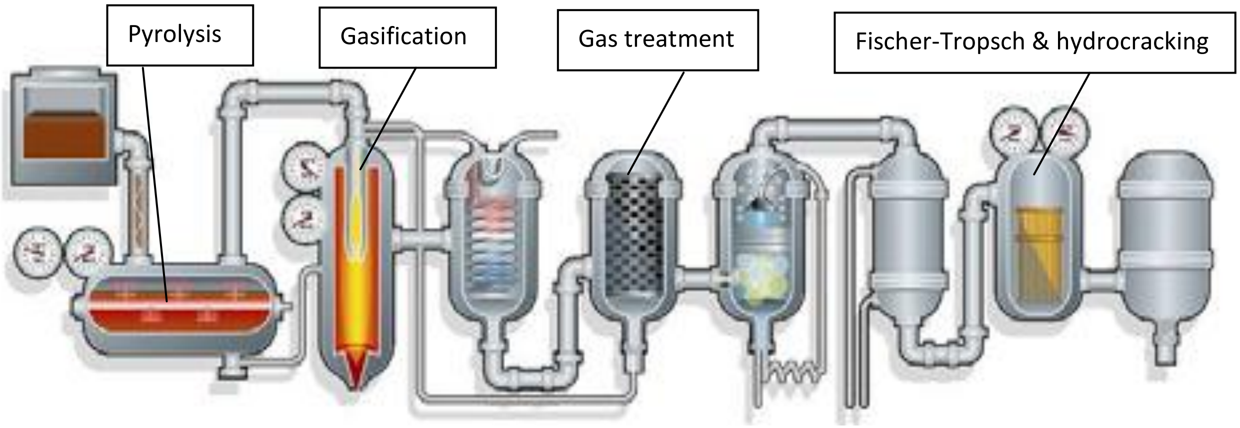

Figure 13. The Choren process for producing syngas using paddle pyrolysis reactors (Bienert, 2007).

3.2. Heat Transfer Rate

The heat transfer rate during pyrolysis is one of the most important parameters for determining the yield and property of products. High rate heating of lignocellulosic materials typically yield up to 75 mass % bio-oil, and approximately 15 mass % biochar. High heating rates can only be achieved when using very small particles (i.e. < 2 mm). Depending on the particle heat transfer rate achieved, it is possible to identify two types of pyrolysis reactors: *slow and fast pyrolysis*.

3.2.1. Slow Pyrolysis

With slow pyrolysis, the process of heating biomass is very slow (heating rate: 5-7 °C/min). Slow pyrolysis typically produces less liquid (30-50 mass %) and more char (25-35 mass %) than fast pyrolysis. The liquid produced separates in two phases (a pyrolygneous water and a decanted oil). Any reactor that utilizes particles larger than 2 mm in diameter is considered a slow pyrolysis reactor (kilns, retorts, and converters).

3.2.2. Fast Pyrolysis

With fast pyrolysis, the process of heating biomass is rapid (heating rates: over 300 °C/min). Fast pyrolysis is typically used to obtain high yields of single-phase bio-oil. Fast pyrolysis uses small particles due to the low thermal conductivity of lignocellulosic materials. However, it is possible to use larger particles through fast removal of the low thermal conductivity layer of biochar that forms around the particle. This method is known as *ablative pyrolysis*.

3.3. Mode of Operation

Depending on the mode of operation, pyrolysis reactors can be classified as batch, semi-batch, and continuous.

3.3.1. Batch Operation

Batch reactors are typically used to manufacture biochar while the recovery of byproducts is often of secondary importance (Klark, 1925). This process involves a heating up period in which the product is produced, followed by a nonproductive cool down period that prepares the equipment for the next batch. In a batch kiln, retort, or converter, individual particles remain almost immobile. These reactors only allow the discharge of biochar after it has been cooled. Start up and energy costs to heat and reheat the oven is repetitive and energy intensive. It is also difficult to use the volatiles formed during the process, which are released to the atmosphere causing significant pollution. Batch operations are very common among small reactors.

3.3.2. Semi-batch Operation

The semi-batch operated system is portable and makes better use of hot ovens. Heat containing vapors are recycled between batch reactors. The Carbo Twin Retort (Figures 14- 17), developed by Ekoblok/Carbo Group, is a typical example of a semi-batch operation. The Carbo Twin Retort is a semi-continuous production module. Its capacity is determined by the number of batch runs that can be carried out (Trossero et al., 2008). Some of these systems allow recovery of liquid products, but most are typically used to produce biochar.

Figure 14. Semi-batch reactor - Van Marion Retort (VMR) system (source: http://www.bioforsk.no/ikbViewer/Content/71499/Biokarbonseminar%20%C5s%2011-03-2010%20Morten%20Gr%F8nli.pdf) (date accessed: Nov., 14, 2010).

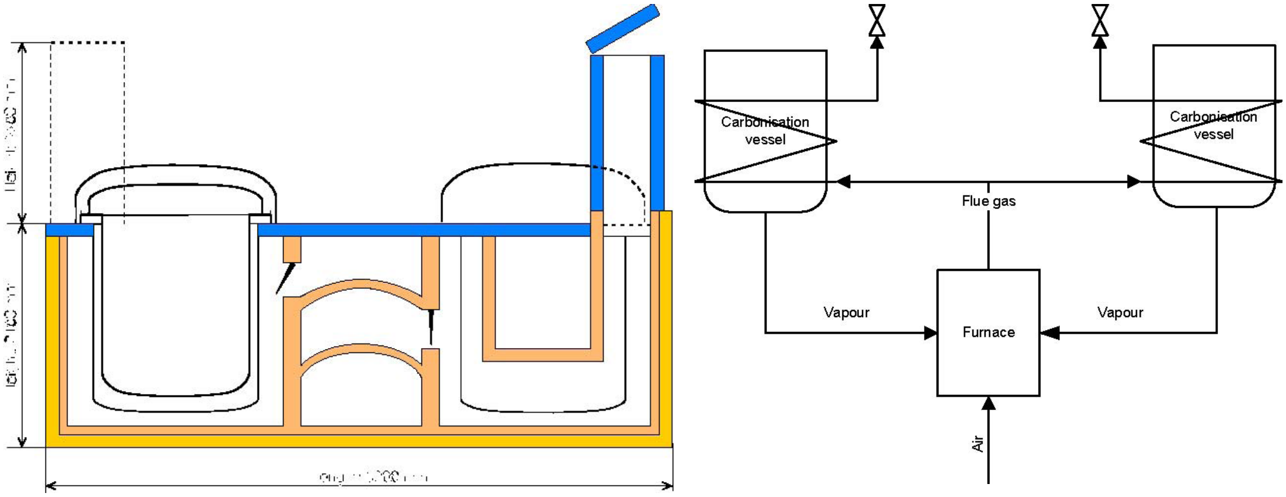

Figure 15. Cross section of the Carbo Twin Retort and operating principles (Trossero et al., 2008).

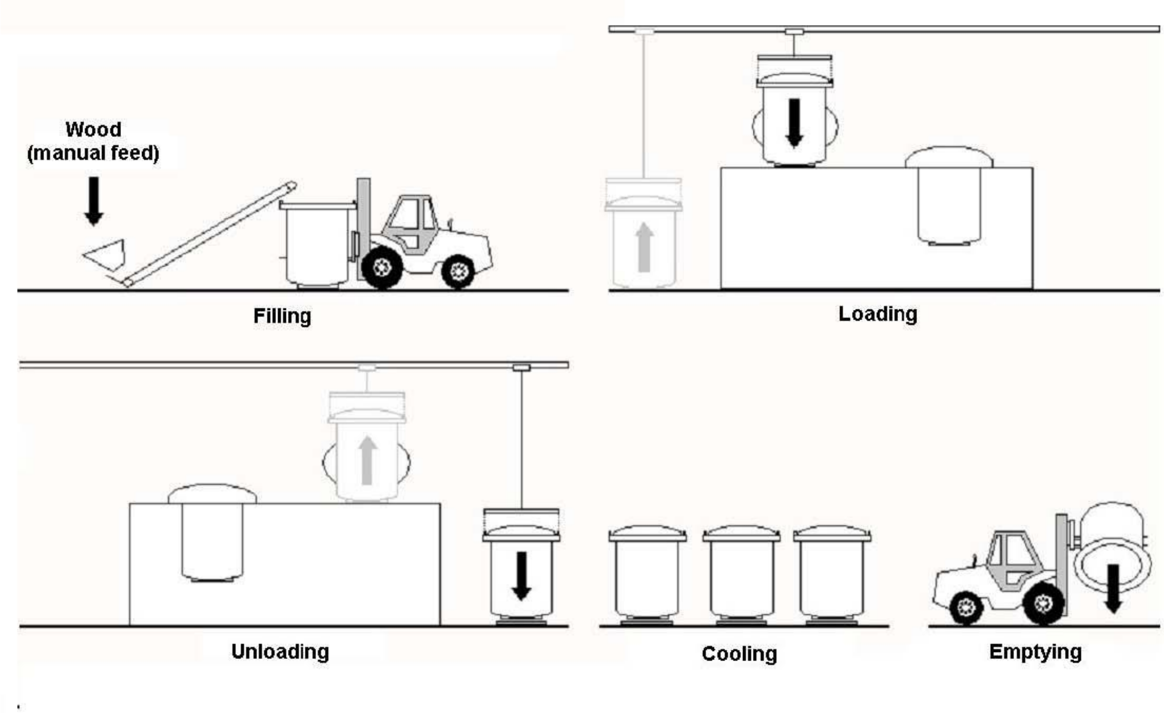

Figure 16. Operating principles of a semi-batch system (Carbo-Twin Retort) (Trossero et al 2008).

A similar concept is being commercialized by a company called Bioenergy LLC based in St Petersburg, Russia. The semi-batch stationary systems built by this company are commercialized under the name of POLIKOR and EKOLON. In this technology the removable retorts are inserted inside the firewood box. The retorts have a special device at the bottom that allows the pyrolytic vapors to enter into the combustion chamber and generate part of the heat needed to drive the process. The mobile units developed by this company are called POLYEVKA and KORVET. These semi-portable steel kilns have two advantages: they can be moved easily (which may be useful for small-scale production) and shorter cycles result when biomass is dispersed and the kilns cool quickly (Emrich, 1985).

3.3.3. Continuous Operation

Continuous operation reactors are designed to run nearly continuously with occasional down time for maintenance. Typically, the unit attainment, (i.e., the percentage of the available hours in the year that the plant operates) is usually 90-95%. Most continuous operation reactors are justified only if the flow rate is high. A typical continuous unit for the production of biochar has a capacity over 2.75 ton/h. These systems usually have proven designs for creating products with well-established markets. They are often more economical for large-scale production. Figure 17 shows a continuous wagon reactor. This technology is currently being commercialized by Impianti Trattamento Biomasse based in Milan, Italy. Continuous pyrolysis may seem like a simple matter, but in practice the process requires a higher level of training (Klark, 1925).

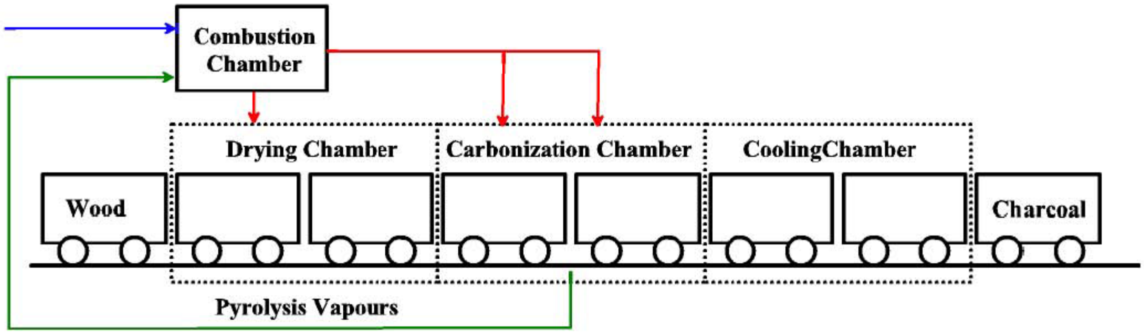

Figure 17. Continuous carbonization operations use pyrolytic vapors to heat the combustion chamber (Trossero et al., 2008).

3.4 Heating Methods

Nearly all pyrolysis reactors require the biomass particle dimensions to be well specified. If the particles are not of the proper dimensions, penetration of heat will be slow and the necessary heating rate will not be reached. If the feedstock is kept in steady movement, heat exchange can be improved significantly. There are two general strategies to heat pyrolysis reactors. The first one uses a hot carrier (typically a gas) produced by the combustion of wood, oil, gas, etc. in an external combustion chamber. The second strategy allows a limited amount of combustion to occur inside the pyrolyzer by burning part of the wood and using this heat to dry and carbonize the remaining wood (Emrich, 1985). Some authors (Dumesny and Noyer, 1908; Fournier, 2009) further break out pyrolysis reactors into three categories depending on the heating method used: (1) pyrolysis by partial combustion (auto-thermal systems), (2) pyrolysis by injection of a hot gas in the load (direct heating with an inert hot gas), and (3) pyrolysis in an enclosed reactor or retort (indirect hearting). Figure 18 shows diagrams of each of these systems.

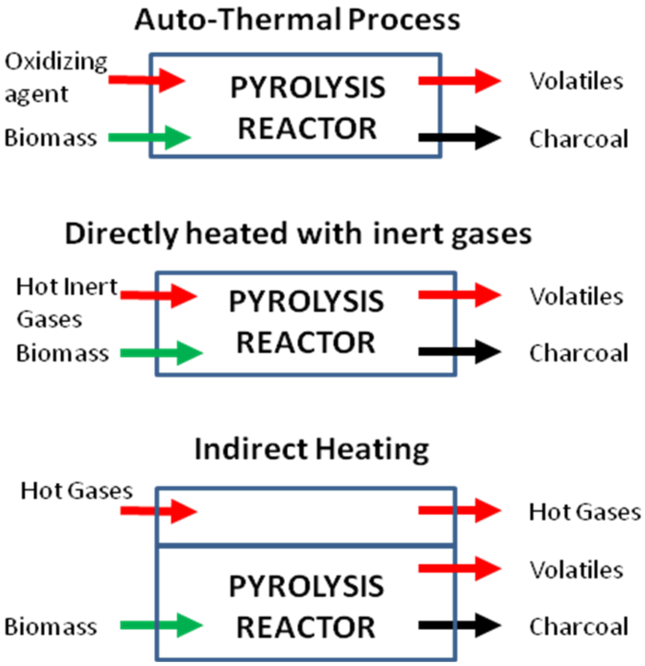

Figure 18. Types of pyrolysis technologies according to the heating method used (Fournier, 2009).

3.4.1 Partial Combustion (Auto-thermal Processes)

Partial combustion of pyrolysis vapors and biochar is most common for small-scale operations (Emrich, 1985). Burning part of the raw material with a controlled air inlet provides the energy necessary for the process. This technique requires that a portion of the biomass be combusted, which in-turn reduces the yield of biochar. Therefore, it is best to operate these systems in areas where raw materials are cheap. These systems typically have low capital cost partly because no heat surfaces are needed and condensable products are usually not recovered.

3.4.2 Carbonization by Contact with Hot Gases

Hot gases from an external source that come into direct contact with the fuel charge provide the energy required for carbonization. This method reduces the need for expensive heat transfer surfaces, however, costs are associated with heating the required inert gases. The fuel used to heat the heat carrier, typically wood of inferior quality or leaves, is combusted in an outside furnace (Klark 1925). Overall biochar and byproduct yields are high making this system suitable for medium to large plants (Emrich, 1985).

3.4.3 Indirect Heating

With indirect heating the retort/converter is heated from the outside and strictly excludes oxygen from the inside. The fuel charge is placed in a sealed container and an external heat source, partially fueled by the off gases, transmits the heat necessary for pyrolysis through its walls. Once the carbonization process has started, pyrolytic gases released by the process can be used as fuel to provide part of the energy needed to sustain pyrolysis reactions. Other than its own off gases, any combustible material can also feed the heat source. Some systems use molten salts as a heat carrier. This type of system is ideal for the recovery of volatile products and yields large amounts of biochar and byproducts (Toole et al., 1961).

*3.4.3.1 Internal radiators: 7*Hot pipes placed inside the reactor supply the necessary heat for pyrolysis (Toole et al 1961). The benefit to this type of reactor is the provision of the radiator system inside the reactor, which increases the heat transfer area (Klark, 1925). Internal radiators must be used for large reactors.

3.4.3.2 Heating through reactor walls. All heat required for pyrolysis is transferred through the walls of the reactor. Since the heat transfer inside the biomass bed is relatively slow, large reactors cannot depend solely of this heating method. For large reactors, heating through the external walls should be accompanied by the use of internal radiators or by direct heating.

3.5 Construction Materials

3.5.1 Earth

Since the dawn of carbonization history, earth has been used to keep out oxygen and to insulate the carbonizing wood against excessive heat loss. The obvious low cost of this method has kept it alive for centuries. Readily available and non-combustible, earth is an excellent choice as a sealant for enclosing carbonizing wood. There are two methods of using earth as barrier in the carbonization process: underground and on the surface. The underground method involves digging out a pit, placing firewood in the pit, and then covering the hole with the excavated earth to seal and insulate the chamber (pit kilns). The second method consists on covering a pile of wood resting on the ground with earth, sand, and leaves, which forms a necessary gas-tight layer behind which biocharring can take place.

3.5.2 Masonry, CinderBlocks, and Concrete

To control the amount of oxygen during carbonization, concrete, masonry, or cinder blocks can take the place of earth as a sealant. The recommended basic wall material is either concrete or cinder blocks composed of both coarse and fine aggregates of crushed and screened cinders from bituminous coal clinkers (Toole et al., 1961). Another material commonly used is reinforced concrete (Toole et al., 1961). In most cases, the firebricks used for the kiln are made by the operator rather than purchased (Emrich, 1985). These brick kilns are typically auto-thermal and have a very long lifespan that usually exceeds their usage periods. One advantage of these brick kilns is their portability. In many developing countries, the bricks are dismantled and sold as building materials once the carbonization operation needs to be moved to a new location. (Emrich, 1985).

3.5.3 Steel or Cast Iron

Retorts, converters, and fast pyrolysis reactors are commonly built with steel or cast iron because heat can easily be transferred through walls or radiators made from these materials.

3.6 Portability

3.6.1 Stationary Pyrolysis Units

Stationary units are typically large installations that can process more than 100 tons/day (Figure 19). Because these units are permanent, transportation of the raw material from its source adds to the cost of a project (Dumesny and Noyer, 1908). Due to transportation and building expenses, these reactors are justified when large amounts of biomass are available for the production of biochar and bio-oil. Some stationary units are designed to be dismantled and sold in parts after they are no longer useful.

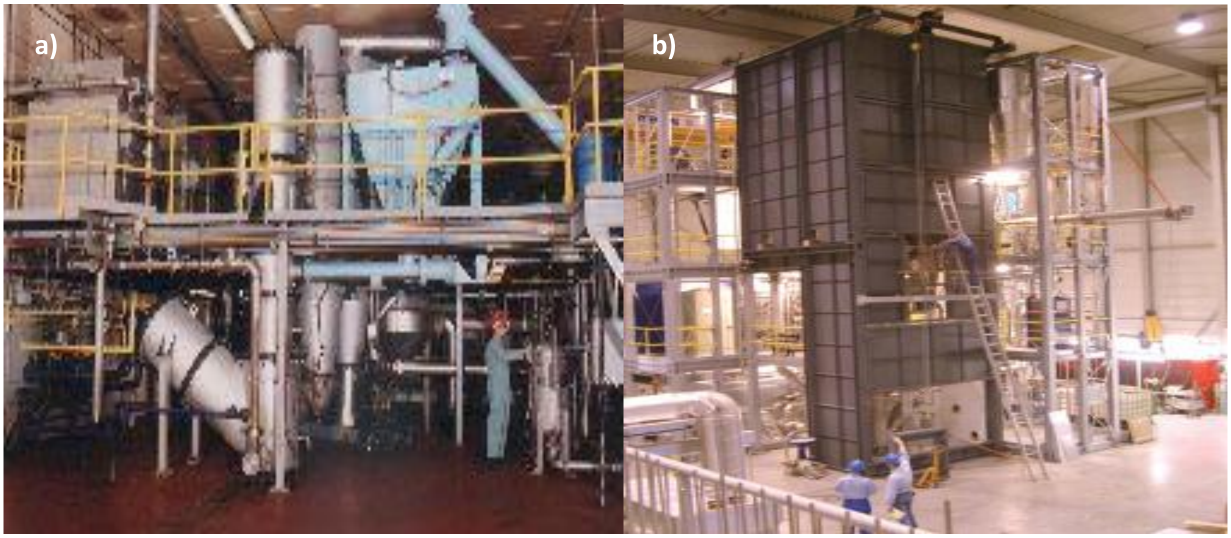

Figure 19. Stationary fast pyrolysis reactors for industrial settings (a) Ensyn, http://www.ensyn.com; date accessed: Nov. 15, 2010 and (b) BTG, http://www.btgworld.com; date accessed: Nov. 15, 2010.

3.6.2 Semi-portable Pyrolysis Reactors

Some components of these systems are stationary but the most expensive components are portable. As seen in Figure 20, the furnace (left), which generates heat for the pyrolysis reactor, is stationary, while the reactor and condensers (right) are portable.

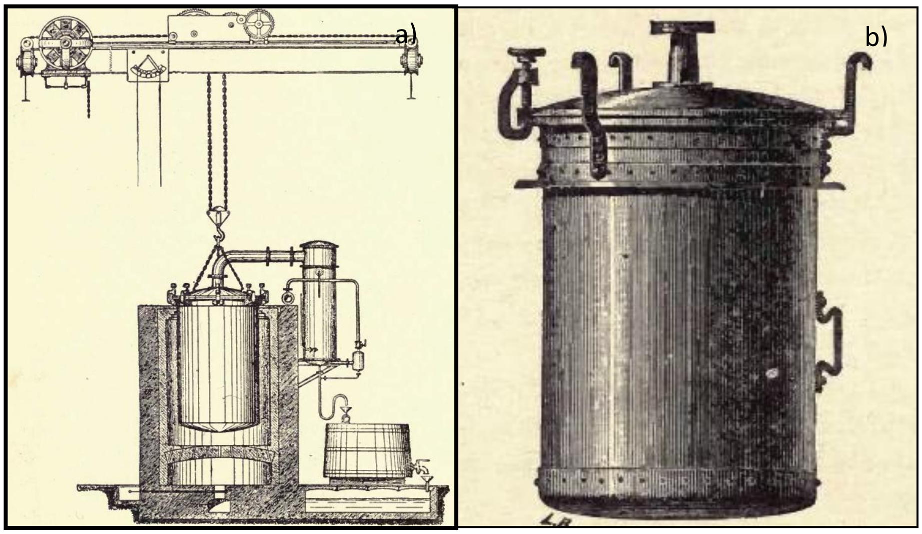

Figure 20. Semi-portable vertical steel retort unit (5 m^3) (a) Klark, 1925 (b) Dumesny and Noyer, 1908.

Another example of a semi-portable reactor is shown in Figure 21. Portable wagon retorts were typically coupled with a stationary brick furnace in the old wood distillation industry.

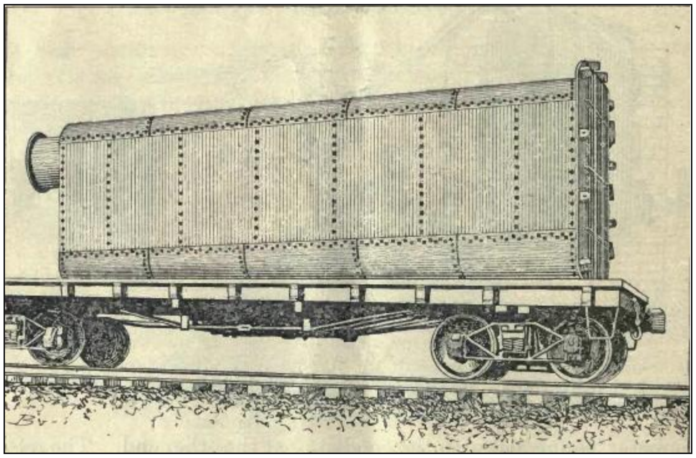

Figure 21. A semi-portable retort (Veitch, 1907)

3.6.3 Portable or Mobile Units

These fully transportable units consist of equipment and accessories that can be easily and rapidly assembled and disassembled using simple tools (Figures 22 and 23).

Figure 22. This 50 t/day portable (Mobile Pyrolysis Unit, ABRI) must be disassembled for transportation (source: http://www.advbiorefineryinc.ca/home; date accessed: Nov., 15, 2010).

Figure 23. Mobile pyrolysis reactor developed by JF Biocarbon, Canada (source: http://terrapreta.bioenergylists.org/taxonomy/term/1175; date accessed: Nov., 15, 2010).

Another type of unit consists of several portable sections specially designed and built from metal sheets (Figure 24). This system can be moved to a site that may have more available resources.

Figure 24. Examples of portable metal kilns (kilns assembled from portable sections) (Paddon and Harker, 1980).

3.6.4 Built-in-Place Kilns

Kilns that are built in place typically are constructed from soil or other local materials, are located close to biomass resources, and are small (Figure 25). They are economically viable if the cost of construction and transportation of the biochar is lower than the cost of transporting and processing the biomass.

Figure 25. Earth kilns built in place (source: http://www.biocoal.org/10.html; date accessed: Nov., 15, 2010).

3.7 Reactor Position

The horizontal or vertical positioning of pyrolysis reactors (Figure 26) is inadequately discussed in the literature. The reactor's position is important because it has significant consequences for how biomass is loaded and how the pyrolysis unit is operated.

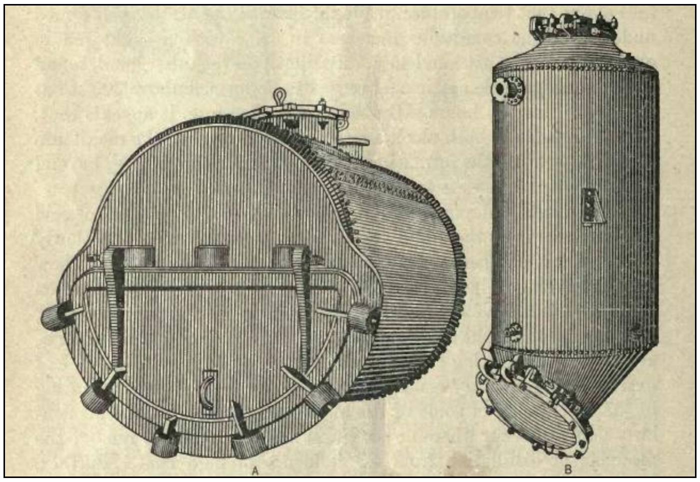

Figure 26. Horizontal and vertical retorts used in distilling turpentine (Veitch, 1907).

3.7.1 Horizontal Reactors

During the 19th century, Great Britain, Sweden, and Germany typically pyrolyzed wood in retorts laid horizontally (Dumesny and Noyer, 1908). The standard retort was cylindrical and made from cast iron, which later was replaced by steel.

3.7.2 Vertical Reactors

The French mainly used vertical retorts during the 19th century. Vertical reactors can be difficult to load but take advantage of gravitational forces to help move biomass. This made them the main reactor type used for converters (Dumesny and Noyer, 1908; Veitch, 1907).

3.8 Raw Materials

The size and type of available raw materials may determine the specific type of kiln, retort, or converter (Emrich, 1985). As a rule, batch kilns and retorts are chosen to carbonize raw materials that are over 100 mm long and over 25 mm in diameter. These systems cannot suitably carbonize smaller particles such as sawmill chips, nutshells, husks, hulls, leaves, small twigs, or bagasse (Emrich, 1985). These types of feedstocks can be carbonized in converters or must be further ground in order to be processed by fast pyrolysis reactors. Three main types of wood typically used are: (1) cordwood, (2) sawmill chips and pellets, and (3) fine particles (less than 2 mm diameter).

