

Thermal Depolymerization of Biomass with Emphasis on Gasifier Design and Best Method for Catalytic Hot Gas Conditioning

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This paper reviews ways that biomass can be converted by thermal depolymerization to make synthetic gas, *i.e.* syngas. Biomass, being carbon neutral, is considered as a form of solar energy stored during the growing season by photosynthesis. An effective biomass is one with low moisture and ash content, high lignin content, high calorific value, and small particle size. Woody biomass with low ash content (<1%), nut shells with high lignin content (30 to 40%), and municipal solid waste with synthetic polymers are effective at creating value-added synthetic gases. An allothermal downdraft gasifier produces a low tar syngas (99.9% tar conversion) at 850 °C and provides a simple and low-cost process. Integrated gasification combined cycle (IGCC) improves thermodynamic efficiency. To avoid thermal loss, a hot gas filtration system uses trona sorption material for sulfur and halogen compounds. Secondary systems can use multiple cyclones followed by reactors employing calcined dolomite, olivine, and others for adsorption or reaction with residual sulfur, ammonia, metals, and halogens. Reforming of residual tar to syngas can take place within chambers with ceramic tubes doped with nano-nickel particles. Syngas can then be used in boilers, gas turbines for production of electricity or production of chemicals by Fischer-Tropsch conversion.

Keywords: Biomass; Depolymerization; Catalyst; Gasifier; Thermochemical; Syngas; Gasification; Pyrolysis; Tar; Reforming

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INTRODUCTION

Overview of the Article Topics

The main focus of this review article is the unit operations needed to obtain fuel value from the thermal decomposition of biomass, while avoiding operational problems and harm to the environment. As shown in the list of contents, there are five main sections: the introduction, an overview of biomass materials, discussion of thermochemical processes, considerations of different gasifier designs, and discussion of gas cleaning methods. Due to the wide-ranging scope of this article, readers are encouraged to use the index and topic headings to locate information of greatest interest and concern to them.

Biomass as an Energy Source

Biomass has been defined as a biological organic matter (plant or animal) that has stored energy (Bain 2004). Wood is considered the largest biomass source, which includes forest residues, wood chips, sawdust, yard clippings, and part of municipal solid waste (MSW). The Energy Policy Act (EPACT) (Sec. 206(a)(6)(B) of 2005 has defined biomass as "...any organic matter that is available on a renewable basis, including agricultural crops and trees, wood and wood wastes and residues, plants (including aquatic plants), grasses, residues, fibers, and animal wastes, municipal wastes, and other waste materials." It has been stated that biomass feedstock includes trees, agricultural crops, agricultural residues, animal wastes, and municipal solid waste (Lucia 2015); this feedstock could be used to produce ethanol, diesel, heat, electricity, plastics, solvents, chemical intermediates, pharmaceuticals, adhesives, fatty acids, acetic acid, carbon black, dyes, pigments, and detergents. Biomass, whether it comes from MSW, agriculture, or forest operations, is a viable and important source of energy. Its importance has been increasing due to the fact that it has great potential for biofuels and chemicals. The 2011 Billion Ton Study Update (Male 2015) showed that there was enough feedstock to potentially displace 30% of our current petroleum consumption in the US and reduce CO₂ emissions by 400 million tons. The advantages of biomass as an energy source include its abundance, renewability, carbon neutrality, suitability as a hydrocarbon source, contribution to energy security (as a domestic resource), contribution to rural jobs, and protection of air quality (low sulfur content, *etc.*).

Biomass is being looked at as the most important energy source for the future, and it has been increasing in importance. It has a diverse role including providing energy, food, fabrics, building materials, chemicals, and paper products. There is 5 to 8 times more energy stored through photosynthesis in biomass than we currently could consume from all possible sources (Prins 2005). Kumar *et al.* (2009) noted that photosynthesis by plants captures approximately 4,000 EJ/year in the form of energy in biomass and food. Biomass energy in the United States has gradually increased from 3.88 quads (quad is a unit of energy equal to 10¹⁵ Btu) in 2008 to 4.49 quads in 2013 (Park 2014). In the United States in 2010, biomass provided approximately 4% of the energy used, with 46% coming from wood biomass, 43% from mainly ethanol biofuels, and 11% from MSW (Biomass Renewable Energy 2017). The potential of MSW for energy often has been overlooked. Typical MSW components in landfill that could be converted to energy include paper, yard waste, scrap wood, furniture, pallets, processed lumber, packaging material, tree debris, and plastic. Plastic materials are recalcitrant and if left in landfills they will not degrade for several decades. In the United States, the EPA has collected numbers for generation and disposal of MSW for over 30 years. From 1960 up to 2011, MSW generation has

increased in volume from 88.1 million tons per year to 250.4 million tons per year (EPA 2012). In the United States during the 1960's, the contents of landfill sites were often burnt for volume reduction, and even today in some countries this is still going on because of limited regulations. In 2012, there were 68.62 million tons of paper and paperboard generated and only 64.6% recovered. In addition, there were 15.82 million tons of wood generated and only 15.2% recovered. Plastic, which is high in carbon, generated 31.8 million tons, of which only 8.8% were recovered (EPA 2012). By thermally converting MSW (which is an energy rich carbon sink) to energy, we would:

- Reduce contaminated soils and ground water
- Reduce amounts of atmospheric gases such as methane, CO₂, ammonia, hydrogen sulfite, CO, and non-methane organic compounds such as trichloroethylene
- Reduce HAP and VOC's such as benzene, toluene, and vinyl chloride
- Reduce land usages for handling MSW
- Reduce transportation costs for MSW that is hauled out of some states
- Reduce use of fossil fuels by converting energy from waste

Processes for Thermo-chemical Conversion: Overview

Processes for thermo-chemical conversion of biomass to process heat, biopower, or biofuel include combustion, gasification, pyrolysis, and torrefaction (Bridgwater 2003). For centuries, humans have used biomass combustion for heat, and now it is being used to create biopower through steam and expansion over a turbine. Combustion can be defined as a rapid oxidation of biomass, or municipal solid waste (MSW), occurring at extremely high temperatures and producing high concentrations of gas with minor amounts of char and vapor/liquid. Incineration plants, sometimes called "waste-to-energy" plants, consists of the following components: waste handling and storage bunker, one or more combustion units with bottom ash handling systems, boiler with turbine generator, pollution control system (nitrogen oxide, mercury, dioxin, acid gas, and particulate removal), pollution control test, and emissions stack. Typical combustion plants use fabric filters or electrostatic precipitators for particulate removal, wet scrubbers for removal of sulfur, acids and halogenated compounds, activated carbon for removal of dioxins, furans, and mercury, and nitrogen oxides are eliminated by catalytic reduction. The attractive features of combustion of biomass include the following: a well-developed and commercially obtainable technology, reductions in the volume of solid waste destined for landfills, recovery of energy from controlled combustion of waste, decreases in carbon emissions by reduction in energy from fossil fuel, and reductions in methane generation from landfills. Disadvantages include the high cost to build and operate such a plant, the need for skilled personnel for the operation, and inefficient operation of small-scale plants. Currently, China is building the world largest waste-to-energy plant in Shenzhen that will convert 5,000 tons/day of waste to energy. The plant is expected to be running by 2020.

Gasification methods have been in use for decades (McKendry 2002; Alonso *et al.* 2010). In the early 1800s, gasification of coal and peat was used for illumination and cooking. Due to the shortage of petroleum, wood-gas generators were used during World War II to create producer gas that powered motor vehicles. Gasification is an endothermic process that converts a carbon rich material, at high temperatures, under partial oxidation into large quantities of combustible gases and lower amounts of char, ash and liquid. The external oxidant can include air, oxygen, water, and carbon dioxide. Gasification of biomass goes through four conversion zones, which include drying, pyrolysis, combustion,

and reduction. The combustible gases and volatiles include hydrocarbon gases, hydrogen, tar, carbon monoxide, carbon dioxide, and water vapors. The by-products, which are not vaporized, include char and ash. Char can then be reacted with oxidants to release heat that is used for the endothermic reactions. The quantitative and qualitative productivity of gases formed during gasification are strongly governed by biomass type and size, moisture content, reaction temperature, gasifying agent, ash content, catalyst, pressure inside reactor, and gasifier design. Typical gasifier designs include fixed bed (downdraft, updraft, crossdraft), fluidized bed (bubbling, circulating), and entrained flow. Methods for gas cleaning include: particulate removal by multiple cyclones, barrier filters, or ESP, tar reforming using mineral and synthetic catalyst, and sulfur, nitrogen, and halogen removal can take place using calcined dolomite or nickel and iron based catalyst. Combustible gas can then be used for heat or electricity, or processed into biofuels. Advantages of gasification plants versus waste-to-energy plants include lower capital cost, higher efficiency, small and modular size units, and the fact that syngas can be used for process heat, biofuel, or biopower. The disadvantage of gasification is that some systems such as updraft can produce high volumes of tar, while the downdraft and fluidized bed gasifiers produce large amounts of particulate matter (PM) which require extensive gas cleaning.

Pyrolysis is an endothermic reaction that takes place in an oxygen-depleted atmosphere converting biomass feedstock into gas, oil, and char (Mohan *et al.* 2006; Bridgwater 2012). Pyrolysis can be categorized as slow, intermediate, fast, and these different processes can determine the yield of gas, oil, and char. Fast pyrolysis, which has reaction times in seconds, produces large amounts of bio-oil, while slow and intermediate pyrolysis produce larger volumes of char. Pyrolysis advantages include a process that enhances energy density and thus reduces transportation and handling costs. There are a number of reactors that are used for pyrolysis including bubbling fluidized bed (BFB), circulating fluidized (CFB), auger reactor, rotating cone, and ablative reactor. Both BFB and CFB reactors have commercial potential for fast pyrolysis due to high oil yields and high heat transfer with fast separation of char and vapors. Typical systems for pyrolysis gas cleanup are similar to gasification due to the fact that the gases can be used in a steam generator for production of electricity *via* steam turbine. Gas cleanup can include cyclones, tar conversion catalyst, sorbents for S, N, halogen conversion, and fabric filters.

Torrefaction of biomass feedstock is a similar process to slow pyrolysis in that a lower temperature, in the absence of oxygen, removes water with depolymerization and devolatilization of hemicellulose with moderate decomposition of cellulose and lignins (van der Stelt *et al.* 2011). The final product is a hydrophobic, energy dense solid fuel with lower moisture content and reduced biological presence. Reactors used for torrefaction of biomass include rotating drum, auger screw, and fluidized bed. Gas produced during torrefaction can be sent to a combustor, which is used for torrefaction processes or biomass drying. Gas products are composed mainly of water, acetic acid, aldehydes, alcohols, ketones, and lipids such as terpenes, fatty acid, and waxes.

To improve thermal efficiency, both gasification and pyrolysis systems can use hot gas conditioning methods such as cyclones, guard bed using calcined alkaline earth metals, granular bed filters, and ceramic tubes or fibers doped with nano-nickel based catalyst.

Pyrolysis and gasification (the focus of this study) are thermochemical processes that involve thermal depolymerization of biomass. It is worth noting that during thermal treatment, hemicellulose, cellulose, and lignin react differently at different temperatures, which results in a range of products. The conditions of processing can be adjusted in order to target the production of value-added products. Pyrolysis depolymerizes organic material

in the absence of air or oxygen at temperatures in the range of 500 to 800 °C, while gasification is relatively higher at 800 to 1,000 °C. Typically, three products are produced: gas, bio-oil, and biochar. Gaseous products are sometimes referred to as syngas or producer gas. Sadaka (2017b) refers to syngas as a mixture of hydrogen and carbon monoxide, which is the product of high temperature reaction between biomass and steam or oxygen. Gandhi *et al.* (2012) define producer gas as a mixture of combustible gases such as carbon monoxide, hydrogen, and methane and non-combustible gases including nitrogen and carbon dioxide, which are the products of air gasification at low temperatures (1292-1832 °F).

Active Biomass Energy Projects

Lane (2015) in *Biofuels Digest* has listed the top pyrolysis projects for 2015. They include:

1. Ensyn Corporation. This corporation, with headquarters in Wilmington Delaware, has produced 37 million gallons of renewable fuel and chemicals over 160,000 hours of operation. Their core business converts non-food biomass from forest and agricultural to yield light liquids. The process they used is called Rapid Thermal Processing (RTP), which produces a renewable fuel oil (RFO) that is used in the heating sector and can also be used as a feedstock for bio-refineries. In 2012, Ensyn entered into a joint venture with Fibria cellulose of Brazil, which is one of the major leaders in pulp production, for production of liquid fuels and chemicals to be used in the United States and Brazil (ENSYN 2017). In May of 2014, Ensyn and Honeywell announced that their pyrolysis procedure was capable of producing fuel at a target price of \$45 per barrel. A five-year contract was signed in 2014 with Memorial Hospital in New Hampshire where they would supply 300,000 gallons per year of Ensyn's renewable fuel oil. This has allowed the hospital to replace their petroleum heating fuels, thereby reducing GHG by 85%. In addition, Ensyn has signed a seven-year renewable contract with Valley Regional Hospital in New Hampshire where they would supply 250,000 gallons of RFO and by this they would eliminate all of their heating oil requirements.
2. Battelle. Battelle has headquarters in Columbus Ohio and is a nonprofit research and development organization that has over 22,000 employees at more than 60 locations globally. Battelle has partnered with Marathon Petroleum and Pacific Northwest National Lab (PNNL) to produce around 60 gallons of finished hydrocarbon fuel from 1 ton of dry feedstock. They have also succeeded in developing a catalyst that can withstand 1,000 hours of bio-oil hydro-treatment that produced transportation fuel from biomass pyrolysis. Because of its small size, their pyrolysis system can be transported to production sites by a flatbed 18 wheel truck.
3. Empyro BV. Empyro, located in Henglo, The Netherlands, will produce electricity, steam, and oil from woody biomass and residue. Their technology is based on flash pyrolysis and the experience gain by BTG Technology through a 50 ton/day pyrolysis plant in Malaysia.

Table 1. North Carolina Biomass Facilities

Company	Plant Name	Location	Nameplate Capacity (MW)	CHP Capability	Co-fire Coal	Fuel Feedstock	Plant Status
Capital Power Corp.	CPI USA North Carolina LLC	Southport, NC	55	Yes	Yes	Wood residue, tire derived fuel	Operational
Capital Power Corp.	Roxboro Facility	Roxboro, NC	67.5	Yes	Yes	Wood, tire derived fuel	Operational
CMS Energy	Craven County Wood Energy	New Bern, NC	50	No	No	Mill residue	Operational
New Hanover County	New Hanover County WASTECC	Wilmington, NC	10.3	No	No	Municipal Solid Waste	Idled
ReVenture Park	ReVenture Park	Charlotte, NC	3.6	Yes	No	Landfill gas	Operational
Riverstone Holdings	Coastal Carolina Clean Power	Kenansville, NC	35	Yes	No	Woody Biomass	Operational

4. Anellotech. Anellotech, located in Pearl River New York, has partnered with IFP Energies Nouvelles and Axens to commercialize a process for low-cost production of benzene, toluene, and xylene (BTX) from bio-based feedstock including palm wastes, bagasse, corn stover, and woody biomass. This process is based on Catalytic Fast Pyrolysis (CFP) of non-food biomass.
5. Avello Bioenergy. Located in central Iowa, Avello has partnered with ConTech (EPC), Borrengaard (Product R&D), Cargill (Biofuel oil demo), Virent (R&D), Iowa State (biomass & product R&D), Iowa DOT and USDA as advisors to develop biomass fast pyrolysis, from which products will be in the range of \$50-\$65/bbl oil equivalent range. Using a rapid heating process (fast pyrolysis), Avello produces Bioasphalt, Chemical Feedstock, Biofuel Oil, and Biochar. The proposed feedstock includes forestry pine residue, mill residue, corn stover, switchgrass, and hybrid poplar.
6. Proton Power Incorporated (PPI). PPI, located in Lenoir City Tennessee, has developed a renewable system (CHyP-Cellulose to Hydrogen Power) that produces hydrogen from biomass and waste sources. PPI system includes

biomass prep, biomass mixer, cellulose to hydrogen power (96% CH₄P + 4% biochar), and gas cleanup (65% H₂, 30% CO₂, 5% CO). The advantages of PPI system include: high yield of H₂ (65%) in syngas, very low concentration of tars and particulates (cuts back on expensive syngas clean-up), and a process that can tolerate high moisture (45%) content (which eliminates drying) (Proton Power 2017).

In the 2016 United States Biomass Power Map, there were 227 U.S. Biomass Power Facilities. Table 1 lists the biomass facilities in North Carolina and their capacity, feedstock, and plant status. Of the total 227 facilities, 191 plants were operational, 17 sites were idled, 15 were proposed sites, and four sites were under construction. To qualify for this map, a plant must: 1) supply all or part of their power to the grid, 2) biomass in fuel mix must be greater than 40% by volume, and 3) the plant must have a nameplate capacity equal to or greater than 1 MW. Typical fuel feedstocks that are used in operational units includes corn stover, straw, switchgrass, woody biomass, forest residue, tire-derived fuel, municipal solid waste, logging and sawmill residue, sugarcane, orchard and vineyard prunings, nut shells, stone fruit pits, whole tree chips, rice hulls, bagasse, paper mill sludge, construction and demolition (C & D) material, hogged fuel (grounded up or powdered wood), peanut hulls, paper making residues, biogas, landfill gas, black liquor, softwood, and railroad ties. The four under construction had listed the following fuel feedstocks: sweet sorghum, eucalyptus, albizia, urban wood waste, forest residue, pecan shells, and peanut hulls. The top 10 biomass power producing states include Florida (1,089 MW), California (806 MW), Virginia (523.9 MW), Maine (464.2 MW), New York (450.3 MW), Minnesota (373.5 MW), Washington (288.4 MW), Michigan (282 MW), New Hampshire (266.7 MW), and Connecticut (262.8 MW) (U.S. 2016).

Failed Biomass Energy Projects

Charles Kettering, an American inventor, engineer, businessman, and holder of 186 patents, once said that “99% of success is built on failure”. Below is a list of companies that have had failures in converting biomass to value added products and reasons for failure. The intent here is to highlight the reasons for failures so that they won’t be repeated.

1. KiOR was founded in 2007 by Khosla Ventures and a group of scientists whose vision was to make renewable fuels from cellulose. The production facility, located in Columbus Mississippi, used a biomass fluid catalytic cracking procedure for turning wood chips into hydrocarbons. These hydrocarbons then would go into vehicles, refineries, or pipelines. Approximately one year after startup, KiOR filed for bankruptcy with losses amounting to \$629.3 million. Reasons for failure were: 1) a conveyer system for feeding wood chips frequently jammed, 2) blades for turning wood into chips were the wrong size, 3) tar build-up in part of the plant that was used for treating feedstock, 4) in the lawsuit it was mentioned that the problem was a design issue involving how the equipment was put together too hastily, and 5) the bio-oil conversion to gasoline was very poor, most being converted to CO₂ and H₂O (Mufson 2014). It was stated in one article that during the initial stage of catalytic fast pyrolysis, the most reactive components were being converted to coke, gas, and water with only a small yield of liquid product (PyroWiki 2017a). KiOR stated in its annual report that “The

- costs and time involved in operating our Columbus facility have been much higher than we initially anticipated” (Fehrenbacher 2014). KiOR has been very tight about their procedure, but some have suggested that the catalyst system had been destroyed and overwhelmed by the very alkaline ash in the biomass.
2. Oak Ridge National Laboratory (ORNL) in Tennessee constructed a \$60 million plant in 2012 that turned wood chips to gas. The gas was then used as fuel in a boiler. After about a year and a half of operation, the plant was shut down due to problems with thinning of vessels and transfer lines. These problems were caused by weak organic acids. The steam plant was designed by Nexterra, and financing and construction were given to Johnson Controls Inc. (JCI) (Munger 2014).
 3. The University of South Carolina in 2007 was going to take wood byproducts and create steam, which was to be used to supply 85% of the campus energy. There were a few incidents from a steam joint rupturing on December 8th, 2007, an expansion joint rupturing on February 9th, 2008, and on June 28th, 2009 a fuel auger rupturing, sending a metal panel 60 feet toward a control office. Reports stated that in a two-year time frame, the plant provided steam for 98 days. Some USC officials have stated that the plant has been a \$20 million disaster that was not properly planned and was built by a company that had never constructed a power plant before. The biomass boiler was built by Nexterra, and Johnson Controls Inc. was in charge of construction of the plant (Washington 2011).
 4. Arbre project, located near Eggborough in the United Kingdom, was built as an 8 MW IGCC plant with low pollution controls based on a circulating fluidized bed gasifier. Production began in 2001 with locally grown wood, and in 2002 the project went into liquidation. The original cost was estimated to be \$40 million. Failure was attributed to insufficient control and monitoring, technical problems, and gas cooling and cleaning was described as the major problem (Black & Veatch 2008; Ernsting 2015)
 5. Ebara Corporation commercialized the Bailie Process. The Bailie Process is a dual fluid bed process that permitted the use of air for conversion of biomass to gas. There were three plants in Japan that operated on RDF feedstocks. They included a 36 tpd pilot plant, a 91 tpd, and a 408 tpd commercial plant. All of these plants have been shut down (Klass 1998). No data were found on the reason for shutting down.
 6. Brightstar Environmental is a subsidiary of a company from Australia (Energy Developments Limited-EDL) that develops and operates power generation and waste resource recovery and energy projects. The commercial system was installed in Wollongong, Australia and was based on a two-step gasification unit with a primary pyrolysis reactor followed by secondary steam gasification. Even though their system was successful on a pre-commercial scale, it failed to perform on a full-scale commercial size plant, which resulted in dismantling and financial losses from investors and a loss in value of EDL stock of \$120 to 140 million. Problems with this system were: a) design issues with the material handling system, b) removal of hot char (400 to 500 °C) from the primary reactor caused problems due to ignition of char between the primary and secondary gasification

- reactor, c) a switch to a wet char quenching system, which resulted in more problems due to the wet system not being inert and some deposited with pyrolysis oils preventing carbon conversion and problems with the emission parameters, d) after a lengthy shut down of the secondary reactor, char and pyrolysis oil from primary reactor began to build up, creating a waste and operational problems, e) in 2001, emissions tests showed arsenic exceeded limits, SO₃ & NO_x levels were high, CO levels were very high, and they also found emissions of dioxin, HCl, HF, and polycyclic aromatic hydrocarbons (PAH). This article also states, "Brightstar's website admitted to emissions of dioxins, heavy metals, and other chemicals of concern". The facility was shut down in March of 2004 (Brightstar Environmental 2014; Incinerators 2006).
7. Thermoselect, a Switzerland-based company, provided the technology for gasification of MSW followed by combustion. The plant was located in Baden-Wurttemberg, Germany and was designed to process 225,000 tons of MSW per year. The plant was temporarily closed in 2000 due to release of toxic gases and operational problems including explosion, cracks in a concrete chamber (due to corrosion and heat), and a leaking basin that held cyanide wastewater. In 2002, the plant was having trouble with high levels of TOC (Total Organic Carbon) and nitrogen oxides and exceeded emission levels for particulates. This article also stated that 120,000 cubic meters of wastewater was disposed of in the Rhine River in 2003. Despite the claims that their technology completely destroys dioxins, furans and other harmful substances found in waste, it was shown that the company's emissions included dioxins/furans, SO₂, CO, HCl, HF, Hg, cadmium, thallium, and other heavy metals. The plant was closed in November 2004, resulting in a loss of approximately \$500 M (Incinerators 2006).
 8. Scotgen, waste to energy company, installed a plant at Dargavel in Dumfries, Scotland that was to gasify over 20,000 tons of MSW and hazardous waste per year for production of electricity. The plant began operating in 2009 and was shut down in April of 2011. During that period, they had over 200 breaches on emission limits. Other problems included fires, explosions, pipe burst, steam explosion, and a very low energy recovery. One of the main pollutants was dioxin. The World Health Organization (WHO) listed dioxin as a carcinogen that can cause reproductive and developmental problems and can damage the immune system (The Herald 2003; Waukesha County 2017).
 9. Caithness Heat and Power was started in 2004, in Wick Scotland, as a combined heat and power plant. It was to provide heat to approximately 500 homes in the area and sell power back to the grid. The biomass gasifier was to create gas that had to be cleaned before going to gas engines to create power. After several years of technical and financial problems, the plant was closed with a net lost to tax payers of \$11.5 million (Express 2014; McCall 2014; Ernsting 2015).
 10. Biomass Engineering built a 1 MW plant in 2006 on a poultry farm near Calthwaite, UK. The gasifier was to produce gas that proceeded to a gas cleaning area and then to the internal combustion engine. The system did not work and was soon shut down (Ernsting 2015). It is suspected that the gas cleaning system

failed because of high ash content from chicken litter (Table 3 Ash content for chicken litter was 19.3%). Elemental analysis of the ash showed high levels for phosphorus, calcium, potassium, silicon, magnesium, and sodium (Bain 2004; Bock 2004).