3.8.1 Cordwood

Cordwood usually consists of material > 1 m in length, but also may range from 10 to 40 cm in length (Toole et al, 1961). Wood that is preferable for a given fuel charge should be of the same general size and moisture content. This simplifies handling the wood and creates more uniform carbonization. Round wood with a cross section greater than 20 cm should be split or cut into smaller pieces (Toole et al, 1961). Figure 27 shows example of cordwood yards.

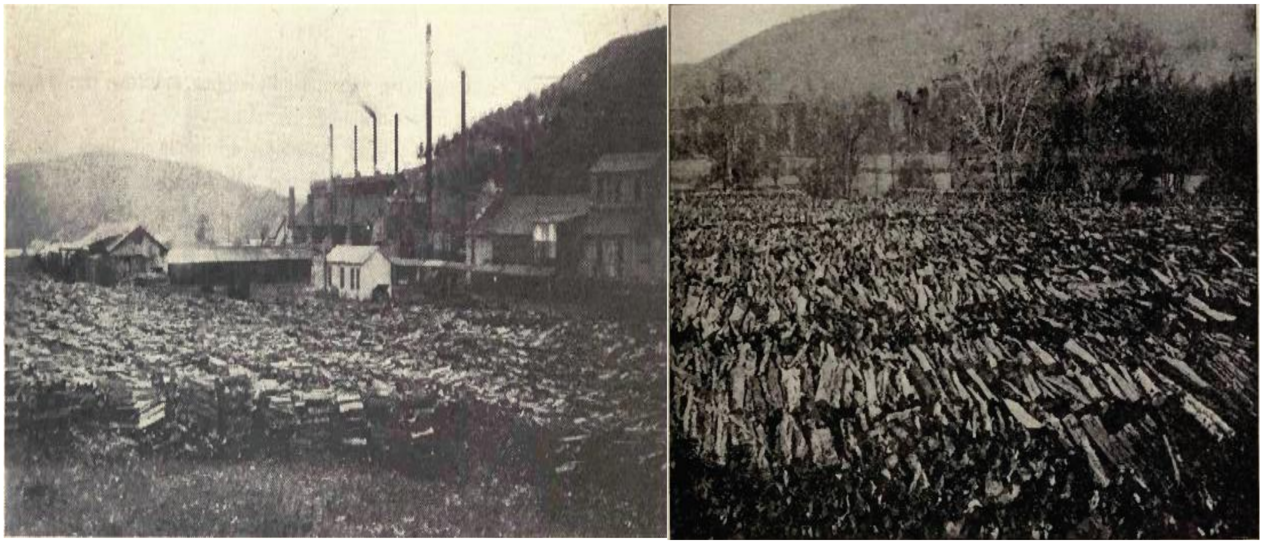

Figure 27. Cordwood used by the wood distillation industry historically (Bates, 1922; Brown, 1917).

3.8.2 Chips

Chips can be produced directly from woody biomass, but transporting them from their source to pyrolysis plants requires planning. The main advantage of processing chips is that they are easy to handle.

3.8.3 *Fine Particles*

Fine particles (< 2 mm diameter) are typically used with fast pyrolysis reactors (fluidized bed reactors, and circulating bed reactors). In order to achieve necessary heat transfer rates, small particles (< 2 mm diameter), typically produced from grinding chips, are needed. Grinding and pretreatment represent additional energy and cost to the total process cost.

3.9 Loading and Discharge Methods

To use the kiln effectively, the wood must be stacked so that combustion gases can freely circulate through the pile. Since labor is a major operation cost, labor for loading and unloading should be minimized. The location of the air entry and smoke outlet openings and the type of wood affects how a kiln is loaded and unloaded. Loading can be accomplished manually, mechanically, and with the use of wagons.

3.9.1 Manual Loading

Cordwood and slabs are loaded and unloaded by hand through a door (Toole et al., 1961; Bates, 1922). To use kiln capacity effectively, wood must be stacked to allow combustion gases to circulate freely through the pile (Toole et al., 1961). Stacking wood inside the kilns is labor intensive. All of the logs must be packed as close together as possible with thinner pieces against the wall and thicker logs towards the center (Emrich, 1985).

3.9.2 Mechanical Loading

Using mechanized yard handling equipment has several distinct advantages. Conveyer belts, bucket elevators, and tractor scoops can quickly and efficiently move the discharged biochar from the kiln (Toole et al., 1961). Tractor scoops (Figure 28) move larger material, while smaller pieces (chips) are fed into the reactor with a conveyor or bucket elevator (Toole et al., 1961).

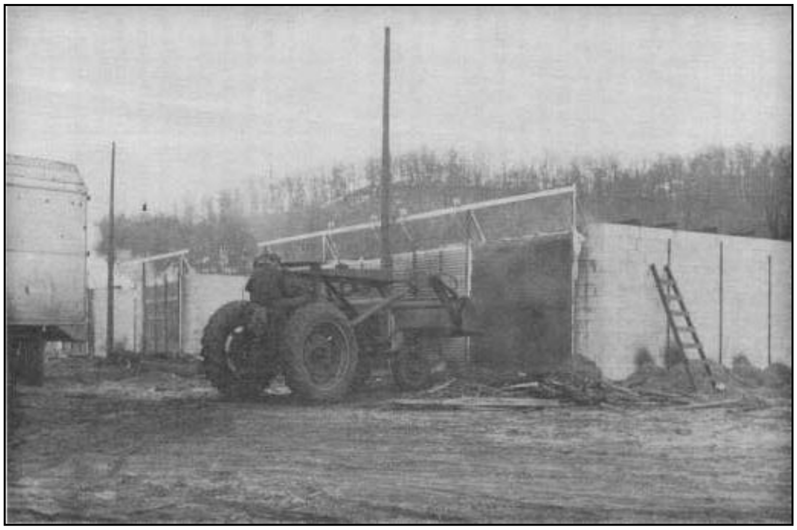

Figure 28. Tractor with a scoop being used to discharge a kiln (Toole et al., 1961).

3.9.3 Use of Wagons

Using wagons (Figure 29) to load and unload the pyrolysis reactor can reduce costs considerably. Wagon cars carry feedstock directly into the oven on a track and then back out of the oven with the resulting biochar. However, maintaining wagons that are frequently subjected to the extreme temperatures of the ovens (thermal fatigue) contributes to operation costs.

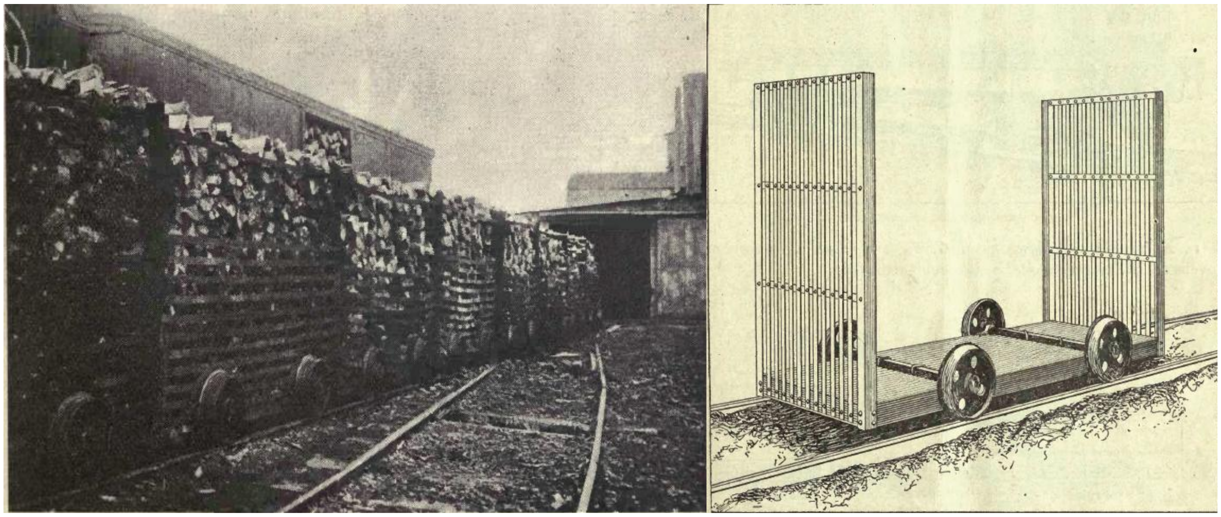

Figure 29. Cars used to load wood into the oven (Bates 1922, Veitch 1907).

3.10 Kiln Size

Once a suitable location has been selected, the size and shape of the kiln must be determined. The size, or gross capacity, of the kiln depends on: (1) weekly or monthly volume of raw material to be carbonized, (2) shape and size of the raw material (i.e., chunk, short-length, round wood, long slabs, or other mill residues) (Emrich, 1985). Small kilns typically hold up to ten cords (25.4 tons). Masonry kilns should not be larger than ten-cords (25.4 tons) because the carbonizing temperature tends to cause considerable expansion (Toole et al., 1961). Large kilns can hold more than 100 tons.

3.11 Charge Ignition Methods

Moisture content of wood determines the amount of fuel needed for ignition. Fuels used to ignite pyrolysis reactors include dry kindling wood, brands, leaves, natural gas, biochar, and fuel oil. Three methods most commonly used to ignite the biomass are: (1) ignition by fuel placed at the charge, (2) ignition by auxiliary fuel either with a torch, or 3) a dedicated ignition system.

3.11.1 Ignition Fuel at Midpoint or in the Front of the Charge

This method involves placing oil soaked fabrics or glowing biochar through the air inlet holes at the base or through the center hole in the top to ignite the kindling wood. Once the kiln has been ignited, the operator determines how the contents are reacting by the color of the smoke. For instance, a dense white smoke for the first few days would indicate that the wood has high moisture content and that water is evaporating (Toole et al., 1961).

3.11.2 Ignition by Gas-fired Torch

Using kerosene or a gas-fired torch is one of the most efficient methods to ignite a charge (Figure 30) (Toole et al 1961). These inexpensive torches are a good source of heat capable of efficiently and quickly igniting the charge (Toole et al., 1961). It usually takes anywhere from five to ten minutes of directing the torch flame through the air ports before the charge is burning. Torch ignition eliminates time spent preparing other fuels, which furnish variable heat and may not properly ignite the charge. Ignition is practically assured with a torch. Using a torch also allows more space for the charge (Toole et al., 1961).

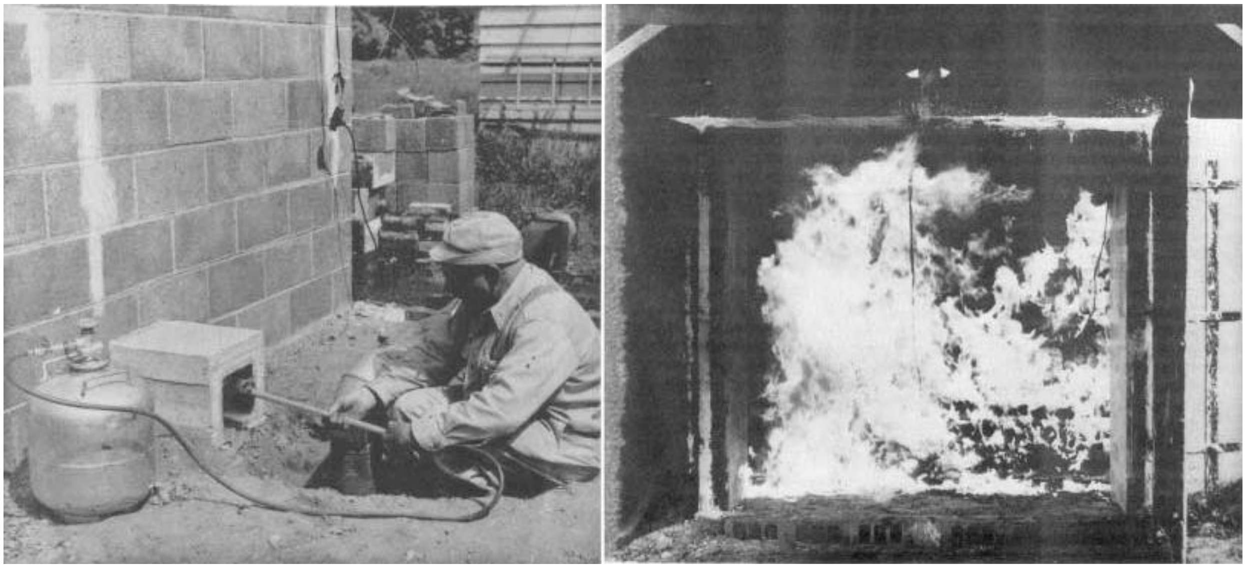

Figure 30. Igniting the kiln charge with a gas torch (left); and ignition of the charge by the open door method in an auto-thermal process (right) (Toole et al., 1961).

3.11.3 Use of Dedicated Burners

Ignition can also be achieved with a dedicated burner (Figure 31). Auxiliary fuel is halted once the proper pyrolysis temperature has been obtained and the heat to keep the temperature of the reactor is generated from the combustion of the pyrolysis vapors (Pro-natura 2004).

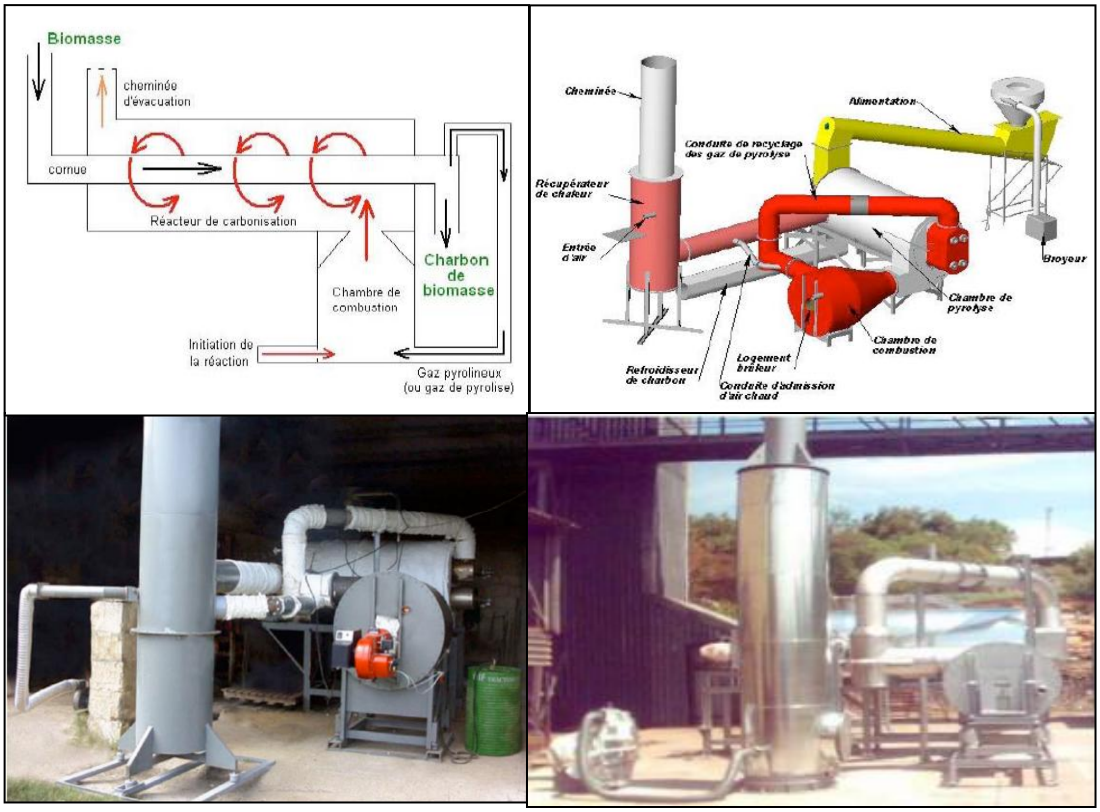

Figure 31. Continuous reactor indirectly heated through the walls with the heat released from the combustion of pyrolysis vapors (source: http://www.pronatura.org/index.php) (date accessed: Nov., 15, 2010).

3.12. Process Control

To achieve good yields of high quality products, reaction conditions must be well controlled. The heat generated must be sufficient to dry the wood and maintain a temperature for efficient carbonization. Burning also must be limited in order to obtain the proper amount of heat to produce quality biochar. The temperature in the reactor is the most important variable to control during pyrolysis (Toole et al 1961). Two ways to control heat conditions of pyrolysis reactors: are (1) to observe the color of vapors produced and (2) to measure and control the temperature inside the reactor either manually or using standard feedback control systems.

3.12.1. Control by Observation of Vapor Color

This approach is typically used in carbonization reactors without heat or bio-oil recovery. The production of steam results in white smoke that indicates the drying of the biomass, whereas a black smoke is typically associated with pyrolysis. After pyrolysis begins, the smoke becomes more transparent as the process continues. Once the carbonization process is completed (no more smoke is produced), the cooling cycle is started by sealing all of the air ports. Though all of the air intake ports are sealed, the chimneys must remain open until all smoking has ceased. This prevents the accumulation of gas pressure within the kiln and releases any smoke that may form during the cooling process. Chimneys are usually left open for about one to two hours until the smoking stops, at which point they should be closed immediately. This prevents any fresh air from entering the kiln which may support combustion or result in an explosion (Toole et al., 1961). Toward the end of the carbonization period the smoke color and volume do not provide much information about the progress of the carbonization.

3.12.2. Direct Temperature Measurement

Since the carbonization process is controlled by time and temperature, it is important to monitor both. A direct and reliable measurement of the carbonization progress can be done by monitoring the temperature (Toole et al., 1961). Although it is safe to open the reactors and discharge the char once the temperature is lower than 65 °C (Emrich 1985), the reactor should be checked for localized hot spots before discharging begins.

3.13. Pressure

Pyrolysis reactors can be operated at atmospheric pressure, in a vacuum, or at high pressure. Operating a reactor in a vacuum results in increased production of liquid products enriched with levoglucosan, while operation under high pressures results in greater yields of biochar and gases.

3.13.1. Atmospheric Pressure

Most pyrolysis reactors operate under atmospheric conditions due to its simplicity. Because it is not necessary to create a vacuum of high pressure, the cost of auxiliary equipment is drastically reduced.

3.13.2. Vacuum Pyrolysis

Reactors that operate in a vacuum are more complex due to the necessity of avoiding air leaks. This technique is typically used to enhance the production of liquid products, yielding an amount of oil that is comparable to that of fast pyrolysis reactors.

3.13.3. Pressurized Pyrolysis

Operating a reactor under pressure results in limited production of liquids. However, pressurized reactors produce much higher yields of biochar and syngas. A high-pressure reactor developed by the University of Hawaii is seen in Figure 32.

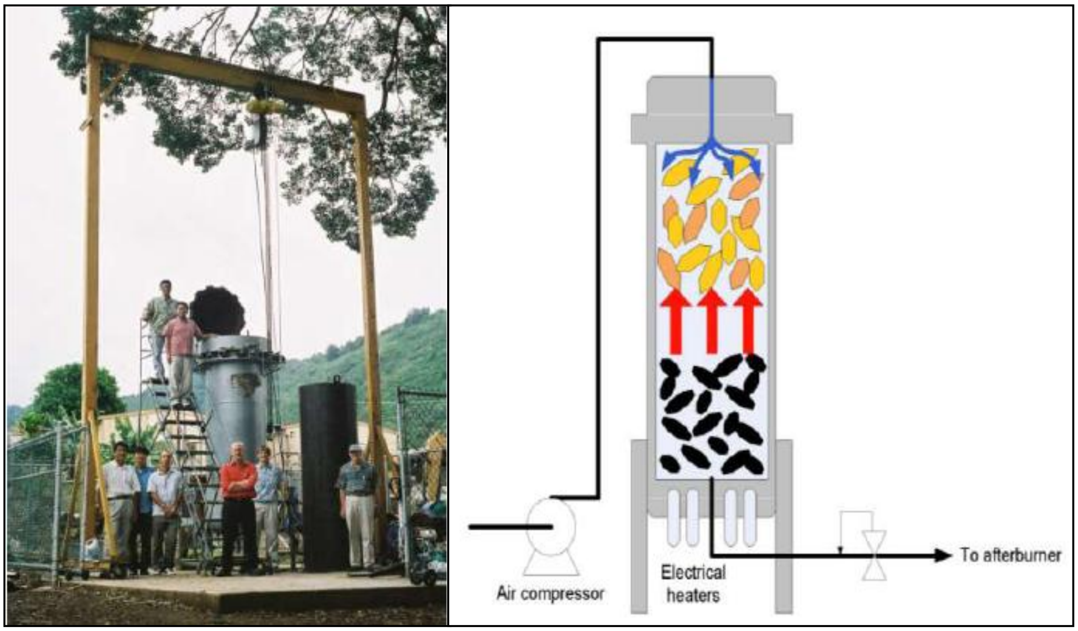

Figure 32. High-pressure pyrolysis reactor at the University of Hawaii (Antal, 2009) (www.hnei.hawaii.edu; date accessed: Nov. 13, 2010).

3.14. Pretreatment of Feedstock

Feedstock is rarely fed directly into the pyrolysis reactor without any pretreatment (Cummer and Brown, 2002). In order to improve the efficiency of pyrolysis, the feedstock must be dried, reduced to the proper size, and free of alkaline compounds (Cummer and Brown, 2002).

3.14.1. Drying

Most pyrolysis units work best using a feedstock with moisture content in the range of 10-20% (Cummer and Brown, 2002). Freshly harvested biomass can have a moisture content of up to 60% and is likely to clog the feeding system and result in a lower heating value of oil (Cummer and Brown, 2002). A fairly large energy input is required for the drying process. Although the drying process can reduce the overall efficiency of a pyrolysis plant, directing the waste heat from the pyrolysis units to the dryers can mitigate this inefficiency (Cummer and Brown, 2002).

During the drying process, volatile organic compounds may be released from the vaporization of volatile components in the biomass. Therefore, exhaust formed during drying should be monitored. A slightly smoky exhaust plume called “blue haze” sometimes forms from biomass driers. Feedstock should not reach 100 °C, the temperature at which these emissions are usually released. Cleanup equipment such as cyclones and absorption beds may be necessary to reduce the environmental impact of drying (Cummer and Brown, 2002).

The simplest biomass drying system utilizes a perforated floor. This system works by passing hot gases through the perforation in the bottom of large bins, a process called through circulations (Cummer and Brown, 2010). For continuous systems, band conveyor dryers and rotary drum dryers are typically used; and can handle a wide range of materials.

3.14.2. Particle Size Reduction (Comminution)

Knife chippers and hammer mills are the two most common devices for reducing biomass to the appropriate size for pyrolysis. Knife chippers are better suited for grinding wood, and consist of high-speed rotary devices. Any metal that may be mixed in with the wood to be sized can severely damage the knives (Cummer and Brown, 2002). Hammer mills are also rotary devices that crush the biomass with large metal hammers. The hammers crush the falling biomass into a breaker plate. The crushed biomass is then pulverized between another hammer and a screen at the bottom of the mill. The screen at the bottom determines the size of the comminuted particles.

Since this type of device requires the feedstock be less than 4 cm, an auxiliary crusher may be necessary (Cummer and Brown, 2002).

3.14.3. Alkali Removal (Biomass Washing)

Feedstock containing high amounts of alkali may lead to the formation of extra char (Scott et al., 2001). The removal of the alkali prior to subjecting the biomass to pyrolysis is needed to obtain high yields of bio-oil. A simple washing of the biomass readily dissolves most alkali since it is water-soluble (Scott et al., 2001). Washing the biomass in water, then mechanically dewatering it is a process known as leaching. Leaching can remove more than 80% of the potassium and sodium, and more than 90% of the chlorine found in herbaceous biomass (Cummer and Brown, 2002, Scott et al., 2001).

4. KILNS

The kilns described in this section are part of our review of historical designs, and are not intended to represent the objectives of this project. This report is meant to identify weaknesses of these designs in order to propose improved concepts designed to achieve (as close as possible) zero emissions to atmosphere, water and land. A detailed review of several traditional methods for biochar production can be found in the Handbook of Charcoal Making by Emrich (1985).

4.1 Earth Kilns

Historically, crude earth kilns were the forerunners of modern kiln design in the United States. During the nineteenth century earth kilns were replaced by so called “beehive kilns” (Toole et al., 1961). Earth kilns are still very popular in Africa. Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Batch operation
Heating method: Partial combustion of foliage (auto-thermal process)
Construction materials: Earth
Portability: Built in place
Reactor Position: Horizontal/vertical
Raw material used: Cordwood
Loading and discharge methods: Manual
Size of the kiln: Small/medium
Charge ignition method: Small kindled wood at midpoint
Process control: Observing color of produced vapors
Pressure: Atmospheric
Pretreatment needed: Seasoned wood

One advantage of constructing earth kilns is that they are simply made of earth and can be built in the same area as the source of the biomass. For instance, building a kiln on the logging site to carbonize the wood obtained from that area can significantly reduce freight charges. Figure 33 illustrates early forms of earth kilns. A detailed description of the construction of earth mounds can be found in the publication, Simple Technologies for Charcoal Making (FAO, 1987).

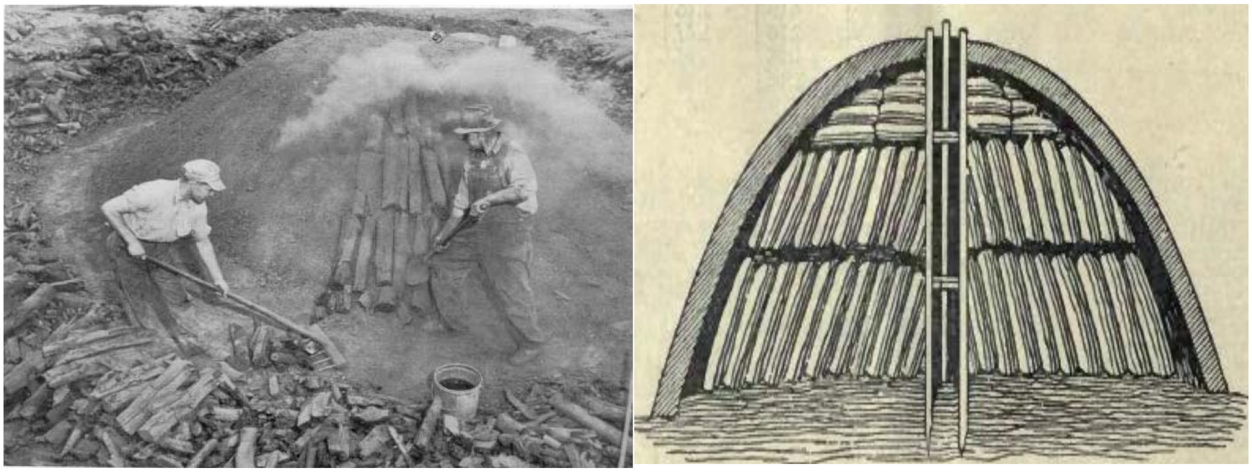

Figure 33. Earth kilns (earth-mound) (Veitch, 1907).

To protect the wood from outside air, soil is used as a barrier for oxygen attack. The attack of oxygen causes high losses of products. Earth is mounded over the wood (Figure 33) tightly enough to provide a firm closure, but not so tightly that air is prevented from leaking through to the wood. Utilizing a previously used site for construction is beneficial. To ignite the charge, the chimney is filled with small pieces of lit wood. Once the kiln has reached full combustion, no more fuel is added. To allow the combustion products to escape, the vents are opened starting from the top and working downward. When no more smoke is produced, the cooling stage is started by covering the stack with a layer of moist earth. The cooling process takes several days before the earth is removed and the biochar produced is separated from the surrounding imperfectly carbonized portions.

Rain can create problems with the quality of the biochar. The foliage layer and the outer covering layer of earth tend to contain condensed pyroligneous gases that get washed back down by the rain and reabsorbed by the biochar. Although a majority of these types of kilns are constructed to collect biochar, several have been modified to primarily collect the tars that are produced (see Figure 34).