In summary, failures of systems for biomass gasification to energy have resulted from poorly designed conveyor systems, walls of vessels and transfer lines thinning, steam and expansion joints ruptured, fuel auger ruptured, technical problems, insufficient control and monitoring, major problems with gas cooling and cleaning, material handling system, ignition of hot char removal, emission limits exceeded (in particular dioxins), operational problems including explosions, cracks in concrete chambers due to heat and corrosion, leaks in basins that held waste water, release of toxic gases, fires, pipe burst, energy recovery low, bio-oil conversion to gasoline very poor, and tar build up being major problems.

On the other hand, successful biomass gasification systems have benefited from having excellent technical personnel with companies that have funds, such that they can upgrade and solve problems when they occur. For example, Avello partnered with ConTech, Borrengaard (Product R&D), Cargill (Biofuel), Virent (R&D), Iowa State (biomass and product R&D) and Iowa DOT and USDA.

In light of the mixed record of plant implementation and operation, the purpose of the present study is to:

- Find the best method for conversion of polycyclic aromatic hydrocarbons (PAH) to lower chain carbons.
- Learn from past successes and failures to help propose a gasification/pyrolysis system that will convert biomass to chemicals, fuels, or energy.
- Find the best method for high temperature gas conditioning of particulate matter, haloacids, sulfur compounds, nitrogen derivatives including ammonia, carbon dioxide, heavy metals, dioxins, and furans.
- Find the most efficient gasifier for biomass conversion to fuels, chemicals or energy.

BIOMASS MATERIALS AND FUEL PROPERTIES

As will be shown in subsequent sections, the gasification of biomass can be highly sensitive to its chemical composition, particle size, density, moisture, and a variety of other detailed attributes. This section gives an overview of such attributes in the case of biomass types that have been most often considered for gasification.

Lignocellulose

Lignocellulosic biomass refers to plant materials (mainly softwood and hardwood) whose structures are composed mostly of three polymeric compounds. These include cellulose, hemicellulose, and lignin, with smaller amounts of extractives and inorganics. Lignocellulosic biomass is not an ideal fuel due to its generally low density and heating value, high moisture and ash content, and fibrous nature with low grindability. However, during photosynthesis, biomass stores energy from sunlight. When biomass is combusted during gasification or pyrolysis, this energy can be released in the form of stored chemical

energy, or the atoms can rearrange to form syngas or higher molecular compounds such as polycyclic aromatic hydrocarbons (PAH). When considering ways to solve our environmental pollution problems, we need to turn to lignocellulosic biomass, the most abundant material for production of bio-fuels (Lucia 2008).

The chemistry and properties of the main components of lignocellulose have been well described in other sources, so their description here will emphasize issues pertaining to pyrolysis. Briefly stated, cellulose is a polymer of glucose monomers (McKendry 2002) having a typical molecular mass of 100,000 g/mole. Hemicellulose, like cellulose, is a polysaccharide but has a branched polymer structure consisting of C5 and C6 carbon sugars. It is a co-polymer of two or more sugars and sugar acids with monomers that can include glucose, mannose, galactose, arabinose and 4-O-methylglucuronic acid, and it has a low DP of 120-200 (Park 2014). Like cellulose, it is a carbohydrate and thus has the formula $C_n(H_2O)_n$. Lignin is a large biopolymer molecule composed of phenylpropanol units; its structure is complex, highly variable, and amorphous, with a branched three-dimensional dendritic network (Campbell and Sederoff 1996; Novaes *et al.* 2010; Park 2014). Lignin's energy content is 40% of the total energy content of ligno-cellulosic biomass (Leisola *et al.* 2012). Percentages of the main components can vary considerably from one biomass to another. Table 2 list cellulose percentages from woody biomass to herbaceous and agriculture biomass to other biomasses. For example, on the low side, leaves and grasses can have very small amounts ranging from 15 to 25% cellulose, while paper and cotton seed hairs can have on the high side 95 to 99% cellulose (Table 2, Dakar 2017; Goyal 2017).

Table 2. Percent Cellulose, Hemicellulose, & Lignin of Various Biomass Materials (Dry Basis)

Biomass Material	% Cellulose	% Hemicellulose	% Lignin	Reference
Hardwood	40-50	25-35	20-25	Goyal
Softwood	40-50	25-30	25-35	Goyal
Grasses	25-40	35-50	10-30	Dakar
Leaves	15-20	80-85	0	Dakar
Paper	85-99	0	0-15	Dakar
Newspaper	40-55	25-40	18-30	Dakar
Switchgrass	45	31.4	12	Dakar
Cotton seed hairs	80-95	5-20	0	Dakar
Nut Shells	25-30	25-30	30-40	Dakar

Extractives from lignocellulosic biomass are low molecular weight compounds such as terpenes, tall oil, fatty acids, esters, triglycerides, waxes, resins, tannins, polyhydric alcohols, alkaloids, starches, pectins, and phenolics. The extractives function to protect trees from insects and fungi and can have a rather high heating value of 35 ± 2 MJ/kg (The Bioenergy System Planners Handbook 2017).

Ash

Inorganic mineral, also called ash, in biomass is the residue left after ignition or incineration and is often combined with oxygen. It consists of minerals comprising silicon (SiO_2), aluminum (Al_2O_3), calcium (CaO), magnesium (MgO), phosphorus (P_2O_5), sulfur (SO_3), iron (Fe_2O_3), potassium (K_2O), and sodium (Na_2O). As noted in Table 3, the ash content can be quite high, as in agricultural and herbaceous biomass. Herbaceous biomasses contain an order of magnitude more ash than wood biomass (Henrich *et al.* 2008;

Sikarwar *et al.* 2016). For example, the ash content is very high in rice hulls (18.34%), sorghum stalks (12.50%), wheat straw (11.40%), sugarcane bagasse (9.79%), and corn stover (6.26%) (Table 3). However, the ash content for wood and woody biomass is lower as noted for black locust (0.97%), poplar (1.16%), ponderosa pine (0.30%), white fir (0.20%), and Douglas fir (0.01) (Table 3).

Table 3. Ultimate Analysis of Various Biomass Materials

Ultimate Analysis (% dry weight)									
Biomass	HHV (dry) MJ/kg	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Chlorine	Ash	Reference
Alfalfa straw	18.45	46.76	5.40	40.72	1.00	0.02	0.03	6.07	Park 2014
Almond shells	19.38	44.98	5.97	42.27	1.16	0.02	-	5.60	Park 2014
Bituminous coal	17.0-23.3	73.20	4.70	9.10	1.00	1.00	-	11.00	Park 2014; Engineering Tool Box 2017
Black liquor (pine)	-	39.00	4.00	33.40	0.10	4.50	-	19.00	Park 2014
Black locust	19.71	50.73	5.71	41.93	0.57	0.01	0.08	0.97	Park 2014
Chicken litter	14.68	32.00	5.48	34.45	6.64	0.96	1.14	19.33	Bain 2004
Corn cobs	18.77	46.58	5.87	45.46	0.47	0.01	0.21	1.40	Park 2014
Corn stover	17.65	43.65	5.56	43.31	0.61	0.01	0.60	6.26	Park 2014
Corn grain	17.20	44.00	6.11	47.24	1.24	0.14	-	1.27	Park 2014
Cotton Stalk	18.26	43.64	5.81	43.87	0	0	-	6.68	Gaur & Reed 1998
Cotton Stalk	15.83	39.47	5.07	39.14	1.20	0.02	-	17.30	Jenkins <i>et al.</i> 1985
Douglas fir	20.37	50.64	6.18	43.00	0.06	0.02	-	0.01	Park 2014
Cottonwood	19.50	-	-	-	-	-	-	1.1	Stevens 2001
Hemlock (western)	19.89	50.40	5.80	41.40	0.10	0.10	-	2.20	Park 2014
Manure cattle, fresh	17.36	45.40	5.40	31.00	1.00	0.30	-	15.90	Park 2014
MSW	19.87	47.60	6.00	32.90	1.20	0.30	-	12.00	Park 2014
Oak bark	19.47	49.70	5.40	39.30	0.20	0.10	-	5.30	Park 2014
Orchard prunings	19.05	49.20	6.00	43.20	0.25	0.04	-	1.38	Park 2014
Ponderosa pine	20.02	49.25	5.99	44.36	0.06	0.03	0.01	0.30	Park 2014
Poplar	19.50	47.05	5.71	41.01	0.22	0.05	<0.01	1.16	Bain 2004
Redwood (combined)	20.72	50.64	5.98	42.88	0.05	0.03	0.02	0.40	Park 2014
RDF	17.40	42.50	5.84	27.57	0.77	0.48	0.57	22.17	Park 2014
Rice hulls	16.14	40.96	4.30	35.86	0.40	0.02	0.12	18.34	Park 2014
Sorghum stalks	15.40	40.00	5.20	40.70	1.40	0.20	-	12.50	Park 2014
Sugarcane bagasse	17.33	44.80	5.35	39.55	0.38	0.01	0.12	9.79	Park 2014
Swine feces	15.12	45.00	6.90	31.20	4.00	0.40	0.30	12.20	Koger <i>et al.</i> 2002
Switchgrass	18.64	47.45	5.75	42.37	0.74	0.08	0.03	3.50	Park 2014
Walnut shells	20.18	49.98	5.71	43.35	0.21	0.01	0.03	0.71	Park 2014
Wheat straw	17.51	43.20	5.00	39.40	0.61	0.11	0.28	11.40	Park 2014
White fir	19.95	49.00	5.98	44.75	0.05	0.01	0.01	0.20	Park 2014
Yard waste	16.30	41.54	4.79	31.91	0.85	0.24	0.30	20.37	Park 2014

Table 4. Percent Elemental Ash Composition of Different Biomass Materials

Sample	SiO ₂	CaO	K ₂ O	P ₂ O ₅	Al ₂ O ₃	MgO	Fe ₂ O ₃	SO ₃	Na ₂ O	TiO ₂	Reference
Poplar bark	1.86	77.31	8.93	2.48	0.62	2.36	0.74	0.74	4.84	0.12	Kang <i>et al.</i> 2014
Willow	6.1	46.09	23.40	13.01	1.96	4.03	0.74	3.00	1.61	0.06	Kang <i>et al.</i> 2014
Hybrid poplar	5.90	49.92	9.64	1.34	0.84	18.40	1.40	2.04	0.13	0.30	Jenkins <i>et al.</i> 1998
Wood residue	53.15	11.66	4.85	1.37	12.64	3.06	6.24	1.99	4.47	0.57	Kang <i>et al.</i> 2014
Wood pellets (Pine)	4.30	55.90	16.80	3.90	1.30	8.50	1.50	-	0.60	-	Roy 2017
Bamboo whole	9.92	4.46	53.38	20.33	0.67	6.57	0.67	3.68	0.31	0.01	Kang <i>et al.</i> 2014
Miscanthus	56.42	10.77	19.75	5.54	0.79	3.01	0.94	2.28	0.47	0.03	Kang <i>et al.</i> 2014
Sorghum grass	73.21	7.02	8.97	4.43	1.83	2.21	0.95	1.11	0.25	0.02	Kang <i>et al.</i> 2014
Switchgrass	66.25	10.21	9.64	3.92	2.22	4.71	1.36	0.83	0.58	0.28	Kang <i>et al.</i> 2014
Bana grass	38.59	4.09	49.08	3.14	0.92	1.96	0.73	-	0.44	-	Roy 2017
Corn stover	51.99	8.99	26.38	2.79	0.28	6.09	1.12	2.20	0.08	0.01	Gresham 2012
Cotton gin trash	41.80	10.80	10.50	2.60	3.10	3.30	0.70	5.90	0.60	-	Capareda 2014
Wheat straw	50.35	8.21	24.89	3.54	1.54	2.74	0.88	4.24	3.52	0.09	Kang <i>et al.</i> 2014
Rice husks	94.48	0.97	2.29	0.54	0.21	0.19	0.22	0.92	0.16	0.02	Kang <i>et al.</i> 2014
Sugarcane bagasse	46.79	4.91	6.95	3.87	14.60	4.56	11.12	3.57	1.61	2.02	Kang <i>et al.</i> 2014
Sunflower husks	23.66	15.31	28.53	7.13	8.75	7.33	4.27	4.07	0.80	0.15	Kang <i>et al.</i> 2014
Chicken litter	5.77	56.85	12.19	15.40	1.01	4.11	0.45	3.59	0.60	0.03	Kang <i>et al.</i> 2014
Mixed waste paper	28.62	7.63	0.16	0.20	53.53	2.40	0.82	1.73	0.54	4.37	Kang <i>et al.</i> 2014
RDF	38.67	26.81	0.23	0.77	14.54	6.45	6.26	3.01	1.36	1.90	Kang <i>et al.</i> 2014
Sewage sludge	33.28	13.04	1.60	15.88	12.91	2.49	15.70	2.05	2.25	0.80	Kang <i>et al.</i> 2014
Wood yard waste	60.10	23.92	2.98	1.98	3.08	2.17	1.98	2.46	1.01	0.32	Kang <i>et al.</i> 2014

Ash content plays a vital role in combustion, gasification, and pyrolysis. Klinghoffer (2013) found that char from gasified poplar wood was acting as a catalyst in depolymerization of tar compounds. He discovered that the char had active minerals on the surface, and when these metals were removed by acid washing, the catalytic activity fell by 19%. Catalytic activity was also attributed to the high surface area of char, which was stated as being higher than most commercial catalysts.

Alkaline earth oxides including calcined dolomite CaMg(CO₃)₂ have proven to be very effective at thermally depolymerizing polycyclic aromatic hydrocarbons (PAH) (Alden *et al.* 1988; Orio *et al.* 1997a,b; Dayton 2002; El-Rub *et al.* 2004; Balas *et al.* 2008;

Yung *et al.* 2009; Zwart 2009; Nemanova *et al.* 2010; Ay *et al.* 2012; Milhe *et al.* 2013; Mohammed *et al.* 2013; Akudo and Theegala 2014). On the negative side, ash under high temperature, *i.e.* combustion and gasification, can cause corrosion, sintering, slagging, deposition, and agglomeration (sticking of metals to solid surface). Group I metals such as potassium can react with silica and sulfates, forming potassium silicate (K_2SiO_3) and potassium sulfate (K_2SO_4). Wang *et al.* (2008) stated that both compounds are capable of depositing on reactor walls, leading to sintering and defluidization problems. The alkali salts can react with silica to form a low melt eutectic mixture, which can lead to agglomeration. Klein and Themelis (2003) reported that the main elements causing alkali slagging were potassium, sodium, chlorine, and silica. Sahni *et al.* (2015) observed no slagging for biomass having ash content below 5 to 6%, while severe slagging can be expected for biomass with 12% and above. From Tables 3 and 4, one can see that problems could develop if the feedstock was 100% rice hulls, sorghum stalks, or wheat straw. These problems are due to high levels of ash and the ash containing high percentages of SiO_2 . Also, syngas needs to be free of alkali metals before being sent to gas turbines due to corrosion and deposition problems.

Thermal Degradation

During thermal destruction, cellulose, hemicellulose, and lignin are the main polymers that undergo depolymerization. Carbohydrates (hemicellulose and cellulose) are the least stable and begin to depolymerize first. Hemicelluloses, which contains heteropolysaccharides, are the first to thermally degrade (Rivilli *et al.* 2011), and it has been stated that hemicellulose content decreases from approximately 85% to 60% at 330 °C (Park *et al.* 2013). Lv *et al.* (2010) noted that hemicellulose thermally degrades within a temperature range of 180 to 340 °C. Compared to cellulose, hemicellulose undergoes rapid decomposition and produces less tar, less char, and more gas, methanol, and acetic acid (Sadaka 2017a; Mohan *et al.* 2006). Rivilli *et al.* (2011) reported that cellulose, hemicellulose and lignin react independently during pyrolysis of different biomass, giving a unique pattern of products.

Park *et al.* (2013) stated that thermal degradation of cellulose takes place at higher temperatures (300 to 400 °C) compared to hemicellulose. Mohan *et al.* (2006) noted that cellulose degradation occurs at 240 to 350 °C. This thermal destruction of cellulose produces anhydrocellulose and levoglucosan (Mohan *et al.* 2006; Jin *et al.* 2013).

Lignin begins to thermally depolymerize at a similar temperature as hemicellulose due to its heterogeneous structure. However, lignin is also more difficult to dehydrate and produces greater amounts of residual char than cellulose or hemicellulose (Mohan *et al.* 2006; Jin *et al.* 2013). Other products produced during lignin pyrolysis include:

1. Liquid part includes menthol, acetic acid, acetone, and water
2. Gaseous part include methane, ethane, and carbon monoxide

A high percentage of oxygen content is indicative of biomass material (Table 3), and this high oxygen content leads to dilution of calorific values. It is imperative that during gasification and pyrolysis, decreases in oxygen content take place; this occurs during torrefaction. This reduction in oxygen content is accompanied by the loss of volatile compounds including CO and CO_2 and by dehydration reactions (Park *et al.* 2013).



Fig. 1. Corn being harvested with corn stovers left behind (Source: Lori Potter, Hub Staff Writer, Kearney Hub Newspaper; figure used with permission of the copyright holder)

Worldwide there are approximately 140 billion metric tons of waste biomass produced every year including residual stalks, straw, leaves, roots, husk, nut, seed shell, waste wood, and animal waste. This waste biomass is equivalent to approximately 50 billion tons of oil (Converting Waste Agricultural Biomass 2009).

With the increased demand for ethanol and food exports, there will be a continual increase in the generation of corn stover (Fig. 1). Corn stover by definition includes the leaf, husk, and cob that remain after collecting the grain. As noted in Table 3, corn stover has a heating value of 17.65 MJ/kg (dry) with carbon and hydrogen of 43.65% and 5.56%, respectively. The negatives include high contents of the following: 1) oxygen 43.31%, 2) nitrogen 0.61%, 3) chlorine 0.60%, and 4) ash 6.26%.

Syngas fermentation is being researched heavily. In this process, biomass (corn stover and others) is being thermally converted to carbon monoxide and hydrogen. Several metabolic systems including *Clostridium ljungdahlii* are being used for the synthesis of products such as ethanol and butanol (van Kasteren *et al.* 2011; Daniell *et al.* 2012; Devarapalli and Atiyeh 2015). Whitham *et al.* (2016) published an extensive review on *Clostridium ljungdahlii* for the development of industrial biocatalyst and found that this ethanologenic acetogen could grow while producing energy-rich ethanol. They concluded that acetogen would be an excellent choice for industrial application because of its unique physiology, known metabolic pathways, and considerable genetic background work. Syngas fermentation takes place by microbial metabolism, producing bio-fuel. Daystar *et al.* (2013) used a NREL thermochemical model and SimaPro for GHG analysis and life cycle assessments on corn stover, loblolly pine, eucalyptus, miscanthus, and switchgrass. They found that corn stover had the lowest alcohol yield and highest GHG emissions per liter of ethanol, and this was attributed to its high ash content. Daniell *et al.* (2012) has stated that while there are many challenges with the scale-up of syngas fermentation, this process has many advantages over regular fermentation and thermochemical depolymerization. These advantages include feedstock flexibility and production cost.



Fig. 2. Wheat Straw (Source: Landscape Unlimited; figure used with permission of the copyright holder)

Rathmann and Illerup (1995) found from pyrolysis experiments on pulverized wheat straw (Fig. 2) that when the heating rate of 30 °C/min (150 to 1000 °C) were used, the char yield increased by 15%, 20%, and 22% as pressure increased from 1.5, 20, and 40 bars, respectively. Because of the high ash content (11.40% Table 3), problems could develop in gasification and pyrolysis including sintering, deposition, high temperature corrosion, and slagging. Shao *et al.* (2012) noted that straw presented high fouling problems because of the highly active alkali and alkaline metals. These metals could form sticky layers on heat exchangers or heat transfer surfaces by forming vapor phase chloride compounds. Table 3 lists the ultimate analysis for chlorine at 0.28%, and Table 4 list the elemental ash content for potassium at 24.9%. This according to Shao *et al.* (2012) is the most problematic elements during biomass combustion.