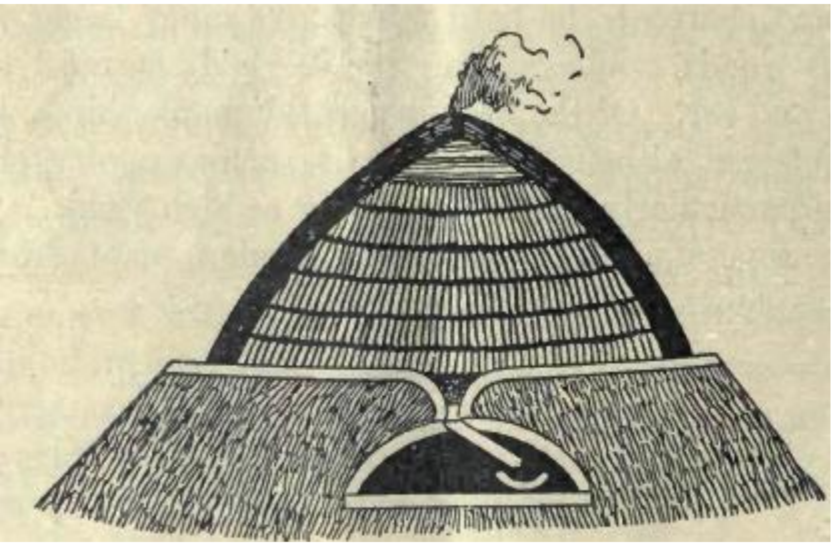

Figure 34. Early form of kiln in which biochar and tar are recovered (Veitch, 1907).

In the 1970s and 1980s some improvements were made to traditional biochar making equipment including the use of oil drums as chimneys on earth kilns (Casamance kilns), and small-scale steel or brick kilns. Earth-mound kilns equipped with a chimney (Figure 35) are most advanced among earth kilns. The construction process is virtually the same as described previously. The ability to alter the chimney diameter according to the oxygen demand, and precise control of the draft of the chimney, which is dependent on height, results in better control of the pyrolysis process (Emrich, 1985). With a few necessary modifications to the chimney section, it is a small step from the chimney kiln to a biochar operation that allows for tar recovery (Figure 35) (Emrich, 1985).

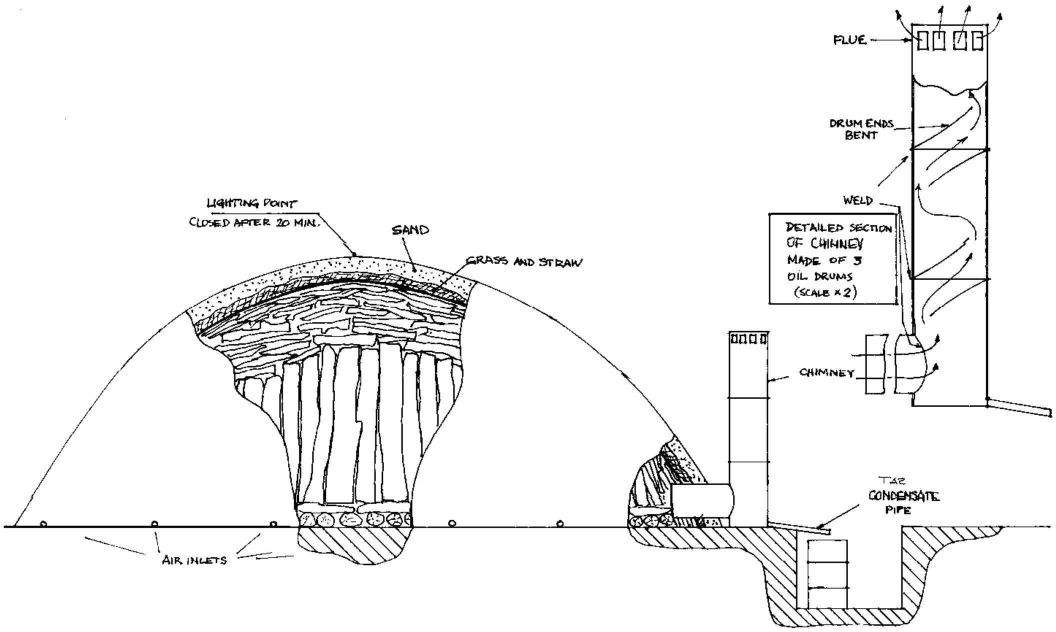

Figure 35. An earth-mound kiln with pyrolysis oil recovery (FAO, 1987). *Image courtesy of the Food and Agriculture Organization of the United Nations.*

The principles of building a biochar pit are similar to those to build an earth-mound kiln. The basic principle is to lead the air from one end of the chamber to the other, routing the flow under the bottom of the pit (Figure 36). Before the pit is charged with fuel wood, bed logs are laid to form a crib on which the charge is placed. The crib consists of logs cut to the same dimensions as the width of the pit and evenly spaced along the entire length (Emrich, 1985). Logs cut equal to the length of the biochar pit are to then be placed on the top of this first layer. A detailed description of the construction of earth pits can be found in the publication, Simple Technologies for Charcoal Making (FAO, 1987).

Figure 36. Biochar pit showing logs placed lengthwise across the crib (FAO, 1987). *Image courtesy of the Food and Agriculture Organization of the United Nations.*

Using a 6 m x 2.7 m x 1.2 m pit (depth at the ignition point) and a team of five people, it is possible to obtain up to 360 t of biochar per year (Emrich, 1985). Applying a steel sheet to cover large pits is done in many cases in order to prevent soil from falling in and contaminating the biochar when the kiln is uncovered at the end of carbonization (Emrich, 1985) (Figure 37).

Figure 37. Improved earth kiln design. A semi-permanent, low-cost, earth-metal kiln in Madagascar (Girard, 2002).

4.2 Cinder Block and Brick Kilns

The basic difference between earthen kilns and cinder block and brick kilns is the construction materials. These kilns have a long lifespan and several types have proved their economic viability for over fifty years. An estimated 250,000 of these kilns were being operated in 1985 all over the world (Emrich, 1985). A detailed description of the construction of these kilns can be found in the publication, Simple Technologies for Charcoal Making (FAO, 1987). Some of the main characteristics of these kilns are:

Final Product Targeted: Biochar
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Batch operation
Heating method: Partial combustion (auto-thermal)/contact with hot gases
Construction materials: Cinder/brick/concrete/Iron bands
Portability: Stationary
Reactor Position: Horizontal
Raw material used: Cordwood
Loading and discharge methods: Manual/mechanical
Size of the kiln: Small-large
Charge ignition method: Small kindle wood/burning oil/gas fired torch
Process control: Observing color of vapors or temperature measurements
Pressure: Atmospheric
Pretreatment needed: None

Common designs of these kilns can be differentiated by their shape. Hangar kilns which are a rectangular or square shape, and round brick kilns (Emrich, 1985). Some of the most commonly used hangar kilns are the Missouri kiln, the Ottelinska furnace, and cinder-block kilns. The most commonly used round brick kilns are the American kiln, the Argentine kiln (Half Orange), and the Brazilian kiln. The Missouri, cinder-block, American, Argentine, and Brazilian kilns are all auto-thermal kilns which burn part of the charge wood within the kiln. The Ottelinska furnace uses a central fire grate to produce hot flue gases that pass through the kiln supplying the heat required for drying and heating the wood to start carbonization.

4.2.1 The Brazilian Beehive Brick Kiln

These internally heated, fixed, batch-type kilns are widely operated and successful in some parts of Brazil, especially in the state of Minas Gerais and in the Amazonian region. Several thousand of them are operated by iron and steel companies to produce the biochar needed for their operation (Emrich, 1985). The construction material consists of ordinary firebricks which are positioned in a circular shape with a domed roof (Figure 48). A detailed description of the methods to build and operate these kilns can be found in the publication, Simple Technologies for Charcoal Making (FAO, 1987).

Some of the more advanced modifications to Brazilian kilns are the attachment of an external heating chamber and the reduction of the number of smoke stacks (Figure 38) (Emrich, 1985). Branches, brushwood, and other residue material, which is not suitable for kilning and would be wasted otherwise, is used to heat the kiln. The kiln behaves like a biochar retort with all of its advantages because the necessary energy for carbonization is transferred by gases leaving the fire chamber. Advantages of this type of kiln are high biochar yields because no wood is burned away, and high fixed carbon content because the terminal temperature of the carbonization cycle can be very well controlled. The yield of charcoal obtained with these kilns is about 20 mass %. The raw material used for carbonization is typically cordwood obtained from dedicated plantations or from forest clear cutting (Emrich, 1985).

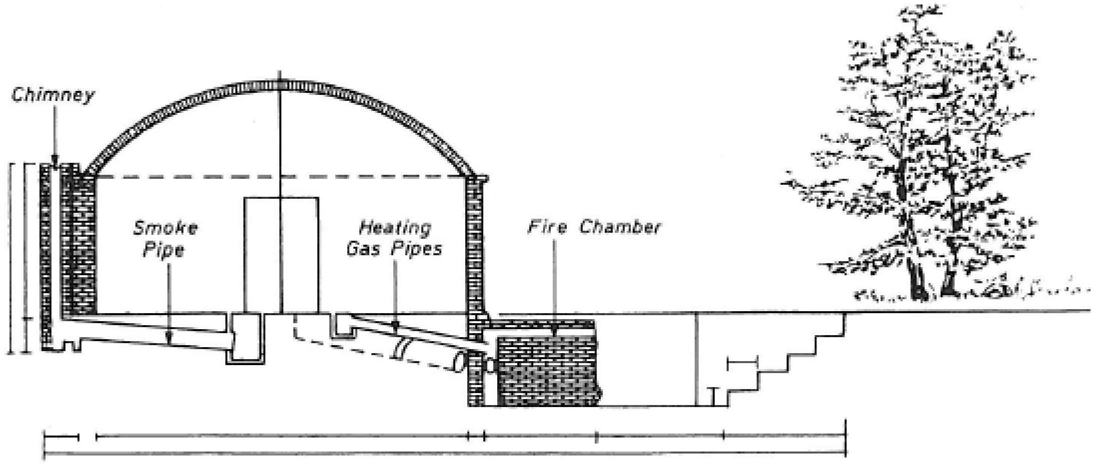

Figure 38. The Beehive fire brick kiln with external heating (Emrich, 1985).

Grouping a large number of Brazilian beehive brick kilns together in batteries can produce massive amounts of product. This simplifies the logistics for the transportation of both raw materials to the batteries and biochar from the batteries (Emrich, 1985). Figure 39 shows an ideal set up of the biochar producing site.

Figure 39. Batteries of Brazilian beehive kiln (Levine, 2010).

These kilns can be modified to recover pyroligneous water and decanted oil. The Brazilian company Biocarbo Ind. Com. Ltda (http://www.biocarbo.com/index.htm, date accessed: Nov. 13, 2010) specializes in the development of products from these condensable fractions.

4.2.2 The Argentine Beehive Brick Kiln

The Argentine kiln is also generally referred to as the "Half Orange Kiln" due to its hemispherical shape (Figure 40). Like many others, these kilns can be large, medium, or small. Unlike the Brazilian kiln, Argentine kilns are built completely out of bricks with no iron parts (Emrich, 1985). A detailed description on how to build and operate a half Orange kiln can be found in the publication Simple Technologies for Charcoal Making (FAO, 1987).

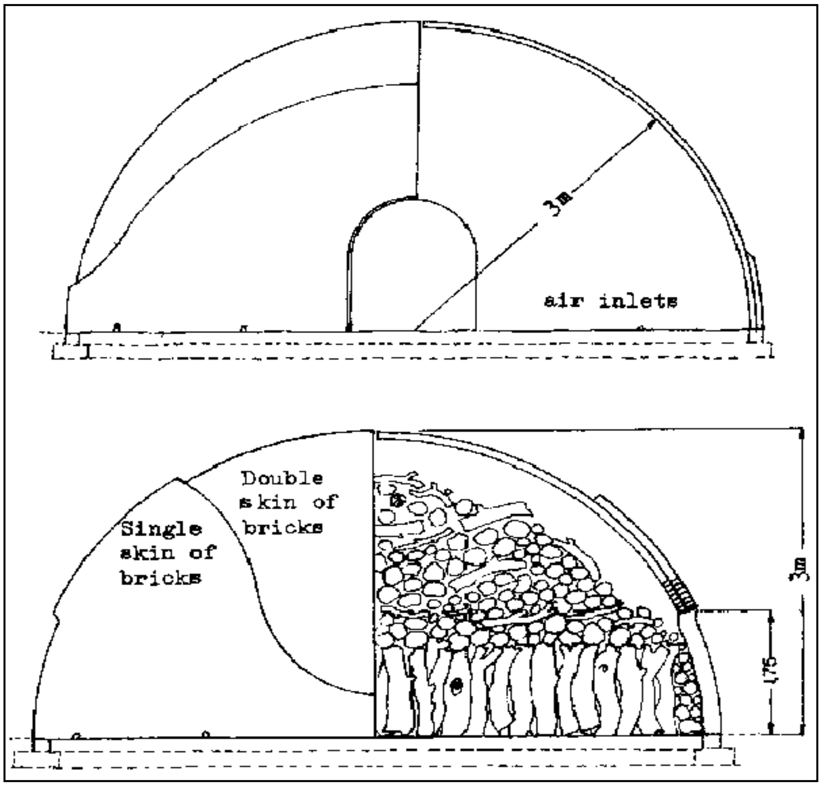

Figure 40. The Argentine half-orange kiln (FAO, 1987). *Image courtesy of the Food and Agriculture Organization of the United Nations.*

4.2.3 Other Small Masonry Kilns

The kilns described in this section operate on the same principles as the Brazilian and the Argentine kilns. The style of construction is what separates them from one another (Figures 41 and 42). All of these kilns support their masonry walls with a continuous perimeter-type reinforced concrete footing. This footing is set in permeable soil so water can freely drain, and it is at least 25 cm below the surface. Laying the first course of blocks in a full bed of mortar is crucial for construction (Toole et al., 1961). It is also desirable to construct a roof structure, though not part of the kiln, to protect ceiling parts from corrosion. If roof trusses are used to support a steel ceiling, then the roof structure is necessary (Toole et al., 1961). A detailed description on how to build these kilns is provided by Toole et al. (1961).

Figure 41. Experimental single wall, masonry kiln (Toole et al., 1961).

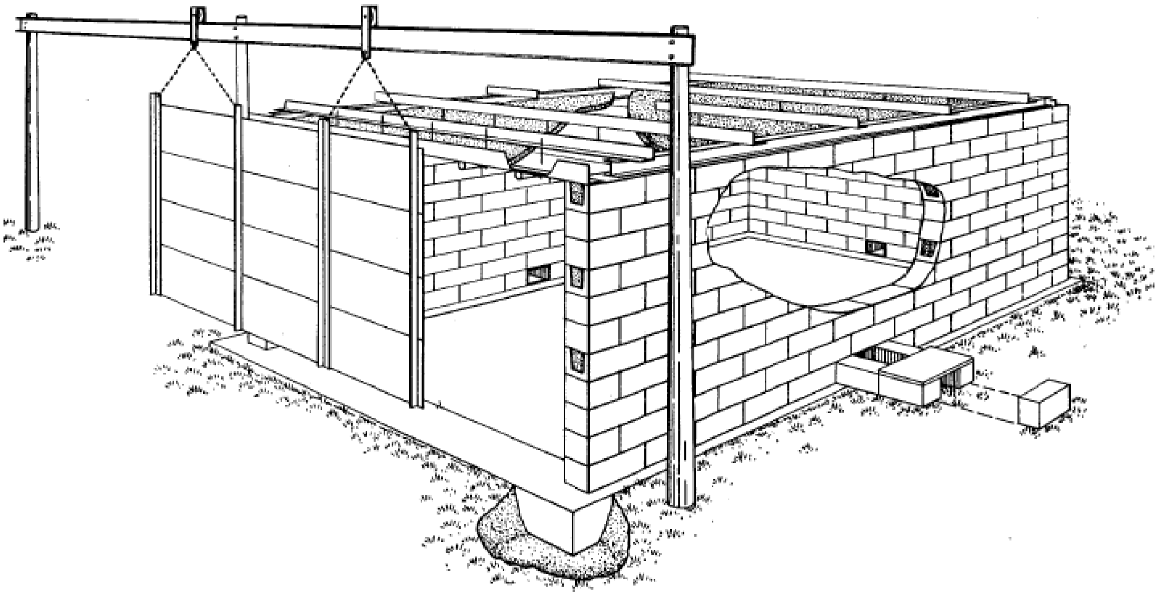

Figure 42. A single wall masonry block kiln of seven cord capacity (cinder block biochar kiln) (Toole et al., 1961).

The Adam+ Partner group, (Germany) (http://www.biocoal.org/index.html, date accessed: Nov. 15, 2010) developed the so called “adam retort” or Improved Charcoal Production Systems (ICPS). This small retort (3 m^3), designed for use in developing nations, is built with locally available construction materials and is able to produce about one ton of charcoal per week. This group claims higher economy and better efficiency (35-35 %) than traditional charcoal systems. This increase in efficiency is achieved by recycling and cleaning pyrolysis gases that are produced. The company claims that this method of operation reduces the emission of harmful volatiles into the atmosphere up to 75% compared with traditional earth mount kiln. The process starts with the combustion of residual biomass (e.g. leaves, crust, charcoal dust, branches) in a separate fire box to dry and heat the wood. After moisture has evaporated, gases rich in pyrolysis vapors are rerouted into the hot fire chamber to reduce pollution. The additional energy is used to further accelerate the heating process. The process last only 10 hours, compared with 4-14 days of a conventional carbonization retort. The recovery of the wood vinegar in the first phase is possible (http://www.biocoal.org/3.html, date accessed: Nov. 15, 2010).

Figure 43. Improved Charcoal Production Systems (ICPS) or Adam retort (source: http://www.biocoal. org/3.html, date accessed: Nov. 15, 2010).

4.3 The Missouri Kiln

Missouri-type kilns are mid-sized, manually loaded and unloaded kilns that produce about 17.6 tons of biochar during a three week cycle (Figure 44). The Missouri kiln is a well-proven kiln with a footing that consists of concrete and reinforced steel. High costs associated with large quantities of steel and concrete construction materials, as well as its immobility are disadvantages of the Missouri kiln. It is recommended to build this kiln within an economic haul distance with a ten year supply of wood because these kilns cannot be demolished and rebuilt like the brick kilns. More information on the design and operation of this kiln can be found elsewhere (Emrich, 1985).

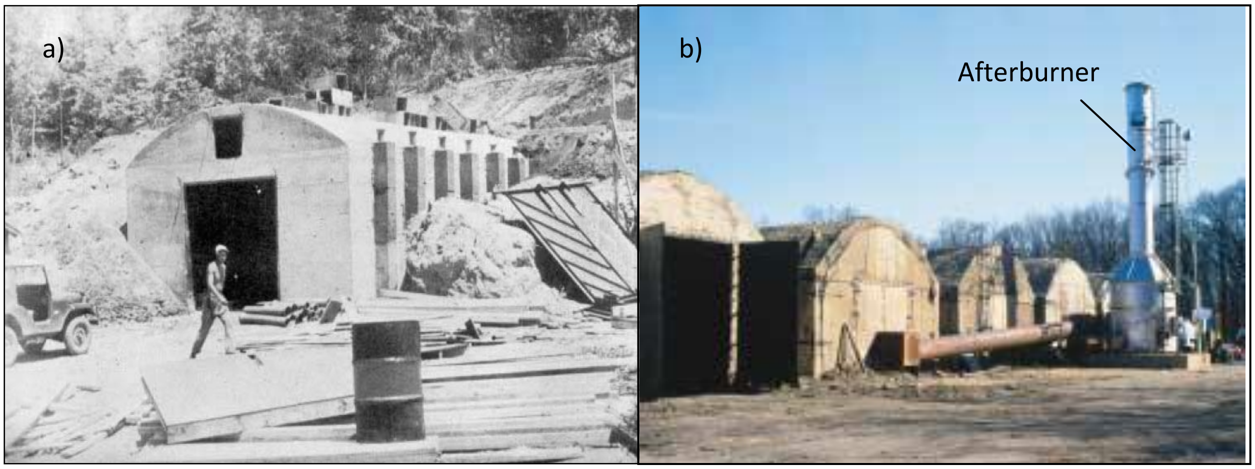

Figure 44. Concrete kiln (Missouri type) a) 100 cord capacity kiln without afterburner (Toole et al., 1961) and b) with afterburner (Source: (http://www.dnr.mo.gov/env/apcp/1999%20AnnualReport/99AirQualityHiLites.pdf, date accessed February 6, 2011).

4.4 Large Kilns with Recovery of Pyrolytic Vapors

The predominant kiln in the United States during the nineteenth century was the "American beehive kiln" which spawned from early biochar pits (Figures 45 and 46) (Toole et al., 1961). This kiln's brickwork chamber was shaped like a beehive with an opening in the top where wood was kindled, and which could be closed and sealed using a plate and clay. The charge of wood was introduced through an opening in the bottom, and the biochar was discharged through another opening that was level with the bed of the kiln. Iron hoops and clay held the iron plate doors to the openings tightly in place. Holes used for air ports were located around the kiln and could be opened or closed as desired using bricks of a corresponding shape. The outlet pipe guided gases and vapors through the bottom where it was equipped with a damper/trap. This pipe then ran into the main vapor pipe, which contained condensers that led to a fan propelling the vapors under the stacks where it was burned (Dumesny and Noyer, 1908; Klark, 1925). Some of the main characteristics of these kilns are:

Final Product Targeted: Biochar, bio-oil and gases
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Semi-batch operation
Heating method: Partial combustion/contact with hot gases
Construction materials: Firebrick/iron
Portability: Stationary
Reactor Position: Horizontal
Raw material used: Cordwood
Loading and discharge methods: Manual/mechanical
Size of the kiln: Large
Charge ignition method: Small kindle wood/burning oil/gas fired torch
Process control: Observing produced vapors/temperature measuring
Pressure: Atmospheric
Pretreatment needed: Seasoned wood

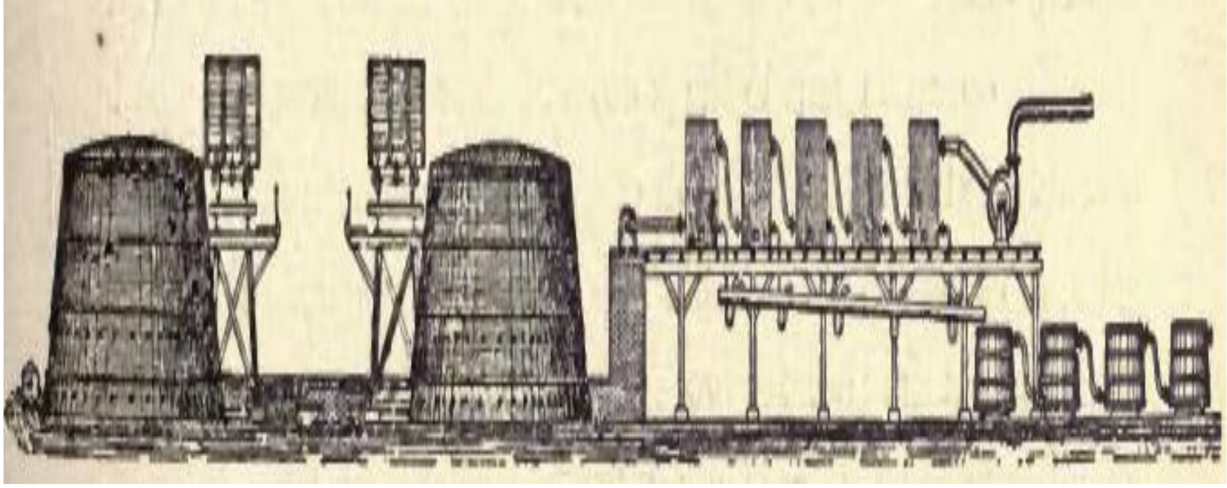

Figure 45. Masonry stack ovens (American "beehive" kilns) or furnaces for wood distillation on very large scale and appropriate condensation plant (Dumesny and Noyer, 1908).

Several American kilns were operational until the 1960's (Toole et al., 1961). These kilns had openings in a dome-shaped ceiling which were used for loading and firing. To enable loading, these kilns were built along the base of a hill or bank. Another opening at the base also allowed for wood piling and biochar discharge. The remaining partially carbonized billets from the previous cycle, ranging from 150 to 200 mm, were spread over the bed before charging the next cycle (Klark, 1925).

Figure 46. Stationary large "American" kilns for biochar production (Klark, 1925).

A pipe for collecting the products of distillation ran along a row of ten of these kilns. Four collecting pipes from four different rows of ten ovens all united at a central pipe that could receive products from four more rows of kilns. This central pipe then led to a central condensing system where it split into several branches. These branches then led to a number of tubular condensers in which vapor passed through round tubes while water flowed through them. With 40 kilns, each possessing a 300 m^3 capacity, it was typical to have seven condensers connected in a series inside of four different systems. Fans were used to draw in air through the air ports of the kiln as well as to push the products of combustion and carbonization through the outlet pipes, into the collecting pipes, and through the central condenser system. Using a central condenser system allowed the condensers to be utilized much more efficiently than with separate condensers. Artificially inducing the flow of air and the movement of the carbonization products using a central condensing system was advantageous because condensation did not depend on the weather.

The larger of the American kilns had an estimated total height of 24 feet, a diameter of 30 feet (volume of 16956 ft^3 or 557 m^3) and a wall thickness of about one foot (Toole et al., 1961). The ability to buy wood at low bulk prices made high-volume production of beehive kilns possible. About 30 to 90 cords of wood (76.2 to 228 tons) could be processed through these types of operations (Baker et al., 1985). It took anywhere from 15 to 30 days to completely manufacture the biochar, including charging and discharging (Bates, 1922; Klark, 1925). These kilns were similar to those described in previous sections except for the fact that their large size allowed them to recover liquid products as well. With the ability to produce upwards of 700 pounds of biochar per cord of seasoned wood, and the objective to manufacture around 100 tons per day, while simultaneously recovering its byproducts, it is doubtful that any other type of kiln could compete in terms of capital and costs of labor (Klark, 1925).

5. RETORTS

This section describes retorts developed to produce biochar. Retorts described in this section are part of our review of historical designs, and are not intended to represent the objectives of this project. This report is meant to identify weaknesses of these designs in order to propose improved concepts designed to achieve (as close as possible) zero emissions to atmosphere, water and land. The main types of retorts discussed here include: 1) small retorts without recovery of liquid products, 2) retorts with liquid by-products recovery, and 3) wagon retorts. A more detailed description of many of the systems can be found in the handbook of charcoal making technologies by Emrich (1985).

5.1. Small Retorts without Liquid By-product Recovery

Since the beginning of the 20th century, small retorts have been made for the production of biochar using bulky sawmill waste and branches and brushwood. When biochar gas-producers for fueling motor vehicles became practical and economically feasible, interest in small portable metallic retorts increased. From 1939 to 1945 (World War II) the use of these retorts reached a maximum in some Western European countries. Oil supply shortages associated with the war resulted in biochar becoming the most commonly used fuel for combustion engines. This vogue of portable kilns passed when normal fuel supplies returned.

Portable metallic kilns are more economical in terms of labor because they require much less supervision. Retorts can be constructed from oil drums (Figure 47). A pipe used for the evacuation of vapors is installed at the end of the retort. The simplest design leads the gas through a pipe underneath the retort where it is burned in the fire chamber. Sometimes the retorts are placed inside of brick structures which serve as the fire chamber (Emrich, 1985). Curved trays made from sheet metal with a cross section designed to fit the retort as best as possible are used to load the raw feed and are left in the retort until the biochar is ready (Emrich, 1985).

Some of the most important characteristics of these kilns are:

Final Product Targeted: Biochar
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Semi-batch operation
Heating method: Indirect heat
Construction materials: Brick/metal
Portability: Portable
Reactor Position: Horizontal
Raw material used: Sawmill chips
Loading and discharge methods: Manual
Size of the kiln: Small
Charge ignition method: External combustion with leaves and bark
Process control: Observing produced vapors
Pressure: Atmospheric
Pretreatment needed: None

Figure 47. Small retort constructed of oil drums (http://www.twinoaksforge.com /BLADSMITHING /MAKING% 20CHARCOAL.htm, date accessed: Nov. 13, 2010).