Fig. 3. Cotton Residue (Source: "Photo credit Ollivier Girard-CIFOR, Retrieved picture from Feedipedia; figure used with permission of the copyright holder)

Cotton residue (Fig. 3) is the waste that is left in the field after cotton has been harvested, which includes stalks, leaves, seeds, cotton lint, and bolls. Umesh *et al.* (2015), using a bomb calorimeter, found that cotton stalk has a value of 16.01 MJ/kg, which as he stated is "good characteristics for gasification because higher heat generated during combustion leads to high temperature in reaction zone". These results were in accordance with Jenkins and Ebeling (1985), who reported 15.83 MJ/kg for cotton stalks. Although cotton stalk has good values for gasification, there are other herbaceous residues such as alfalfa straw and corn stover that has higher calorific values (Engineering Tool Box 2017) Table 3).

Capareda and Parnell's research work (2007) showed that bio-oil produced from cotton gin trash (CGT) by thermal conversion is 40% less by weight and 20% by volume than No. 6 fuel oil. The bio-oil density (1.3 g/mL) was much higher than No. 6 Fuel Oil (0.98 g/mL) due to polycyclic hydrocarbons and other heavier fractions. They mention that the bio-oil could be hydrogenated to produce numerous fuel feedstocks and with the use of different catalyst, this feedstock could produce dimethyl ether (DME) and aviation fuel (JP-8). Capareda and Parnell (2007) concluded by saying that "electrical power and heat energy production from cotton gin trash *via* gasification is already a proven technology".



Fig. 4. Switchgrass (Dennis Pennington, Bioenergy, Michigan State University; figure used with permission of the copyright holder)

Co-gasification of coal and biomass is a way of lowering problems from both sectors, which includes harmful emissions from coal and low calorific value from biomass. For example, by blending biomass with coal, one would reduce harmful emissions from coal such as heavy metals and sulfur, which is a contributor to acid rain. Some of the elements found in coal and coal waste include: arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), antimony (Sb), copper (Cu), sulfur (S), molybdenum (Mo), tin (Sn), magnesium (Mg), manganese (Mn), beryllium (Be), aluminum (Al), barium (Ba), cobalt (Co), iron (Fe), strontium (Sr), nickel (Ni), silver (Ag), selenium (Se), vanadium (V), zinc (Zn), potassium (K), and sodium (Na) (Schweinfurth 2009; Nalbandian 2012).

Biomass has low energy density due to high oxygen and moisture content. This disadvantage will be offset by the high energy density of coal. Masnadi *et al.* (2015) noted

in their experiment with coal and switchgrass (bubbling fluidized bed at 800 to 860 °C) that there was a considerable decrease in tar. They attributed this decomposition of tar to alkali and alkaline earth metals (AAEM) in switchgrass. They concluded that switchgrass (Fig. 4) ash can act as an inexpensive catalyst for gasification, which means that one can lower the gasification temperature without an increase in tar percentages. Tchabda and Pisupati (2014) also found that AAEM dispersed in biomass fuels will induce catalytic activity during co-conversion with coal.



Fig. 5. Wood Crops (Business Alabama; Nancy Mann Jackson); figure used with permission of the copyright holder



Fig. 6. Urban Wood Waste (eNewsLink, King County); figure used with permission of the copyright holder



Fig. 7. Forest Thinning (Photo by Juris Repsa, Lake States Forest Management); figure used with permission of the copyright holder



Fig. 8. Harvest Forest Residue (Source: Gestion Cyclofor Inc.); figure used with permission of the copyright holder



Fig. 9. Damaged Trees (Source: Pixabay); figure used with permission of the copyright holder

Thermal energy from trees can come from wood crops, forest thinning, harvest residue, damaged trees, or urban wood waste (Figs. 5 to 9). Urban wood waste (Fig. 6) includes pallets, used lumber, trees, branches, debris from construction and demolition, and stumps. The United States Department of Agriculture (USDA) reported that a large volume of wood waste is still being landfilled, and in 1998 they reported that over 160 million tons of wood waste was generated (Successful Approaches to Recycling Urban Wood Waste 2002). Steve Kelley (Ph.D. Department of Forest Biomaterials at North Carolina State University) was quoted in (Wood) Waste to Energy that 40 percent of milled logs end up as either sawdust, trimmings, or other odds and ends, and this represents a tremendous energy source (Woolston 2013). These products could be used in gasifiers or co-fired with coal to reduce CO₂, SO_x, NO_x, and reduction in emissions of heavy metals, conservation of landfill space, and conservation of natural resources. The USDA reported that wood composition makes up approximately 17% of material going into landfills in the United States. In the report on "Successful Approaches to Recycling Urban Wood Waste" (2002), the ultimate analysis on waste wood showed:

- % Carbon 41.20
- % Hydrogen..... 5.03
- % Oxygen..... 34.55
- % Nitrogen..... 0.24
- % Chlorine..... 0.09
- % Sulfur..... 0.07
- % Moisture..... 16.00
- % Ash..... 2.82

Heating Values

While it is difficult to establish a set Btu value for all waste wood, Conway (2010) in "Calculating the Heating Value of Wood Waste for Fueling Heat Treating Operations" has recorded some values, and these are noted in Table 5.

Table 5. Estimates of Heating Value of Different Wood Groups (Conway 2010)

Wood Group	Heating Value Btu/lb (Dry)	Heating Value MJ/kg (Dry)
Eastern Oaks	9510	22.12
High Density Eastern Hardwoods	9360	21.77
Bigleaf Maple/Oregon Ash	8400	19.54
Medium Density Eastern Hardwoods	8400	19.54
Western Hardwoods	8110	18.86
Red Alder	8000	18.61
Yellow Poplar	9360	21.77
Low Density Eastern Hardwoods	8800	20.47
Southern Yellow Pine	10,380	24.14
Douglas Fir	9200	21.40
Hem-Fir	8500	19.77
Spruce Pine Fir (SPF)	9100	21.17

1 MJ/kg = 429.923 Btu/lb

When considering the thermal decomposition of biomass by gasification or pyrolysis, one has to examine the moisture content of the biomass. Freshly cut trees have a much higher percentage of moisture than seasoned wood. Seasoned or air-dried firewood typically has about 20 to 25% moisture, while freshly cut wood can have up to 75% moisture. The heating value of biomass or wood is directly proportional to its dry weight. It has been stated in numerous articles that one pound of dry wood (zero moisture and hardwood species) has a heating value of approximately 8,600 Btu/lb ($36,000 \text{ kJ}\cdot\text{kg}^{-1}\text{K}^{-1}$). Additionally, it takes approximately 1,200 Btu to vaporize one pound of water (Schalau 2015; Stelzer 2015; Stark 2017). With the amount of energy it takes to reduce moisture content, it becomes apparent that moisture reduction is very important before gasification or pyrolysis.

Waste Materials

Companies are being awarded funds for biomass gasification systems for converting wood waste to energy. For example, Birmingham Bio-Power was awarded a \$47.8 million dollar contract to build and maintain a new 10.3 MW waste wood gasification plant in Tyseley, Birmingham UK. Wood waste will be supplied under a long-term sustainable contract with local suppliers and will include approximately 67,000 tons per year. Nexterra will supply the gasification system, which includes four gasifiers, high-pressure boiler, and a flue-gas treatment system. The gasification system will work by combustion of waste wood to create steam. Steam is then used to drive a turbine, which generates electricity. The system, over a 20-year lifespan, is expected to reduce GHG by an estimated 2.1 million tons and prevent 1.3 million tons of waste wood from going to landfills. After completion, the project will add 19 full time jobs (Birmingham Bio-Power 2013).



Fig. 10. Municipal Solid Waste (Source: RecycleReminders); figure used with permission of the copyright holder

Municipal solid waste includes paper, cardboard, plastic, leather, yard waste, wood, tires, rubber waste, cans, metals, glass, used oil, food waste, mattresses, electronics, batteries, concrete, medical waste, and dirt that comes from homes, schools, hospitals, and businesses. Paper, cardboard, plastic, leather, yard wastes, wood, tires, rubber waste can be sorted, shredded, ground and used in combustion, pyrolysis, or gasification systems to create energy or syngas. Tires (Table 7) have a high heating value of 29.20 MJ/kg; however, the sulfur to chlorine ratio is 1.36, and this will burden the gas cleanup system.

The synthetic leather market is growing rapidly in the U.S., and the calorific value of approximately 20 MJ/kg makes it an excellent substrate for gasification. Table 7 lists the oxygen and nitrogen content of leather at (27.8%) and (9.9%). These values are high and will dilute the calorific value. In the synthetic leather molecule, O₂ and N₂ numbers originate from the reaction between polyol (oxygen content) and isocyanates (nitrogen content). These are the intermediates used in synthetic leather production.

Kaplan *et al.* (2009) mentioned that MSW used to generate electricity through waste-to-energy and landfill-gas-to energy (LFGTE) accounts for close to 14% of U.S. non-hydro renewable electricity generation.

Table 6 lists the heating values of several plastics, and it points to an energy-dense substrate. Several plastics, including PE, PS, PP, ABS, HDPE, and LDPE, have a greater caloric value than anthracite coal (32.5 to 34.0 MJ/kg), which has the highest carbon and caloric content of all types of coal (Engineering Tool Box 2017).

According to the 2014 ERC directory, there are 84 facilities in the United States that produce waste to energy (WTE) (Michaels 2014). While other power plants have used coal, oil, or natural gas to produce electricity, WTE plants use trash as fuel and this trash is burned in a combustion chamber. The combustion chamber heats tubes of water that are located in the boiler walls. This process turns water to steam, which is used to drive a turbine generator that produces electricity. Michaels (2014) states that of the 84 WTE facilities, 64 of these facilities use mass burn technology, in which MSW is not pre-processed before combustion, and 13 facilities use a pre-processed method (RDF) in which the waste can be separated, shredded, dried, and then mixed and ground. The remaining facilities are either under construction, idle, or in different stages of development. The 84 plants produce various forms of energy, which include: 62 plants only sell electricity to the grid, 18 are combined heat and power (CHP), and four plants produce only steam. When the steam value is expressed in megawatts, the 84 plants will have a generating capacity of 2,769 megawatts. Figure 11 gives a picture of the design of a WTE plant and how they control emissions such as NO_x, Hg, dioxin, acid gas, and particulates (Waste to Energy Plant 2017). The emissions are tightly controlled through a continuous emission monitors, and they comply with federal and state emissions requirements.

In Europe, where land is at a premium, there is no movement against WTE because the alternative is shipping MSW or creating more landfills. In addition, WTE creates jobs and reduces the use of fossil fuels. The European countries that have the highest WTE programs, such as Denmark, Germany, Sweden, Austria, and the Netherlands, also recycle their waste at a rate of 27 to 54%. Denmark, with a population of 5.5 million, has 27 WTE facilities, and the European Union has approximately 429 plants in operation (Tenenbaum 2011). In addition, many of the European WTE facilities are co-generation and are located in cities where the steam can be used to heat buildings. This process is a more energy efficient way of extracting greater power from combustion. Both Europe and the United States are seeing a big drop in air pollution from WTE. Joseph DeCarolis (Assistant professor of water resources and environmental engineering at North Carolina State

University) stated, "According to EPA [Environmental Protection Agency] data on waste-to-energy facilities in the U.S., depending on the pollutant, the levels are significantly below their standards". In addition, he states that most levels are less than half the EPA limit (Tenenbaum 2011).

Table 6. Ultimate Analysis of Various Plastics

Ultimate Analysis (% dry weight)									
Plastics	HHV (dry) MJ/kg	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Chlorine	Ash	Reference
Polyethylene	40.50	86.00	14.00	0	0	0	0	-	Becidan 2007
Polystyrene	44.50	92.00	8.00	0	0	0.04 S/Cl	0.04 S/Cl	-	Becidan 2007
Polypropylene	43.40	86.00	14.00	0	0	0	0	-	Becidan 2007
PMMA	25.80	60.00	8.00	32.00	0	0	0	-	Becidan 2007
PA	26.49	55.38	8.65	26.03	9.95	-	-	0	Othman <i>et al.</i> 2008
PVC	19.20	38.00	5.00	0	0	0	57		Becidan 2007
PC	26.71	69.56	5.33	24.86	0.08	-	-	0.17	Othman <i>et al.</i> 2008
PET bottles	32.01	68.50	8.00	21.90	0.16	0.08	0.08	1.30	Bailie <i>et al.</i> 1999
ABS	35.16	76.82	7.45	8.59	6.13	-	-	1.01	Othman <i>et al.</i> 2008
PBT	15.72	43.28	3.56	22.38	0.04	-	-	-	Othman <i>et al.</i> 2008
HDPE	46.40	86.10	13.00	0.90	-	-	-	-	Becidan 2007
LDPE	46.60	85.70	14.20	0.05	0.05	0	0		Becidan 2007
POM	14.47	40.86	6.90	51.50	0.07	-	-	0.67	Othman <i>et al.</i> 2008
PUF	27.00	63.20	6.70	13.50	6.60	0.1/9.6 S/Cl	0.1/9.6 S/Cl	-	Becidan 2007
PS	39.48	86.30	7.90	3.40	0.28	0.30	0.12	1.80	Bailie <i>et al.</i> 1999
PA6/PE	39.5	79.70	13.30	4.20	2.60	<0.01	<0.01	-	Becidan 2007
Nilamid	-	63.1	9.80	15.00	12.10	-	-	-	Becidan 2007

The dilemma is to find a collection system in which one can combine all the discarded waste and proceed to gasification or combustion, where the waste is not treated (mass burn technology) or it is pre-processed (RDF). Currently, a large amount of attention is being focused on reducing the amount of alkali and heavy metals, chlorine, sulfur; this would reduce or prevent the formation of polychlorinated dibenzodioxins/furans (PCDD/F) (Tursunov 2014). Because of economics, these facilities will have to be located close to the point of waste. While most companies such as Unifi cannot handle non-recycle

plastics; however, systems like combustion, gasification, and pyrolysis units can depolymerize this material into usable products.

When MSW (paper, plastic or any of the other numerous waste materials) is recycled by converting to yarns, gases, bio-oils, or chemical intermediated, the greenhouse gases are reduced, and this reduces dependence on foreign oils, reduces the landfill requirements, and provides greater energy security.

Table 7. Ultimate Analysis of Various Materials

Ultimate Analysis (% dry weight)									
Materials	HHV (dry) MJ/kg	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Chlorine	Ash	Reference
Newspaper	17.99	43.80	5.90	44.40	0.29	0.24	0.14	5.20	Bailie <i>et al.</i> 1999
Cardboard	16.90	48.60	6.20	44.96	0.11	0.13 S/Cl	0.13 S/Cl	-	Becidan 2007
Magazines	13.55	35.00	5.00	39.40	0.05	0.08	0.07	20.40	Bailie <i>et al.</i> 1999
Tobacco residue	14.98	42.39	6.49	48.48	2.23	0.41	0	13.26	Akalin <i>et al.</i> 2011
Grass clippings	17.92	43.30	5.90	37.60	2.60	0.30	0.60	9.70	Bailie <i>et al.</i> 1999
Leaves	18.68	50.00	5.70	36.00	0.82	0.10	0.10	7.30	Bailie <i>et al.</i> 1999
Tire	29.20	71.90	4.70	7.00	1.36	1.36 S/Cl	1.36 S/Cl	-	Becidan 2007
Leather	~20	53.01	7.74	27.75	9.94	1.56 S/Cl	1.56 S/Cl	-	Becidan 2007; Jones 2010
Food waste	20.92	45.40	6.90	32.30	3.30	0.32	0.74	11.00	Bailie <i>et al.</i> 1999
Asphalt	17.1-18.4	83-87	9.9-11	0.2-0.8	0.3-1.1	1.0-5.4	-	-	Othman <i>et al.</i> 2008
Tar Sands Athabasca Bitumen	41.64	83.60	10.30	0.20	0.40	5.50	-	-	Bain 2004

THERMO-CHEMICAL PROCESSES

Combustion

Thermo-chemical conversion processes can be classified as combustion, gasification, pyrolysis, and torrefaction. Combustion (Fig. 11) takes place at extremely high temperatures (~1100 °C for 1 to 2 seconds) with excess air as the normal oxidant for complete conversion, and products include vapor/liquid (0 to 2%), char/liquid (0 to 5%), and gas (90 to 95%) (Park 2014). Air's composition on a dry basis by volume is 78% nitrogen, 21% oxygen, 0.93% argon, and trace amounts of monatomic gases such as neon,

helium, krypton, and xenon (Weast and Astle 1980-1981). Although biomass contains a high percentage of oxygenates, which lowers its energy content, bio-oxygen can be used in the conversion to fuel. Kirubakaran *et al.* (2009) stated that "every biomass has sufficient quantity of oxygen (bio-oxygen) to convert the solid combustible matter in it to gaseous fuel".

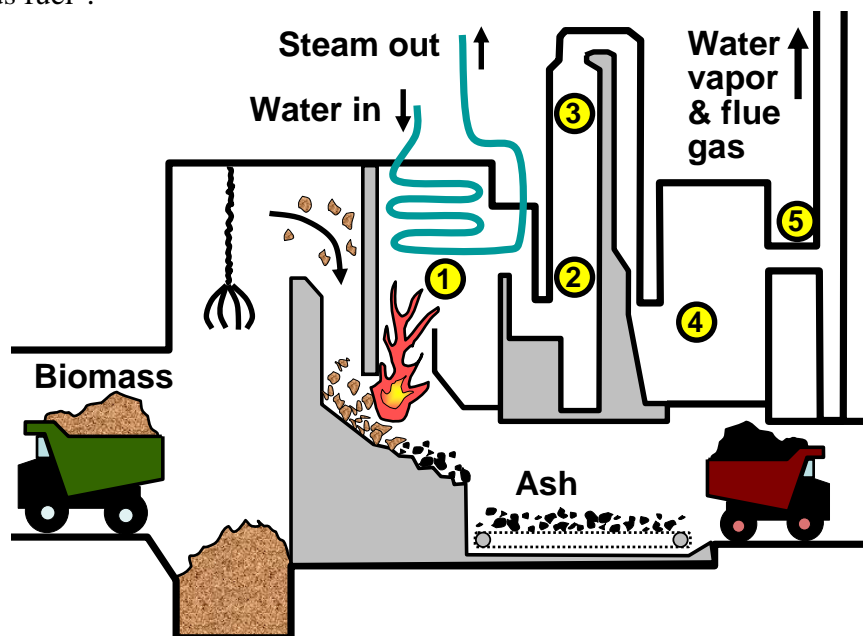


Fig. 11. Waste-to-Energy Process. 1: Location of nitrogen oxide removal system; 2: Mercury & dioxin removal; 3: Acid gas removal; 4: Particulate removal; 5: Pollution control testing (Redrawn based on: Ecomaine (2017), Kevin Roche CEO); figure used with permission of the copyright holder)

The theoretical oxygen demand (ThOD) for complete combustion is the minimum amount of oxygen required to burn the fuels (C, H, S), so they are converted to CO₂, H₂O, and SO₂. For air at 79% nitrogen and 21% oxygen, the theoretical air demand in moles is equal to: ThOD/0.21 (Park 2014). In a typical biomass combustion system that is used to produce power via steam turbine, the electric generation efficiency will vary from 20% for older systems to over 30% for newer systems.

Dell'Antonia (2017) lists biomass combustion conversion in three steps:

1. Drying of fuel and vaporizing of water
2. Pyrolysis/Gasification in the presence or absence of externally supplied oxygen (air)
3. Oxidation of the charcoal and flue gases

Hasan *et al.* (2011) quoted Bridgwater as listing combustion efficiencies (ratio of useful Btu's recovered to Btu's of heat input) as being low in small capacity plants. With this complete conversion, there are no value-added gases and the final product is heat, which can be converted to electricity by steam-driven turbines.

Combustion products include:

1. $C + O_2 \rightarrow CO_2$ (411 kJ/kmol)
2. $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ (121 kJ/kmol)
3. $S + O_2 \rightarrow SO_2$ (9.2 kJ/kmol)

Imperfect mixing of fuel and combustion air will lead to carbon monoxide and hydrocarbons. Nussbaumer (2003) stated that incomplete combustion can lead to high emissions of unburned pollutants such as soot, CO, and polycyclic aromatic hydrocarbons.

Sulfur emissions can take the form of sulfur dioxide (SO₂). Sulfur dioxide can then be oxidized to sulfur trioxide (SO₃), and the water in flue gas can react with SO₃ to form sulfuric acid (H₂SO₄), which is harmful to boilers and the environment. Sulfur can be captured by adding limestone into the furnace to form calcium sulfate as shown below.



Nitrogen can react with combustion air to form NO and NO₂ and with hydrocarbon radicals to form HCN and NH, which may then react to form NO_x. To eliminate NO_x, ammonia or urea solutions can be injected to produce nitrogen and water as shown below.



During combustion, MSW has inert materials that cannot be destroyed during the process. Inert materials are typically classified as bottom ash and fly ash. Bottom ash is the material that falls from the grate together with the sifting. Fly ash is the fine material that becomes airborne in the primary chamber and settles either in the ducts or becomes the particulate matter that is removed from the exhaust gases by the pollution control devices. Table 8 lists test results from elemental analysis from combined bottom and fly ash. As shown in the table, Niessen (2002) reported that the dominant elements are silicon, iron, calcium, and aluminum. These results are similar to the metal concentrations of common soil except for the high Fe content, as noted in Table 9. Also, Table 9 shows an enormous increase in concentration in fly ash for heavy metals, including mercury, cadmium, and chromium compared to bottom ash. Cadmium especially has a large increase from bottom to fly ash of 0-170 mg/kg to 2-78,000 mg/kg respectively. These metals are very toxic at low concentrations, and monitoring procedures have to be established. From Table 10, the range of metal concentrations is large and depends on the source of ash, with baghouse filters showing the highest concentrations for heavy metals. Table 11 list the melting points of inorganic elements and oxides that appear during gasification, incineration, and pyrolysis of biomass, MSW, and co-gasification with biomass and coal. At a typical gasification temperature of 850 °C, metals such as aluminum, zinc, cadmium, calcium, tin, mercury, lead, barium, and strontium will be in a vaporized form and can be filtered during cooling and gas clean-up.