5.2 Retorts with By-product Recovery

Until the middle of the 19th century, the potential value of the byproducts contained in pyrolysis vapors went unnoticed. A pressing need for the supply of organic acids, methanol, and acetone compounds emerged with development of the chemical industry. These high-demand chemicals were present in the condensates produced by biochar plants (Emrich, 1985). Following the brick kiln, the iron retort was the first device to efficiently collect the vapors from carbonization for creating wood alcohol, acetate of lime, and various other chemicals from distilling pyroligenous acid (Klark, 1925). These systems were typically heated from an external fire box that was located underneath the retort (Figure 48). Some of the most important characteristics of these reactors are:

Final Product Targeted: Biochar, bio-oil and gases
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Semi-batch operation
Heating method: Indirect heat through the walls
Construction materials: Steel/iron/brick
Portability: Stationary
Reactor Position: Horizontal
Raw material used: Cordwood/softwood/chips
Loading and discharge methods: Manual
Size of the kiln: Small
Charge ignition method: External combustion chamber
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: None

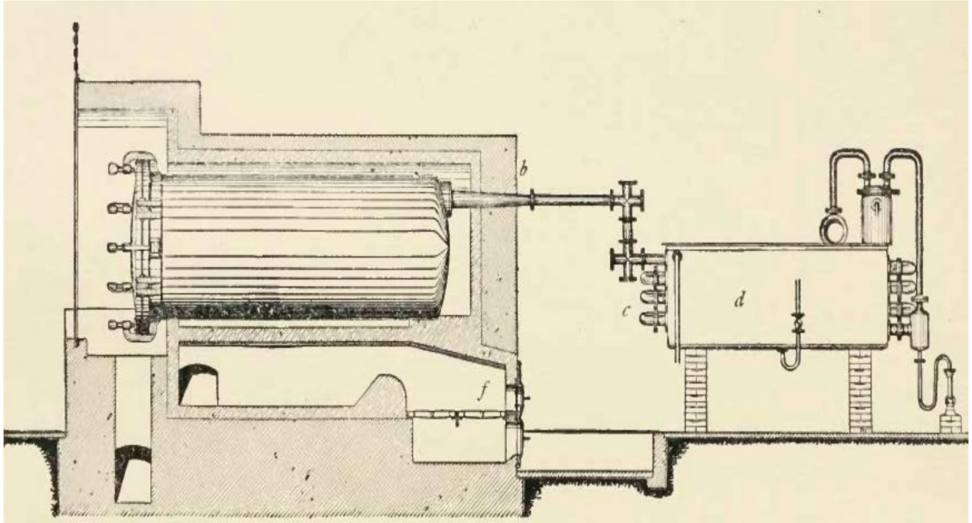

Figure 48. Horizontal steel retort (capacity 1.5 stacked m^3, operating period 12-16 hours a-retort, b-retort neck, condenser tubes, d-condenser tank, f- furnace) (Klark, 1925).

5.3 The Wagon Retort

Compared to other methods the wagon retort required a substantial amount of labor (Emrich, 1985). Figure 49 illustrates the principle of a wagon retort plant. Wagon retorts commonly used raw material made up of round wood and split round wood with an average length of 1.0 to 1.2 m. A limited quantity of shorter pieces was also charged (Emrich, 1985). The following components make up the wagon-retort plant (Klark, 1925): (1) 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. One or two vapor outlets provided on the side, top, or at one end and a rail track for running retort cars located on the floor of the chamber. (2) A furnace for the heating process. (3) A condenser connected to the retort. (4) A steel chamber with a door at each end for cooling biochar placed in front of the retort and fitted with a similar rail track. (5) A section of rail that connects the retort with the biochar cooler that can be moved as needed. (6) Mechanical equipment for moving the cars. (7) The retort wagons (Klark, 1925). Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar/bio-oil
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Continuous operation
Heating method: Indirect heat
Construction materials: Steel
Portability: Stationary
Reactor Position: Horizontal
Raw material used: Cordwood
Loading and discharge methods: Use of wagons
Size of the kiln: Small to large
Charge ignition method: Heating with an external combustion chamber
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: Drying

Each car is packed with 5 to 7 m^3 of wood. Four of these cars form one retort charge. As soon as the cars have been processed in the retort they are withdrawn and four freshly loaded cars are charged back into the retort. The cars either move individually or are linked together with a wire cable and driven by an electric or mechanical winch. A tongue fitting tightly into a groove in the door frame seals the door. The retort is then heated, in some cases with the combustion of the non-condensable gases provided by other retorts that are further along in the process. The distillation process varies depending on the amount of moisture in the wood, the type of furnace being used, and the firing method (Klark, 1925).

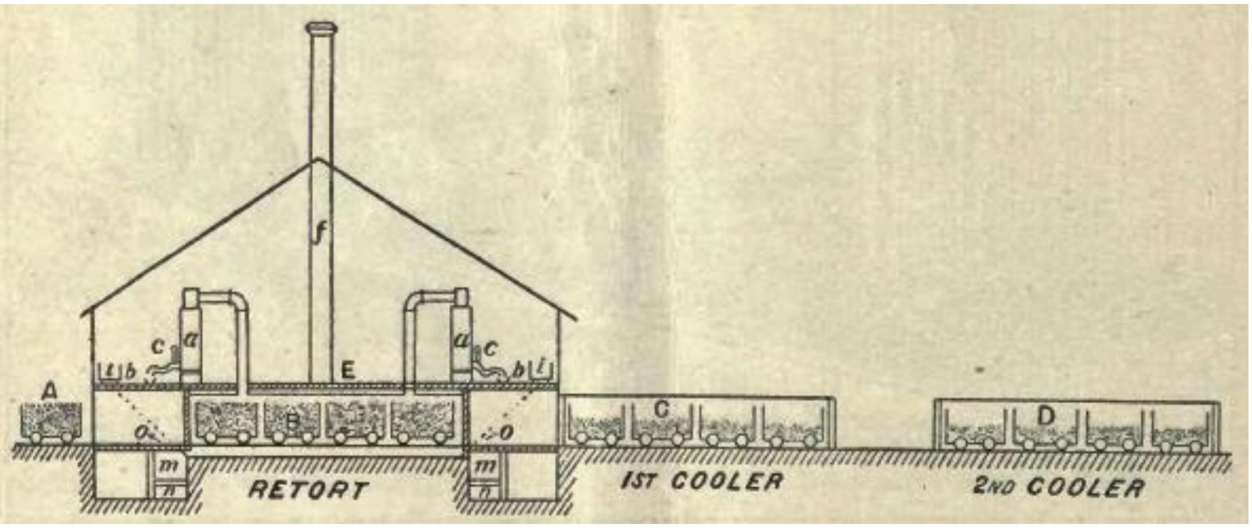

Figure 49. Plan of a American destructive distillation plant in continuous operation. A: car, B: retort, C: first cooler, D: second cooler, E: acetate drying floor (Veitch, 1907).

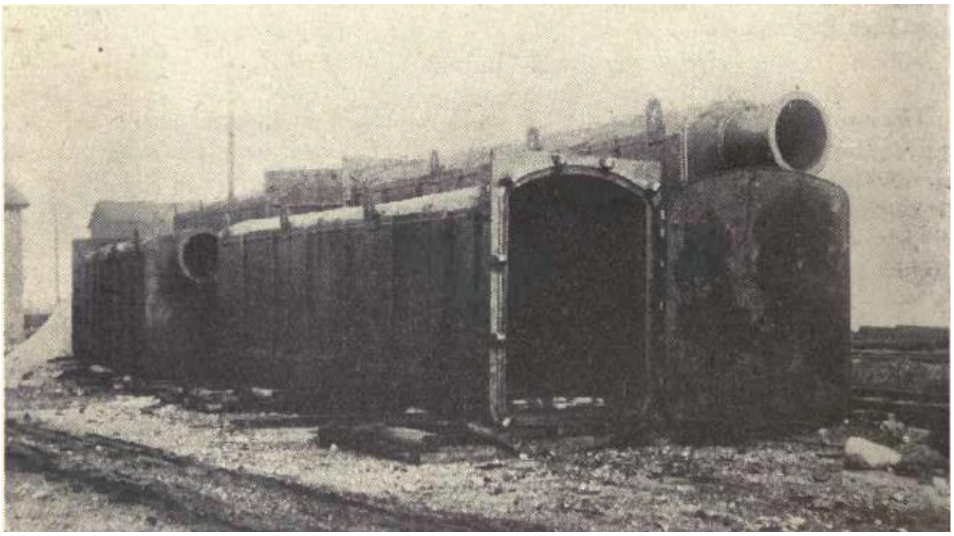

Figure 50. Ovens of a six-cord capacity retort awaiting installation (Bates, 1922).

Retorts 8 to 9 m long and up to 2.5 m in diameter up are standard (Figure 50). These steel retorts are inserted into a brick structure fitted with ducts for the heating gases. During the operation, the wagon retort is heated using an external heating system. Once the pyrolysis process has been completed, the first step is to transfer the wagons with the biochar into the cooler (Figures 51 and 52). The cooled biochar is then discharged. Once the cars are empty they are immediately taken to the wood yard to be refilled. The freshly loaded wood is then moved to the drying chambers, which in some instances are positioned opposite or alongside the retorts.

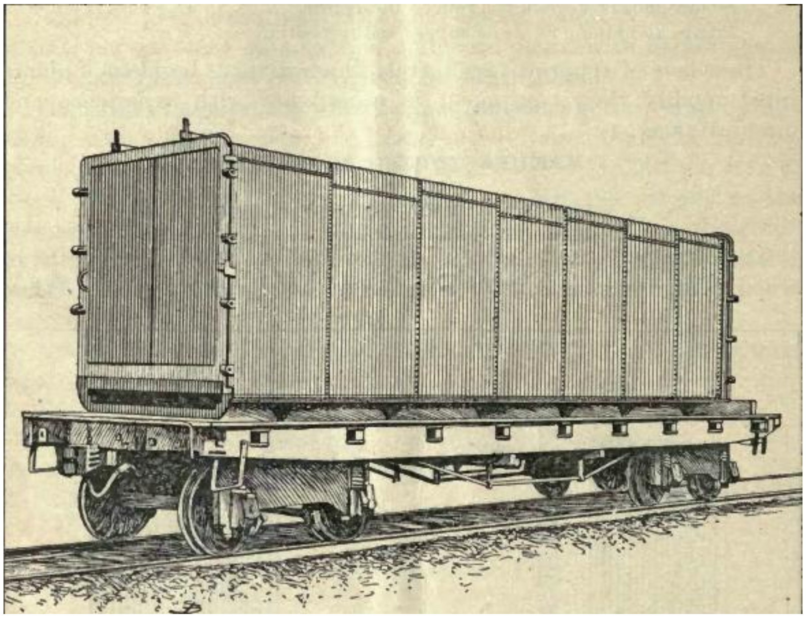

Figure 51. Biochar cooler used with oven retort (Veitch, 1907).

Figure 52. Looking down an alley between two sets of cooling ovens, Cadillac MI (Brown 1917).

After a 24-hour cooling period, the trucks are moved from the ovens on the right to the ovens on the left to be cooled further. In one charge, each 17 m cooling oven can hold a total of four trucks (Brown, 1917).

Every retort plant requires that the biochar be gradually cooled. Cooling begins in the cooling ovens immediately in front of the retort house. The first cooling oven is a mere 2.5 – 3 m in front of the charring oven, and the second is an equal distance beyond the first cooling oven. The arrangement of the cooling ovens in relation to the retorts can be seen in Figure 52. The construction of the cooling oven is similar in size and shape as the ovens themselves. The difference is that the walls are only 3/16 inch thick steel and typically doors are at both ends. Cooling ovens simply rest on the ground and do not require a bottom floor. Dirt is pilled around the base and used as a seal to prevent air from entering (Brown, 1917). In order to reduce the chance of the biochar reigniting and losing valuable product, as soon as the door of the retort is opened the train of biochar filled cars is quickly drawn into the cooler which is then closed as rapidly as possible. This operation takes several seconds and, if done properly, the risk of loss is no greater than that of a small retort of only 1 to 5 m^3. Much of this operation relies on the smooth action of the retort and cooler doors, and the hauling arrangements of the cars. Serious consequences can result from slight errors in the construction due to a lack of experience (Klark, 1925).

Many of these types of systems were used widely. They varied greatly in size from 20 to 112 cords per day in Canada, and 100 to 200 cords per day in the United States. In some of the lake states plants consumed as much as 200 cords per day. In the State of New York, the largest plant consumed 80 cords of wood per day and had an annual capacity of 24,000 cords (Brown, 1917). The area required for these plants ranges from 10 to 40 acres for wood yards and buildings (Bates, 1922). The capacities of different plants vary depending on the size and number of ovens.

Wagon reactors are currently commercialized by Impianti Trattamento Biomasse (an Italian company) (Figure 53). With plants in Milazzo and Mortera (Italy) this company produces up to 6.000 tons/year of charcoal. The process is now called O.E.T. Calusco (former Carbolisi) (http://www.itbiomass.com/site/home.html, date accessed: Nov. 13, 2010). Alterna Biocarbon a company based in Prince George, BC, Canada (http://www.alternaenergy.ca/, date accessed: Nov. 13, 2010), is also commercializing an upgraded design of the wagon retort. The main products targeted by this company are energy pellets, activated carbon, products for mercury recovery and biochar for soil applications.

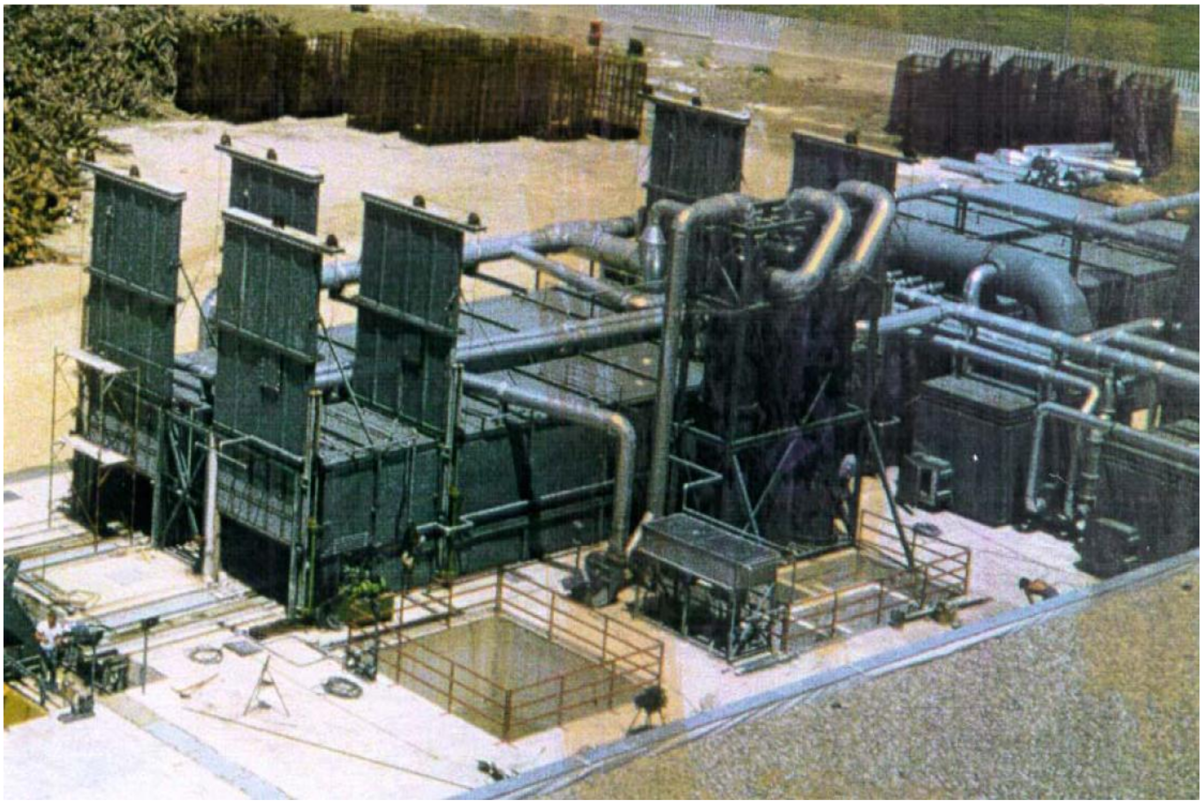

Figure 53. O.E.T. Calusco process (source: Groenli,, 2010).

6. CONVERTERS FOR PROCESSING WOOD LOGS

The converters (Reichert, the French SIFIC process) described in this section are part of our review of historical designs, and are not intended to represent the objectives of this project. This report is meant to identify weaknesses of these designs in order to propose improved concepts designed to achieve (as close as possible) zero emissions to atmosphere, water and land. A more detailed description of converter designs can be found in Emrich's Handbook of Charcoal Making (1985).

6.1 The Reichert Converter

A large-scale retort with the capacity of 100 m^3 of raw material is the center piece of the Reichert converter (Figure 54). Logs used in this batch-wise process must be cut to one third of a meter (Emrich, 1985). Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Semi-batch operation
Heating method: Direct contact with hot gases
Construction materials: Metal
Portability: Stationary
Reactor Position: Vertical
Raw material used: Cordwood
Loading and discharge methods: Mechanical
Size of the kiln: Large
Charge ignition method: N/A
Process control: Direct measurement
Pressure: Atmospheric
Pretreatment needed: None

The recirculation and use of hot off gases is a significant feature of Reichert converter's heating system (Figure 54). Once wood has been charged to maximum capacity through an access hole on the top, the valve is closed and the main heating pipe is opened permitting hot gases into the interior. The downdraft design of this system starts the carbonization in the upper layers of the charge where it first comes in contact with the entering hot gases. The carbonization zone then continues to move toward the bottom.

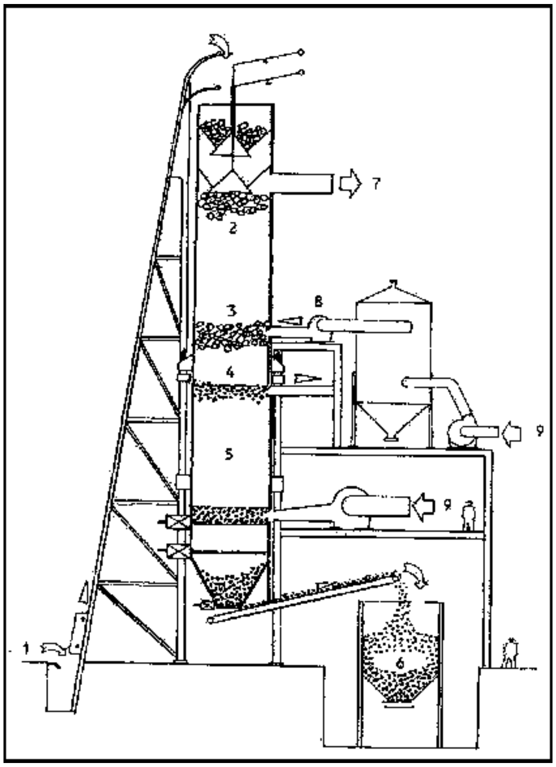

Figure 54. The Reichert converter (FAO, 1985). *Image courtesy of the Food and Agriculture Organization of the United Nations.*

After the scrubbing process, the gases are sent to a burning chamber where parts of them are burned to raise the temperature of the exiting heating gases to 450 °C. After the carbonization process has reached the top and stopped, the biochar is discharged through the bottom of the retort into airtight containers to prevent self ignition and the loss of good biochar. Cold inert gases passing through the biochar assist in the cooling process.

Large retorts with recirculated gas heating have been commercially used for more than sixty years. In countries where labor is expensive, these retorts can operate economically with the use of mechanical equipment for conveying, loading, discharging, and preparing raw material. Widespread use has been hindered by high investment costs only until recently (Emrich, 1985).

6.2 The French SIFIC Process

When it comes to the production of biochar the French SIFIC process is one of the most successful technologies. To keep the retort continuously full, the level of pre-dried wood or other raw material that enters the top of the retort through a lock can be controlled electronically. Throughout the biocharring process the wood slowly moves toward the bottom. The middle of the retort, known as the hot temperature zone, is where the wood is decomposed into biochar and gases. The gases released from this section are drawn upward by a fan. Once the biochar is discharged, it is loaded on the converter plenum and carried away to storage. Since the lower segment of the retort acts as the first step in the cooling process, there is no need to separate the biochar cooler. To save on labor costs, small automatically controlled lorries move the char to desired locations (Emrich, 1985).

Final Product Targeted: Biochar and bio-oil
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Continuous operation
Heating method: Contact with hot gases
Construction materials: Metal
Portability: Stationary
Reactor Position: Vertical
Raw material used: Cordwood
Loading and discharge methods: Mechanical
Size of the kiln: Large
Charge ignition method: Hot gases generated in an external oven
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: Pre-died

As a result of several attempts to simplify the SIFIC process, the CISR Lambiotte Retort was developed. An internal combustion device heats the retort using part of the recycled pyrolysis vapors (off gases) (Emrich 1985). These plants have been run commercially for a number of years. Some of the main features of this design are seen in figure 55. The Lambiotte & Cie company (http://www.lambiotte.com, date accessed: Nov. 13, 2010) commercializes automatic continuous carbonization retorts (type SIFIC/CISR) producing 2,000 tons or 6,000 tons of biochar per year. In this system, wood is dried in a first zone at the top of the retort, and undergoes carbonization in the second zone. Lambiotte & Cie excels in the elaboration of Acetal innovative solvents. Lambiotte 6000 (H=18.4, D=4.3 m) has a capacity of 6000 tons/year. Several units operate in Europe and Russia.

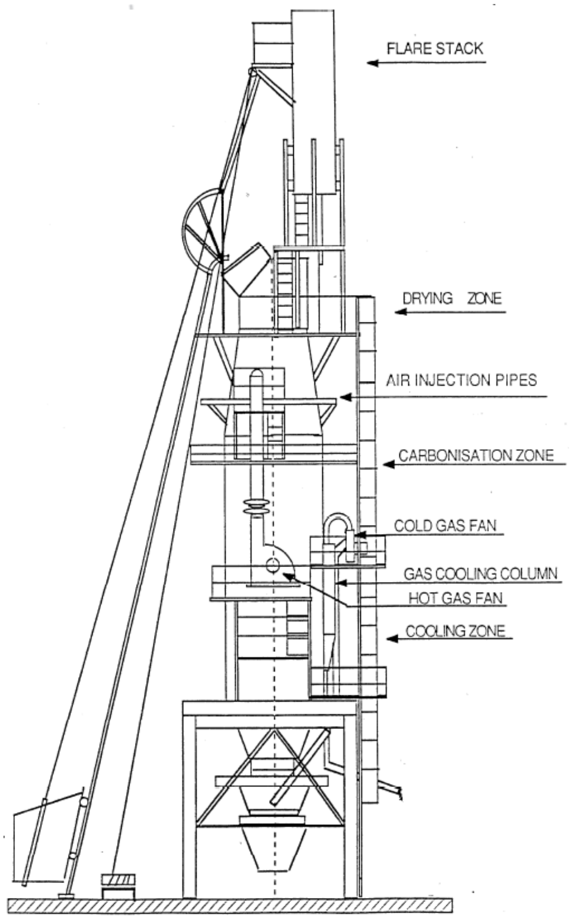

Figure 55. Scheme of a Lambiotte Plant (Groenli, 2010).

The Lurgi Process (Figures 56 and 57) operates by the same principle as the Lambiotte process. Lurgi GmbH has built one charcoal plant in Bunbury, Western Australia with a capacity for producing 27,000 tons/year.

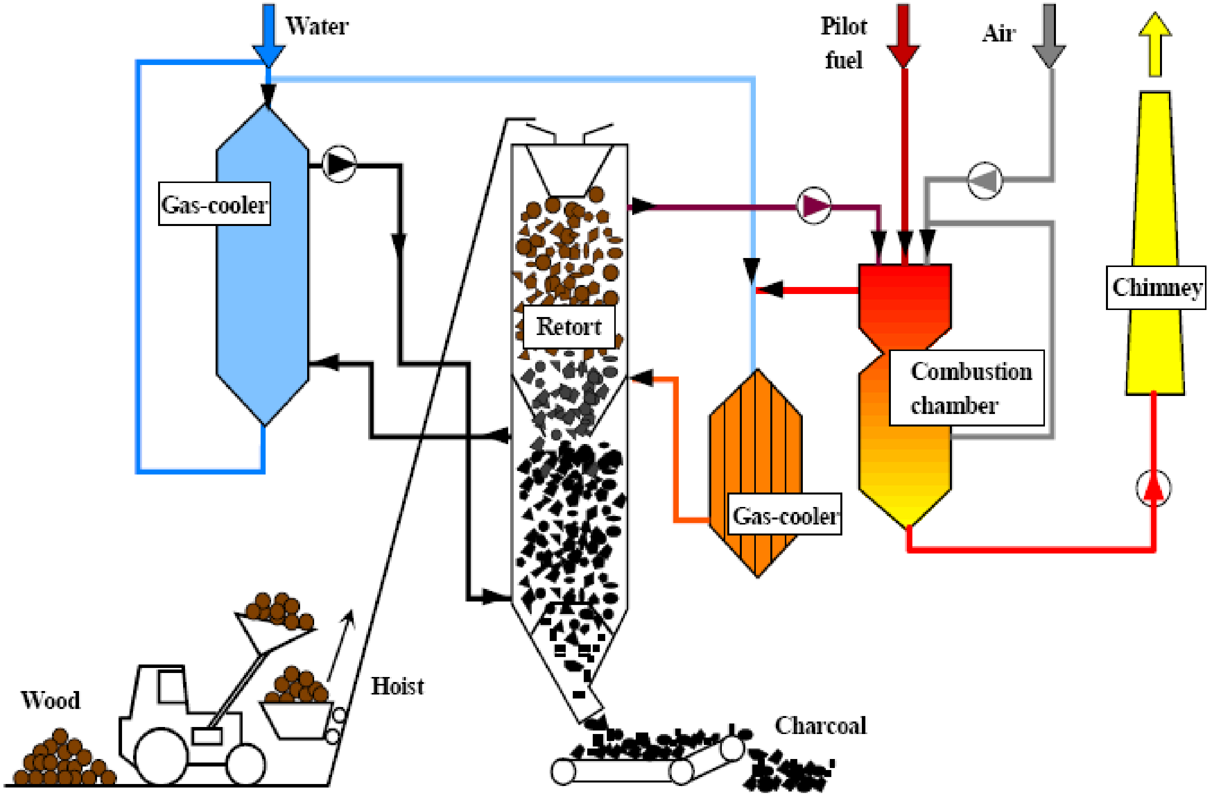

Figure 56. Lurgi process (Groenli, 2010).

Figure 57. Lurgi process - charcoal production plant in Bunbury, Western Australia (http://www.biochar.bioenergylists.org/files/Gronli.pdf, date accessed: Nov. 13, 2010).

A similar principle (continuous downdraft pyrolysis reactor) but using chips or pellets is being commercialized by Biochar Engineering (http://www.biocharengineering.com/biochar/index.html, date accessed: November 10, 2010), a company based in Colorado. The system commercialized by this company (Figure 58) is a mobile downdraft auto-thermal gasifier able to convert 225 kg/h of biomass into synthesis gas and biochar.

Figure 58. Picture of the mobile downdraft gasifier to produce biochar and heat from wood chips (source: http://www.biocharengineering.com/technology/, date accessed: Nov. 13, 2010).

7. CONVERTERS FOR PROCESSING WOOD CHIPS

Converters described in this section are part of our review of historical designs, and are not intended to represent the objectives of this project. This report is meant to identify weaknesses of these designs in order to propose improved concepts designed to achieve (as close as possible) zero emissions to atmosphere, water and land.

Many attempts to carbonize forest and agricultural waste using inexpensive and simple kilns have been made within the past few decades. The kiln technique described in Section 6 is used for relatively large fragments and is not suitable for the small fragments and particles found in waste matter without some sort of modification. If one of the large kilns is charged with small waste particles such as sawdust, there will be an insufficient penetration of gases unless the cargo is continuously rotated or moved. This is due to the small particle load being too tightly compact in the kiln (Emrich, 1985).

Many technical difficulties occur during the process of carbonizing powdery and bulky material such as saw dust (Klark, 1925). Small powdery wood particles pack much more tightly than larger wood pieces. This hinders circulation of gaseous products and prevents particles from acting as heat carriers (Klark, 1925). Since the conduction and radiation of the heated surface almost exclusively supplies heat for carbonization, devices with large diameters are essentially useless. Penetration of heat to the material is hindered by an insulating layer of biochar that forms against the heated surface of the container (Klark, 1925).

This section describes reactors able to handle chips and pellets, in addition to deliberately crushed or chopped material such as sugarcane bagasse, bark, twiglets, coconut shells, etc. Some converters used to process wood chips or fine particles described here include: the Herreshof furnaces, rotary drums, Auger reactors, and shelf reactors. A disadvantage of these converters is that they produce biochar in the powdery form for which there is a relatively low demand. This process is not profitable unless the biochar is converted into briquettes or pellets.

7.1 Herreshoff Multiple-Hearth Furnace

The Herreshoff furnace is a continuous multiple-hearth furnace designed to convert raw materials in the form of sawdust, shavings, or milled wood and bark (Figure 59). It was patented in 1921 by R.D. Pike. These systems are typically employed for large capacity units producing at least one ton of biochar per hour, converting four tons of biomass per hour or 100 tons of biomass per day. The yield of dry biochar for this process is about 25 mass % by weight. The first Herreshoff furnace was used in 1984, and by 1985 there were 16 Herreshoff furnaces in use in the United States producing over half of the total biochar produced from wood and bark (Baker, 1985, Anotonini and Hazi 2004).

Herreshoff furnaces are vertical kilns containing several circular hearths enclosed by a refractory lined steel shell. A vertical rotating 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 spiral exposes the material to the gases by constantly agitating it before dropping it through a hole to the next level. Controlled quantities of hot gases are supplied by combustion air blowers drawing the air through burners or ports. The power draw and fuel demand is minimized by automatic draft and oxygen monitoring equipment that ensure clean combustion. Of the many types of multiple-hearth furnaces on the market, the influencing factor when selecting a furnace is the ability to be flexible and handle a wide variety of materials varying in both physical and chemical characteristics. Some of the main characteristics of these ovens are:

Final Product Targeted: Biochar
Heat transfer rate achieved: Typically slow pyrolysis (but could be used eventually for fast pyrolysis)
Mode of operation: Continuous
Heating method: Contact with hot gases
Construction materials: metal
Portability: Stationary
Reactor Position: Vertical
Raw material used: Chips/fine particles
Loading and discharge methods: Mechanical
Size of the kiln: Large
Charge ignition method: External combustion chamber to produce hot gases
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: Ground in chips/fine particles

Compared to retorts and small scale converters, the investment cost for a multiple-hearth furnace is very high. As a result of high investment costs, they need to have a high biochar capacity, and an increased rate of productivity. Estimated figures for an economic operation are production of 15,000 to 18,000 tons of biochar per year which requires 100,000 tons of biomass per year.

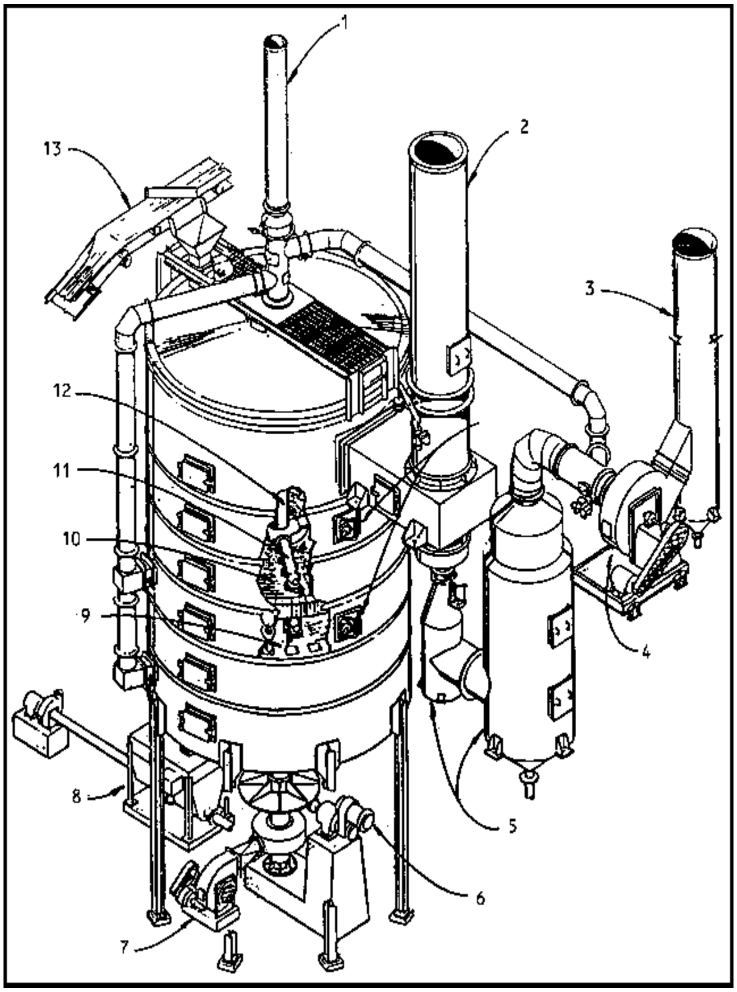

Figure 59. Cross section of the multiple-hearthfurnace (FAO, 1985). *Image courtesy of the Food and Agriculture Organization of the United Nations.*

Figure 60 shows a mobile Herreshoff pyrolysis rector commercialized by BIG Char (Black is Green Pty Ltd), a company with based in Queensland, Australia. This company is commercializing a patented mobile multiple-hearthfurnace (the unit is mounted on a truck) (http://www.bigchar .com.au/, date accessed: Nov. 13, 2010) that produces biochar and heat with the capacity to process up to one ton per hour of biomass. The biochar produced is available in a briquetted form.

Figure 60. Mobile multiple-hearthfurnace commercialized by Black is Green Pty Ltd (http://www.bigchar.com.au/about.html, date accessed: Nov. 13, 2010).

NESA has commercialized multi-hearth large pyrolysis units for waste treatment with afterburners (Figure 61) (http://www.cmigroupe.com/nesa/pdf/Pyrolysisof.pdf, date accessed February 2010). In this reactor the material processed is conveyed through hearth to heath from the top of the reactor to the bottom while the gases flow upwards. The heat needed for the process is produced from the combustion of all of a part of the volatiles.

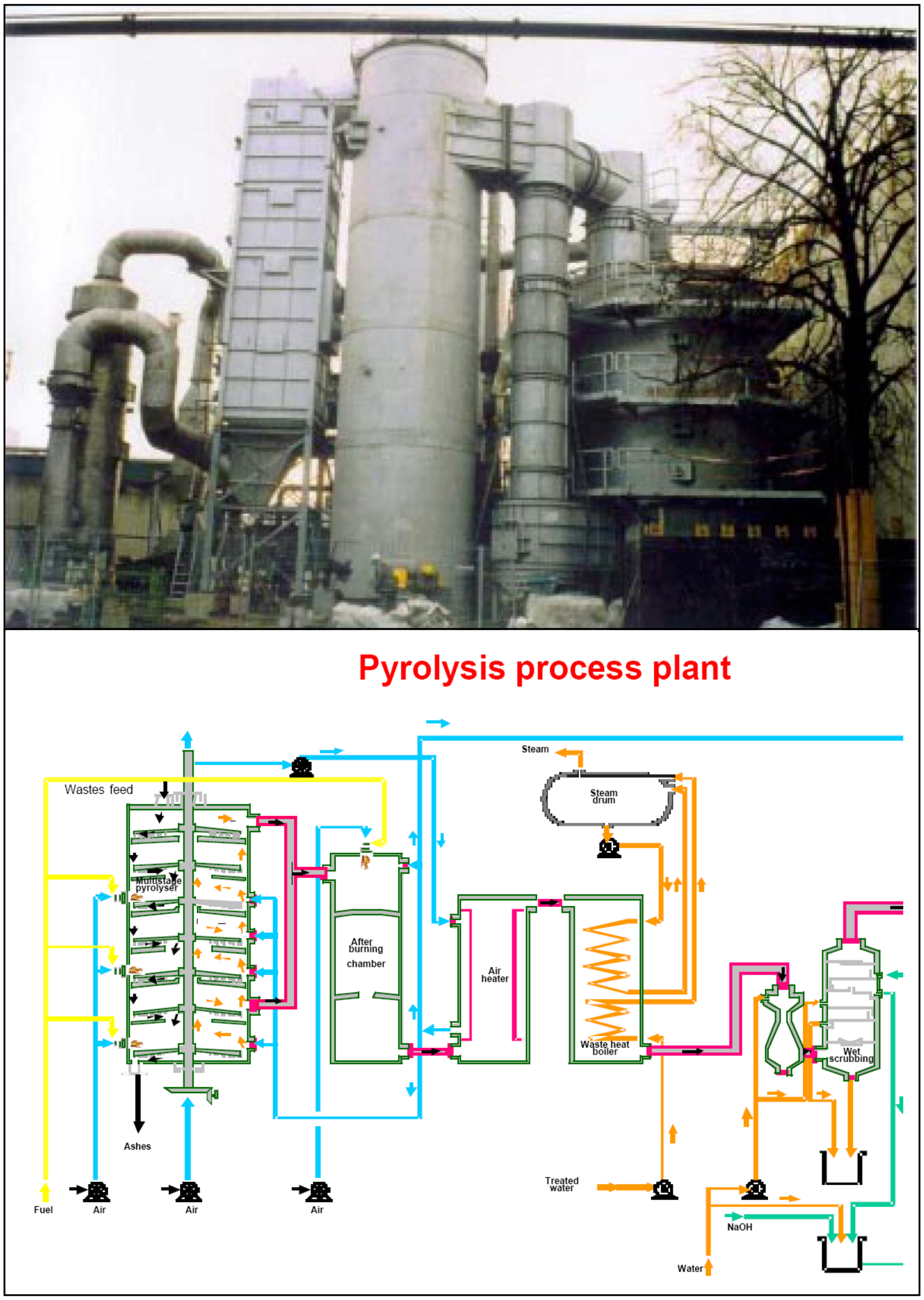

Figure 61. NESA stationary multiple hearth kiln ([http://www.cmigroupe.com /nesa /pdf/ Pyrolysisof.pdf](http://www.cmigroupe.com/nesa/pdf/Pyrolysisof.pdf), date accessed February 2010).

7.2 Rotary Drums

The rotary drum reactor (Figure 61) is a very reliable system for converting solid materials. The angle of the reactor as well as the rotation of the drum alters the residence time of the particles and the conversion achieved. Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar/heat
Heat transfer rate achieved: Slow or potentially fast pyrolysis
Mode of operation: Continuous operation
Heating method: Contact with hot gases
Construction materials: Steel
Portability: Stationary
Reactor Position: Horizontal
Raw material used: Chips
Loading and discharge methods: Mechanical
Size of the kiln: Small
Charge ignition method: N/A
Process control: Direct measurement
Pressure: Atmospheric
Pretreatment needed: Ground into chips

A rotary drum converter is comprised 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. The biomass travels continuously into the carbonization kiln, runs outside the internal concentric tube, and is then moved through various sections at increasing temperatures. The temperature of the biomass is increased to 500 °C by high temperature fumes entering the furnace and flowing counter current. Heat required for the carbonization process is provided by burning gases and pyrolysis vapors. With the exception of the starting phase where the use of external combustion is necessary, this process is energy independent. The exiting fumes are sent to the stack while the biochar leaving the separator is transferred into a stocking silo by means of suitable screws (Conti et al., 2002). These reactors (Figure 62) have been used by companies such as Siemens and Mitsui for recycling waste materials. Mitsui seeks to produce heat and biochar.

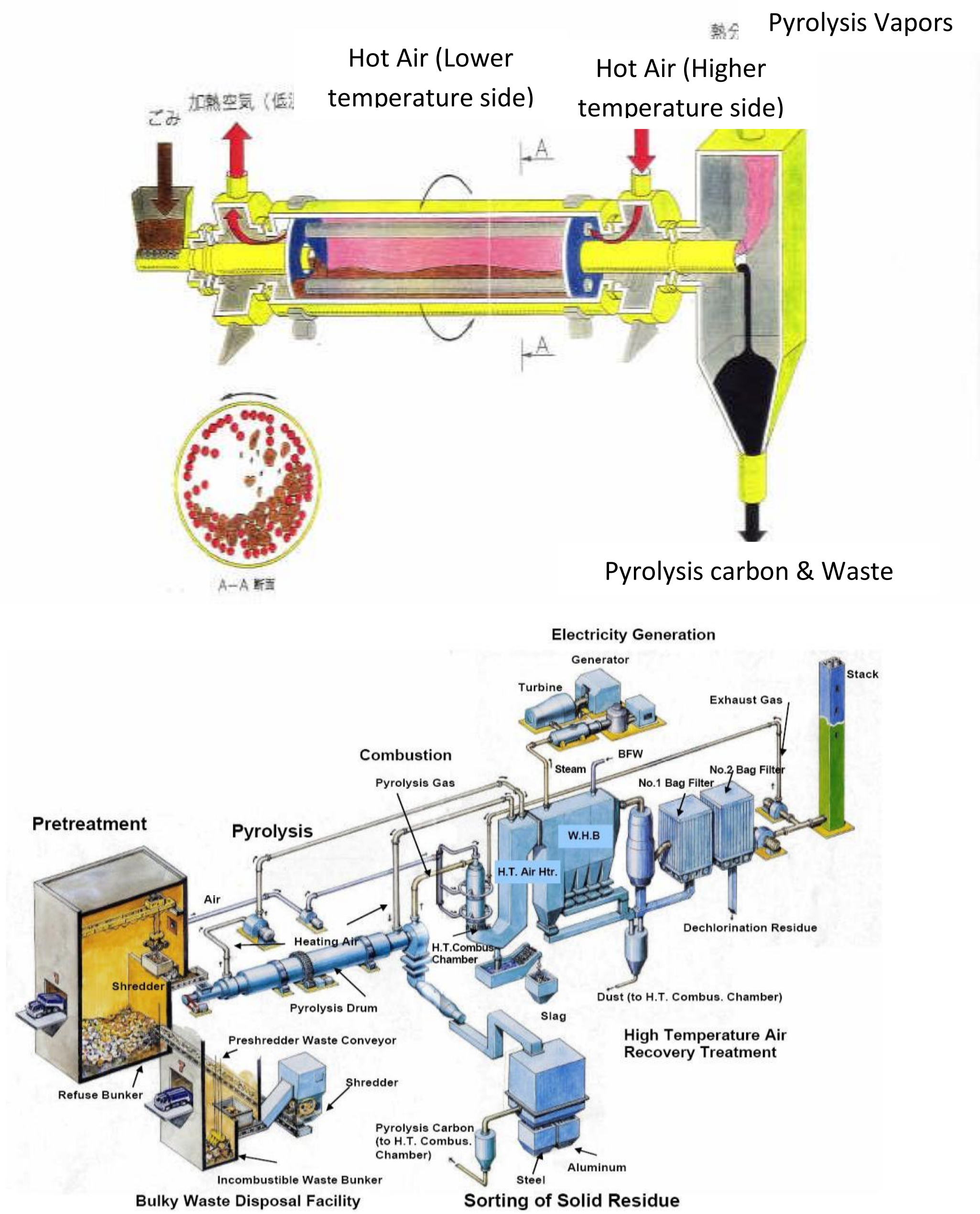

Figure 62. Pyrolysis rotary drum, Mitsui Recycling (http://www.ieabcc.nl/meetings/ Tokyo_Joint _Meeting /02Mitsui.pdf, date accessed: Nov. 13, 2010).

Pyrolysis of municipal solid waste (MSW) has been applied mostly in Japan and Europe because landfill space is limited (Hackett et al 2004). Technologies developed to process MSW serve as valuable models to develop new technologies to process biomass. The pyrolysis concept for processing MSW is based on the combination of kiln and combustion chamber to treat MSW thermally while producing steam in a heat recovery steam generator (HRSG) to generate electricity via a steam turbine (Malkow 2004). Metals are recovered and biochar can be burned or marketed as a coke-like by-product (as in the case of the EDDITh process commercialized by Thide Environmental SA) (Malkow 2004). In Japan, more than two million tons of materials are processed every year (Hackett et al. 2004). Mitsui Backbock and Takuma (http://www.takuma.co.jp/english/, date accessed February 3, 2011) have been applying the technology developed by Seemens to the Japanese market. However, Seemens withdrew from the market in 1999. A table with a list of the rotary drum reactors built by Mitsui Babcock, Techntrade, Takume and Thide Hitachi can be found elsewhere (http://www.nyfederation.org/pdf2007/64_PytlarT.pdf, date accessed: February 3, 2011).

In Europe, a limited number of facilities are operating at a scale above 50,000 TPY for municipal solid wastes (Hackett et al 2004). One of the longest running plants (since 1987) is located in Burgau, Germany (40,000 tons per year) (Hackett et al 2004). Thide-Environmental has a 50,000 ton per year facility in Arras, France (Hackett et al 2004). Other companies commercializing drum pyrolysis reactors for MSW treatment are: Ethos Energy (http://www.ethosenergy.co.uk/, date accessed: February 3, 2011), Graveson Energy Management (GEM) (http://www.gem-ltd.co.uk/, date accessed: February 3, 2011), TechTrade (http://pyrolysis.de/index.html, date accessed: February 3, 2011), the PIT Pyroflam process commercialized by SERPAC Environment of France (Malkow 2004), the PKA technology commercialized by Umwelttechnik GmbH & Co (Malkow 2004), the PyroMelt technology commercialized by ML Entosorgungs and Energieanlagen GmbH (Malkow 2004), Siemens/KWU Schwel-Breen technology and Noell-KRC conversion process (Malkow 2004).

In 2009, Amaron Energy designed, constructed, and began tests of a unique indirectly-heated rotary kiln for pyrolysis of biomass to produce bio-oil and biochar (Figure 63). Although pyrolysis in rotary kilns is customarily described as slow pyrolysis and oil yields are typically much lower than oil yields from fluidized bed reactors, Amaron has achieved char yields and bio oil yields close to those from fast pyrolysis fluid beds. The Amaron rotary reactor consists of: (1) a cylindrical reaction section heated by multiple high-intensity, gaseous, fueled burners located and controlled to optimize heat transfer into the materials being heated; (2) a feed section with an auger arrangement that suppresses slow 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 a stationary end closure supporting a vapor and gas withdrawal pipe.

Figure 63. Amaron rotary drum reactor (Courtesy of Coates Engineering, http://www.coatesengineering.com, date accessed: Nov. 13, 2010).

Vapors are condensed in multiple units designed to operate without problems caused by condensation of tars in the interconnecting piping. Following successful testing of the ½ ton per day prototype reactor, Amaron Energy filed a patent application covering the design of the reactor and the method of withdrawal and condensation of the bio-oil. The location and control of the multiple burners of the Amaron kiln are described in a prior patent application entitled "Method and Apparatus for Maximizing Throughput of Indirectly Heated Rotary Kilns." In designing the Amaron kiln, consideration was given to widely reported observations that excessive residence times at high temperature or overheating of the pyrolysis vapors result in decomposition of pyrolysis vapors into solid carbon and non-condensable gases. To optimize oil yields multiple burners are controlled to maintain optimum reactor wall temperatures. The equipment required to operate the rotary kiln pyrolysis reactor of this invention, in addition to the biomass preparation and feeding equipment include: (1) a means to rotate the kiln; (2) multiple burners that heat the kiln; (3) a blower from recycling product gas to the burners; and (4) a blower to supply air to the burners.

7.3 Auger Reactor

The auger pyrolysis reactor is one of the most attractive designs developed today (Figure 64). The reactor is typically fed with wood waste at one end of the retort through a hopper. A screw (auger) then gradually leads the wood waste into other extremities where it is carbonize. The gases and vapors are extracted and led to a condenser, and the resulting very finely divided wood biochar falls to the bottom of the retort (Dumesny and Noyer, 1908). The discharging biochar exits through a single tube leading to airtight metal receivers. The lowest level of the main structure consists of a combustion chamber that provides heat to the area in which the carbonization process is continued utilizing heat furnished from the burning of its own gases (Toole et al., 1961).

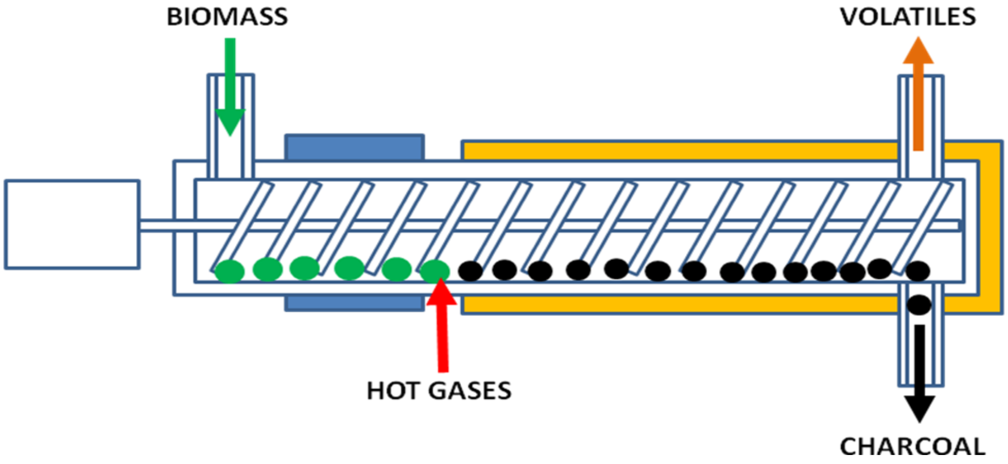

Figure 64. Auger reactor.

Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar/bio-oil/gases
Heat transfer rate achieved: Slow or fast pyrolysis
Mode of operation: Continuous
Heating method: Can use indirect heat through the walls, hot sand, or hot gases
Construction materials: Metal
Portability: Stationary or portable
Reactor Position: Horizontal
Raw material used: Chips or fine particles
Loading and discharge methods: Mechanical
Size of the kiln: Small
Charge ignition method: Heating with an external combustion chamber
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: None

Several companies are currently commercializing auger pyrolysis reactors. Companies that focus on producing bio-oil and biochar are: Renewable Oil International (http://www.renewableoil.com/, date accessed: Nov. 13, 2010), Biogreen (http://www.biogreen-energy.com/biogreen.html, date accessed: Nov. 13, 2010), Advanced Bio-refinery (http://www.advbiorefineryinc.ca/products/, date accessed: Nov. 13, 2010), and Forschungszentrum Karlsruhe (FZK) (http://www.bioliq.com/schnell.html, date accessed: Nov. 13, 2010). International Tech Corporation (http://www.internationaltechcorp.org/IT-info.htm, date accessed: Nov. 10, 2010), eGenesis (http://www.egenindustries.com/, date accessed: Nov. 13, 2010) and Agri-tech producers (http://www.agri-techproducers.com/, date accessed: Nov. 10, 2010), on the other hand focus on producing biochar and heat.

7.3.1 Production of Bio-oil and Biochar

ABRI-Tech (a joint venture between Advanced BioRefinery Inc and Forespect Inc based in Ottawa, Canada) (http://www.advbiorefineryinc.ca/products/, date accessed: Nov. 10, 2010) has been developing heated auger reactors using hot metal beads as high density heat carriers (Vonderbosch and Prins 2009). They are now building and selling 1 t/day and 50 t/day units. This company specializes in designs for transportable pyrolysis plants. Forschungszentrum Karlsruhe (FZK) developed a twin-screw mixer reactor also using hot sand as a heat carrier. A 500 kg/hour pilot plan was concluded but the yield of products obtained has not yet been reported (Venderbosh and Prins 2009). Renewable Oil International® LLC (ROI) is a company based in Alabama also targeting the development of mobile pyrolysis technologies using auger reactors (Figure 65, http://www.renewableoil.com/, date accessed: Nov. 13, 2010).

Figure 65. Renewable Oil International Mobile Unit using an auger pyrolysis reactor (Alabama USA).

Biogreen (http://biogreen-energy.com; date accessed: Nov. 13, 2010) is a French company developing auger pyrolysis reactors (Figure 66) for the production of bio-oil and biochar. This is a trademark and process developed by ETIA, an engineering company founded in 1989 specialized in processes of thermal treatment. This company produces bio-oil, biochar and synthesis gas.

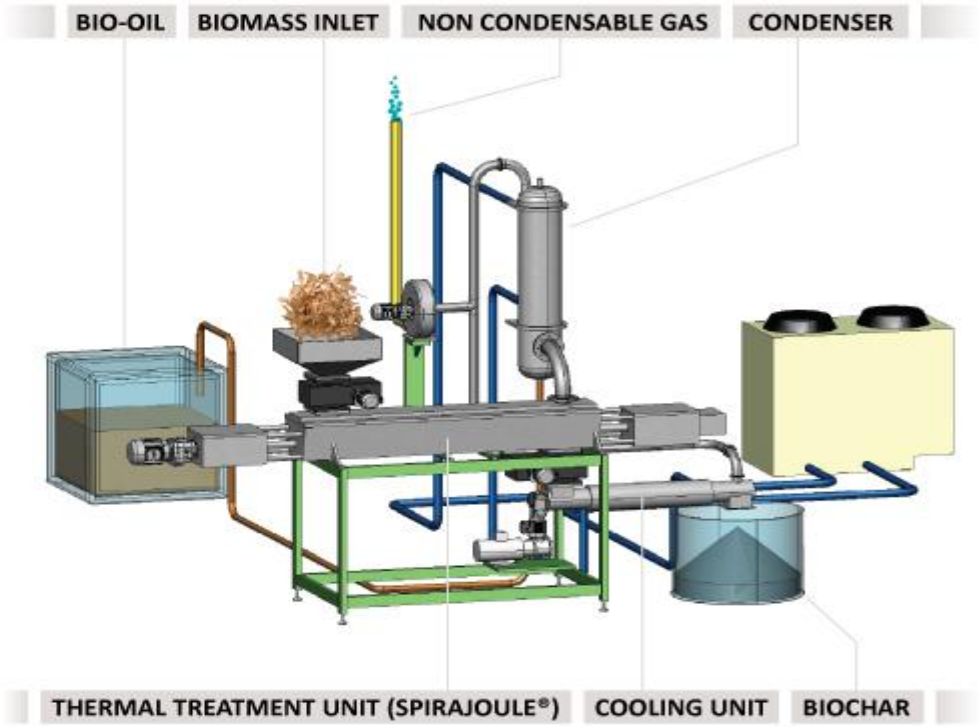

Figure 66. Auger pyrolysis reactor commercialized by Biogreen^{R} (http://www.biogreen-energy.com/biogreen.html, date accessed: Nov. 13, 2010).

7.3.2 Production of Biochar and Heat

Agri-Tech Producers (ATP) is a company based in Columbia, South Carolina which is using auger reactors for torrefaction and pyrolysis (Figure 67). This company started to work in partnership with Kusters Zima Corporation in biomass and bioenergy initiatives in 2005 (http://www.agri-techproducers.com/About-Us.html). Kusters Zima is a company with more than 40 years experience in engineering and manufacturing machinery.

Figure 67. Picture of the torrefaction machine commercialized by Agri-Tech Producers, LLC (source: http://www.agri-techproducers.com/, date accessed: Nov. 13, 2010).

Another company commercializing design of auger pyrolysis units is International Tech Corp (http://www.internationaltechcorp.net/). Its thermal recovery unit combusts all pyrolysis vapors to produce heat (Figure 68). The heat can then be converted into steam. This company develops products such as activated carbons, soil enrichments and custom carbon products. The system is designed to destroy most forms of solid wastes, and can process 50 tons of biomass per day. This kind of system costs $450,000 and requires 16 weeks to manufacture.