Table 8. Range of Elements/Compounds from Combined MSW Bottom and Fly Ash (Styron and Gustin 1992; Niessen 2002)

Element/Compound	Weight Percent	Element/Compound	Weight Percent
SiO ₂	40-50	Na ₂ O	3-6
Al ₂ O ₃	5-15	SO ₃	0.5-1.5
TiO ₂	0.75-1.50	P ₂ O ₅	0.5-0.75
Fe ₂ O ₃	12-25	CuO	0.06-0.15
CaO	8-15	PbO	0.04-0.15
MgO	1-2	ZnO	0.12-0.22
K ₂ O	0.75-1.5	LOI*	1-3

*Loss on ignition at 750 °C

Table 9. Range of Metal Concentrations in Common Soil, Refuse Combustibles, Bottom Ash, and Fly Ash (mg/kg) (Goldin *et al.* 1992; Niessen 2002)

Metal	Common Soil	Refuse Combustible	Bottom Ash	Fly Ash
Al	10,000-300,000	3,000-25,000	18,000-177,000	31,000-177,000
As	1-50	0-15	2-2,000	3-750
Ca	7,000-500,000	2,300-50,000	4,100-96,000	33,000-86,000
Cd	0-1	0-90	0-170	2-78,000
Cr	1-1,000	2-200	10-2,000	20-3,000
Cu	2-200	20-3,400	40-18,000	200-5,000
Fe	7,000-550,000	500-45,000	400-480,000	3,100-320,000
Hg	0-0	0-2	0-4	1-100
Ni	5-500	1-90	7-600	10-29,000
Pb	2-200	30-1,600	30-44,000	200-140,000
Zn	10-300	40-8,000	90-128,000	2,000-280,000

Table 10. Range of Total Metal Concentrations at Various Locations (mg/kg) (Korn and Huitric 1992; Niessen 2002)

Ash Type	Cadmium	Copper	Lead	Zinc
Bottom Ash Grate	<1.0-48.2	420-12,600	300-2,750	903-2,420
Bottom Ash Siftings	<0.68-67.6	122-21,200	738-103,000	412-46,100
Fly Ash Boiler Tube	130-389	534-988	4,280-16,100	11,100-24,300
Spray Dryer	38.0-59.4	312-880	1,060-1,710	2,830-9,630
Baghouse	40-578	142-4,399	1,100-10,340	280-92,356
Combined	7.7-120	445-17,355	561-5,100	733-53,800

Table 11. Physical Constants of Inorganic Elements and Oxides (Handbook of Inorganic Compounds CRC Press)

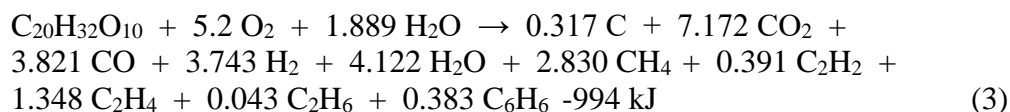
Name	Formula	Mol. Wt.	m.p. °C	Density g/cm ³
Aluminum	Al	27.0	660.3	2.7
Aluminum oxide	Al ₂ O ₃	102.0	2053	4.0
Calcium	Ca	40.1	842	1.5
Calcium oxide	CaO	56.1	2898	3.3
Cadmium	Cd	112.4	321.1	8.7
Chromium	Cr	52.0	1907	7.2
Copper	Cu	63.5	1084.6	9.0
Iron	Fe	55.8	1538	7.9
Iron oxide	Fe ₃ O ₄	231.5	1597	5.2
Mercury	Hg	200.6	-38.8	13.5
Nickel	Ni	58.7	1455	8.9
Lead	Pb	207.2	327.5	11.3
Zinc	Zn	65.4	419.5	7.1
Magnesium oxide	MgO	40.3	2825	3.6
Potassium oxide	K ₂ O	94.2	350	2.4
Silicon Dioxide	SiO ₂	60.1	1722	2.3
Titanium (IV) oxide	TiO ₂	79.9	1843	4.2
Sodium oxide	Na ₂ O	62.0	1132	2.3
Sulfur	S	32.1	115.2	2.1

Table 11, continued

Name	Formula	Mol. Wt.	m.p. °C	Density g/cm ³
Sulfur trioxide	SO ₃	80.1	16.8	1.9
Arsenic	As	74.9	817	5.8
Phosphorus oxide	P ₂ O ₅	142.0	562	2.3
Antimony	Sb	121.8	630.6	6.7
Tin	Sn	118.7	231.9	7.3
Molybdenum	Mo	96.0	2622	10.2
Beryllium	Be	9.0	1287	1.9
Barium	Ba	137.3	727	3.6
Selenium	Se	79.0	220.5	4.8
Cobalt	Co	58.9	1495	8.9
Strontium	Sr	87.6	777	2.6
Vanadium	V	50.9	1910	6.0
Silver	Ag	107.9	961.8	10.5

Gasification

Gasification is a complex thermal and chemical process for conversion of organic material under partial oxidation to syngas (hydrogen and carbon monoxide) at temperatures of approximately 870 °C for 1 to 2 seconds with a limited amount of oxygen, air, or steam. Sadaka (2017c) stated that gasification technology has been extensively used for production of commercial fuels and chemicals. As stated, the products of biomass gasification include vapor/liquid (0 to 2%), char/solid (0 to 10%), and gas (85 to 90%) (Park 2014). Gasification, when compared to combustion, produces gas that is lower in volume and heat. This provides a chance to clean and condition the gas prior to use. An example of the chemical reaction during this process was demonstrated by Angelova *et al.* (2014) and is listed below:



Gasification of biomass is an intricate process consisting of reactions that are homogeneous and heterogeneous. Homogeneous reactions are those in which the reactants and products are in the same phase as in numbers 2, 4, and 5 (when 5 is a gas as in methane, ethane) in oxidation reactions below. Heterogeneous reactions are those in which there are both solid and gas phases in reactants and products as in numbers 1 and 3 below.

Below are the main reactions that occur during gasification (Angelova *et al.* 2014; Shakorfo 2016b).

OXIDATION REACTIONS

	ΔH
1. C + ½ O ₂ → CO	-111 MJ/kmol
Carbon partial oxidation	
2. CO + ½ O ₂ → CO ₂	-283 MJ/kmol
Carbon monoxide oxidation	
3. C + O ₂ → CO ₂	-394 MJ/kmol
Carbon oxidation	

4. $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ -242 MJ/kmol
Hydrogen oxidation
5. $\text{C}_n\text{H}_m + n/2 \text{O}_2 \leftrightarrow n\text{CO} + m/2 \text{H}_2$ Exothermic C_nH_m
partial oxidation

GASIFICATION REACTIONS INVOLVING STEAM

 ΔH

6. $\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$ +131 MJ/kmol Water-gas reaction
7. $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ -41 MJ/kmol Water-gas shift
reaction
8. $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$ +206 MJ/kmol Steam methane
reforming
9. $\text{C}_n\text{H}_m + n \text{H}_2\text{O} \leftrightarrow n\text{CO} + (n + m/2) \text{H}_2$ Endothermic Steam reforming

GASIFICATION REACTIONS INVOLVING HYDROGEN

 ΔH

10. $\text{C} + 2\text{H}_2 \leftrightarrow \text{CH}_4$ -75 MJ/kmol Hydrogasification
11. $\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$ -227 MJ/kmol Methanation

GASIFICATION REACTIONS INVOLVING CARBON DIOXIDE

 ΔH

12. $\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$ +172 MJ/kmol Boudouard reaction
13. $\text{C}_n\text{H}_m + \text{CO}_2 \leftrightarrow 2 n\text{CO} + (m/2)\text{H}_2$ Endothermic Dry reforming

DECOMPOSITION REACTIONS OF TARS AND HYDROCARBONS

14. $p\text{C}_x\text{H}_y \rightarrow q\text{C}_n\text{H}_m + r\text{H}_2$ Endothermic Dehydrogenation
15. $\text{C}_n\text{H}_m \rightarrow n\text{C} + m/2\text{H}_2$ Endothermic Carbonization

Biomass, as it is being gasified, goes through four conversion zones. They are:

1. Drying Zone (>150 °C)
2. Pyrolysis or devolatilization Zone (150 to 700 °C)
3. Combustion (Oxidation) Zone (700 to 1500 °C)
4. Reduction Zone (800 to 1100 °C)

In the drying zone, energy is received through heat transfer from the other zones. Water in the biomass is removed by vaporization to moisture levels below 20%. Thermal efficiency of the gasification system is lost when moisture content is more than 40% by weight (Asadullah 2013, 2014; Shakorfo 2016a). Asadullah reported that this loss of thermal efficiency for high moisture content was due to heat being absorbed by unreacted steam and this occurring in three steps:

1. Heating of moisture from room temperature to 100 °C
2. Latent heat of vaporization
3. Heating of steam to gasification temperature is totally lost from the system

Shakorfo (2016a) noted that a certain amount of moisture can be converted to steam, which in turn can act as a gasification agent and react with PAH and char, producing syngas and hydrogen through the water gas shift reaction.

The rate of drying depends on the density of biomass, temperature, moisture content, velocity, external surface of biomass, internal rate of diffusion of moisture, and

how tightly bound water is to the biomass. Bhavanam and Sastry (2011) noted that the water (vaporized as steam) can be mixed with the gas flow, and if the temperature is high enough the water gas reaction can take place. They also noted that the biomass moisture will have a large effect on the operation of the gasifier and also on the quality of syngas. In the pyrolysis zone, heat is used to decompose the dried biomass into solids, liquids, and gases. The three phases are: charcoal (fixed carbon) for the solid part, tar for the liquid part, and syngas for the gaseous part, and a 70% weight loss is shown after devolatilization (Bhavanam and Sastry 2011; Yadav *et al.* 2013). The combustion (oxidation) zone is where the volatile gases and some of the char are oxidized at high temperatures to form carbon dioxide and small amounts of carbon monoxide and this heat is used to provide energy for the other zones.

Yadav *et al.* (2013) noted that during combustion carbonized biomass and hydrogen that is present will react with oxygen, forming CO₂ and H₂O with release of large amounts of heat. Oxygen from biomass (bio-oxygen) will be used in the combustion zone, thus reducing the amount of oxidant needed. In the reduction zone, with no free available oxygen, activated charcoal is used to reduce CO₂ and H₂O to products that are mostly H₂ and CO (Reactions 6 and 12 above). Reaction 12 is endothermic and will not take place until the temperature is above 900 °C (Biomass, The Sustainable Energy Handbook 2017). In gasification systems such as Fluidized Bed, the biomass is mixed with gasification medium (steam, air, oxygen) and hot solid material (sand) and the four zones are indistinguishable due to mixing (Obernberger and Thek 2008).

Depending on the type of biomass, the gas after gasification can vary in calorific value from 7.5 to 17.5 MJ/m³ (Angelova *et al.* 2014), and this gas, after conditioning, can be used to produce electricity, heat, or chemicals. Because of its high nitrogen content, air (oxidant) will dilute the Btu value of waste gasification gas and nitrogen will constitute about 50% of the final gas volume. Angelova *et al.* (2014) reported a value of 6 to 9 MJ/m³ for gasification of MSW with air as an oxidant and 10 to 20 MJ/m³ when the oxidant was steam and oxygen. Sikarwar *et al.* (2016) reported that the ratio of steam to biomass (S/B) will affect the input energy requirements, outlet gas quality, and product quality. They noted that low S/B ratios will result in high amounts of char and CH₄, whereas high S/B ratios will result in higher H₂ yields and higher calorific values. In addition, increased S/B ratio produces low concentration of tar, and this could be attributed to steam reforming (reaction 9 above) and cracking reactions.

The calorific values for steam and oxygen biomass ratio were reported to be high enough to be used in synthesis of methanol and gasoline hydrocarbons (Angelova *et al.* 2014). Rapagna *et al.* (2000) and Sikarwar *et al.* (2016) reported a calorific value 4 to 7 MJ/m³ and 12 to 28 MJ/m³ for gasification of biomass using air and pure oxygen, respectively. However, steam gasification yielded the highest concentration of H₂.

During gasification, carbon in the feedstock reacts with stoichiometric amounts of air and steam to produce syngas. Angelova *et al.* (2014) stated that the ratio of CO/CO₂ in the gasifier is determined by temperature and the Boudouard reaction (Reaction 12 above). They report that at temperatures above 700 °C, most of the product will be CO, whereas below 700 °C, more of the product will be CO₂.

The quality of product gas during gasification depends on biomass type and dimensions (size, shape, density, moisture content), reaction temperature, gasifying agent, ash content, catalyst, gasifier design, and pressure inside the reactor (Kirubakaran *et al.* 2009; Feng *et al.* 2011; Radwan 2012; Roy *et al.* 2013; Parthasarathy and Narayana 2014; Sikarwar *et al.* 2016). Researchers have found a direct correlation between biomass size,

shape and density and the quality of the gas yield. The smaller the pieces of biomass, the more consistent temperature and reaction will be throughout the particles, which yields a consistent composition of gases. When the particles are large, the maximum temperature will be on the outside of the particle and minimum temperature on the inside, which yields a non-uniform composition of gases. For example, during pyrolysis of biomass (cellulose), particle size less than 2 mm are controlled by chemical reactions throughout the particle, particles between 2 and 60 mm are controlled by chemical reaction and heat transfer, and particles larger than 60 mm are controlled by heat transfer (Kirubakaran *et al.* 2009). Niessen (2002) reported that there were four classes of equipment used for MSW size reduction. They include:

1. Swing hammer type hammermills (horizontal or vertical shaft)
2. Vertical ring grinder shredders
3. Flail mill (lightweight swing hammermill for very coarse reduction)
4. Rotary shear (slow turning cutting type device with circular cutter disks)

Biomass with high porosity has a large surface area for reaction. Consistent composition of producer gases can be obtained due to uniform reactions taking place throughout the particle and uniform temperature throughout the biomass. On the other hand, when the biomass is large and less porous, the temperature will vary from maximum on the outside to minimum on the inside. When there is inconsistency in temperature, the processes of drying, pyrolysis, and gasification take place at the same time, yielding non-uniform producer gases and higher amounts of char (Kirubakaran *et al.* 2009; Sikarwar *et al.* 2016).

Feng *et al.* (2011) noted that biomass gasification products (H_2 , CO, CO_2 , CH_4) vary with temperature, pressure, residence time, particle size, and catalyst. They listed that particle size had a great influence on product composition and less influence on gas yield, and temperature had a great influence on yield and product composition. Rapagna and Latif (1997) reported an increase in gas yield and gas compositions during steam gasification when almond shell particle size was reduced from 1090 μm to 287 μm . Luo *et al.* (2009) used a lab scale fixed bed reactor to study the influence of biomass particle size during steam gasification. Results showed that by decreasing particle size from 1.2 mm to 0.075 mm, there was an increase in H_2 , CO, dry gas yield, carbon conversion efficiencies, and the content of tar and char decreased. Sikarwar *et al.* (2016) stated that in general, the higher the cellulose and hemicellulose content, the greater the amount of gaseous products that are produced. They mentioned that hardwood, softwood, wheat straw, and bagasses are more likely to form gaseous products than sunflower seed hull, coconut shell, and almond shell.

The efficiency of gasification is greater than combustion. As the amount of nitrogen from the atmosphere is reduced to the gasifier, the Btu value of the syngas can increase from 12 to 21 MJ/NM³ (Sadaka 2017b). Sadaka stated that biomass gasification is currently being used to produce bioenergy and bio-products. Products of gasification are being used in dual-mode engines to produce power, heat, steam, and electricity (Sadaka 2017b).

Allothermal and Autothermal

In autothermal gasification, the heat that is needed to gasify the biomass is provided by combustion of only a part of the biomass. In allothermal gasification, the heat needed to gasify the biomass is provided from an external source. Milhe *et al.* (2013) built a pilot-

scale reactor to study the continuous fixed bed pyrolysis in either allothermal or autothermal mode using air as an oxidant. They found that in allothermal mode, tar cracking reactions are influenced below 500 °C and in autothermal experiments volatile products are preferentially oxidized and organic condensates production drops to 17 wt. % on a dry basis. They concluded that: “during autothermal pyrolysis in fixed-bed conditions, the presence of oxygen promotes oxidation of volatile matter and cracking reactions, thereby increasing the production of pyrolysis of water and permanent gases”. They observed a significant increase in yields of CO₂ and CO, while the yield of char remained comparable to that in allothermal experiments. Kienberger *et al.* (2009) found that an allothermal gasification system was necessary to produce syngas out of woody biomass.

Pyrolysis

Pyrolysis is a thermo-chemical decomposition of organic matter in the absence of oxidizing agents or oxidants to a limited degree so that gasification does not occur to any substantial amount. There are three types of pyrolysis technology, and these depend on process conditions. They include slow, intermediate, and fast pyrolysis. Product yield (liquid, char, gas) from these pyrolysis types depends on reactor, reaction conditions, feedstock, and process type. Typical yield ranges are (Brownsort 2009):

- Slow pyrolysis – liquid 20 to 50%, char 25 to 35%, and gas 20 to 50%
- Intermediate pyrolysis – liquid 35 to 45%, char 30 to 40%, and gas 20 to 30%
- Fast pyrolysis – liquid 50 to 70%, char 10 to 25%, and gas 10 to 30%.

Fast pyrolysis, sometimes referred to as flash pyrolysis, is an endothermic rapid thermal decomposition of organic feedstock in the absence of air that produces mainly liquid bio-oils. The temperature of pyrolysis is 450 to 600 °C with residence time of 1 to 2 seconds. Bidy *et al.* (2013) used fast pyrolysis of woody biomass (10% moisture) mixed with hot sand and reactor temperature at approximately 500 °C to produce predominately condensable vapors, non-condensable gas, and char. They used a circulating fluidized bed with a pyrolysis reactor, cyclone, and combustor. The char and sand, which is separated from vapors in the cyclone, is sent to a combustor to burn the char and this heat is used to reheat the sand. Brown and Holmgren (2008) used fast pyrolysis at temperatures between 400 and 500 °C, with residence times of 0.5 to 2 seconds, and the yields were similar to Brownsort’s fast pyrolysis data as shown below.

- Oil at 60 to 70%
- Char at 12 to 15%
- Gas at 13 to 25%

Hydrophilic bio-oils are very acidic (pH <3) due to organic acids such as formic and acetic. They also contain significant amounts of metal ions, especially if the pyrolysis reactor is fabricated from metals other than stainless steel (Sadaka 2017a). With the significant amount of oxygenated components present, the oil does not mix readily with hydrocarbons due to its polar nature. Bio-oils are mixtures obtained from pyrolysis of cellulose, hemicellulose, and lignin with calorific value of approximately 17 MJ/kg. The fractions of bio-oils can be divided into three product streams, which include (PyroWiki 2017a):

- Pyrolytic lignin ~35% of original carbon
- Sugar syrup ~45% of original carbon
- Aqueous phase ~20% of original carbon.

Special attention has to be paid when transporting the hydrophilic bio-oil due to its acidic nature and tendency to phase separate. The water content of bio-oils is typically 15 to 35%, and phase separation occurs when the water content is higher than 30 to 45 percent. Bio-oils have been receiving a lot of attention in the past few years due to (Jahirul *et al.* 2012):

- Fuels in boilers, engines, turbines, power generation, and industrial processes
- Low cost and green energy
- Second generation bio-oil feed stock and MSW
- Transportation and storability
- High energy density
- Conversion to motor fuels, additives, or special chemicals.

Reactors that work well for fast pyrolysis include fluidized bed, circulating fluidized bed, auger or twin screw reactor, rotating cone, and ablative reactor (Hornung 2008).

Intermediate pyrolysis is the preferred process for non-woody biomass and is capable of processing large particles up to pellets and chips and also biomass with moisture content up to 40%. Feedstock can include coarse, shredded, chopped, or finely ground material with particle size from dust to several centimeters. The heat transfer rate to the biomass is much lower than fast pyrolysis, and because of this, there is less tar coming from a more controlled reaction. Intermediate pyrolysis will accept large size feedstock, and some of the feedstock can include algae, energy grass, wood residue, and agriculture and forest residue (Hornung *et al.* 2011). Yang *et al.* (2014) described the use of an intermediate pyrolysis system to produce solid, liquid, and gas from pelletized wood and barley straw feedstock. They found that 34.1% (wt.) of the wood pyrolysis liquid formed pyrolysis oil and only 12.0% (wt.) for barley straw. The remaining liquid was an aqueous phase, while the char yields were 28.5% (wt.) for wood and 30.1% (wt.) for barley straw. Both wood and barley straw oil are high in heterocyclic and phenolic compounds with a heating value of 24 MJ/kg. The char heating values for both are similar to sub-bituminous coal. Gas was produced with heating values similar to a downdraft gasification system that produces gas, and calculations of the product energy yields indicated the efficiency at approximately 75%.

Slow pyrolysis yields a higher proportion of char and has been used for thousands of years. Due to its high vapor residence time (5 to 30 minutes), there is a continual reaction with components in the vapor phase, and this leads to formation of high solid char (Jahirul *et al.* 2012). During slow pyrolysis, the temperature is lower than fast pyrolysis (approximately 400 °C). Traditional methods using mounds or pits did not recover byproducts such as liquids and gases. However, recent developments have shown that retorts operating in batch or continuous modes could recover the organic liquid part, and gases could be used for process heat (Brownsort 2009). The cited author reported that before the availability of petrochemicals, slow pyrolysis was used to produce organic liquid components such as acetic acid and methanol. Phan *et al.* (2008) used a slow pyrolysis process on waste wood, cardboard, and textile residues. They found that the char contained about 38 to 55% of the energy content of the raw material, liquid contained about 20 to 30% of the energy content of the raw material (gross calorific value of 10 to 12 MJ/kg), and two thirds of the gases were comprised of carbon monoxide and carbon dioxide.