Figure 68. International Tech Corporation pyrolysis unit with heat recovery (http://www.internationaltechcorp.org/IT-info.htm, date accessed: Nov. 13, 2010).

eGenesis Industries is also developing auger pyrolysis reactors for the production of biochar and heat. The company is based in California (http://www.egenindustries.com; date accessed: Nov. 13, 2010). Their CR-2 unit can operate at 40 kg/h producing an energy output from the syngases of 64 kW (Figure 69). The clean syngas can be used as source of heat or for power generation. The company is currently designing Model CR-3 for a capacity of one ton per hour.

Compact Power Ltd of the UK is commercializing a technology based on multiple auger pyrolysis reactors to convert different waste materials into heat and biochar. Municipal solid waste is conveyed by an auger through heated tubes for pyrolysis (Malkow 2004). A pilot plant of 500 kg/h was built at the Avonmouth site near Bristol (Malkow 2004).

Figure 69. eGenesis CR-2 pyrolysis unit for the production of biochar and synthesis gases (http://www.egenindustries.com/, date accessed: Nov. 13, 2010).

7.4 Moving Agitated Bed

This kind of reactor has been used as part of the design of the vacuum pyrolysis unit built by Pyrovac. This process was scaled up by the team led by C. Roy at the Pyrovac Institute in Quebec, Canada. In the reactors commercialized by Pyrovac International, biomass is conveyed by patented mixers over a horizontal surface heated by molten salts. The molten salt used is a mixture of potassium nitrate, sodium nitrate and sodium nitrite (Venderbosch and Prins 2009). A 3.0 ton/h demonstration unit was built and operated in the city of Saguanay Quebec, Canada between 1999 and 2002 (Figure 70). The reactor operated satisfactorily until operational problems with the condensation towers developed (Venderbosch and Prins 2009). A group of investors led by NewEarth Renewable Energy (http://www.newearth1.net/e-oil.html) is raising capital to restart the plant (Venderbosch and Prins 2009). Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar/bio-oil
Heat transfer rate achieved: Fast/slow
Mode of operation: Continuous
Heating method: Indirect heating (sometime molten salts)
Construction materials: Metal
Portability: Stationary
Reactor Position: Horizontal/vertical
Raw material used: Chips/fine particles
Loading and discharge methods: Mechanical
Size of the kiln: Medium/large
Charge ignition method: External oven
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: Pre-dried

Figure 70. Moving bed system commercialized by NewEarth (http://www.newearth1.net/e-oil.html, date accessed: Nov. 13, 2010).

7.5 Shelf Reactors

In a horizontal retort, trucks containing a certain amount of shelves entered these retorts through two sliding doors. The material to be distilled was spread in a thin layer on these shelves. During the carbonization process in one of the retorts, the initial drying process occurs in the other. Once the wood has been carbonized, the trucks carry the shelves out and in to the cooling chambers (see Figure 71). Using shelves does away with the need for mixing, lowering costs, and allowing for immediate charging and discharging of the retorts (Dumesny and Noyer, 1908).

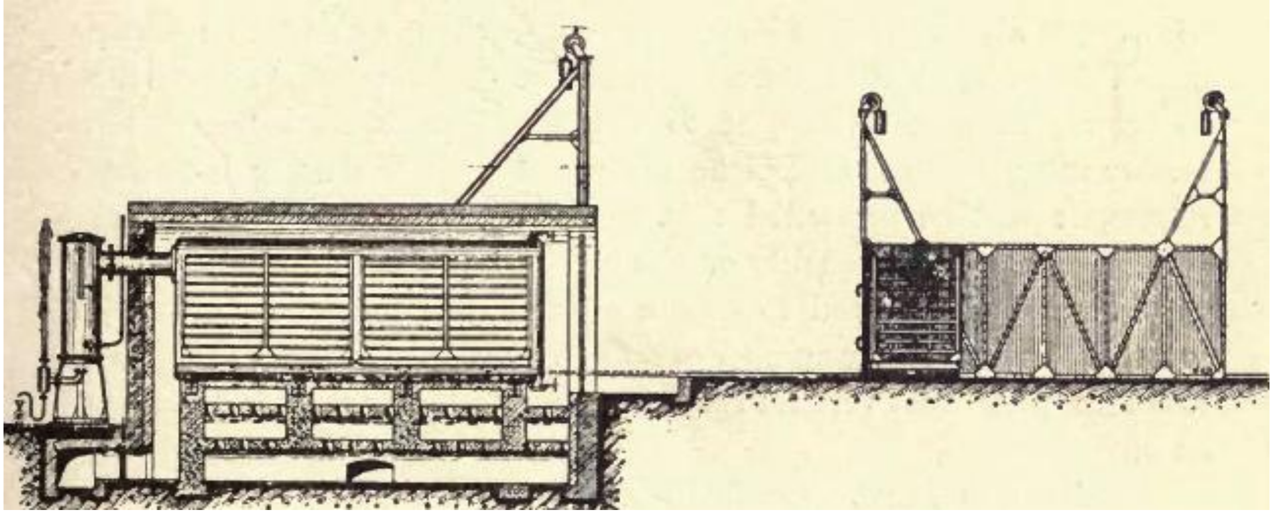

Figure 71. Retort for carbonization of small wood waste, and coolers for cooling the retorts after an operation (Dumesny and Noyer, 1908).

Once the waste material has been spread out into thin layers on plates or trays, it is brought into a horizontal retort or suspended in a vertical retort. Large scale trials have proven that this carbonization method produces good products. However, a major drawback is that the loading of the trays must be done by hand. The operation of the reactors tested was intermittent (Klark, 1925).

Although unsuitable for handling vary large quantities of raw material, in addition to other disadvantages mentioned previously, this design can be trusted to operate continuously with absolute certainty for an unlimited period (Klark, 1925). Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar and bio-oils
Heat transfer rate achieved: Slow or fast pyrolysis
Mode of operation: Continuous operation
Heating method: Indirect heat
Construction materials: Metal
Portability: Stationary
Reactor Position: Horizontal/vertical
Raw material used: Chips
Loading and discharge methods: Manual/mechanical
Size of the kiln: Small
Charge ignition method: Direct measurement
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: Pre-dried

7.6 Paddle Pyrolysis Kiln

Paddle pyrolysis reactors have been used by companies such as BEST (http://www.bestenergies.com/companies/bestpyrolysis.html, date accessed: Nov. 13, 2010) (Figure 72). The paddle pyrolysis reactor is also part of the design of Choren's low temperature gasifier (Figure 73). The main features of this reactor are the internal mechanisms to move and mix the biomass which increases the heat transfer on the surface of the material. Some of the main characteristics of these reactors are:

Final Product Targeted: Biochar
Heat transfer rate achieved: Slow pyrolysis
Mode of operation: Continuous
Heating method: Indirect heat
Construction materials: Metal
Portability: Stationary
Reactor Position: Horizontal
Raw material used: Chips
Loading and discharge methods: Mechanical
Size of the kiln: Small
Charge ignition method: External heater
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: None

The pyrolysis units commercialized by BEST are designed to generate syngas to be used as engine fuel to generate electricity. The system has a unique gas cleanup system effectively destroying tars and making the syngas clean for downstream applications. (http://www.bestenergies.com/companies/bestpyrolysis.html).

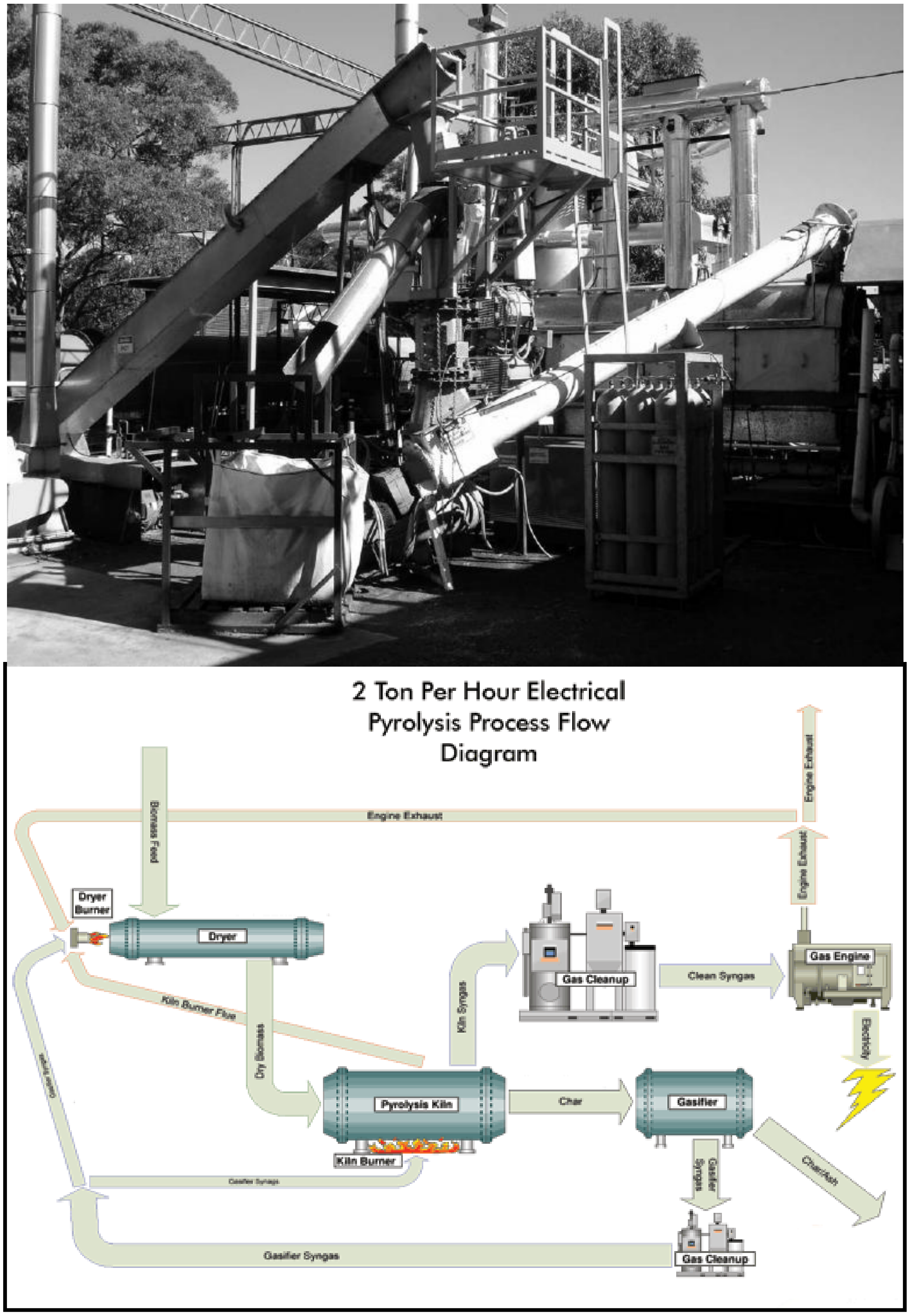

Figure 72. BEST unit using paddle reactors (http://www. bestenergies.com/companies/ bestpyrolysis.html, date accessed: Nov. 13, 2010).

Figure 73. Paddle pyrolysis reactor used by Choren (http://www.fnr-server.de/cms35/fileadmin/allgemein/pdf/veranstaltungen/BtL_Berlin_2008/4_Blades.pdf, date accessed: Nov. 13, 2010).

8. FAST PYROLYSIS REACTORS TO PRODUCE HIGH YIELDS OF BIO-OILS

In the 1970s, new concepts and processes targeting increased yield of liquid fractions provoked a renaissance in the pyrolysis of biomass. The basis of modern fast pyrolysis was developed at the University of Waterloo in the 1980's (San Miguel et al 2011). From this time to the early 1990s, research performed in the U.S., Canada, and Europe has made fast pyrolysis what it is today. New and improved technologies such as fluidization, ablation (the removal of material from the surface of an object by vaporization), and vacuums were being aggressively researched for application in new pyrolysis reactor designs (Pelaez-Samaniego et al., 2008).

Pyrolysis companies like Ensyn Technologies, Dynamotive, BTG, Fortum, Pyrovac, and Bioware developed due to extensive scale-up and new understanding of the thermochemical phenomena. Several different styles of reactors began to be used by these companies. Some of these reactors included the fluid bed, the circulating bed, the rotating cone, the ablative reactor, and the vacuum reactor. The state of the art pyrolysis technologies were reviewed extensively and published by Meier at el. (1999) and Bridgwater et al. (1994, 2001). All of these reviewed reactors were designed for converting fine particles of biomass only, excluding designs in which logged biomass was used (Pelaez Samaniego et al., 2008). Many of these pyrolysis reactors are capable of converting up to 70 mass % of the biomass into crude-oil (Bridgwater and Peacocke, 1994; Czernik and Bridgwater, 2004; Mohan et al., 2006), 40 mass % of which can be further refined into green gasoline and green diesel (Holmgreen et al., 2008a, b; Marinangeli et al., 2005). Nonetheless, numerous aspects of these technologies have the potential for improvement. These aspects include:

(1) Feedstocks with high alkaline content cannot be used in existing fast pyrolysis reactors.

(2) Despite the ability of lignin to be converted into precursors of green gasoline and green diesel, the conversion of cellulose to these precursors of transportation fuel (e.g. sugars) is not very efficient. This is because when the sugars breakdown they form small molecules with little economic value.

(3) Corrosive and unstable bio-oils are a result of high levels of acetic acid derived from hemicelluloses.

(4) Using large volumes of inert carrier gases causes a dilution of the pyrolytic gases making their energy recovery near impossible.

(5) The market is limited for small condensable molecules with < 5 carbons which are the result of fragmentation reactions. Disposing of small condensable molecules that are not converted into valuable products can cause environmental issues. Our goal is to design a system that produces hydrogen or other valuable products from these burden bearing molecules.

(6) Hydrotreatment of crude bio-oils could intensify coke formation and accelerate the deactivation of expensive catalysts which is of great concern for petroleum refineries.

(7) For this concept to be viable it is critical that mobile pyrolysis units generate their own electricity using a fuel produced onsite (synthesis gas) to run diesel engines or fuel cells.

(8) In order to hydrotreat bio-oils, bio-oil refineries and mobile pyrolysis units need to generate their own hydrogen.

Advancements made in pyrolysis reactor designs for the wood distillation industry can inform new designs. Ignoring these past advancements is a weakness in most pyrolysis designs today. The chemical industry influenced the academic world in developing current pyrolysis technologies. An important aspect of creating a new design is to make a critical evaluation of the existing designs and incorporate whatever device or practice that can contribute to an improvement on that design. The best design quality that a reactor can possess is the ability to be flexible. To be able to adapt components capable of both bio-oil recovery for bio-fuel, or biochar production for stable carbon soils opens doors for opportunity.

In order for heat transfer to occur in a pyrolysis reactor, two conditions are required: (1) heat transfer to the reactor through a medium (a solid reactor wall in ablative reactors, or gas in entrained flow reactors), and (2) from the heat transfer medium to the biomass to be pyrolyzed (Bridgwater et al., 1999). The two main methods to heat biomass particles in a fast pyrolysis system are gas solid heat transfer and solid-solid heat transfer. A fluid bed pyrolysis reactor uses solid-solid heat transfer with a small contribution from gas solid convective heat transfer. In this type of reactor biomass is mixed well so the solid-solid transfers approximately 90% of the heat, while the gas-solid transfers only 10% of the heat to the biomass. Another example that uses both gas-solid, and solid-solid heat transfer is the circulating fluid bed. Part of the energy transferred to the fast pyrolysis reactors is due to radiation (Bridgwater et al., 1999).

In order to obtain an adequate gas-solid heat transfer biomass particles must be very small to fulfill the rapid heating processes required to produce high yields of liquids. This is due to poor thermal conductivity in biomass (0.1 W/mK along the grain and 0.05 W/mK across the grain). A thin reaction layer may achieve a temperature increase of 10,000 °C but the low thermal conductivity of wood prevents temperature gradients throughout the entire particle. As the size of the particle increases, secondary reactions within the particle become increasingly significant, leading to the reduction of liquid yields (Scott and Piskorz, 1984). In circulating and fluidized bed reactors contact of the bed solids with the biomass causes wear on the char and destruction of sandy particles.

8.1 Fluidized Bed Reactors

The fluidized bed and the circulating bed are pyrolysis reactors that use a combination of convection and conduction to transfer heat from a heat source to the particle of biomass. To obtain substantial liquid yields, the particles must be very small (< 2 mm) since the transfer limitation is within the particles (Graham and Bergougnou, 1984). One of the best known examples a fluidized bed reactor is Dynamotive.

The Dynamotive (Figure 74) is the outcome of research performed by the University of Waterloo in Canada, possibly the most extensively published research on this topic. In the early 1980s, a drive to maximize liquid yields from biomass, particularly forest materials, initiated this program. The founding of modern fast or flash pyrolysis reactors can be credited to the University of Waterloo. Some of the main characteristics of these reactors are:

Final Product Targeted: Bio-oil and biochar
Heat transfer rate achieved: Fast pyrolysis
Mode of operation: Continuous
Heating method: Direct and indirect heat/sand
Construction materials: Metal
Portability: Stationary
Reactor Position: Vertical
Raw material used: Fine particles
Loading and discharge methods: Mechanical
Size of the kiln: Large
Charge ignition method: External combustion chamber to heat the carrier gas
Process control: Direct measurement of temperatures
Pressure: Atmospheric
Pretreatment needed: Particle milling and pre-drying

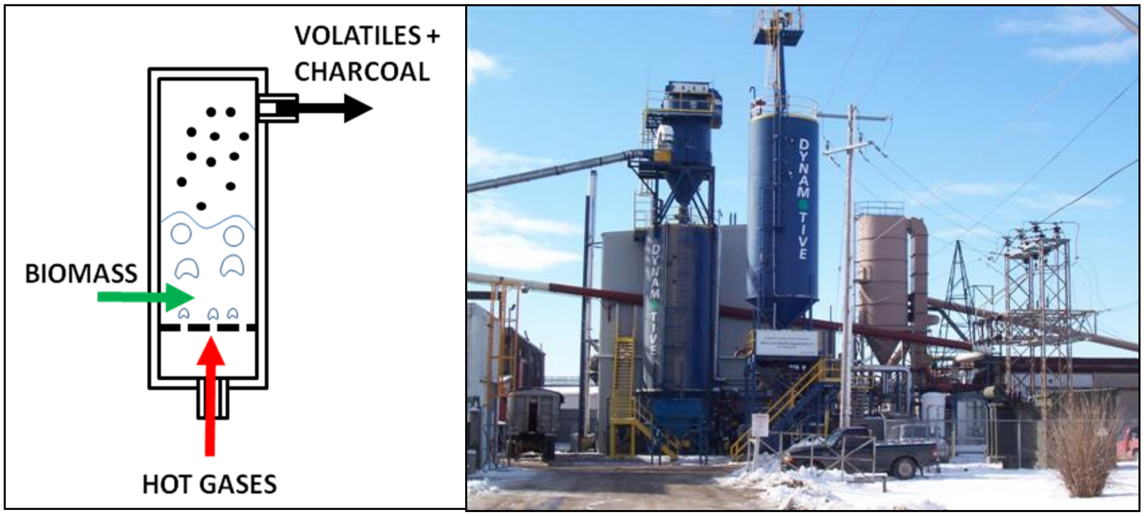

Figure 74. Fluidized bed reactors (Dynamotive, http://www.dynamotive.com/technology/, date accessed: Nov. 13, 2010).

Dynamotive (http://www.dynamotive.com) is based in Vancouver, Canada with offices in the US, UK and Argentina. In most fluidized bed reactors biochar is entrained by carefully controlling the difference between size and density of biomass particles and sand. A precise selection of sand particle size, biomass particle size, bed velocity, and reactor configuration enables this process. This mode of operation called the "blow-through," leaves the sand inside the bed with minimal traces of char making sand circulation or replacement unnecessary (Bridgwater and Peacocke, 2000).

The main features of this type of reactor are: its ability to accurately control temperature; the separation of char is done by entrainment; the use of cyclone separation; easy scaling; the technology is well known and understood; it requires small particles, and it requires large-scale heat transfer to the bed. Dynamotive (Canada) has developed Bench-Scale Plants, a 15TPD Pilot Plant, a 130TPD Plant in West Lorne, ON and a 200TPD Plant in Guelph, ON (http://www.dynamotive.com/technology/).

The heat used in these reactors is generated from the combustion of pyrolysis gases and is typically transferred to the fluidized bed by heating coils. Given the low heat transfer rates between combustion gases and the bed (100-200 W/m2 K), at least 10 to 20 m^2 of surface area is required to transfer the heat required to pyrolyse one ton/hr of biomass. These heat transfer surfaces are very susceptible to attrition from sand (Venderbosch and Prins 2009).

A mobile pyrolysis unit with fluidized bed reactor is being developed by Agri-therm at the University of Western Ontario (http://www.agri-therm.com/). This company is working with the Institute for Chemicals and Fuels from Alternative Resources under the supervision of Franco Berruti (http://www.agri-therm.com/TCBiomass2009_Pyrolysis_CBriens.pdf, date accessed: Nov. 13, 2010). An important feature of the design proposed by Agri-therm is a compact design in which the pyrolysis reactor is built in an annulus with a burner at the core providing the energy needed for pyrolysis process. Agri-therm is now working to improve the performance of their 10 ton per day plan aiming to start commercialization soon.

AvelloR Bioenergy (http://www.avellobioenergy.com/, date accessed: Nov. 13, 2010) in Iowa is also commercializing fast pyrolysis technology. This company was formed in 2009 by Robert C. Brown and three of his graduate students and specializes in the development of fractionation strategies to develop new products from bio-oils.

Bioware (http://www.bioware.com.br, date accessed: Nov. 13, 2010) is a Brazilian company located at the University of Campinas commercializing auto-thermal fluidized bed reactors. This company commercializes technologies to produce bio-oil, biochar and phenolic resins.

8.2 Circulating Bed Reactors

Research performed by the University of Western Ontario in the late 1970s and early 1980s spawned Rapid Thermal Processing (RTP) technology developed by Ensyn. As seen in Figure 75, hot recirculated biomass and sand come into contact with the hearth of the system, which is an up-flowing transported bed reactor. Before feeding this system's reactor, the biomass is comminuted to 6 mm, and then dried to a moisture content of 10% or less. Once the products have passed through two “cyclones” which separates the solids, the produced vapor is rapidly cooled and quenched in a multiple stage system. Precise control of the hot vapor’s total residence time allows it to be set down to one hundred milliseconds which “freezes” the thermally unstable liquid intermediates of the pyrolysis process (Bridgwater and Peacocke, 2000). Ensyn (Canada) has built six plants built, including a 50 t/day plant at Red Arrow, USA and a 100 t/day plant constructed in 2007 in Renfrew (Canada) (San Miguel et al. 2011). Some of the main characteristics of these reactors are:

Final Product Targeted: Bio-oil
Heat transfer rate achieved: Fast pyrolysis
Mode of operation: Continuous
Heating method: Direct heat with carrier gas
Construction materials: Metal
Portability: Stationary
Reactor Position: Vertical
Raw material used: Fines/Chips
Loading and discharge methods: Mechanical
Size of the kiln: Small-Large
Charge ignition method: Heating and external combustion chamber
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: Particle milling and pre-drying

Figure 75. Circulating bed pyrolysis reactor (http://www.uop.com/renewables/10060.html, date accessed: Nov. 13, 2010).

Rapid Thermal Processing (RTP)^{tm} is the only pyrolysis technology in the world that has operated on a long-term commercial basis (http://www.ensyn.com/tech.htm, date accessed: Nov. 13, 2010). Since most of the biochar from this process is utilized for the heating stage, it is not a major product.

The transported bed reactor has several main features including: precise temperature control within the reactor; the ability to use particles of large size; CFBs are suitable for very large throughputs; and the technology is well understood. Additional distinguishing attributes of this reactor are: the complexity of the hydrodynamics; high velocities leave the char more attrited; the separation of biochar; sand and vapors are caused by a "cyclone;" careful control is needed for the closely integrated combustion; and a large scale heat transfer to the bed is required.

A similar technology using catalysts instead of inert sand is being developed by KIOR (http://kior.com/, date accessed: Nov. 15, 2010), in Huston, Texas. KIOR uses a proprietary catalyst system with biomass to produce a deoxygenated bio-oil in a Fluid Catalytic Cracking (FCC) reactor.

8.3 Ablative and Cone Reactors

Ablative pyrolysis entails a heated surface in which wood is pressed against and moved rapidly leaving an oily film which then evaporates. Larger particles of wood can be used for this process and the limiting factor is the rate of heat supplied to the reactor. These reactors are intensive (can process large amounts of biomass in little volume), compact, and do not require carrier gases (Figure 76). NREL (Golden, CO) conducted most of the first studies on ablative reactors. BBC from Canada built and operated an ablative reactor with a capacity of 10-25 kg/hr in the 1990s (Venderbosch and Prins 2009). A disadvantage is that it requires a surface area controlled system and operates with moving parts at high temperatures (Bridgwater et al., 1999). An important feature of ablative heat transfer is that when biomass comes into contact with the hot solid, ablation occurs and exposes fresh biomass to the hot surface. This allows for no limit on particle size in certain ablative reactors. Another drawback to this process is that micro-carbons are produced which are difficult to remove from the vapor phase and usually end up in the liquid product. Some of the main characteristics of these reactors are:

Final Product Targeted: Bio-oil
Heat transfer rate achieved: Fast pyrolysis
Mode of operation: Continuous
Heating method: Indirect heating
Construction materials: Metal
Portability: Stationary
Reactor Position: Horizontal/vertical
Raw material used: Chips
Loading and discharge methods: Mechanical
Size of the kiln: Large
Charge ignition method: External combustion chamber
Process control: Direct measurement of temperature
Pressure: Atmospheric
Pretreatment needed: None

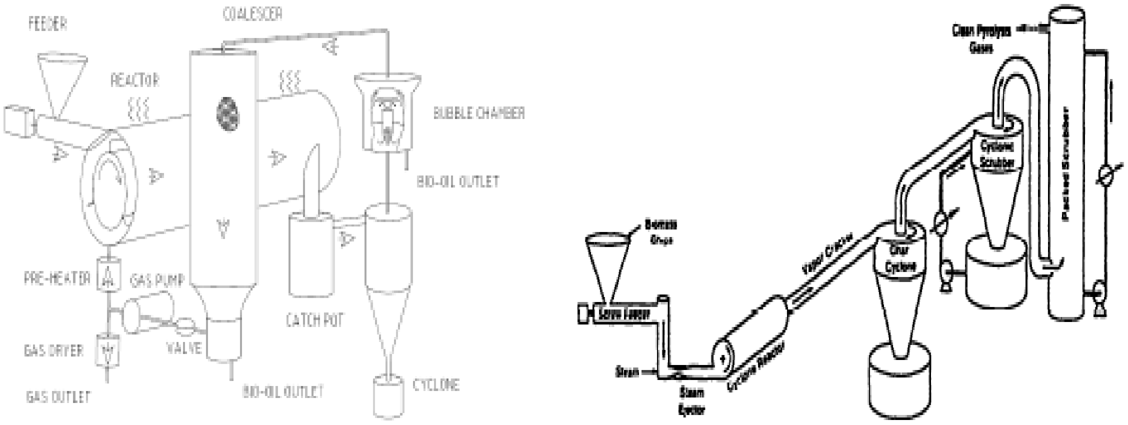

Figure 76. Ablative fast pyrolysis reactors (Graham et al., 1984).

Vortex and cyclone reactors use a flow of high velocity gas to suspend the particles of biomass. A tangential introduction of these gases into the reactor uses centrifugal actions to force the particles against the heated walls of the reactor. Even though both of these reactors are inherently mechanically simple, they require motive gas in large volumes relative to the volume of the biomass feed.

On the other hand, ablative reactors like the pyrolysis mill, and the ablative plate or tube have mechanical systems inside the reactors. These mechanical systems, in the form of mill stones or scrapers, force the biomass against the wall of the reactor. Potential negative aspects of these reactors are the use of mechanical systems which increase their complexity, and inevitable wear and tear of the moving components (Bridgwater et al., 1999).

The University of Hamburg, another group active in the development of ablative reactors, built two plants. The first plant was developed for research and has a capacity of 20 kg/h; the second, with a capacity of 2 t/h is a demonstration unit (see Figure 77 and 78).

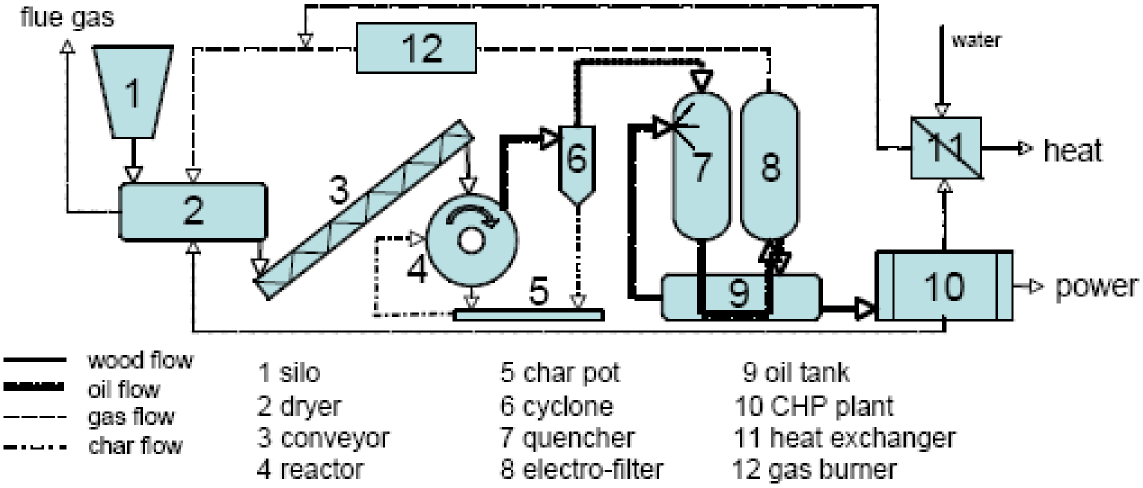

Figure 77. Pytec’s biomass to oil ablative pyrolyser from the University of Hamburg (Venderbosch and Prins 2009).

At present, ablative reactors are only being developed by the German company Pytec. This company has a pilot plant of 250 kg/hr near Hamburg and a 2 t/hr demonstration plant in Mecklenburg-Vorpommern (Venderbosch and Prins 2009).

Figure 78. PyTec 2 t/h demonstration unit built in Germany (University of Hamburg).

The University of Twente in the Netherlands developed a novel type of fast pyrolysis reactor called the rotating cone reactor. This design requires an impeller mounted at the base of the heated rotating cone into which particles of biomass are fed. The impeller, along with a flow of inert particles, pushes the feed onto the heated surface pyrolyzing it while transporting it spirally upward along the hot wall of the cone (Figure 79). This reactor takes advantage of the fast heat transfer between biomass and hot inert particles without using carrier gas (Venderbosch and Prins 2009). Basically, this design mixes the hot sand and the biomass mechanically. Since this reactor does not require a gas carrier, the size and cost of the secondary oil collection system is reduced significantly. BTG in Malaysia built an up-scaled version of the rotating cone technology capable of processing up to 50 t/day (San Miguel et al., 2011).

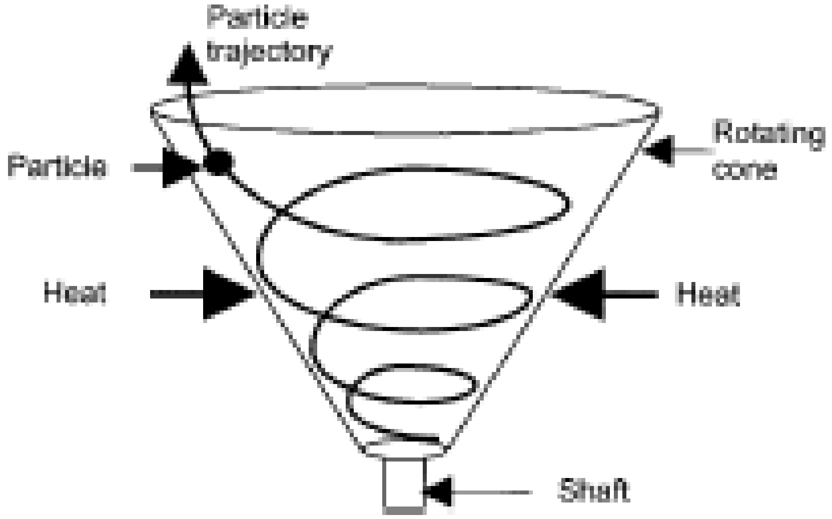

Figure 79. University of Twente rotating cone principle (Bridgwater and Peacocke, 2000).

9. VEHICLE GASIFIERS USING BIOCHAR AS FUEL

During World War II, small gasifiers able to utilize biochar as fuel to operate vehicles, boats, trains, and small electric generators were developed. In 1939, all oil transports to Europe were halted. The military got top priority for gasoline use, so the civilian population was forced to find their own transportation fuels. As a result, approximately one million gasifiers came into operation around this time. About 90% of Sweden's vehicles were powered by gasifiers, and by the end of the war there were more than 700,000 wood gas generators. Figure 80 shows some examples of vehicle gasifiers and Figures 81 and 82 show the working principles of these systems.

Two main concepts of gasifiers were used to operate these engines: updraft and downdraft gasifiers. An updraft gasifier can be used without cleanup if the gas is going to be applied to a burner. However, if gas is to be fed into an engine, a downdraft, or another tar cracking gasifier, must be used and the gas must be conditioned and cleaned. A downdraft gasifier produces hot gases that are usually laden with dust and contain up to 1 mass % of tar and particulates. Costly and troublesome problems dealing with the maintenance, repairs, and reliability of the vehicles can occur if the dust and tar are not removed properly. The leading cause of gasifier engine system failure is the improper removal of these syngas contaminants. During the initial start up, the gas is very dirty and must be burned in the gasifier until the system is fully functional.

Figure 80. Vehicle gasifiers constructed after the fuel crisis in the 1970s. (SERI, 1988).

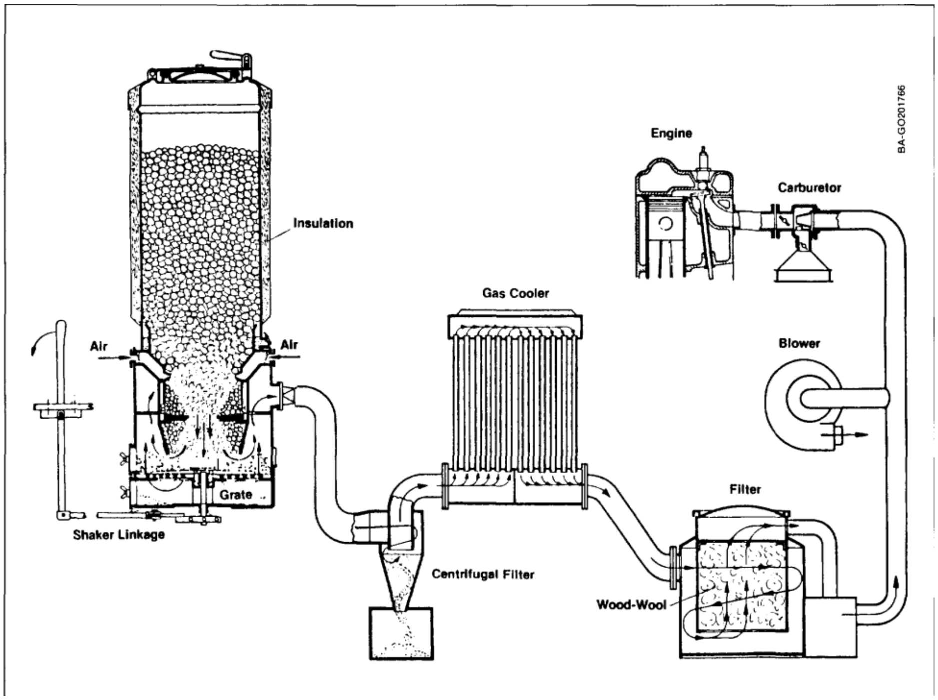

Figure 81. Typical vehicle gasifier showing cyclone and gas cooler (SERI, 1988).

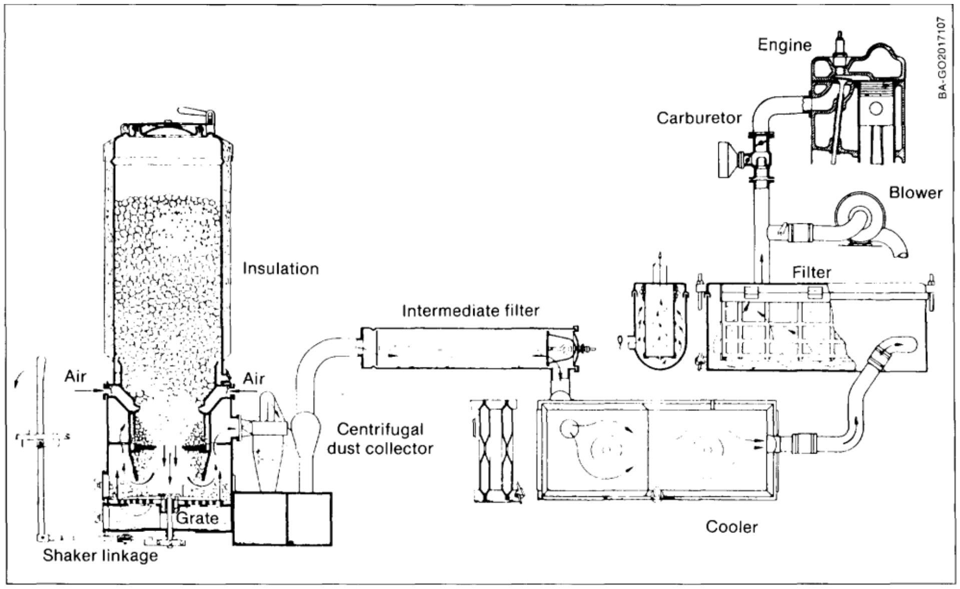

Figure 82. Producer gas engine for spark ignition system (SERI, 1988).

In order for the gasifier process to become an economic oil fuel replacement, it is necessary to take into account costs. Biochar currently costs $300 per ton. With current gas prices at about $0.79 per liter (592 $/ton), the maximum cost of biochar should be $470. Biochar costs less in most developing countries. Comparing the use of biochar to the convenience of liquid fuel, a fair margin is necessary in order to make the installation of the proper equipment worthwhile. Partially replacing gasoline with producer gas has been quite successful. Replacing up to 70% of petroleum derived fuel with producer gas for running stationary engines is a worthwhile investment. There are very clear advantages of replacing imported petroleum with producer gas, however, giving the convenience of liquid fuels many users prefer to pay more.

10. ENVIRONMENTAL IMPACTS OF BIOCHAR PRODUCTION

Biochar production is associated with greenhouse gas emissions as well as water and land pollution. Such impacts are of critical importance for designing low environmental impact pyrolysis units.

Biochar production is one of the largest industries in the world today. In 2009, 220 million tons of biomass were converted into 44 million tons of biochar. Most of this production came from highly polluting and inefficient kilns like earth or pit kiln, drum kilns, beehive kilns, and others. Inevitably, environmental impacts arise as a result of using feedstock inefficiently and releasing pollution from carbonization into the atmosphere.

In developing nations, biochar production is a major source of income and environmental degradation in rural areas; and in urban areas it is a primary fuel source (Kammen et al., 2005). In Africa, the production, transportation, and combustion of biochar represent important economic and energy systems (Kammen et al., 2005). Most of the detrimental effects of biochar are related to inefficiency of production, land and forestry degradation, and long transportation distances. Due to immense batch sizes, biochar production is often associated with clear cutting of forests. In Brazil, for example, large areas of forests, mainly in the Amazon, are cut to produce char for the metallurgical industry. Well-managed plantations offer the best option for producing biochar, but more typically feedstock comes from land cleared for agricultural purposes or small areas of land cleared specifically for biochar production (Kammen et al., 2005).

Rural residents and biochar producers in many countries often cannot afford to use biochar. Instead, demand for biochar is generated in urban areas, which means that charcoal must be transported via truck to the area of demand, sometimes up to 1000 km away. Use of fuel wood by urban dwellers leaves rural dwellers with decreased access to biomass supplies (Kammen et al., 2005). A large amount of the biochar feedstock comes from unsustainable harvesting, resulting in net carbon dioxide emissions. Further, pyrolysis without product recovery results in the emissions of gases such as methane which can more significantly impact global climate change than carbon dioxide (Kammen et al., 2005).

Although only one tenth of biochar production accounts for the energy use in certain areas of Africa, it has a large impact on forests for two reasons. First, since the production process is inefficient, the wood fuel equivalent is 4-6 times larger. Also harvesting wood for biochar production is an intensive process and is concentrated in a small area over a short period of time leading to the consumption of much of the forests, and in some cases fuel wood is illegally taken from state land (Kammen et al., 2005). The wood collected by the rural wood fuel users is done daily in small amounts resulting in much more dispersed and less severe impact on the forests (Kammen et al., 2005). About 80% of the biochar produced in Africa comes from land clearing (Kammen et al., 2005).

10.1. Environmental Impacts of Biochar Production

Atmospheric pollution and forest degradation are two main environmental concerns of biochar production. Water and waste water pollution are outside the scope of this report.

10.1.1. Atmospheric Pollution

Because pyrolysis kilns are designed to only partially combust wood, gases harmful to the environment such as methane, carbon monoxide, alkanes, oxygenated compounds, and particulate matter, as well as organic compounds such as ethane, ethanol, and polycyclic organic matter (POM) are released directly into the atmosphere. Additionally, if tars remain uncombusted, they may solidify and form emissions of particulate matter (PM), pyroacids, and aerosol. The gases that are released have a much greater impact on climate change than carbon dioxide. Studies show that producing biochar releases more gross emissions than actual combustion of biochar in a stove.

Traditional biochar production creates five types of products and byproducts: 1) biochar, 2) non-condensable gases (carbon monoxide, carbon dioxide, methane, and ethane), 3) pyroacids (primarily acetic acid and methanol), 4) tar and heavy oils, and 5) water. When pyrolysis oil and heat are not recovered, they are released with kiln exhaust. The type and distribution of biochar products vary depending on the raw materials chosen and the carbonization parameters.

Biochar production units are usually located far from populated areas due to the smoke they produce. Kiln smoke naturally settles and travels near the ground at atmospheric pressures. Therefore, it is preferable to construct a site on high ground so the prevailing winds will carry the smoke into the upper air strata. In order for biochar to be produced in the United States non-polluting technology must be developed (Toole, 1961).

Continuous production of biochar is more amenable to emissions control than batch production, because the composition and flow rate of emissions are relatively constant. After burners and cyclones control the emissions from continuous multiple hearth kilns. They are also used for product recovery and to reduce PM, CO, and volatile organic compounds (VOC) (by at least 80%). It is difficult to control emissions from batch type kilns because the process and consequently the emissions are cyclical. Some batch kilns have after burners to help control emissions but most do not.

The biochar briquetting process also produces emissions. Particulate matter and PM-10 may be produced during the crushing, screening, and handling of the raw biochar. Depending on the additives used, VOC may be emitted from the briquette pressing and drying process. A centrifugal collector or fabric collector with control percentages of 65% and 99% respectively, may control some particulate matter emissions from the briquetting process. It also may be beneficial to use pellets for slow pyrolysis systems. Emission factors for criteria pollutant emissions from the manufacture of biochar without emission control devices are shown in Table 1. The emission factors for organic compounds released to the atmosphere by carbonization units without heat recovery are shown in Table 2.

Table 1. Emission factors for pollutants[a] associated with biochar production (Shreve, 1967; Hartwing, 1971; Maxwell, 1976).

Source	lb / ton of char produced				
	Total PM[b]	NO_x	CO	VOC	CO_2
Biochar kiln[c]	310	24	290	270	1,100
Briquetting[d]	56	ND	ND	ND	ND

[a] Factors represent uncontrolled emissions (emission factors units are lb/ton of product, one lb/ton = 0.5 kg/Mg). ND = no data.

[b] Includes condensable and consists primarily of tars and oils.

[c] Applicable to both batch and continuous kilns without pollution controlling devices or product recovery.

[d] For entire briquetting process.

Table 2. Emission factors for organic pollutants[a] associated with biochar production (Shreve, 1967; Hartwing, 1971; Maxwell, 1976; Moscowitz, 1978).

Source	Pollutant	Emission factor, lb/ton of char produced
Biochar kiln[b]	Methane	110
	Ethane	52
	Methanol	150
	POM	0.0095

[a] Factors represent uncontrolled emissions.

[b] Applicable to both batch and continuous kilns.

The ultimate goal of this project is to identify or develop biochar production facilities that are exempt from air permitting with emissions below the values in the exemption table (173-400-102 WAC) and de minimis levels (173-460-150 WAC). Otherwise, facilities may apply a best available control technology (BACT) and keep emissions below either the Small Quantity Emission Rates (SQER) or the Acceptable Source Impact Levels (ASILs) with air dispersion modeling.

Facilities emitting below exemption and de minimis levels do not require an air emissions permit, while facilities that can only achieve ASILs must go through an air emissions permitting process. For pyrolysis, these standards can only be met in systems where pyrolysis vapors are used to produce heat or other valuable products.

10.1.2 Forest Degradation

Biochar production can be quite damaging to the environment because most feedstock comes from forests. Trees are often felled for this industry and not replaced. In the absence of sustainable forest management practices, production of biochar will outpace the replenishment of forests. This is further exacerbated by inefficient char production facilities. The extent to which biochar production alone contributes to deforestation warrants further investigation. Nonetheless, more sustainable biochar production is possible using agricultural waste, small shrubs and plants as biochar feedstock. With the appropriate technology, using alternative sources would help reduce deforestation and could potentially increase yields.

11. SAFETY CONCERNS OF BIOCHAR PRODUCTION

Biochar production presents a high-risk environment (e.g., fire and high temperature operating conditions) where safety protocols are critical (Toole, 1961). This section describes safety concerns of biochar production including safety equipment, operating protocols, storage and transportation.

11.1. Safety Concerns in Biochar Production

One of the goals of this project is to develop designs with enhanced safety features. All the risks identified for traditional carbonization industrials must be taken into account as new designs are developed. Carelessness and complacency can lead to unnecessary loss of product and can endanger workers. The fact that kilns are fairly simple to operate can cause operators to overlook basic safety practices. The operator must closely monitor weather conditions, the integrity of the kiln structure, the temperature of the kiln, and the time of the process for every production cycle. Additionally, the operation area should be fenced or posted with warning signs around the perimeter to control unwarranted traffic around the kiln area (Toole, 1961, FAO 1985). Explosions, fire, and carbon monoxide poisoning are the most significant hazards of biochar production.

11.1.1 Explosion Hazards

Improperly used kilns can explode, burn, or collapse causing harm to people. Respiratory and skin problems can also arise from the release of harmful fumes as a result of improper kiln use. Explosions caused by a mixture of methane, hydrogen, and air that is admitted at the air inlets are a potential risk. While the explosions themselves may not be severe, they can damage the structure of a kiln which may cause more serious problems and potential injury (Toole, 1961).

Puffing, the release of kiln gas pressure, is controlled with temperature regulation through proper air inputs. Although puffing occurs even during proper kiln operation, it can indicate the slow build up of explosive gases (Toole, 1961). Developing a well-instrumented kiln is critical to reducing the risk of explosion.

11.1.2. Fire Hazard

Explosions typically lead to fires. An explosion or extended heating can create cracks in the kiln wall, allowing air to freely enter resulting in the combustion of the coaling wood. When operating a kiln after an explosion, the operator must be prompt and careful in sealing the air admitting cracks (Toole, 1961). In addition to explosions, improper maintenance and preparation of the biochar production cycle as well as an improper monitoring of the heating and cooling stages can lead to fires. Because every kiln operates differently, guidelines (rather than strict rules) should be developed to direct the biochar production process. Differences in stock and changes in weather make it necessary to operate each cycle differently. The operator should never assume that a kiln is working properly. Because of obvious fire hazards, biochar production kilns should be located a proper distance away from other buildings, brush, or other flammable materials (Toole, 1961).

11.2 Safety Equipment

It is important to control burning conditions in the kiln using temperature detection and control equipment should. Temperature can be monitored using inexpensive thermocouples. It can be controlled using air inlets to regulate the amount of air let into the kiln (Toole, 1961; FAO 1985). Intake and vent closure plates are necessary to prevent explosion or fire hazards. If excessive puffing occurs, automatic mechanisms can close air intake ports. When operating a kiln with a vent or a chimney there should always be a device that will allow the gases to escape (Toole, 1961). Water should be available in a storage tank or piped to the kiln site. Other safety equipment including back pack water pumps, large capacity fire extinguishers, or a hose with a nozzle should be available for immediate use to provide some measure of fire protection (Toole, 1961). Workers should wear gloves when working around the kiln door, and avoid tripping or falling. First aid materials should be kept on site at all times.

11.3 Safe Operation

Safe kiln operation centers on moisture content of feedstock and ignition practices. To avoid kiln damage and burns extra care should be taken during the carbonization process. The moisture content of the wood varies the pattern of the biocharring. Seasoned wood heats rapidly and therefore poses a greater risk of explosion than unseasoned wood. To prevent control hazards in the carbonization process the moisture content of the wood should not be less than 30 to 40 % (Toole, 1961).

Closed-door ignition involves highly flammable fuel oil and an abundance of air, which could lead to vigorous and rapid combustion. With this method, fuel should not be allowed to rest on the fuel bed. Explosion or backfire can result. Low flash point fuels should never be used and fuel should be poured over the bed immediately before ignition. Fuels with low flash points such as gasoline should never be used (Toole, 1961). Ignition of the charge with gas or oil torches can sometimes overheat the charge and cause structural damage. Raw fuel from the burner has the potential to vaporize and increase the chance of explosion if it is let into the kiln. So extra care should be taken to make sure the burner is operating properly. Once the kiln has cooled, gases may linger. Workers should wear masks and the kiln should be well ventilated to prevent inhalation of these gases.

11.4 Storage of Biochar

In most parts of the country demand for biochar is seasonal (FAO, 1985). Therefore, during summer biochar producers must create a considerable stockpile of inventory, or temporarily stop operations (Toole, 1961). Although biochar is very stable once it has cooled, precautions must be taken to prevent spontaneous combustion during storage.

Immediately after biochar has been removed from the kiln it tends absorb oxygen, which can lead to combustion and thus loss of product. Biochar fines should be removed before the biochar is stored (Toole, 1961; FAO, 1985). Occasionally, material that is still burning is missed during removal of the charge even after the cooling cycle. It is important to prevent this “hot coal” from reaching the storage area by allowing it to sit in an open dry area for 24 hours before it is stored (Toole, 1961). During this safe cooling period, the biochar should be protected from rain in an open shed or under a tarpaulin. Once the biochar has been safely cooled and there is no evidence of heat or active fire, it is considered safe for warehouse storage (Toole, 1961). Biochar fines should be protected from rain as well but exposed to air in a separate pile from the lump biochar for at least five days (Toole, 1961).

12. CONCLUSION

The need for advanced fuels and bio-chemicals to reduce our dependency on imported oil, the need for advanced biochar to store carbon and enhance soil fertility, and the need for new technologies to convert waste biomass resources into valuable products are the main market drivers for the development of pyrolysis technologies in Washington State.

Two types of pyrolysis technologies adapted to the conditions of Washington State should be developed: (1) slow pyrolysis units to produce biochar and heat; and (2) fast pyrolysis to produce biochar and bio-oil. Bio-oil has to be further processed in a rural refinery to obtain stabilized bio-oil compatible with existing petroleum refineries and high value products.

Despite the obvious potential benefits of producing second generation transportation fuels and chemicals using the bio-oil obtained from the pyrolysis process, the commercial production of bio-oils cannot happen until the development of fully operational bio-oil refineries. The market conditions and technologies available at this time favor the development of pyrolysis units that produce biochar and heat. Once bio-oil refineries are developed or the pyrolysis units are able to produce bio-oil compatible with existing refineries, these conditions will experience a drastic change. The economies of scale will favor the production of bio-oils and the further conversion of these oils to fuels and chemicals as a result of the development of bio-oil refineries. The development of high value products from bio-oil is also critical to enhance the economic viability of bio-oil refining technologies.

Using the current slow pyrolysis technologies to produce biochar and heat is most viable short term option available. With this in mind we are proposing to deploy pyrolysis units in the state of

Washington that can produce heat and biochar but can easily be modified to become fast pyrolysis units for when the bio-oil refineries are operational and there is an established market for these bio-oils. There should be a further evaluation on the development of reactors that can be used for slow or fast pyrolysis once bio-oil refineries have been established. This will enable the current biochar producers to increase their income by switching pyrolysis methods to produce bio-oils when the time comes.

Programs aimed at substituting fossil fuels in rural communities could utilize the heat generated from the pyrolysis volatiles. Using waste streams such as forest thinning, cereal straws, municipal solid wastes, and digested fibers as feedstocks to generate high value products with the produced biochar will increase the revenue for biochar production. There is also a large unexplored market in the soil applications of biochar as well as in the use of syngas as a supplier of electricity for farms. A further investigation should be performed involving the development of small biochar gasifiers able to generate power for tractors as well as electricity for isolated communities.

A balanced investment in the creation of new knowledge (science), in the design, testing and scale up of new technologies (for pyrolysis reactors and for rural bio-oil refineries) (technology) and in the development of new products (from bio-oil and biochar) (Market) to build a shared vision that take advantage of existing infrastructure and is achievable in small steps are all critical for the deployment of a viable biomass economy based on pyrolysis technologies.

Biochar and bio-oil production technologies, batch size, and marketing to the available resources and end user population needs to match up with the analysis of transport, marketing, and the economics for specific conditions (Kammen et al, 2005). A proper analysis of these criteria is crucial to design policies at the state, federal, and international level.

13. REFERENCES

Andrews R.G., Zukowski S., Patnaik P.C., Feasibility of Firing an Industrial Gas Turbine Using a Biomass Derived Fuel. Developments in Thermochemical Biomass Conversion. A.V. Bridgwater and D.G.B. Boocock, Eds. Blackie Academic and Professional, London, UK, 1997, p. 495-506.

Antal MJ. Biocarbon Production: The State of the Art. Presentation made at TCBiomass2009, Sept 17, 2009 Chicago.

Antonini G, Hazi M, Edute ADEME/PROCEDIS: Pyrolyse-Gazeification de dechets solides- Juin 2004, Partier 1: Etat de l'art des procedes existants Feasibilite de traitement de un dechet par Pyrolyse ou Gasification.

Baglioni P, Chiaramonti D, Bonnini M, Soldani I, Tondi G., Bio-crude oil/diesel Oil Emulsification: Main Achievements of the Emulsification Process and Preliminary Tests on Diesel Engine. In Progresses in Thermochemical Biomass Conversion; Bridgwater AV, Ed. Blackwell Science, Oxford, 2001, p. 1525-1539

Baker AJ: Biochar Industry in the U.S.A. In: Symposium on Forest Product Research International. Achievements and the Future: Vol. 5, 1985, April 22-26: Pretoria. Republic of South Africa. South African Council for Scientific and Industrial Research. National Timber Research Institute, 1985: 15 p.

Banks G.N., Wong J.K.L., Whaley H., Combustion Evaluation and Heat Transfer Characterization of Fast Pyrolysis Product, 1992, Division Report ERL 92-35 (CF) CANMET, Energy Mines and Resources Canada, Ottawa, Canada.

Bates JS. Distillation of hardwoods in Canada. Forestry Branch-Bulletin # 74, Department of the Interior, Canada. 1922.

Baker AJ. Biochar Industry in the U.S.A. In : Symposium on Forest Products Research International – Achievements and the Future : Vol. 5, 1985 April 22-26. Pretoria. Republic of South Africa. South African Council for Scientific and Industrial Research, National Timber Research Institute 1985, 15 p.

Barbucci P., Costanzi F., Lagasacchi S, Mosti A, Rossi C., Bio-fuel Oil Combustion in a 0.5 MW Furnace. In Proccedings: Second Biomass Conference of the Americas NREL/CP 200-8098, Golden, USA, 1995

Bech N, Jensen PA, Dam-Johansen K: Ablative Flash Pyrolysis of Straw and Wood: Bench Scale Results.