Torrefaction

Torrefaction (sometimes called roasting, or slow and mild pyrolysis) is a thermochemical process with temperatures between 200 and 300 °C that leads to depolymerization and devolatilization of hemicellulose (Medic *et al.* 2012; Medic 2012). During torrefaction, there is a loss of moisture and a partial loss of volatile compounds. This volatile loss results in destruction of fibrous material from hemicellulose with minor destruction of the cellulose component. The charred product is one that is brittle and easy to grind for pelletization. Prins (2005) found that during torrefaction there were more acetic acid and methanol in volatiles from deciduous wood such as beech and willow than from coniferous wood such as larch. He concluded that these compounds were derived from methoxy and acetoxy groups that are on side chains in xylose molecules. He surmised that torrefied willow could be used in co-combustion because of its increase in caloric value from 17.7 MJ/kg (untreated) to 20.7 MJ/kg (torrefied). Bergman (2005) did research work on combining torrefaction and pelletization (TOP process) to create a high quality bio-pellet. His work was geared to producing TOP pellets that could be used for co-firing in existing coal fired power stations. He concluded that TOP pellets had:

- Bulk density of 750 to 850 kg/m³
- Net calorific value of 19 to 22 MJ/kg
- Volumetric density of 14 to 18.5 GJ/m³ (bulk)
- Durability higher than conventional bio-pellets
- Process has a net energy efficiency of 92%

From his experiments, Bergman (2005) concluded that there could be a major economic savings in using TOP bio-pellets in biomass to electricity.

Torrefaction advantages include (Koppejan *et al.* 2012; Nordin *et al.* 2017):

- Alternative feedstock
- Pelletization
- Increased bulk energy density
- Increased heating value
- Reduced oxygen content
- Dry and hydrophobic nature
- Reduced biological presence
- Reduced chlorine content
- Reduce cost of transportation
- Compatible properties to coal
- Grindability

The design of gasifiers play an important role in the qualitative and quantitative composition of not only the producer gas but also on the side stream of contaminants. Below is a description of various gasifiers with the pros and cons of each system.

GASIFIER DESIGNS

As described in the subsections that follow, there are a few main types of gasifiers that can be considered. As shown in Fig. 12, fixed bed reactors can be either downdraft, updraft, or crossdraft.

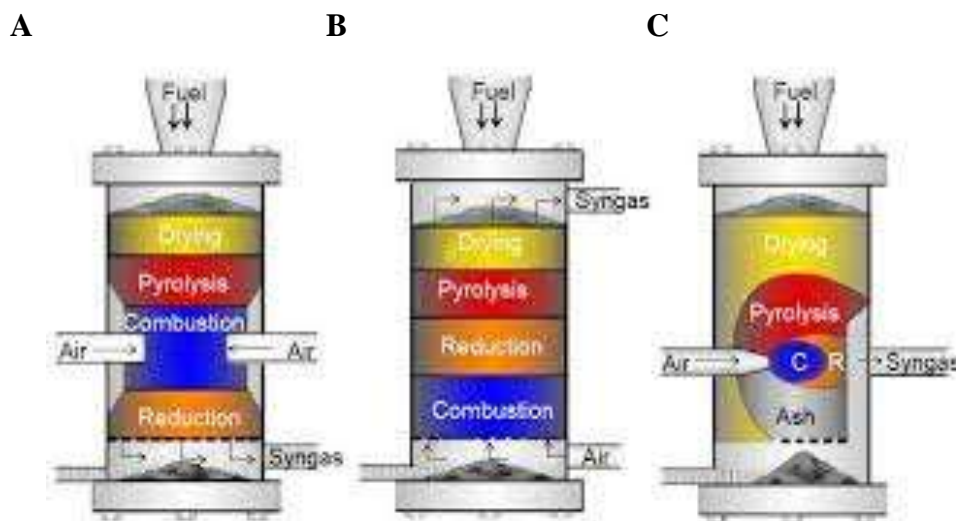


Fig. 12. **A** = Downdraft Fixed Bed, **B** = Updraft Fixed Bed, **C** = Cross Draft Fixed Bed (Biomass Conversion Technologies, Gasifying Reactors, IZES, Slide Share); figure used with permission of the copyright holder.

Downdraft

Design of reactors or gasifiers depends upon several factors that include type of feedstock (moisture, ash, and particle size), position of oxidants into the fuel mix, and whether a gasifier is stationary or portable. It has been written that "gasifier design determines where pyrolysis takes place, how the tar reacts with oxidants, and the temperature of the reactions" (Capital Energy 2015). Stevens (2001) with Pacific Northwest National Laboratory stated in Hot Gas Conditioning that the design of a gasifier plays a major role in determining the primary characteristic of the product gas, its energy content, concentration of tars and particulates, and the quantitative amounts of the producer gas, including hydrogen, carbon monoxide, and carbon dioxide. Basu (2006) stated that the height of the gasifier should be sufficient to allow a gas residence time needed for tar cracking inside the gasifier. In the downdraft gasifier, also called co-current flow gasification, the gasifying agent and product gases flow in the same direction as the biomass (Fig. 12-A). The feedstock or biomass is inserted at the top of the reactor, where it is ignited with air or oxygen (with or without steam) in the reaction zone. This reaction generates pyrolysis gas/vapor, which burns, leaving 5 to 15% char and hot combustion gases (Ciferno and Marano 2002). These gases, including acids and polycyclic aromatic hydrocarbon, react with char (800 to 1200 °C) in the combustion zone, generating CO and H₂. Typical tar conversion is greater than 99% in the downdraft design due to the gases (PAH) being sent through a hot bed of charcoal. This conversion thermally cracks and partially oxidizes PAH in the combustion zone with char (800 to 1200 °C) (Roos 2010; Whitty 2015). In the reduction zone, greater amounts of CO and H₂ are formed with CO₂ and H₂O being reduced by the hot char. The gases exit at 700 to 800 °C, while unconverted char and ash pass through the bottom grate. The primary advantages of downdraft gasifier include (Ciferno and Marano 2002; Couto *et al.* 2013):

- Approximately 99.9% of tar is converted to lower-chain hydrocarbons, which require minimal cleanup.

- Minerals that are created by biomass combustion remain with the char and ash, which reduces the need for cyclones.
- The technology is proven, simple, and low cost.

Because of rapid thermal depolymerization of organics, there are low levels of organic compounds in the condensate. Because of these low levels, there is less of an environmental impact than updraft (Couto *et al.* 2013). The disadvantages for downdraft include (Ciferno and Marano 2002; Zafar 2009; Roos 2010; Couto *et al.* 2013):

- Moisture content needs to be less than 20%, which requires drying of feedstock.
- Gases exiting the reactor requires cooling.
- Carbon (4 to 7%) is unconverted.
- Fluffy low density feedstock creates problems with flow and excessive pressure drop, which requires pelletization.
- Feedstock with high ash content tends to have slagging and clogging problems, and this requires fuel such as wood with low ash content.

Gandhi *et al.* (2012) noted that downdraft gasifiers with throats are known to produce the highest quality gas for engines.

Updraft

The updraft gasifier, also called counterflow gasification, is the oldest and simplest of the gasifiers. As noted in Fig. 12-B, the feedstock is inserted at the top of the reactor (refractory lined) and the oxidant (air, oxygen and/or steam) is introduced below the grate, where ash is removed. The grate is at the bottom of the reactor supporting the reacting bed. In the combustion zone (bottom of gasifier), char burns creating CO₂ and H₂O with temperatures approaching 1200 °C (Roos 2010; Whitty 2015). This exothermic reaction provides the energy necessary for reduction of the hot gases to H₂ and CO (syngas), and these gases are cooled to 750 °C in the reduction zone (Ciferno and Marano 2002). These hot gases proceed upward where they pyrolyze the descending feedstock and dry the incoming material and then exit the reactor at a temperature of approximately 500 °C (Ciferno and Marano 2002; Hu *et al.* 2012). Whitty (2015) and Roos (2010) reported lower exit gas temperature (80 to 100 °C and 250 °C, respectively) than Ciferno and Marano (2002) and Hu *et al.* (2012) whose outlet temperatures were approximately 500 °C. The major advantages for updraft gasification are (Ciferno and Marano 2002; Breault 2010):

- Simple and low cost
- Good thermal efficiency
- Little tendency toward slag formation
- Small pressure drop
- Ability to handle high moisture and inorganic content (MSW)
- Proven technology

The main disadvantage is the generation of 10 to 20% tar (wt.), which requires expensive gas cleanup before turbine, engine or synthesis applications (Ciferno and Marano 2002; Breault 2010; Mandl *et al.* 2010; Hu *et al.* 2012; Couto *et al.* 2013; Whitty 2015). Because of the high tar content in syngas, which can cause problems with ESP and plugging in-line equipment, the updraft gasifiers are normally operated in a close coupled

mode to a furnace or boiler in which steam or hot water can be produced (Sangeorzan 2008; Zafar 2009; Whitty 2015). While the updraft gasifier has a fuel capacity of 1.1 to 12 MW, compared to 1 kW to 1 MW for downdraft, it is still used in coal gasification and has been the primary gasifier in coal processing for 150 years (Zafar 2009; Roos 2010; Gandhi *et al.* 2012).

Cross Draft

Cross draft gasifiers (Fig. 12-C), same as downdraft gasifiers, are considered co-current flow gasification. Biomass is added at the top of the gasifier, and air or a mixture of air/steam is introduced into the side of the gasifier. Syngas is collected on the opposite side of where air or air/steam is introduced. Unlike a downdraft gasifier, the ash bin and reduction zone are separated. Because of this unique design, it is limited to low ash biomass types such as wood, charcoal, and coke. Some advantages of cross draft are (Njikam *et al.* 2006; Breault 2010; Biomass 2017; PyroWiki 2017b):

- Start-up time of 5-10 min, which is faster than downdraft and updraft gasifiers
- Adapted for use on charcoal, which gives low tar content
- Easy to clean equipment with only particulates having to be removed
- Short design height
- Flexible gas production
- Gasifier system is simple, cheap and easy to operate

Disadvantages for cross draft gasifiers include (Breault 2010; Biomass 2017; PyroWiki 2017b):

- High sensitivity to slag formation
- High pressure drop
- Operates in small scale typically of less than 10 kW
- High exit temperature
- Poor CO₂ reduction
- High gas velocity
- Gasifier design limits feedstock to low ash such as wood, charcoal and coke.

Entrained Flow

The term entrain, when used in chemical technology, means to draw or carry suspended particles along in a current or vapor phase. Entrained flow gasifiers (Fig. 13) are defined by finely ground or pulverized biomass or coal (mixed with oxygen, air or steam) that are fed into the top of the gasifier. This results in the pulverized feedstock being entrained with oxidant and steam as they flow through the gasifier. Lettner *et al.* (2007) stated that the ground feedstock is generally smaller than 10 μm . Some entrained flow gasifiers use pulverized coal in which the particles are entrained in a steam oxygen feed, and the product gas is separated from the slag under high temperature or as an ash under lower temperatures (Thermal Conversion 2017).

Most entrained flow gasifiers use oxygen instead of air because they have a short residence time, which requires high temperature (1300 to 1400 °C). This temperature allows the reactor to operate above the slagging temperature. There are two types of entrained flow gasifiers: slagging and non-slagging. Slagging gasifiers are characterized by ash-forming components that melt in the gasifier and flow down the walls of the reactor, forming a slag. If the reactor is operated under slagging conditions, there will be little to

no tars and oils in the product gas. It was noted by van der Drift *et al.* (2004) that limestone or a calcium rich chemical is often used as a fluxing material to create a liquid slag for coal-fired plants, and silica or clay seemed to be the best material as a fluxing material for biomass. Manufacturers of entrained flow gasifiers include Shell, GE Energy (formerly Chevron Texaco), Krupp-Uhde, Future-Energy, E-gas, Siemens, PRENFLO, ECUST, EAGLE, HCERI, Tsinghua OSEF, Mitsubishi Heavy Industries, Hitachi, and Choren (van der Drift *et al.* 2004; Entrained Flow Gasifiers 2017).

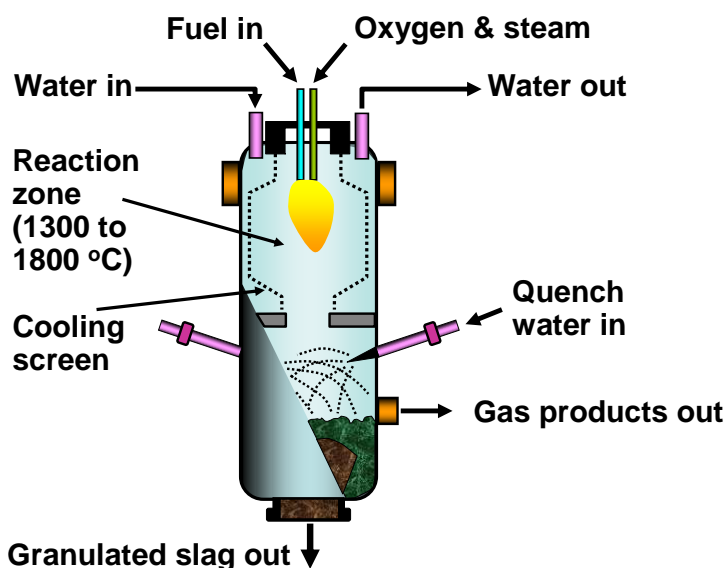


Fig. 13. Entrained Flow Gasifier (Redrawn based on figure from Siemens, Top fired, dry feed, oxygen blown gasifier); figure used with permission of the copyright holder.

In a non-slagging entrained flow gasifier, the walls are kept free of slag, and the process yields fuel that contains small amounts of ash/minerals. This class of gasifier is ideal for fuels with little ash (1% is typically the maximum allowable amount). The Shell Gasification Process is using this type of gasifier on oil residues in the Netherlands (van der Drift *et al.* 2004).

Entrained flow gasifiers are noted for the following (Chen and Coates 1986; Stevens 2001; Kim 2004; van der Drift *et al.* 2004; Lettner *et al.* 2007; Review of Technologies 2009; Energy Technology 2010; Mashingo *et al.* 2014; Park 2014; Henrich *et al.* 2015; Biofuels Academy 2017b; Encust Entrained 2017; Entrained Flow Gasifier 2017; Thermal Conversion 2017):

- High feedstock flexibility (coal, MSW, biomass)
- Short residence time
- High and uniform temperature within the reactor
- Large oxidant requirements, which can be oxygen or air
- High carbon conversion (conversion efficiency of 98 to 99%, where 1 to 2% carbon remains as solids)
- Slagging and non-slagging operation
- Minute amounts of tar in gas
- Removal of ash as molten slag
- Low methane in syngas

- Environmentally most benign
- Syngas consist mainly of hydrogen, carbon monoxide, and carbon dioxide

The entrained flow gasifier seems to be an ideal gasifier for MSW, biomass or co-gasification due to the fact that it can accept different types of feedstock, has uniform temperature inside the reaction zone, has high carbon conversion, and has a short residence time.

Fluidized Bed

Bubbling

The first fluidized bed (FB) gas generator was advanced in the 1920s by Fritz Winkler in Leuna Germany for coal gasification (Adlhoch *et al.* 2000). In the 1930s, American Petroleum Industry started researching ways that FB technology could be used for catalytic cracking oils to smaller chain compounds (Silva *et al.* 2012; ACS 1998; Fluidized Bed Combustion 2017). FB reactors are used in many industries including petroleum, chemical, mineral, and pharmaceutical. Currently, FB technology has been applied to (Taib *et al.* 2001; Luckos *et al.* 2007; Sarkar 2015):

- Fluid catalytic cracking
- Gas-solid reaction
- Calcination of alumina
- Roasting of ore
- Waste treatment
- Bioprocesses

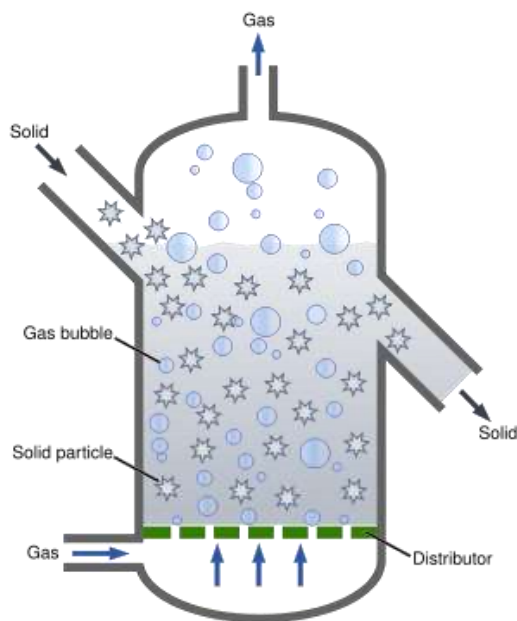


Fig. 14. Bubbling fluidized bed (Source: Wikipedia); figure subject to the Creative Commons license specified by Wikipedia

Fluidized bed gasifiers can be classified as bubbling fluidized bed (BFB) or circulating fluidized bed (CFB). BFB gasifiers (Fig. 14) are generally characterized by

larger cross section, shorter height, lower fluidization velocities, and denser beds (Gasifiers & Gasification 2017). Bubbling fluid bed densities are approximately 720 kg/m^3 compared to 560 kg/m^3 for circulating fluid bed density (PSSurvival 2008). BFB operation takes place when a stream of gas (oxygen, air or steam) is passed upward (1 to 3 m/s) through a bed of solid inert material such as sand, limestone, dolomite, olivine or alumina with particle size ranging from 0.1 to 1 mm (Lettner *et al.* 2007; PSSurvival 2008; Review of Technologies 2009; Whitty 2015). Solid inert material is selected based on density, size, and thermal properties. As the gas is forced through the solid inert material, it functions as a fluidizing medium and also as an oxidant for combustion and cracking of high molecular weight compounds. At a point where the gas velocity shows bubbling and channelling of the solid material (without overflowing the reactor), feedstock is then fed in from the side through an auger. The feedstock mixes with gas and inert material and forms syngas, which flows upward toward the reactor top and through a cyclone, which remove fines. Typical operating temperatures range from 900 to 1000 °C (control by air/biomass ratio) with tar content ranging from 1 to 15 g/Nm³ and particulate content from 2 to 20 g/Nm³ (Roos 2010; Couto *et al.* 2013). The BFB reactor chamber generally has a cylindrical configuration in which size reduction and drying between the gas and solids can be obtained. The constant turbulence of the feedstock and bed material make it appear as though the mixture is in a boiling state. Some of the advantages of BFB gasification are (Ciferno and Marano 2002; Zafar 2009; Couto *et al.* 2013; Fluidized Bed Combustion 2017):

- Uniform mixing with frequent particle-particle and particle-wall collisions
- High heat transfer between inert material, feedstock and gas
- Extremely high surface area contact between fluid and solid per unit bed volume
- High relative velocities between the fluid and the dispersed solid phase
- Yield of a uniform product gas
- High conversion with low tar and unconverted carbon
- Efficient reactions
- Acceptance of a wide range of feedstock particle sizes including fines
- Suitable for generators with capacities greater than 10 MW

Some of the disadvantages for BFB gasification are (Ciferno and Marano 2002; Fluidized Bed Combustion 2017):

- Large bubble size, which may result in gas by-pass through the bed
- Increased reactor vessel size due to expansion of bed material in the reactor
- Particle entrainment with fine particles becoming entrained in the fluid
- Erosion of internal components

Circulating

Circulating Fluidized Bed (CFB) reactors are different from BFB reactors in that the gas flow is increased from 1.5-3.7 m/s (BFB) to 9.1 m/s, causing the turbulent bed solids to flow to the cyclone (PSSurvival 2008). In the cyclone, the solids are separated from the gases and returned to the bed, forming a solids circulation loop. The BFB has a defined interface between the reaction zone of the fluidized bed and the freeboard above the bed surface, while CFB (Fig. 15) has no distinct interface between the fluidized bed and the freeboard (Henrich *et al.* 2015). Ciferno and Marano (2002) describe the CFB gasifier as having gas velocities higher than the minimum fluidization point, resulting in

entrainment of the particles in the gas stream. Then, the gas and particles are separated in the cyclone, where the gas exits the top of the cyclone and is cleaned downstream. The particles exit the bottom of the cyclone, where they are returned to the reactor. CFB gasifiers operate at temperatures below 900 °C to prevent ash from melting and sticking and are generally noted by their taller height, smaller cross section, and higher fluid velocities (Review of Technologies 2009; Gasifiers & Gasification 2017). Typical tar content range from 1 to 15 g/Nm³ and particulate contents from 10 to 35 g/Nm³ (Roos 2010).

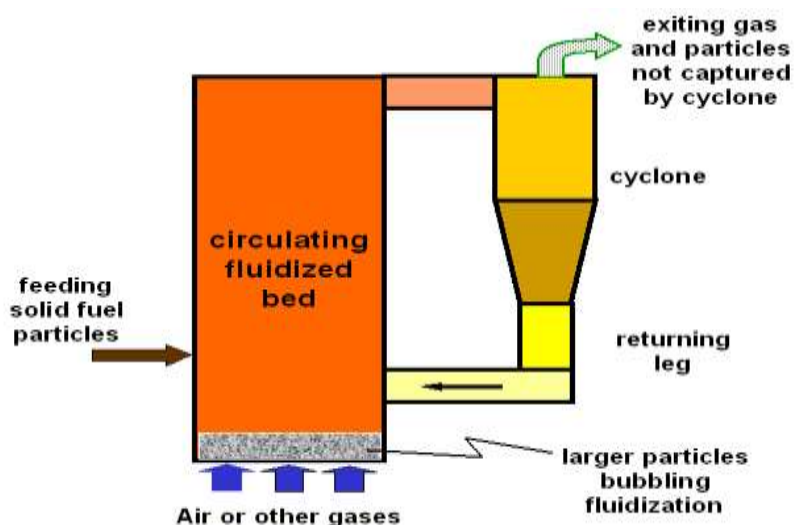


Fig. 15. Circulating fluidized bed gasifier (Source: Dr. Marcio de Souza-Santos); figure used with permission of the copyright holder.

Standard Oil Company in 1942, at the Baton Rouge Refinery, was the first to commercialize a circulating fluid bed reactor (ACS 1998). Their process involved using catalysts in a continuous operation, and this allowed cracking of high molecular oils to produce high-octane fuels.

Advantages for CFB gasification are (Ciferno and Marano 2002; Zafar 2009; Couto *et al.* 2013):

- Suitable for rapid reactions
- Has the capacity to process different feedstock with varying compositions and moisture content
- High heat transport rates possible due to high heat capacity of bed material
- High conversion rates

Disadvantages for CFB gasification are (Ciferno and Marano 2002; Hu *et al.* 2012; Couto *et al.* 2013; Fluidized Bed Combustion 2017):

- Temperature gradients occurring in the direction of solid flow
- Size of fuel particles determining minimum transport velocity
- Heat exchange less efficient than BFB
- Erosion, corrosion, and attrition problems
- Poor operational control using biomass

Currently, fluidized bed reactors are used worldwide in the petrochemical industries. FB reactors and technology are also used in the following (ACS 1998; Naz *et al.* 2015):

- Manufacturing of acrylonitrile, phthalic anhydride, aniline, and maleic anhydride
- Production of polymers such as rubber, vinyl chloride, polyethylene, styrene, and polypropylene
- Coal gasification
- Oil decontamination of sand
- Radioactive waste solidification
- Acetone recovery
- Biomass gasification
- Particles coating
- Water and waste treatments

Plasma Gasifier

Plasma is considered the fourth state of matter and is based on the principle that as energy is supplied to matter, it is transformed from a solid to a liquid to a gas, and when more energy is supplied to gas molecules, it ionizes into the plasma state. Kim (2004) described plasma as a partially or fully ionized gas consisting of electrons, ions, atoms, and molecules. These highly charged gaseous atoms, molecules, ions, and molecular fragments react very differently from solids, liquids, or gases.



Fig. 16. Plasma Gasifier (Source: Alter NRG Corp.); figure used with permission of the copyright holder.

Typically, the electrons in the three less energetic states of matter stay within the nucleus; however, if electric current flows through a solid or liquid, there can be electron movements from adjacent nuclei, and if an atom loses some of its electrons, it is considered an ion. In plasma, there is such a high energy level that no nucleus can hold the energetic electrons, and these ions are considered super-ionized gas. Plasma applications include: electric lamps, lasers, medicine (surface treatment, instrument sterilization), polymer science, surface processing, flue gas treatment, metal recovery, waste treatment, welding, and cutting (Rouse 2005; Byun *et al.* 2012; Ferrell *et al.* 2013; Plasma Science 2017; Plasma Air 2017; Plasma Technology 2017; Coalition for Plasma 2017). Another plasma application is inductively coupled plasma mass spectrometry (ICP-MS).

Plasma's existence was first discovered by Sir William Crookes in 1879, and the term plasma was coined by Irving Langmuir in 1928. Plasma is not such a rare event, as it is present on earth in the form of lightning. Lightning occurs when an electrical discharge through air (78% N, 21% O, Ar, CO₂, CH₄) ionizes the atoms by removing electrons. Plasma can be classified as thermal plasma (hot plasma) or non-thermal plasma (cold plasma). Thermal plasma is close to being completely ionized and has electrons and particles at the same temperature where they are in thermal equilibrium. Non-thermal plasma has only a small fraction of the gas molecules ionized and has ions at a much lower temperature.

Plasma gasification is an allothermal process that is being used for creating syngas from biomass and MSW. Because feedstock varies in physical form, moisture content, ash content, and chemical composition, a plasma reactor must be designed to meet these differences. Therefore, a single plasma reactor design would not apply for all waste treatment cases (van der Walt *et al.* 2012). Rajasekhar *et al.* (2015) described plasma gasification as involving gases such as air, oxygen, nitrogen, or noble gases, and this produces extremely high temperatures, which depolymerizes feedstock to individual atoms such as carbon, hydrogen, and oxygen. These atoms then react with each other to form high quality syngas. At these high temperatures, the inorganic part (metals, glass, silicates) extrudes from the bottom of the reactor (Fig. 16) and forms an inert, non-leachable vitrified slag that can be landfilled or used as insulation material, flooring tiles, garden blocks, or road construction material (Bosmans *et al.* 2012, 2013; Campos *et al.* 2015). Mercury, zinc, and lead are vaporized at these high temperatures and must be treated downstream. Campos *et al.* (2015) wrote that by utilizing plasma arc technology, it was possible to generate 816 kWh per ton of MSW, as shown in Table 12; this is a higher energy producer than incineration, pyrolysis, or conventional gasification.

Table 12. Summary of WTE Technology and By-products (Campos *et al.* 2015)

WTE Technology	Operating Temperatures (°F)	Energy Production (kWh/ton MSW)	By-products
Incineration	1,000-2,000	544	High pressure steam, ash, exhaust gases
Pyrolysis	1,200-2,200	571	Raw syngas, bio-oil, ash, char, metals
Conventional Gasification	1,450-3,000	685	Raw syngas, bio-oil, ash, slag, metals
Plasma Arc Gasification	7,200-12,600	816	Raw syngas, inorganic materials, vitrified slag

Non-thermal plasma has been used to convert elemental mercury to mercury (II) oxide, which is a solid at room temperature and pressure, and HgO can be collected using a fabric filter or electrostatic precipitator (ESP) (Using Non-Thermal Plasma 2005).

Plasma gasification has the following benefits compared to conventional gasification (Using Non-Thermal Plasma 2005; Heberlein and Murphy 2008; Gray 2014; Sirillova 2015):

- Better environmental benefits through lower emissions
- Vitrified slag has numerous usages compared to ash, metals and slag from gasification
- Disposal of hazardous wastes (dioxins)
- Higher gross energy recovery resulting from complete decomposition to elemental level
- Smaller installation size
- Increased process controllability

The disadvantages associated with plasma gasification include (Heberlein and Murphy 2008; Sirillova 2015):

- Lack of reliability
- High energy consumption
- Energy source is electricity, which is economically costly
- High initial investment

Auger Reactor

The auger reactor has attracted a lot of attention over the past few years because of its design and ability to process various feedstocks with continuous operation and with little to no carrier gas.

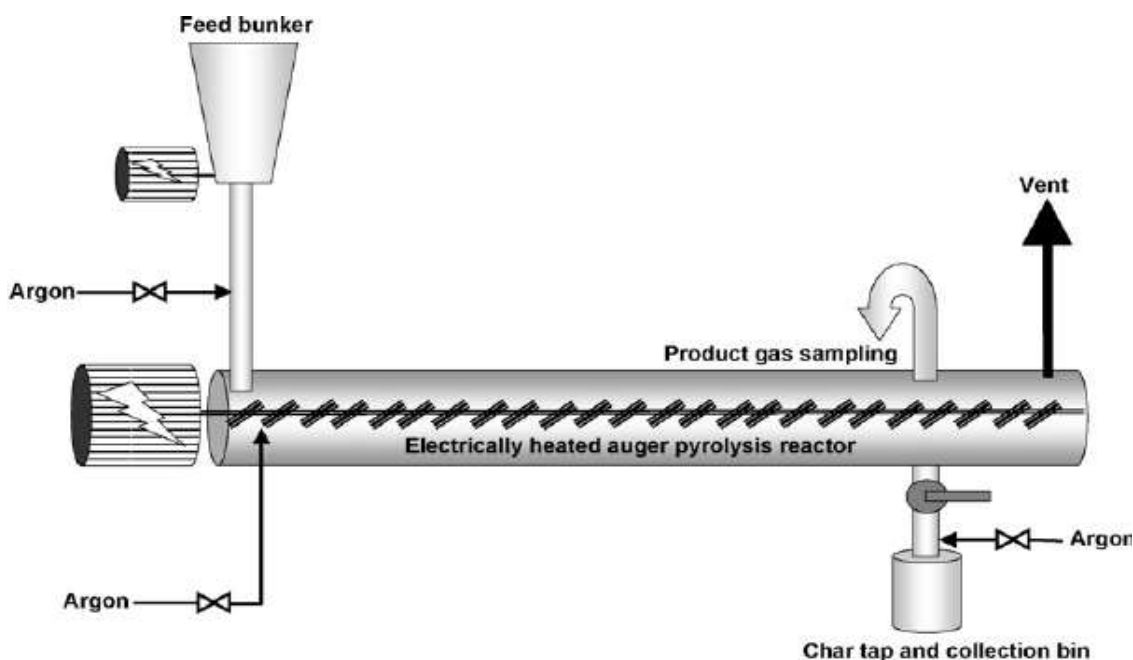


Fig. 17-A. Auger Reactor (Source: Journal of Analytical and Applied Pyrolysis, 85, 2009, Dr. P.J. de Wild); figure used with permission of the copyright holder

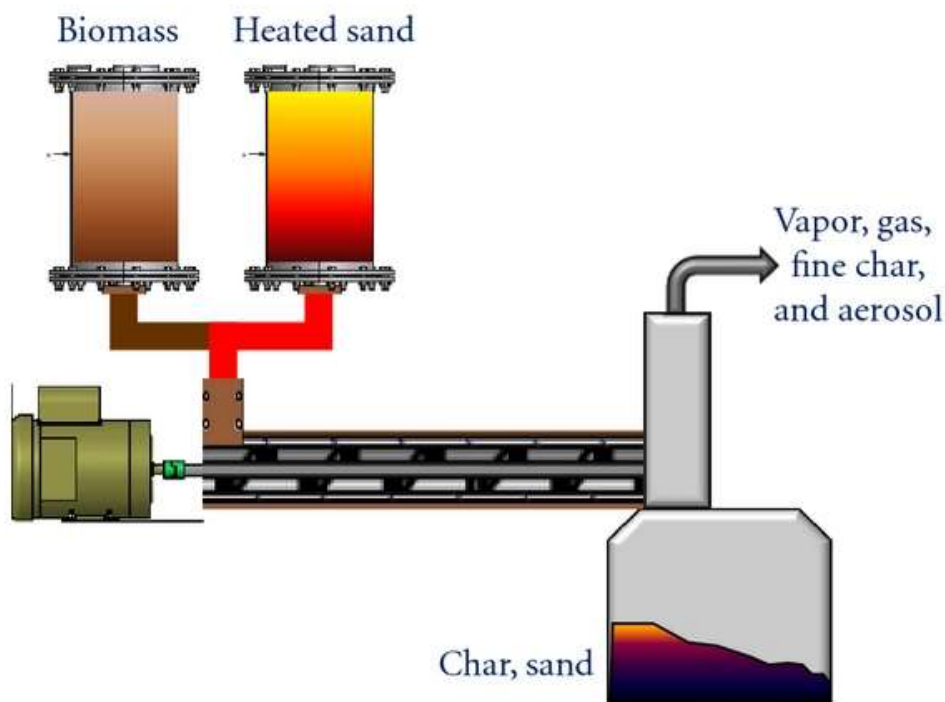


Fig. 17-B. Auger Reactor with heated carrier (Source: Hindawi, Biofuels Production from Biomass by Thermochemical Conversion; M. Verma, S. Godbout, S.K. Brar, O. Solomatnikova, S.P. Lemay, J.P. Larouche); figure used with permission of the copyright holder

The design is simple, with the feedstock being conveyed into the reactor, where it is pushed through with an auger screw. The speed can be easily varied, which will increase or decrease the retention time of the gases. An inert gas, *e.g.*, nitrogen, argon, *etc.*, can be used as the carrier gas (Fig. 17-A), while in some auger reactors a bulk solid heat transfer material (sand or steel shot) (Fig. 17-B) is heated independently before being metered into the reactor with the feedstock (Verma *et al.* 2012; Marshall 2013).

Verma *et al.* (2012) noted that the biomass temperature is controlled for pyrolysis during the flow through the heated zone by manipulating the auger rotational speed, diameter, flight-pitch, biomass particle size, and heating mode. Aramideh *et al.* (2015) found that higher tar yields in an auger reactor were the result of a higher nitrogen inlet velocity and that this results in a shorter residence time for vapors, which prevented tars from cracking into syngas. Sadaka *et al.* (2014) in allothermal auger gasification discovered that increasing the reactor temperature from 700 °C to 850 °C resulted in an increase in gas production from 24.3% to 44.1%. They stated that the higher temperature resulted in a higher heat transfer rate from the reactor walls to the biomass. This higher heat transfer rate enhances the volatilization process, increases the depolymerization of tar, and these reactions increase gas production.

Robert Brown at Iowa State University designed a lab-scale auger reactor system that used sand as the heat carrier with corn stover as the biomass. The project's goal was to find a viable alternative (*e.g.* fluidized bed reactors) for bio-oil production *via* thermochemical fast pyrolysis. In the experiment, sand was heated independently and metered into the reactor with corn stover (Fig. 17-B). The average bio-oil yield was 38.5%,

with bio-char averaging 34.8%. It was noted, "on a gravimetric basis, thermodynamic calculations suggest a heat carrier feed rate 20 times the biomass feed rate" (Brown 2009a)

Jared Brown at Renewable Energy Group, Inc. built a lab scale auger reactor for biomass fast pyrolysis using red oak as the biomass feedstock and S-280 cast steel shot as the heated carrier. He concluded the following (Brown 2009b):

- Heat carriers can create high liquid yields by improving heat transfer, but only if the biomass contacts the heat carrier for a short time period.
- High auger speeds and temperature above 525 °C are required to minimize biochar yield (minimize secondary reactions).
- Low auger speeds and temperature below 525 °C minimize biochar yield by promoting mixing.
- Moisture content in bio-oil decreased when increasing heat carrier temperature and feed rate, and these conditions favor high bio-oil yield and low bio-char yield.
- Hydrogen in the bio-oil decreased when increasing heat carrier temperature and feed rate.
- Water insoluble content increased with increasing temperature and heat carrier feed rate.

The advantages of an auger reactor include (Jahirul *et al.* 2012; Verma *et al.* 2012; Marshall 2013; Ronsse (2013); Aramideh *et al.* 2015; Sharara and Sadaka 2015; Kato *et al.* 2016; Fransham 2017):

- Compact design
- No carrier gas required
- Lower process temperature
- High degree of process control (*e.g.*, biomass residence time inside the heated zone)
- Materials of different phases can be mixed to enhance heat transfer
- Easy separation of bio-oil and char
- Continuous process
- Lower energy requirements
- Very high feedstock flexibility due to mechanical auger

The disadvantages for an auger reactor include (Jahirul *et al.* 2012; Verma *et al.* 2012; Marshall 2013; Sadaka *et al.* 2014):

- Moving parts in hot zone with possible mechanical wear
- Heat transfer in large scale is not suitable
- Plugging risk
- Lower bio-oil yield due to higher char formation

Other Auger reactor systems include:

1. Kothari *et al.* (2015) used dried sawdust (babul plant) that was fed to the reactor at the rate between 3 kg/h to 7 kg/h. Heated sand was used as the carrier and was mixed with biomass at a ratio of 2:1 with nitrogen as the carrier gas. Maximum bio-oil yield was 20.4%, temperature of 600 °C, feed rate of 5 kg/h, and residence time of 90 seconds.
2. Rotliwala *et al.* (2013) studied the co-pyrolysis of HDPE, PP, and PS with jatropha (de-oiled) using a 2 kg/h auger reactor at 500 °C under atmospheric conditions in the presence of nitrogen. The plastics and jatropha were blended

in equal mass weights. Co-pyrolysis demonstrated a huge improvement in the quantity of paraffins, olefins, and aromatics from the bio-oil. Co-pyrolysis of PS with jatropha showed a 90% reduction of oxygenates. Overall, co-pyrolysis produces bio-oil with higher heating value with lower water content and viscosity.

3. Saade and Dubljevic (2013) studied the modeling of an auger reactor for biomass torrefaction. They describe the torrefaction process for wood at 200 to 300 °C at a slow rate in an inert environment. Since temperatures above 300 °C produce tars from decomposition of cellulose and lignins, they maintain that it is impossible to control this exothermic process within the desired temperature (280 to 300 °C) without a control algorithm system.
4. Ingram *et al.* (2008) compared bio-oils from fast pyrolysis (450 °C) in an auger reactor to a fluidized bed and vacuum pyrolysis processes. Feedstock included pine wood, pine bark, oak wood, and oak bark. Using GC/MS, GPC, calorific values, elemental analysis, water analysis, ash content, ¹H and ¹³C NMR spectroscopy, they concluded that the bio-oils were similar and that portable auger reactors might be used to produce bio-oils at various forest locations. Because of the less bulky bio-oil versus raw biomass, portable augers would save money in transportation cost to bio-refineries.
5. Wild *et al.* (2009) compared the slow pyrolysis of beech in an auger reactor to a bubbling fluidized bed. They concluded that a bubbling fluidized bed typically yields more water, less permanent gases and char, less methanol and phenols, and more levoglucosan when compared to conventional pyrolysis using an auger reactor.
6. Sharara and Sadaka (2015) investigated the auger gasification of microalgae at three temperatures – 760, 860, and 960 °C. They concluded that temperature increases resulted in a decrease in CO₂ yield followed by an increase in CO concentration from 12.8% at 760 °C to 16.9% at 960 °C. Similar increases were noted for hydrogen, which went from 4.7% at 760 °C to 11.4% at 960 °C. Overall, increasing in temperature resulted in an increase in gas heating value. In addition, temperature profiles during auger gasification indicated that there were different reaction zones, which was similar to fixed bed gasification systems.
7. Kato *et al.* (2016) studied bio-oil produced from Japanese cedar using a bench scale auger pyrolyzer. From the experimental work, they concluded that pyrolysis temperature and residence time of the pyrolysates played a very important role in determining the characteristics of the bio-oil.

Commercial systems for auger reactors include (Hammond and Rodger 2012; Marshall 2013):

1. PYREG GmbH in Dorth, Germany provides environmental technology in the field of waste to energy. The auger reactor that they designed is a continuous screw fed machine that can use a wide range of feedstock at the rate of 100 to 150 kg dry matter per hour. They currently have contracts for four auger reactors (PYREG 500) and they envision their machine being used in most small towns processing woody or sewage wastes.
2. ABRI-Tech is located in Namur, Quebec and is part of the Leggett Group, which is a forest products company. Their design is based on a hot moving

carrier (hot steel shot) around a loop via two screw conveyors. The biomass is heated by steel shots and the produced gas flows out of the reactor through a pipe. This quick and efficient heat transfer allows for larger auger systems because of the rapid heat transfer. After leaving the reactor, the gas then goes through a cyclone to remove entrained char, and after cleaning, the condensable gases are collected. The steel shots and char are kept clean by an inclined auger that is elevated to allow for separation. The char is conveyed out of the system and cooled and the steel shots drop into the reactor for the next run. Marshall (2013) noted that ABRI-Tech has built and sold several 1 dry ton per day units and is currently manufacturing 20 kg/day to 50 dry tons per day systems.

3. Renewable Oil International (ROI), located in Florence Alabama, is a company that provides small and portable reactors for production of bio-oils using an auger reactor (Renewable Oil 2017). Marshall (2013) lists that their auger reactor is capable of handling biomass at the rate of 200 kg/h. ROI's website list the following features with their technology:

- Produces a high-value product with multiple energy and non-energy markets
- Capable of processing virtually any biomass material
- Cost effective at relatively small scale
- Essentially energy self-sufficient
- Simplified design that can be factory fabricated in transportable modules
- Does not require boilers or process water
- Relatively low capital, operating, and maintenance costs

Because of the composition of biomass feedstock and MSW, a reactor's performance will depend significantly on the geometrical characteristics of the particles from the feedstock (Aramideh *et al.* 2015). In each of the gasification systems listed above, the syngas produced can be used in several different ways. This includes (Zafar 2009):

- Syngas can be burned in a boiler to produce steam, which then can be used to power generators or heating systems
- Syngas can be used in gas engines
- Syngas, after clean-up, can be used in gas turbines
- Syngas can be used to produce chemicals.

GAS CLEANING

Removal of Tars

During gasification or pyrolysis of biomass, the raw gas contains a number of contaminants, which can include tars, particulates, nitrogen and sulfur compounds, halogen and their acids, and alkali metals. Tars are formed during pyrolysis, which is initiated at temperatures close to 230 °C, where the biomass polymer chains are broken down to CO, CH₄, CO₂, H₂O, H₂, tar, and char (Le Coq and Duga 2011; Laurence and Ashenafi 2012). High technology application areas require extensive gas clean-up, *e.g.*, catalyst, gas turbines, transportation fuels, chemicals, and hydrogen for use in fuel cells; while low technology areas such as cement kilns do not require extensive clean-up. It is estimated that the share of gasification and gas clean up equipment for a biomass plant that produces synthetic fuels is on the order of 50 to 55% of the total capital investment cost (Hannula

and Kurkela 2013; Simell *et al.* 2014). Simell *et al.* (2014) stated that the most important steps in gas clean up are:

- High temperature gas filtration
- Reforming of hydrocarbon gases and tars to increase the yield of CO and H₂
- Shift conversion to adjust the H₂/CO ratio of syngas for downstream synthesis
- Gas cooling with effective heat integration and waste heat utilization
- Physical absorption of CO₂, total S, and other impurities to acceptable levels

Removal of particulates, tars, and other contaminants is important, as was noted during the early production of fuel gas from biomass. Lack of attention to this issue led to IC engine failures, which resulted from accumulation of tar in valves. Singh *et al.* (2014) reported that allowable levels of tar for gas engines are about 50 mg/Nm³, while gas turbines and fuel cells can tolerate 5 and 1 mg/Nm³, respectively.

One of the most troublesome areas in gas cleanup is the removal of tar components. Tar is a black viscous liquid with a heating value of 20,000 to 40,000 kJ/kg (Basu 2006) that originates from thermo-chemical processing of organic matter and is one of the major problems relating to biomass gasification technology. Tars are mostly aromatics that have carcinogenic properties; however, they contain a significant amount of energy that can be converted to gases such as hydrogen, carbon monoxide, methane, and other low MW hydrocarbons. Bosmans *et al.* (2013) stated that total tar concentration is not the most important parameter. Tar dew point is the most important because it defines when tar starts to form condensate. Tar dew point is defined as the temperature where the real total partial pressure of tar equals the saturation pressure of the tar. Tar dew points typically fall within the range of 150 to 350 °C (Bosmans *et al.* 2013).

Milne and Evans (1998) listed numerous tars as primary, secondary, and tertiary tars. Primary tars are compounds formed with the presence of oxygen in their structure, where the formation temperature ranged from 400 to 600 °C. Cellulose and hemicellulose are precursors for primary tars, which include anhydrosugars, alcohols, ketones, carbon acids, aldehydes, monoaromatics, and phenols. Examples include acetic acid, benzoic acid, xylose, glucose, cellobiosan, methanol, ethanol, cyclopentanone, formaldehyde, acrolein, phenol, furans, glyoxal, resorcinol, and hydroquinone. Secondary tars are compounds with formation temperatures ranging from 600 to 800 °C and include light hydrocarbons such as pyridine, furans, mono and diaromatics, and dioxins. Examples of secondary tar components include methane, ethane, benzene, toluene, phenol, styrene, naphthalene, biphenyl, and methylpyrene. Tertiary tars have formation temperatures ranging from 800 to 1,000 °C and include light hydrocarbons (methane and acetylene) and aromatics including benzene, indene, fluoranthene, pyrene, chrysene, benzoanthracene, benzo [c] phenanthrene, coronene, and other PAH compounds.