Bhattacharya SC, Hla SS, Pham H-L. A study on a multi-stage hybrid gasifier—engine system. Biomass Bioener 2001;21: 445–60.

Bienert, K. 2007. The status of the CHOREN CarboV® gasification. 2nd European Summer School on Renewable Motor Fuels. Warsaw, August 2007. http://www.baumgroup.de/Renew/download/4%20-%20Bienert%20-%20slides.pdf) (date accessed: Nov., 15, 2010.

Boroson M.L., Howard J.B., Longwell J.P., Peters W.A., Product Yield and Kinetics from the Vapor Phase Cracking of Wood Pyrolysis Tar. AIChE Journal, Vol. 35, No. 1., 1989a, p. 120-128

Boroson M.L., Howard J.B., Longwell J.P., Peters W.A., Heterogeneous Cracking of Wood Pyrolysis Tars over Fresh Wood Char Surfaces. Energy & Fuels, 3, 1989, p. 735-740.

Bridgwater A.V., Peacocke G.V.C. Engineering Development in Fast Pyrolysis for Bio-oils. In: Proceedings of Biomass Pyrolysis Oil Properties and Combustion meeting. Sept. 26-28 Estes Park. Co, 1994, p. 110-127.

Bridgwater AV, Meier D, Radlein D: An overview of fast pyrolysis of biomass. Organic Geochemistry 30 (1999) 1479-1493.

Bridgwater AV, Peacocke GVC, 2000. Fast Pyrolysis Processes for Biomass. Renewable and Sustainable Energy Reviews, 4 (2000), 1-73

Bridgwater AV, Peacocke GVC: Fast Pyrolysis Process for Biomass. Renewable and Sustainable Energy Reviews 4 (2000a) 1-73.

Bridgwater AV, Czernik S, Piskorz J. An overview of fast pyrolysis. In: Bridgwater AV, editor. Progress in thermochemical biomass conversion. IEA Bioenergy. Blackwell Sciences; 2001b. p. 977–97.

Bridgwater AV, 2005 Fast pyrolysis based biorefineries. Presentation made to the American Chemistry Society, Washington, DC, 31 August.

Brown N.C: The hardwood distillation industry in New York. The New York State College of Forestry at Syracuse University. January 1917.

Brown RC, Radlein D, Piskorz J: Pre-treatment processes to increase pyrolytic yield of levoglucosan from hervaceous feedstocks. In: J.J. Bosell Editor. American chemical society series no. 784, American Chemical Society, Washington DC, USA (2001) pp. 123-134.

Chum HL, Kreibich RE, 1993. Process for preparing phenol formaldehyde resin products derived from fractionated fast-pyrolysis oils. U.S. Patent 5,091,499, 1993.

CIRAD and Innov-energies. 2007. Carbonisation and Cogeneration Technology: The CML Process. http://www.drveniugljen.hr/assets/files/prezentacije/06_Christian_Bedrossian.pdf, date accessed: Nov. 15, 2010.

Conti L, Mascia S, Scano G, Grassi G, Maggioni E, Pedani P, Ostan R: Commercial Process for low cost production of biochar, activated carbon, bio-hydrogen, form low value biomass. 12 European Conference on Biomass for Energy, Industry and Climate Protection 17-21 June 2002, Amsterdam, The Netherlands.

Czernik S, Bridgwater A.V., Overview of Applications of Biomass Fast Pyrolysis Oil. Energy & Fuel v. 18, n. 2, 2004, pp. 977-997.

Czernik S; French R; Feik C and Chornet E, 2002. Hydrogen by catalytic steam reforming of liquid by products from biomass thermochemical processes. Industrial and Engineering Chemical Research 41:4209-4215

Cummer K.R., Brown R.C: Ancillary equipment for biomass gasification. Biomass and Bioenergy 23 (2002) 113-128.

D'Alessio J, Lazzaro M, Massoli P, Moccia V, Thermo-Optical Investigation of Burning Biomass Pyrolysis Oil Droplets. Twenty-Seventh Symposium on Combustion/ The Combustion Institute, 1998, p. 1915-1922

Diebold J.P., Bridgwater A.V., Overview of Fast Pyrolysis of Biomass for the Production of Liquid Fuels. Fast Pyrolysis of Biomass. A Handbook, Eds. Bridgwater A et al. CPL press, 1999, p. 14-32.

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. London, Scott, Greenwood & Son. "The oil and colour Trates Journal "Offices & Broadway, Ludgate Hill, E.C.1908.

Elliott DC and Baker E, Hydrotreating biomass liquids to produce Hydrocarbon Fuels. In, Energy from Biomass and Wastes, X. Klass D., Ed. IGT Chicago, 1987, p. 765-784.

Elliott DC 2007. Historical developments in hydro-processing bio-oils. Energy & Fuels 2007 (21): 1792-1815.

Emrich W: Handbook of biochar Making. The Traditional and Industrial Methods. 1985, D. Reidel Publishing Company, 1985

Evans R.J., Milne T.A., Molecular Characterization of the Pyrolysis of Biomass I. Fundamentals. *Energy & Fuels*, Vol. 1, No 2, March/April 1987a, p. 123-137.

Evans R.J., Milne T.A., Molecular Characterization of the Pyrolysis of Biomass II. Applications, Energy & Fuels, Vol. 1, No 4, July/August 1987b, p. 311-319.

Faaij APC. Bioenergy in Europe: changing technology choices. Energy Policy 2006;34:322–42.

Fagernas L. Chemical and Physical Characterization of Biomass-Based Pyrolysis Oils. Literature Review. 1995, VTT Research Notes.

Food and Agriculture Organization of the United Nations (FAO). Industrial Charcoal Making, 1985. Available at: www.fao.org/docrep/x5555e/x5555e01.htm#TopofPage, date accessed November 13, 2010.

Food and Agriculture Organization of the United Nations (FAO). Simple Technologies for Charcoal Making, 1987. Rome, Italy. http://www.fao.org/docrep/x5328e/x5328e07.htm#TopOfPage, date accessed: Nov. 13, 2010.

Fournier J. Low Temperature Pyrolysis for Biochar Systems. Presenation made to the Conference Harvesting Clean Energy January 25, 2009

Fratini E, Bonnini M, Oasmaa A, Solantausta Y, Teixeira J, Baglioni P 2006. SANS analysis of the microstructure evolution during the aging of pyrolysis oils from biomass. Langmuir 22 (1): 306-312.

Frear C, Zhao B, Fu G, Richardson M, Chen S, Fuchs MR: Biomass Inventory and Bienergy Assessment. An Evaluation of Organic Material Resources for Bioenergy Production in Washington State, December 2005. http://www/ecy.wa.gov/pubs/0507047.pdf

Freel B.A.; Huffman D.R.; Applied Bio-oil Combustion. In: Biomass Pyrolysis Oil, Properties and Combustion Meeting. September 26-28, Estes Park, Colorado 1994, p. 309-315

Freel B.A., Graham R.G., Huffman D.R., The scale-up and development of Rapid Thermal Processing (RTP) to produce Liquid Fuels from Wood, Ontario Ministry of Energy Report (CF) Toronto, Canada, 1990.

Freel, BA; Graham RG., 2002. Bio-oil preservatives. U.S. Patent 6,485,841, filed Oct. 30, 1998 and issued Nov. 26, 2002.

Frigo S., Gentilli R, Tognotti L, Zanforlin S, Benelli G: Feasibility of Using Wood Flash-Bio-oil in Diesel Engines, SAE Technical Paper Series, 982529, 1998.

Garcia-Perez M, Chen S, Zhou S, Wang Z, Lian J, Johnson RL, Liaw S-S, Das O: New Bio-refinery Concept to Convert Softwood Bark to Transportation Fuels. Final Report to the Washington State Department of Ecology. Interagency Agreement No C0800247, 2009.

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

Girard P: biochar production and use in Africa. Unasylva 211, Vol. 53, 2002.

Granatstein D, Kruger C, Collins H, Garcia-Perez M, Yoder J: Use of Biochar from the Pyrolysis of Waste Organic Material as a Soil Amendment. Final Project of Interagency Agreement C0800248, July 2009, http://www.ecy.wa.gov/pub/0907062.pdf

Graham RG, Bergougnou MA, Overend RP: Fast Pyrolysis of Biomass. *Journal of Analytical and Applied Pyrolysis*, 6, (1984) 95-135.

Gronli, M. 2010. Pyrolysis and Charcoal. NTNU. Department of Energy and Process Engineering. http://www.bioforsk.no/ikbViewer/Content/71499/Biokarbonseminar%20%C5s%2011-03-2010%20Morten%20Gr%F8nli.pdf; date accessed, November 13, 2010.

Gronli, M. Industrial Production of Charcoal. SINTEF Energy Research, N-7465 Trondheim, Norway. http://terrapreta.bioenergylists.org/files/Gronli.pdf, accessed November 13, 2010.

Gross S., Pyrolysis liquid as Diesel fuel. Wartsila Diesel International. In: Seminar on Power Production from Biomass II, 27-28.2, 1995, Espoo, Finland

Gust S, Combustion Experiences of Flash Pyrolysis Fuel in Intermediate Size Boiler. In: Developments in Thermochemical Biomass Conversion, Bridgwater A.V., Boocock D.G.B., Eds: Blackie Academic & Professional: London, 1997, p. 481-488

Hackett Cm Durbin T, Welch W, Pence J, Williams R, Jerkins B.M., Salour D, Aldas R: Evaluation of Conversion Technology Processes and Products. Final Draft to the California Integrated Waste Management Board, 2004

Hartwing JR: Control of Emissions from Batch-Type biochar Kilns. Forest products Journal, 21 (9): 49-50, April 1971.

Helle S, Bennett NM, Lau K, Matsuio JH, and Duff SJB 2007 2007. A kinetic model for the production of glucose by hydrolysis of levoglucosan and cellobiosan from pyrolysis oils. Carbohydrate Research 342:2365-2370.

Holmgreen J, Biofuels: Unlocking the potential. Joint ACS/AICHE Meeting Chicago section, January 24, 2008 a.

Holmgreen J, Marinangeli R, Elliott D, Bain R: Conversting Pyrolysis Oils to Renewable Transportation Fuels: Challenges & Opportunities, 2008, NRRA Annual Meeting, March 9-11, 2008b, San Diego, California

Huber GW: Breaking the Chemical and Engineering Barriers to Lignocellulosic Bio-fuels: Next Generation Hydrocarbon Biorefineries. A research roadmapfor making lignocellulosic bio-fuels a practical reality. http://www/ecs.umass.edu/biofuels/Images/Roadmap2-08.pdf

Huber GW, Dumesic JA, 2006. An overview of aqueous phase catalytic process for production of hydrogen and alkanes in a biorefinery. Catalysis Today, 111: 119-132.

Huffman D., Vogiatzis A., Clark D., Combustion of Bio-oil. In: Bio-oil Production and Utilization; Bridgwater A.V., Hogan E, eds., CPI Press Newbury, UK, 1996, p. 227-235.

Huffman D.R., Freel B.A., RTP^{TM} Biocrude: A Combustion / Emission Review. In: Developments in Thermal Biomass Conversion. A.V. Bridgwater and D.G.B. Boocock, eds, Blackie Academic and Professional, London, 1997, p. 489-494

Ikura M, Slamak M, Sawatzky H, Pyrolysis Liquid in Diesel Oil Microemulsions. U.S. Patent 5.820.640, 1998

Jay DC, Sipila KH, Rantanen OA, Nylund NO, Wood Pyrolysis for Diesel Engines. ICE-Vol. 25-3 Fall Technical Conference, Vol. 3, ASME 1995, p. 51-59

Jones SB, Valkenburg C, Walton C, Elliott DC, Holladay JE, Stevens DJ, Kinchin C, Czernik S: Production of Gasoline and Diesel from Biomass via Fast pyrolysis, Hydrotreating and

Hydro-cracking. A Design Case. US Department of Energy, Prepared under Contract DE-AC05-76RL01830. PNNL-18284 Rev. 1, February 2009.

Kambewa P, Mataya B, Sichinga K, Johnson T: Charcoal: the reality. Study of charcoal consumption, trade and production in Malawi, Institute for Environment and Development, London, 2007.

Kammen DM, Lew DJ: Review of Technologies for the Production and Use of biochar. Energy and Resources Group & Goldman School of Public Policy. UC Berkley and NREL, 2005

Kasper J.M., Jasas G.B., Trauth R.L., Use of Pyrolysis Driven Fuel in a Gas Turbine, 1983, ASME Paper N^o 83-GT-96

Klark M, Rule A : The Technology of Wood Distillation. London Chapman & Hall LTd, 1925.

Krug, E. and S.E. Hollinger, Identification of Factors that Aid Carbon Sequestration in Illinois Agricultural Systems, Illinois State Water Survey, Atmospheric Environment Section Office of the Chief Champaign, Illinois, 2003.

Lee S.W., Preliminary Combustion Evaluation of Wood Derived Fast Pyrolysis Liquids Using a Residential Burner, Division Report ERL 93-29 (CF) CANMET, 1993, Energy Mines and Resources Canada, Ottawa.

Leech J., Running a Dual Fuel Engine on Pyrolysis oil. In: Biomass Gasification and Pyrolysis, State of the Art and Future Prospects. Kaltschmitt M, Bridgwater A.V., Eds.: CPL Press: Newbury, 1997, p. 495-497.

Lehmann J, Kern DC, Glaser B, Woods WI (2004) Amazonian Dark Earths: Origin, Properties, Management. Kluwer Academia Publ., New York, 510 p.

Levine, J. 2010. U.S.-Focused Biochar Report. Assessment of Biochar's Benefits for the United States of America. Center for Energy and Environmental Security and The United States Biochar Initiative. http://www.biochar-us.org/pdf%20files/biochar_report_lowres.pdf; date accessed November 15, 2010.

Liao W, Frear C, Chen S: Biomass Inventory Technology and Economics Assessment. Report 1. Characteristics of Biomass. June 27, 2007. Ecology Publication No. 07-07-025, http://www/ecy.wa.gov/pubs/0707025.pdf

Mahfud FH, Ghijen F, Heeres HJ, 2007b. Hydrogenation of fast pyrolysis oil and model compounds in a two-phase aqueous organic system using homogeneous ruthenium catalysts. Journal of Molecular Catalysis A; Chemical 264 (1-2) 227-236.

Maggi R, Elliott D, Upgrading Overview. In Developments in Thermochemical Biomass Conversion, Bridgwater A, Boocock D, Eds.: Blackie Academic and Professional: London, 1997, pp. 575-588.

Malkow T: Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. Waste Management 24 (2004) 53-79

March H, Rodriguez-Reinoso F : Activated Carbon. Elsevier 2006, UK

Marinangeli R, Marker T, Petri J, Kalnes T, McCall M, Mackowiak D, Jerosky B, Reagan B, Nemeth L, Krawczyk M, Czernik S, Elliott D, Shonnard D: Opportunities for bio-renewables in oil refineries: Final technical Report. Submitted to the US Department of Energy. UOP DOE award: DE-FG36-05G015085, 2005.

Mason LC, Gustafson R, Calhoun J, Lippke BR, Raffaeli N: Wood to energy in Washington, The College of Forest Resources. University of Washington. Report to the Washington State Legislature. June, 2009 http://www/ruraltech.org/pub/reports/2009/wood_to_energy/index.asp.

Maxwell WH: Stationary Source testing of a Missouri Type biochar Kiln. EPA-907/9-76-001. U.S. Envronmental Protection Agency, Kansas City, MO, august 1976.

McDonough W. The Hannover Principles. Design for Sustainability. Prepared for EXPO 2000, the World's Fair. Hannover Germany, http://www.mcdonough.com/principles.pdf

Meier D, Scholze B., Fast Pyrolysis Liquid Characteristics. In: Biomass Gasification and Pyrolysis. State of the Art and Future Prospects (Eds. Kaltschmitt MK and Bridgwater AV) CPL Press, Newbury, UK, 1997, p. 516-527.

Meier D, Faix O: State of the art of applied fast pyrolysis of lignicellulosic materials—a review. Bioresour Technol 1999;68:71–7.

Mitsui Recycling. Pyrolysis Gasification & Melting Process http://www.ieabcc.nl/meetings/Tokyo_Joint_Meeting/ 02_Mitsui.pdf; date accessed: Nov., 15, 2010.

Mohan D, Pittman CU, Steele PH: Pyrolysis of Wood/Biomass: A critical review. *Energy &Fuels* (2006), 20 (3), 848-889.

Monsanto Research Corporation. Emission Test Report, Kingsford biochar, Burnside Kentucky, Report prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1980.

Moses C., Fuel-Specification Considerations for Biomass Liquids, Proceedings. *Biomass Pyrolysis Oil. Properties and Combustion Meeting*. September 26-28, 1994. Estes Park Colorado.

Morf P, Hasler P, Nussbaumer T. Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis wood chips. Fuel 2002;81: 843–53.

Mottocks T.W., Solid and Gas Phase phenomena in the Pyrolytic Gasification of Wood. M.Sc. Thesis, Dept. Mech. Aerospace Eng. Princenton Univ., New Jersey, 1981.

Moscowitz CM, Source Assessment: biochar Manufacturing State of the Art, EPA-600/2-78-004z. U.S. Environmental Protection Agency, Cincinnati OH, December 1978.

Nicolaides G.M., The Chemical Characterization of Pyrolytic Oils, M.A.Sc. Thesis, University of Waterloo, 1984.

Oasmaa A, Lappamaki E, Koponen P, Levender J, Tapola E., Physical Characterization of Biomass-based Pyrolysis Liquids. Applications of Standard Fuel Oil Analyses. Espoo Technical Research Center of Finland, VTT Publications, 306, 1997, 46 p

Oasmaa A; Czernik S: Fuel Oil Quality of Biomass Pyrolysis Oils- State of the Art for the End Users. Energy & Fuels, 1999, 13 (4) pp. 914-921.

Oehr KH, Scott DS, Czernik S, 1993. Method of producing calcium salts from biomass. U.S. Patent 5,264,623, filled Jan. 4, 1993, issued Nov. 23, 1993

Paddon AR, Harker AP: biochar production using a transportable metal kiln. Rural Technology Guide 12, 1980, Published by: Tropical Development and Research Institute (TDRI) 1980.

Pelaez-Samaniego M.R., Garcia-Perez M, Cortez LB, Rosillo-Calle F, Mesa J: Improvements of Brazilian carbonization industry as part of the creation of a global biomass economy. Renewable and Sustainable Energy Reviews 12 (2008) 1063-1086.

Pira-Internaional. 2010. Carbon Black Production Forecast to Reach Over 13 Million Tonnes by 2015. http://www.pira-international.com/carbon-black-production-forecast-to-reach-over-13-million-tonnes-by-2015.aspx; date accessed, Nov. 15, 2010.

Piskorz J, Radlein D., Scott D.S. and Czernik S., Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *Journal of Analytical and Applied Pyrolysis* 16 (1989), pp. 127–136.

Piskorz J., Scott D.S., Waterloo Fast Pyrolysis Process. Pyrolysis of Carex (Finland) Peat, Results of Pilot Plant Pyrolysis Test Performed for the Technical Research Center of Finland, Laboratory of Fuel Processing, 1988a, 18 p.

Piskorz J, Radlein D, Scott D.S., Czernik S., Liquid Products from the Fast Pyrolysis of Wood and Cellulose. In Bridgwater A.V. & Kuester J.L. (eds.). Research in Thermochemical Biomass Conversion, Phoenix, Arizona, New York: Elsevier Appl. Sci. 1988b, 557-571

Pro-Natura International. Green biochar Innovation Towards Sustainable development. 2004.

PHMSA, Hazardous Material Regulations. Title 49 – Transportation (n.d.) Available at: www.ecfr.gpoaccess.gov, accessed August 12, 2010

Radlein D, Grinshpun A., Piskorz J., Scott D.S., On the presence of Anhydro-oligosaccharides in the Syrups from the Fast Pyrolysis of Cellulose. Journal of Analytical and Applied Pyrolysis, vol. 12, 1987, p. 39-49

Radlein D, 1999. The production of chemicals from fast pyrolysis bio-oils. Fast Pyrolysis of Biomass: A Handbook, ed. A.V. Bridgwater. Newbury, UK: CPL Press 164-188.

Rossi C., Frandi R., Bonfitto E., Jacobini S., Pistone L., Mattiello M., Combustion Test of Bio-oils from Biomass Slow Pyrolysis. In: Advances in Thermochemical Biomass Conversion. Bridgwater A.V. Ed. Blackie Academic & Professional. London, 1993, p. 1205-1213.

Roy C., Lemieux S., de Caumia B., Pakdel H., Vacuum Pyrolysis of Biomass in a Multiple Heat Furnace. Biotechnology and Bioenegy, Sym. No 15, 1985, p. 107

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. A.V. Bridgwater and D.G.B. Boocock, Eds., Blackie Academic and Professional, London, UK, 1997, p. 351-367.

Roy C., Lu X, and Pakdel H, 2000. Process for the production of phenolic rich pyrolysis oils for use in making phenol-formaldehyde resol resin. U.S. Patent 6,143,856, filed Feb. 5, 1999, issued Nov 7, 2000.

Rudloff M. Biomass to Liquid Fuels (BtL) Presentation made by Choren. Process, Environmental Impact and Latest Developments. Automobile & Environment at Beograd Congress, May 2005.

San Miguel G, Makibar J, Fernandez-Akarregi AR: Conversion of Wood into Liquid Fuels: A review of the Science and Technology Behind the Fast Pyrolysis of Biomass. Chapter 2. In Advanced in Energy Research. Volume 7, Ed. Morena J. Acosta, 2011 Nova Science Publishers, ISBN: 978-1-61122-956-1

Sipila K, Kuoppala E, Fagernas L, Oasmaa A: Characterization of Biomass based flash Pyrolysis Oils. Biomass and Bioenergy, Vol. 14, No 2, 1998, pp. 103-113

Solantausta Y., Nylind N.O., Westerholm M., Koljonen T., Oasmaa A., Wood Pyrolysis Oil as Fuel in a Diesel Power Plant. Bioresour. Technol. 46, 1993, p. 177-188

Solantausta Y, Nylund N.O., Gust S., Use of Pyrolysis Oil in a Test Diesel Engine to Study the Feasibility of a Diesel Power Plant Concept. Biomass and Bioenergy, 7, 1994, p. 297-306.

Solantausta Y., Gust S., Hogan E., Massoli P., Sipila K, Bio Fuel Oil-Upgrading by hot filtration and novel physical methods. 2000, Contract JOR3-CT98-0253 Publishable Final Report, (1998-2000) Research funded in part by the European Commission in the framework of the Non Nuclear Energy Programme Joule III.

Solar Energy Research Institute, 1988. Handbook of Biomass Downdraft Gasifier Engine Systems. US Department of Energy.

Scott DS, Piskorz J, 1984 The Continuous Flash Pyrolysis of Biomass. Can. J. Chem. Eng. 62 (3), 404-412.

Scott D.S, Piskorz J., Radlein D., The Effect of Wood Species on Composition of Products obtained by the Waterloo Fast Pyrolysis Process. In: Canadian Chemical Engineering Conference, Toronto, 1988, 10 p.

Scott DS, Paterson L, Piskorz J, Radlein D: Pretreatment of poplar wood for fast pyrolysis of cation removal. *Journal of Analytical and Applied Pyrolysis* 57 (2000) 169-176.

Shafizadeh F, Furneaux RH, Cochran TG, Scholl JP, Sakai Y: Production of levoglucosan and glucose from pyrolysis of cellulosic materials. *Journal of Applied Polymer Science*, 23 (1979) pp. 3525-3539.

Shah N, Girard P, Mezerette C, Vergnet M: Wood to biochar conversion in a partial combustion kiln: an experimental study to understand and upgrade the process. Fuel 1992, Vol 71 p. 955-962

Shihadeh A., Lewis P., Manurung R, Beer J., Combustion Characterization of Wood-derived flash Pyrolysis Oil in Industrial Scale Turbulent Diffusion Flames. In Proceedings of Biomass Pyrolysis Oil Properties and Combustion Meeting. Estes Park, September 26-28, co, NREL-CP-430-7215, 1994, p. 281-295.

Shreve RN, Chemical Process Industries, Third Edition, McGrw-Hill, NY, 1967

Suppes G.J., Natarajan V.P., Chen A., Autoignition of Selected Oxygenated Fuels in Simulated Diesel Engine Environment, Paper (74 e) presented at AIChE National Meeting, New Orleans, LA, February 1996

Toole AW, Lane PH, Arbogast C, Smith WR, Peter R, Locke E, Beglinger E, Erickson E.C.O.: biochar Production, Marketing and Use. Forest Products Laboratory, Madison Wisconsin. USDA-Forest Service, University of Wisconsin. Report 1961, July 1961.

Trossero M, Domac J, Siemons R: Industrial biochar Production. TCP/CRO/3101 (A) Development of a sustainable biochar industry. FAO, June 2008, Zagreb, Croatia

Underwood GL, 1990, Commercialization of fast pyrolysis products. In Biomass Thermal Processing, eds. E. Hogan, Robert J, Grassi G, and A.V. Bridgwater. Newbury, UK: CPL Press, 226-228.

Underwood GL, Graham RG, 1991. Methods of Producing Fast Pyrolysis liquids for making an high browing liquid smoke composition. U.S. Patent 5,039,537 filed June 6, 1991 and issued August 4, 1992.

US Energy Information Administration Independent Statistics and Analysis. Wasghinton State Energy Profile. http://www.eia.doe.gov/state/state_energy_profiles.cfm?sid=WA; date accessed November 15, 2010.

van de Kamp W.L., Smart J.P., Evaluation of the Combustion Characteristics of Pyrolysis Oils Derived from Biomass. Prepared for the 7th European Conference on Biomass for Industry and Energy, Greece, 1991

van de Kamp W.L., Smart J.P., Atomization and Combustion of Slow Pyrolysis Biomass Oil. In: Advances in Thermochemical Biomass Conversion. Bridgwater A.V. Ed. Blackie Academic & Professional, London, 1993, p. 1265-1274

van Loo S, Koppjan J, editors. Handbook biomass combustion and co-firing. Enschede, The Netherlands: Twente University Press; 2002.

van Rossum G, Kersten SRA, Van Swaaij WPM 2007. Catalytic and non-catalytic gasification of pyrolysis oil. Industrial and Engineering Chemistry Research 46 (12): 3959-3967.

Veitch FP: Chemical Methods for Utilizing Wood. Including destructive distillation, recovery of Turpentin, rosin and pulp, and the preparation of alcohols and oxalic acid. USDA, 1907

Venderbosch RH, Prins W: Fast Pyrolysis technology development. Biofuels, Bio-products and Biorefining. 4, 178-208 (2010), DOI: 10.1002/bbb

Woolf D, Amonette J.E., Street-Perrott A. F., Lehmann J, Joseph S: Sustainable biochar to mitigate global climate change. Nature Communications. 1-56, DOI: 10.1038/ncomms1053 /www.nature.com/naturecommunications.

Wormat M.J.; Porter B.G., Yang N.Y.C., Single Droplet of Biomass Pyrolysis Oils, Energy & Fuels 8, 1994, p. 1131-1142

Warnecke R: Gasification of biomass: comparision of fixed bed and fluidized bed gasifier. Biomass and Bioenergy 18 (2000) 489-497.

Wenzl HFJ: The Chemical Technology of Wood. Academic Press, 1923

Withrow J: The Chemical Engineering of the Hardwood Distillation Industry. Ind. Eng. Chem. Res. Vol. 7, No II, p. 912 (1915)

Woolf D, Amonette J, Street-Perrot A, Lehmann J, Joseph S: Sustainable biochar to mitigate global change. Nature Communications, August 2010

Yang J., Tanguy P.A., Roy C., Heat Transfer, Mass Transfer and Kinetic Study of the Vacuum Pyrolysis of a Large Used Tire Particle. Chemical Engineering Science, 50, 1995, p. 1909-1922

Yronwode P, From the Hills to the Grills. Missouri Resources Magazine, Spring 2000 . website: http://www.dnr.mo.gov/magazine/2000-spring.pdf