Zevenhoven and Kilpinen (2001) stated that a typical tar sample from solid fuel had components of benzene, toluene, phenol, PAH (naphthalene and anthracene), pyridines, and thiophenes. They noted that tar produced in an air-blown FB reactor using wood, peat, and brown coal showed the following:

- Total tars produced from wood is an order of magnitude higher than for coal or peat.
- Benzene and naphthalene are the major products from coal and peat.
- Phenolic products are the major group from wood (higher oxygen content).
- The amount of tar depends on the air factor during gasification.

Tar creates problems by: condensing in cold spots (causes plugging of pipes), corrosion of equipment, creating environmental issues with their carcinogenic character, fouling equipment such as gas engines and turbines, and in general reducing the efficiency of the gasification process. Singh *et al.* (2014) noted that tar removal or conversion is seen as one of the greatest challenges in the successful development of a commercial gasification system. The quantity of tar and composition of the tar from a given gasifier depends on several factors. Fjellerup *et al.* (2005) listed these factors as: 1) temperature/time history of the particles and gas, 2) point of introduction of feed in fluid beds, 3) thoroughness of circulation in fluid beds, 4) properties of bed materials in fluid beds, 5) degree of channeling of fixed beds, 6) feed particle size distribution, 7) gaseous atmosphere, which includes O₂, steam, and 8) geometry of the bed. Tar concentration in producer gas were estimated to be in the order of 100 g/Nm³ for updraft, 10 g/Nm³ for fluid beds, and 1 g/Nm³ for downdraft gasifier (Milne and Evans 1998; Rabou *et al.* 2009).

In March 1998, the International Energy Agency (IEA) stated that tars are all organics that have boiling temperatures above that of benzene. Several authors have listed tars as organic compounds with a MW larger than benzene (Rabou *et al.* 2009; Lahti and Romar 2010; Shen and Yoshikawa 2013; Chiranjeevaraoseela *et al.* 2015; Nakamura and Yoshikawa 2015). Other authors have defined tar as a complex mixture of condensable organic hydrocarbon compounds, *e.g.*, aromatics, oxygen containing hydrocarbons, and complex PAHs with a wide range of molecular weight and chemical characteristics (Zevenhoven and Kilpinen 2001; Bergman *et al.* 2002; Kaminska-Pietrzak *et al.* 2013; Vivanpatarakij *et al.* 2014; Shi *et al.* 2016). Polycyclic aromatic hydrocarbon (PAH) compounds, a component of tar, is very difficult to convert to lower chain hydrocarbons. PAH are organic compounds with a minimum of two fused benzene rings and are considered an environmental contaminant. They are found in air, soil, water, foods, pharmaceutical products, and high concentrations are found in tobacco smoke (Some Non-Heterocyclic 2017). Some of the most notable PAH compounds include naphthalene (C₁₀H₈), anthracene (C₁₄H₁₀), and benzopyrene (C₂₀H₁₂). Tar concentration and composition depends on reactor type, fuel (biomass, MSW, *etc.*), and gasification process. Coll *et al.* (2001) listed some typical composition and percentages of biomass gasification tars, and they include:

• Benzene	37.9%
• Toluene	14.3%
• Other one-ring aromatics	13.9%
• Naphthalene	9.6%
• Other two-ring aromatics	7.8%
• Three-ring aromatics	3.6%
• Four-ring aromatics	0.8%
• Phenolic compounds	4.6%
• Heterocyclic compounds	6.5%
• Others	1.0%

Milne and Evans (1998) showed tar composition and a maturation scheme that was proposed by Elliott (1988) and Basu (2006) as a function of increasing temperatures (Table 13). This table shows that with an increase in temperature, there is a loss of hydroxyl and alkyl groups and an increase in refractory aromatics.

Table 13. Tar Composition and Maturation Scheme

Mixed Oxygenates	Phenolic Ethers	Alkyl Phenolics	Heterocyclic Ethers	Polycyclic Aromatic Hydrocarbons	Larger Polycyclic Aromatic Hydrocarbons
400 °C	500 °C	600 °C	700 °C	800 °C	900 °C

Table 14 (Milne and Evans 1998) gives the chemical components in each temperature regime based on GC/MS analysis of tars. With an increase in temperature, products go from primary compounds to phenolic compounds to PAH, and at extremely high temperature they yield larger PAH compounds, which are more refractory. Elfasakhany (2012) listed primary tars as forming in a temperature range of 400 to 700 °C, secondary tars in the temperature range of 700 to 850 °C, and tertiary tars as forming in the temperature range of 850 to 1000 °C. Kaminska-Pietrzak *et al.* (2013) have listed products for wood pyrolysis as:

- Primary tar compounds – similar to Table 14, conventional flash pyrolysis (acids, ketones, phenols, guaiacols, furans)
- Secondary tar compounds – similar to Table 14, high-temperature flash pyrolysis (phenols, monoaromatic hydrocarbons)
- Secondary/Tertiary compounds – similar to Table 14, conventional steam gasification (monoaromatic hydrocarbons, methyl derivative of aromatics, miscellaneous hydrocarbons)
- Tertiary compounds – similar to Table 14, high-temperature steam gasification (polycyclic aromatic hydrocarbons)

Table 14. Chemical Compositions in Biomass Tars

Conventional Flash Pyrolysis (450-500 °C)	High-Temperature Flash Pyrolysis (600-650 °C)	Conventional Steam Gasification (700-800 °C)	High-Temperature Steam Gasification (900-1000 °C)
Acids	Benzenes	Naphthalenes	Naphthalene
Aldehydes	Phenols	Acenaphthylenes	Acenaphthylene
Ketones	Catechols	Fluorenes	Phenanthrene
Furans	Naphthalenes	Phenanthrenes	Fluoranthene
Alcohols	Biphenyls	Benzaldehydes	Pyrene
Complex Oxygenates	Phenanthrenes	Phenols	Acephenanthrylene
Phenols	Benzofurans	Naphthofurans	Benzanthracenes
Guaiacols	Benzaldehydes	Benzanthracenes	Benzopyrenes
Springols			226 MW PAHs
Complex Phenols			276 MW PAHs

Tars can self-polymerize at ambient temperature or with heat. Vreugdenhil and Zwart (2009) showed the following with tar polymerization reactions from biomass samples:

- In pipes at 200 to 400 °C, tars tend to condense and then polymerize (they noted that these tars first produce a sticky dark brown or black syrupy material and then become brittle, shiny carbon after a longer reaction time).
- Pyrolysis oil will polymerize when stored at room temperature and exposed to air.

- Pyrolysis oil will polymerize when heated to 100 °C or higher.
- Tars that have been separated in a scrubber and exposed to air will gradually polymerize to form a solid; however, if they are stored in water or an organic solvent their stability will increase over a longer time frame.
- Tars that are produced at lower temperatures tend to condense and polymerize when maintained at temperatures between 200 and 300 °C (polymerization first produces a thermoplast and then over time it polymerizes to a hard material).

Tar removal methods can be divided into two classes: 1) Primary methods, which is inside the gasifier, and 2) secondary methods, which take place outside of the gasifier. This paper will be mainly concerned with secondary methods, even though some of the catalyst systems such as dolomite, olivine, iron, and char are used in both the primary and secondary methods for reduction of tar concentration.

Rabou *et al.* (2009) stated that ECN's research work on the effects of fuel properties and operating conditions on tar formation can be summarized as follows:

- Composition of dry fuel has little effect on tar amount.
- Lignin produces slightly more tar than cellulose.
- Higher moisture content of fuel reduces the amount of tar formed.
- Temperature has the most marked effect on tar amount and composition (OH groups disappeared first followed by CH₃ groups).
- Higher temperature promotes polymerization, resulting in a larger number of rings.
- Increasing residence time in gasifier has similar effect as increase temperature but on a smaller scale.

Physical methods for removal of tars

Physical methods for tar removal involve secondary measures downstream that remove tar from the gas without requiring a chemical reaction. These methods can include cyclones, cooling towers, venturi scrubbers, WESP, wet cyclonic separators, filters (baghouses, sand, ceramic), and demisters.

Table 15. Reduction of Particles and Tars Using Various Gas Cleaning Systems (Hasler and Nussbaumer 1999)

Systems	Temp. (°C)	Particle reduction %	Tar reduction %
Sand bed filter	10-20	70-99	50-97
Wash tower	50-60	60-98	10-25
Venturi scrubber			50-90
Rotational atomizer	<100	95-99	
Wet electrostatic precipitator	40-50	>99	0-60
Fabric filter	130	70-95	0-50
Rotational particle separator	130	85-90	30-70
Fixed bed tar adsorber	80		50
Catalytic tar cracker	900		>95

Ceramic filters based on SiC compositions have shown promise because of their mechanical stability. Even above 1300 °C, SiC has shown good mechanical stability with good porosity, and hot gas permeation (Innocentini *et al.* 2011; Foscolo and Bocci 2012; Nacken *et al.* 2012). Nacken's group used a SiC ceramic foam with a MgO-Al₂O₃-NiO catalytic layer that was capable of filtration at 850 °C and naphthalene conversion of 99% with 100 ppmv H₂S in the gas stream. Table 15 lists several methods and their effectiveness for cleaning producer gas. Because of tar's hydrophobic character, water scrubbers are only 30 to 40% effective, while oil scrubbers using vegetable oil (lipophilic) have a much higher tar removal performance at 50 to 90% (Paethanom *et al.* 2011; Nakamura and Yoshikawa 2015).

Cyclones depend on mass and centrifugal force for removal of particles. They have been used in tar removal; however, they are not very efficient and are used mostly for removal of particulates. Cyclones operate by centrifugal forces carrying tar and particles toward the wall of the cylinder. The taper structure of the cyclone's body keeps the spinning effect in motion until the particles fall to a collection chamber below. The gas exits out of the top (Fig. 18). However, smaller particles (fines) leave with the clean gas due to less mass and resistance to change in motion. Cyclones have been used after the gasifier for particulate removal when the temperature in the cyclone is kept above the dew point of the tars. They are often listed as an air pollution control device (precleaners) and are used to reduce the inlet loading of particulates to downstream devices such as fabric filters and electrostatic precipitators. There are cyclones that can effectively remove particles with diameter of 2 to 3 µm, and some are listed as being able to remove particulate matter (PM) at PM₁₀ (10 µm or less) and PM_{2.5} (2.5 µm or less) (Singh and Shukla 2014; Air Pollution Control 2003a). By way of comparison, the human hair has a diameter of approximately 100 µm, so one could place approximately 40 PM_{2.5} particles on the diameter of a human hair.

In general, cyclone effectiveness will decrease with increases in gas velocity, body diameter, gas exit diameter, gas inlet duct area, and gas density. The PM collection efficiency generally increases with (Air Pollution Control 2003a):

- Particle size and density
- Inlet duct velocity
- Cyclone body length
- Number of gas revolutions in the cyclone
- Ratio of cyclone body diameter to gas exit diameter
- Dust loading
- Smoothness of the cyclone inner wall

The biggest advantages of cyclones are low capital cost, the absence of moving parts, low pressure drop, the fact that temperature and pressure limitations depends on construction material, dry collection and disposal, and small space requirements. Disadvantages include inability to handle sticky materials, relatively low PM collection efficiencies, and the fact that high efficiencies units may experience high pressure drops (Air Pollution Control 2003a).

The US EPA has listed leakage of air into the dust outlet as the most common factor for decreased control of PM in cyclones.

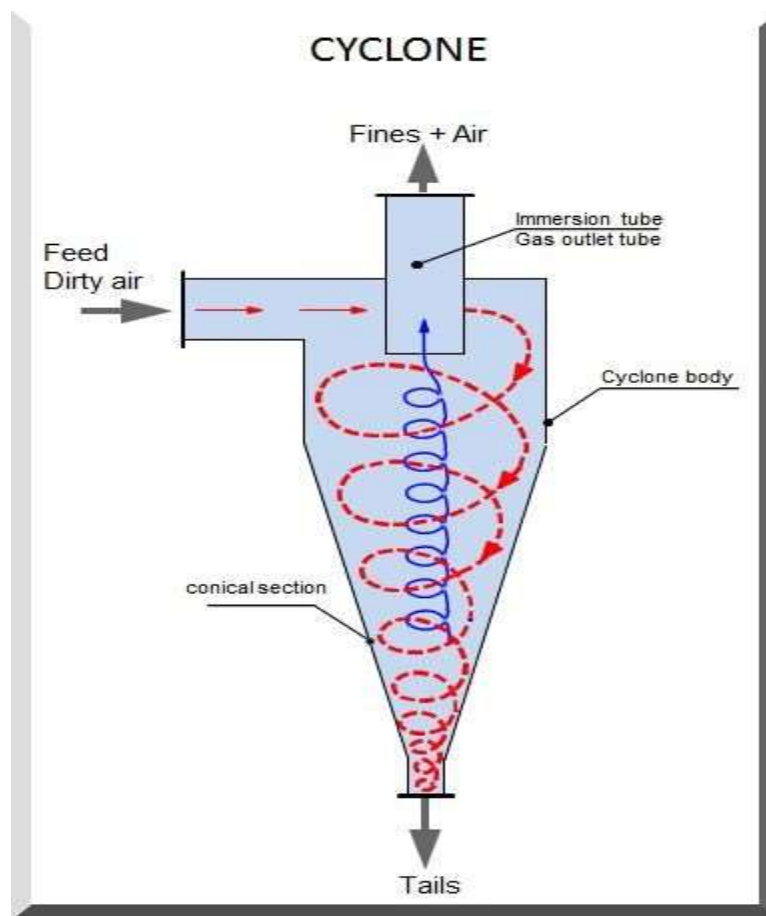


Fig. 18. Cyclone (Source: Marc Piccinin, The Cement Grinding Office); figure used with permission of the copyright holder

Zwart *et al.* (2010) noted that the traditional way to clean gas from a Low Temperature Circulating Fluidized Bed (LT-CFB) gasifier was to use only cyclones; however, this left a large amount of particles in the gas and limited its potential use.

Cooling towers and venturi scrubbers are typically used as the first wet scrubbing units for removal of heavy tar components (Chiranjeevaraoseela *et al.* 2015). In the venturi scrubber (Fig. 19), the dirty inlet gas enters the converging section where gas velocity and turbulence increases.

The scrubbing liquid is stripped from the converging section walls as it is accelerated into the throat section. The turbulence in the throat section causes the scrubbing liquid to be atomized into small droplets that interact with particles and tar compound. The mixture then decelerates, causing the droplets to agglomerate. Next, the wetted matter and excess liquid are separated from the gas stream normally by a cyclonic separator or mist eliminator. Depending on the type of venturi, the maximum inlet gas temperature can vary from approximately 500 to 2200 °F (260 to 1204 °C) (refractory-lined inlet connection). Mist eliminators (Fig. 20) are sometimes installed at the top of the column to separate any remaining liquid droplets from the gas and this reduces re-entrainment of liquid by the gas flow. Wire mesh mist eliminators, made from knitted metal, are the most common used method for removal of entrained liquid drops.



Fig. 19. Venturi Scrubber (Source: AirPol, Inc.); figure used with permission of the copyright holder.



Fig. 20. Mist Eliminator (Source: RVP Process Equipment, Inc.); figure used with permission of the copyright holder.

Wet Electrostatic Precipitators, (WESP) (Fig. 21), use direct energy to the flowing fluid medium to remove tars and particulates. The system uses electrical forces to move particles that have been entrained in an exhaust stream onto a collection plate. The gas is ionized in passing between a high voltage electrode and a grounded electrode. The charged particles and tar droplets are attracted to the grounded electrode, and the moisture in the system makes sure that the collector plates are cleaned. WESP can handle gases that dry ESP cannot handle, such as combustible material, particles that are sticky in nature, and explosive material. The dust in a WESP unit is absorbed in the liquid and drained to the collection plates. This advantage creates a high level of dust removal efficiency. A disadvantage for WESP is high capital cost, and they are not suited for highly variable conditions of variables such as flow rates, temperatures, particulates, and gas composition (Air Pollution Control- 2003d).

An electrostatic precipitator (ESP) is a dry filtration system that removes particles (dust, smoke) from a flowing gas using induced electrostatic charge. The particles that are suspended in gas pass through ionized zones around voltage discharge electrodes. Negatively charged ions are emitted into the gas and then travel to the grounded collecting plates. Particles are negatively charged, causing them to migrate to the grounded positive charge collecting plate, where they agglomerate and the charge dissipates. At preset intervals, the deposited particles are dislodged from the collecting plates by a shaking or brushing mechanism. Particles are then collected in hoppers below the collecting plates for disposal.

ESP size is the most important factor for collection efficiency. The chance of a particle being collected is greater the longer a particle stays in the ESP unit. Collection efficiency is also affected by dust resistivity, gas temperature, particle size distribution, and chemical composition of gas and dust (Air Pollution Control 2003d).

Van Paasen *et al.* (2004) reported results of experiments showing that ESP removes dust and tar droplet efficiently from biomass producer gas. Dust was decreased by more than 99%, and the tar dew point was reduced from 130 °C to 21 °C, which allowed the product gas to be used in gas engines. After 200 hours of operation, negligible fouling of the collector plates was noted. They noted that 4 seconds was enough for total tar removal and that the product gas was clean enough to protect downstream equipment against tar and particles for firing a gas engine. Carlsson (2008) reported that dry ESP can be designed for very high efficiency for all particle sizes and are common after biomass combustion, with several hundred in operation. Large ESP systems are located in CHP plants and are common in all boilers and combustors in the pulp and paper industry. With the construction material being mild steel, the temperature for a dry ESP can reach 350 °C. Dry ESPs can be designed for a wide range of temperatures and some at extreme gas temperatures of 700 °C (Air Pollution Control-2003b). Other advantages include high efficiency for small particles, dry collection and disposal allowing for easier handling, operating cost relatively low, operating under high pressure, and the ability to handle large gas flow rates. Disadvantages for dry ESP include high capital cost, the fact that wire discharge electrodes are high-maintenance items, poor suitability for highly variable processes (flow rates, temperatures, particulate and gas composition, particulate loadings), large space for installation, an explosion hazard when treating combustible gases or combustible particles, and the requirement for highly trained operating personnel (Air Pollution Control-2003b).

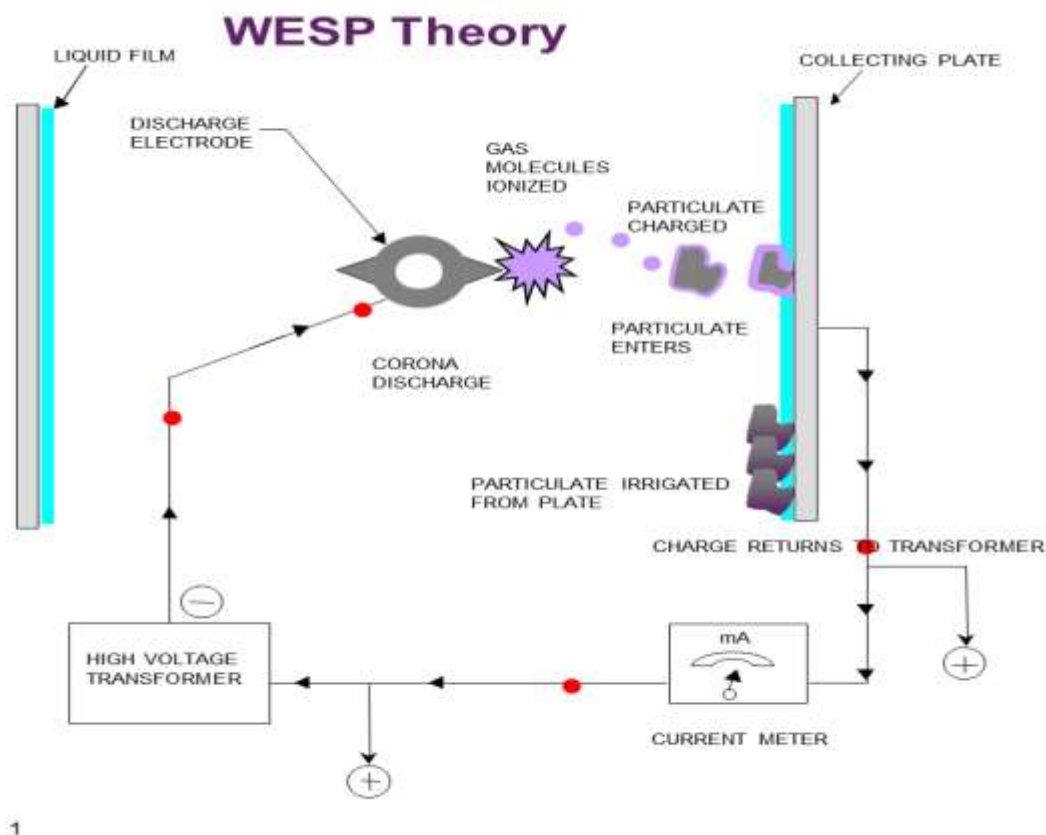


Fig. 21. Wet electrostatic precipitator (Source: AMEC FW Environmental Equipment Company); figure used with permission of the copyright holder

In scrubbers, the gas comes in contact with cooling water and then exits toward other filters to remove remaining tars. The problem with water scrubbers is the necessity of treatment of wastewater and the loss of Btu value from PAH compounds. This lowers the overall efficiency of the gasification process. Wet scrubbers will only transfer the tar dilemma from the gas phase to the liquid phase; whereas, catalytic hot gas conditioning will reduce or eliminate this problem. As noted above, most biomass tars are hydrophobic, and one plant in Austria has used a wet scrubber with bio-oils such as rape methyl esters. This methyl ester, being more lipophilic, will retain more of the tars. In their process, the spent scrubber compounds (tars and condensate) are vaporized and recycled to the combustor (Fjellerup *et al.* 2005).

Fabric filters (FF) are sometimes referred to as baghouses because they are usually configured in a cylindrical bag form. They can be designed for removal of PM₁₀, PM_{2.5}, and hazardous pollutants that are in particulate form. They can remove most metals with the exception of elemental vapor Hg (Air Pollution Control-2003c). Factors that determine collection efficiency include gas filtration velocity, particle characteristics, fabric characteristics, and the cleaning mechanism. FF need to operate under dry conditions because of the difficulty in removing damp dust from fabric; however, a few droplets can be tolerated but must be controlled. In the operation of FF, a dust cake is formed, and this will aid as a filter media until cleaning. FF can be used to absorb hydrated lime and other hydrated material for removal of gaseous impurities such as HCl and SO₂. Mwandila (2010) noted that the dedusting of the laden filter systems can be made by back-flushing with a jet pulse of compressed nitrogen.

The use of fabric filters is a proven technology for de-dusting flue gas at temperatures below 350 °C and not very effective at removing tars, which require higher temperatures. However, with ceramic fibers that can operate at a temperature of 600 °C, tars will not condense, and the efficiency is improved. Advantages for FF include high collection efficiency (course and submicron particles), insensitivity to fluctuation in gas stream conditions, pressure drops not being affected by changes in inlet dust loadings, filter outlet air being very clean, corrosion of components not normally an issue, simplicity of operation and maintenance, and the ability of precoated FF to collect submicron smokes and gaseous contaminants (Air Pollution Control-2003c; Carlsson 2008). Disadvantages for FF include temperature restriction, the fact that some dust may represent a fire or explosion hazard, the possibility that oxidizable dust causes fabric to burn, high maintenance (bag replacement), an inability to function in a moist environment, and the fact that sticky (tars) compounds may cause caking or plugging of the fabric (Air Pollution Control-2003c).

Peukert and Wadenpohl (2001) noted that fabric filters can be made from any available material of construction and are normally used with flow rates from a few cubic meters per hour to several million cubic meters per hour. The separation of particles from gas flow onto fabric is the initial separation. A dust cake is formed, which increases the filtration of particles. With the dust cake forming, there is a pressure drop, and regeneration takes place with pulse jet that produces a pressure wave across the fabric. Typical high-temperature filter elements include glass, ceramic, and metal elements, which can be made of fibers or granules. Metal elements can withstand temperatures up to 600 °C, while ceramic elements can now exceed 850 °C (Peukert and Wadenpohl 2001). Industrial applications of pulse-jet cleaned FF include utility boilers (coal), industrial boilers (coal & wood), commercial/institutional boilers (coal & wood), ferrous metals processing (iron &

steel production), mineral products (cement manufacturing, coal cleaning, stone quarrying and processing), asphalt manufacture, and grain milling (Air Pollution Control-2003c).

Barrier filters allow the gas to flow through while capturing tar material. These filters can include granular bed filters that are packed with sand, gravel, coke, coal, or pebbles. They have been used in biomass gasification to remove tar and dust from biomass gasifier with efficiencies of 80 to 95% and 60 to 95%, respectively (Mwandila 2010). Sand bed filters use mass forces to remove tar and particles and have shown a lot of success for this type removal (Hasler and Nussbaumer 1999; Pathak *et al.* 2007; Carlsson 2008; Laurence and Aschenafi 2012). Hasler and Nussbaumer (1999) reported experiments on tar reduction of raw gas from a fixed bed gasifier and showed the highest reduction to be in venturi scrubbers and sand filters. Sand bed filter had the highest efficiency for particle separation. Pathak *et al.* (2007) reported experimental results showing that reduction in tar and particulate matter was above 90%, using a sand filter for upgrading producer gas that could be used in IC engines. They noted that sand bed filters are effective because sand is:

- Neutral and non-reactive
- Inexpensive and readily available
- Available in different grain size grades
- Able to withstand high gas temperature
- Easy to clean and recycle

Thermal methods to remove tars

Gasification temperature can affect many areas in biomass gasification including gas composition, tar concentration, reaction rate, and ash build-up (Brandt and Henriksen 2000; Fjellerup *et al.* 2005; Kuo *et al.* 2010; Taba *et al.* 2012; Asadullah 2013; Subbaiah *et al.* 2014). Subbaiah *et al.* (2014) carried out experiments with groundnut shells using a FB gasifier. They showed that the concentration of H₂ and CO increased gradually with increase in temperature from 650 to 800 °C and decreased after that. In addition, the experiments revealed that the concentration of CO₂ and CH₄ decreased with increase in temperature. Asadullah (2013) noted that high tar and low yields of CO and H₂ are associated with low temperature gasification. On the other hand, high temperature gasification results in low tar and high yields of CO and H₂. The CO increase at high temperature was attributed to an increase rate of heterogeneous reactions that include the water gas and Boudouard reactions. In addition, an increase H₂ concentration is noted with the water gas reaction. Kuo *et al.* (2010) experimented with FB air gasification of biomass and found that emission concentration of PAHs increases with the operating temperature and that the addition of CaO to the bed reduces the emission concentration of PAHs during gasification. Biomass included a mixture of sawdust and polyethylene bag with average size of about 3 cm x 2.5 cm x 1.5 cm (length x width x height).

Thermal decomposition of tars, without catalyst, requires temperatures in the range of 1100 to 1300 °C to reduce large organic molecules to lower-chain small non-condensable gases. Naphthalene could be reduced by 80% and greater at 1 s at 1150 °C; however, it took 5 seconds at 1075 °C (Fjellerup *et al.* 2005; Brandt and Henriksen 2000; Prabhansu *et al.* 2015). Brandt and Henriksen (2000) reported that temperature of at least 1250 °C (residence time of 0.5 seconds) was needed to achieve high tar cracking of producer gas from an updraft gasifier. They noted a tar content of 32 mg/kg (dry feedstock) at a temperature of 1290 °C. After thermal cracking, soot was measured at 3.6 g/kg dry feedstock, and the energy content of the gas was 19% higher than before cracking with a lower heating value of 6.0 MJ/Nm³.

Hot gas cleaning can include cyclones, hot filters, *e.g.*, ceramic candles, ceramic fibers, ceramic fabrics, metallic fabrics, and ESP. Other methods can include thermal or catalytic cracking and catalytic reforming. Shen and Yoshikawa (2013) reported that catalytic candle filters are capable of particle filtration and catalytic cracking of tar from producer gas in one step. Simeone *et al.* (2010) studied the behavior of a catalytic ceramic candle filter made with SiC porous structure coated with a mullite membrane and integrated with Ni-based layer for naphthalene decomposition. Naphthalene (varying concentration up to 9 g/Nm³) was used as the model compound in a mixture of gases consisting of CO (14%), CO₂ (14%), H₂ (7%), CH₄ (5%), and varying concentrations of N₂ (30, 40, 50%) and H₂O (30, 20, 10%). Gas velocity was 2.5 and 3 cm/s at atmospheric conditions and temperature ranging from 700 to 850 °C. Results included:

- There was higher naphthalene conversion with increasing temperature.
- Temperature at 850 °C and 30% H₂O produced a 99.4% conversion of naphthalene (2.5 g/Nm³ of naphthalene), while only 98.5% with 7.8 g/Nm³ of naphthalene in the gas.
- Higher steam content produced higher conversion of naphthalene.
- Toluene was detected as a product during the reaction, while no benzene was identified.

During biomass thermo-chemical reactions, an increase in temperature results in a loss of hydroxyl groups (OH) followed by methyl groups (CH₃), and this leads to cracking of the heavy aromatic tar compounds into lighter and less problematic smaller-chain compounds. With this increase in temperature, larger ring formation will occur due to fusion. These 4- and 5-member rings are very refractory and require extremely high temperature for depolymerization or cracking. Thermal depolymerization of tars can occur under inert conditions or with reactants in the producer gas such as H₂O, H₂, or CO₂. The experiments of Kuo *et al.* (2010) showed that emission concentrations of PAHs decreased with the increase in operating temperature. Mwandila (2010) stated that Rensfelt and Elstrom had to reach temperatures higher than 1100 °C to reach acceptable levels for thermal cracking of tars. Vreugdenhil and Zwart (2009) concluded the following on thermal cracking and reactivity of tars:

- Depolymerization rate of tars increases with H₂O and CO₂, while it decreases with H₂.
- Production of gas with low tar concentration under a non-catalytic system requires high temperatures approaching 1200 °C for a thermal cracking environment.
- Thermal cracking is also dependent on residence time and tar composition.
- Larger PAH-3 rings and higher (chrysene, anthracene, acenaphthylene) have a greater tendency to form carbon than smaller ring compounds, such as 1 and 2 ring compounds (benzene and naphthalene, Fig. 22).
- Thermal cracking of tars produces some carbon (carbon rich dust or soot).
- Reactivity of carbon in a gasification atmosphere is very low compared with tars.
- Reactivity of carbon in a gasification atmosphere is improved by increasing temperature and/or long residence time.
- Radical reactions play an important role in thermal cracking.
 - I. Breaking of chemical bonds
 - II. Propagation reaction by formation of new chemical bonds
 - III. Hydrogen transfer

IV. Isomerization reactions

V. Termination reactions

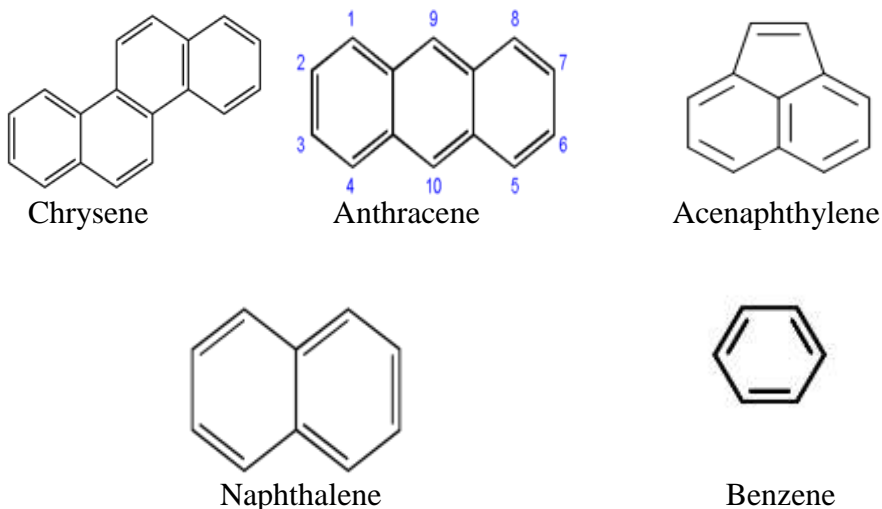


Fig. 22. Structures of Chrysene, Anthracene, Acenaphthylene, Naphthalene, and Benzene

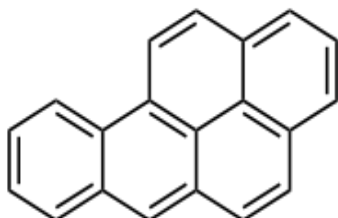


Fig. 23. Benzo[a]pyrene

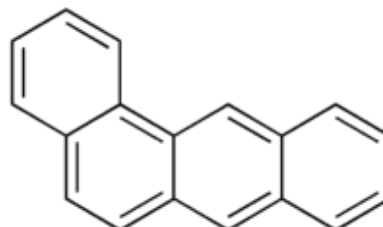


Fig. 24. Benz[a]anthracene

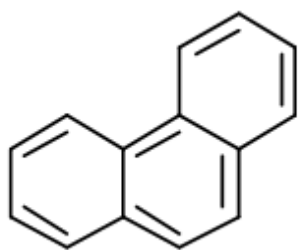


Fig. 25. Phenanthrene

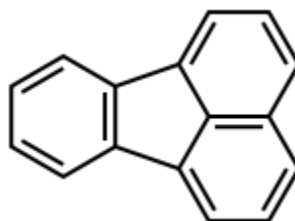


Fig. 26. Fluoranthene

Biomass with reactive structure containing alkyl derivatives and heteroatoms are easily cracked at high temperature. Britt *et al.* (2004) noted that yields of PAH increased with an increase in temperature and gas phase residence time. They stated that isoprene ($\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$), which is a major component of tobacco smoke, forms PAH compounds during pyrolysis at 600 to 800 °C, with benzo[a]pyrene being one of the compounds (Fig. 23). They concluded that terpenes at high temperatures and short residence times produced 3-, 4-, and 5-ringed aromatic hydrocarbons. High temperatures and long residence times produced larger PAH compounds such as benzo[a]pyrene (Fig. 23) and benz[a]anthracene (Fig. 24). These high molecular weight compounds showed a

larger yield than smaller PAH compounds such as phenanthrene (Fig. 25) and fluoranthene (Fig. 26).

Britt *et al.* (2004) stated that the reaction mechanism for formation of PAH involves a free radical pathway. This finding was based on an experiment showing that combustion of 1,3-butadiene in a fuel rich flame produced monocyclic PAH involving free radical pathways with $C_4H_5\cdot$ as the dominant species. Diels-Alder reaction of 1,3-butadiene forming PAH in the flame was not noted due to reaction being too slow and concentration of the reagents too low.

Experimental work by van Paasen and Kiel (2004) using a small scale BFB gasifier on woody biomass at different temperatures and gas residence time, resulted in the following:

- Total tar concentration decreased by a factor of five when the temperature increased from 750 °C to 950 °C.
- Tar composition changed from an alkyl substituted PAH and heterocyclic compounds, to a non-substituted PAH compound.
- Above 800 °C, tars increased in molecular size, which increased the dew point.
- An increase in gas residence time in the freeboard resulted in similar results as gasification temperature increase, but the results were less pronounced.

Vreugdenhil and Zwart (2009) noted that tars produced by biomass and coal will crack at a lower temperatures than PAH model compounds such as naphthalene and phenanthrene. They concluded that this was due to heteroatoms like N and O and pendant groups including -OH and CH_3 . These groups are much more reactive than the aromatic compounds and would de-polymerize at lower temperatures.

Shi *et al.* (2016) noted that when oxygen was added to the gasifier, tar production was suppressed. They stated that under an oxidative environment free radicals were formed, which attacked the weak bonds between tar molecules.

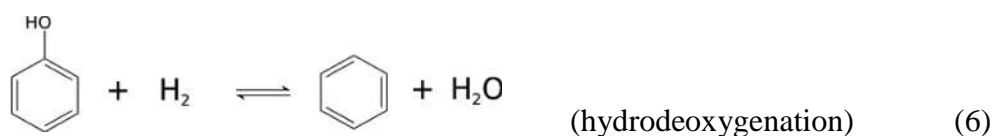
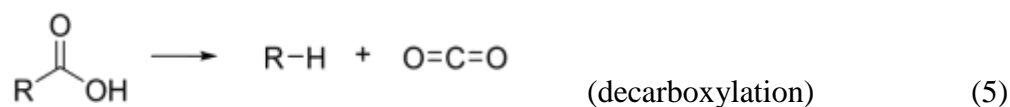
Catalysts

Dolomite, Olivine

Two of the most important indicators of performance for a catalyst are tar reduction and that the catalyst can effectively convert highly oxygenated biomass into hydrocarbon compounds that can be used as fuel or blended with current fuels. How a catalyst reacts to create producer gas is influenced by temperature, particle size, space time, and composition of gas (Capital Energy 2015). Some of the most important properties for choosing a catalyst include effective tar removal, high attrition resistance, resistance to deactivation, easy regeneration, minimal fouling, and low cost (Caraccio *et al.* 2014).

Currently, researchers are looking at catalysts for deoxygenation, hydrogenation, and C-C coupling. Dutta *et al.* (2016) noted that C-C coupling was necessary during pyrolysis vapor upgrading to improve bio-oil quality, which will increase the proportion of diesel/jet fuel range. They stated that downstream hydroprocessing of bio-oil is much more challenging than in the petroleum refinery due to reactive oxygenated species, which can produce coking and other problems during reactor operation. The goal is to reduce oxygenates and chemical reactivity through catalytic upgrading prior to condensation. Deoxygenation can occur through decarbonylation (Eq. 4 with CO removal) and decarboxylation (Eq. 5 with CO_2 removal). As shown, both decarbonylation and decarboxylation proceed through cleavage of C-C bonds, resulting in reduction of oxygen content at the loss of carbon. Between the two methods, decarboxylation is the most

preferred reaction due to the loss of two oxygen atoms per carbon atom. However, the most preferred deoxygenation route is hydrodeoxygenation (Eq. 6). This is preferred due to carbon efficiency, where importance is placed on reducing losses from coke and non-condensable gases including CO and CO₂. Hydrodeoxygenation reaction occurs through the cleavage of C-O bonds and consumes one hydrogen molecule per oxygen atom (Dutta *et al.* 2016).



Alkali and alkaline earth metals have been shown to have catalytic properties for thermal depolymerization of tars. Catalytic activity of calcined dolomite has been widely studied for tar reduction as a primary catalyst and also in a secondary reactor (Leppalahti *et al.* 1992; Timpe and Young 1995; Delgado *et al.* 1996; Delgado and Aznar 1997; Lammers *et al.* 1997; Prez *et al.* 1997; Seshadri and Shamsi 1998; Gil *et al.* 1999; Rapagna *et al.* 2000; Sutton *et al.* 2001; Myren *et al.* 2002; Corella *et al.* 2004; El-Rub 2004; Fjellerup *et al.* 2005; Caglayan 2006; Seitkaliyeva *et al.* 2007; Sundac 2007; Gusta *et al.* 2009; He *et al.* 2009; Li *et al.* 2009; Xie *et al.* 2009; Yu *et al.* 2009; Meng *et al.* 2010; Lisy *et al.* 2012; Kaminska-Pietrzak *et al.* 2013; Simell *et al.* 2014; Husmann *et al.* 2016). Santos *et al.* (2014) even used calcined dolomite as a heterogeneous catalyst to produce methyl esters from soybean oil. It was found to be an effective basic catalyst for the transesterification of triglycerides that could be used in biodiesel production. He *et al.* (2009) used calcined dolomite for catalytic steam gasification of MSW for producing H₂. Hu *et al.* (2006) used calcined dolomite for catalytic steam gasification of apricot stones for producing H₂. Both groups reported that tar reduction using calcined dolomite was notably active only above the temperature of 800 °C. Calcium oxide is now an almost universal catalyst for increasing the yield of H₂ (Sikarwar *et al.* 2016).

At temperatures above 800 °C, calcined dolomite displays its catalytic activity by producing greater H₂ concentration and a lowering of tar amounts in the product gas. Increased concentration of H₂ was achieved at a higher ratio of steam to MSW (S/M), which was due to more steam favoring the water gas shift reaction (He *et al.* 2009). Delgado *et al.* (1996) found that coke formation and elimination by steam gasification increased the life of natural minerals such as dolomite and limestone.

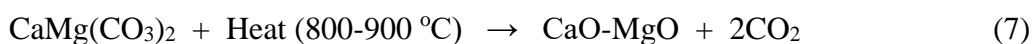
Dolomite is a mineral whose composition is calcium magnesium carbonate-CaMg(CO₃)₂ with minute amounts of iron, aluminum, and silicon oxides (Table 16). Shen and Yoshikawa (2013) reported that the iron content in dolomite promoted tar conversion and the water gas shift reaction. Orio *et al.* (1997a,b) reported a 20% increase in the activity of dolomite for tar elimination by increasing its pore diameter or the Fe₂O₃ content.

Table 16. Chemical Composition of Dolomite, Limestone, and Olivine (%)

Material	MgO	CaO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CO ₂	Reference
Dolomite Norte	20.9	30.9	1.7	0.5	0.6	45.4	Dayton 2002
Dolomite Finnish	18.3	26.6	5.4	2.1	1.1	42	Dayton 2002
Dolomite Chilches	17.5-19.0	29.7-31.3	3.2	0.74-0.80	1.19	47.4	Dayton 2002
Dolomite Malaga	21.2	30.6	--	0.01	0.40	47.3	Dayton 2002
Dolomite Sevilla	21.5	30.5	--	0.01	0.60	47.2	Dayton 2002
Dolomite Northeast USA	16.2	32.6	3.3	--	0.47	41.0	
Dolomite Southeast USA	5.2	19.5	32.5	6.1	9.9	27.0	
Sivrihisar-Eskisehir	22.6	20.3 as CaCO ₃ *	13.3	0.3	1.9	40.7 as others*	Caglayan 2006
Dolomite Kalkkima	18.3	26.6	5.4	2.1	1.1	42	Dayton 2002
Dolomite Myanti	17.8	26	2.8	0.4	0.4	44	Dayton 2002
Dolomite Loukolampi	16	24	14	0.3	7	39	Dayton 2002
Limestone Gotland	0.1	48	1.1	0.1	0.4	49	Dayton 2002
Olivine Magnolithe GmbH	48-50	--	39-42	8-10	--	--	Dayton 2002
Olivine North Carolina	50.5	0.2	40.1	6.7			Redeker 1971

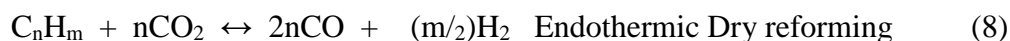
*Calculate 20.3% CaCO₃ as 36.2% CaO. 40.7% others seems to be CO₂. Caglayan (2006) list 0.9% as H₂O.

Dolomite's composition can vary from site to site, but the general formula shows 30% CaO, 21% MgO, and 45% CO₂ (weight basis). After calcination and elimination of CO₂ (Eq. 7), dolomite becomes a highly porous material, making the basic oxides (CaO and MgO) an active catalyst that is capable of tar reduction. This large internal surface area and surface oxides provides calcined dolomite with more catalytic activity than uncalcined. Dolomite, being a nonmetallic oxide that is naturally occurring, is inexpensive and readily available. Dolomite's activity was compared to limestone, olivine, and ilmenite (iron-titanium oxide) with results showing that dolomite had higher activity even when short residence times were applied (Kaminska-Pietrzak *et al.* 2013).



Lammers *et al.* (1997) and Caglayan (2006) studied the catalytic active properties of calcined dolomite as a bed material with and without air addition. Their findings established that a secondary air addition into the gasifier reduced tar compounds and could prolong the activity of dolomite. Gil *et al.* (1999) reported a raw flue gas below 1 g/m³ in

a fluidized bed that contained 15 to 30 wt.% of calcined dolomite and the rest being silica sand. In this experiment, a continuous feed of dolomite (3%) mixed with biomass was used to replace the eroded dolomite from the gasifier bed. Simell *et al.* (1992) demonstrated that the activity for tar decomposition using dolomite increased with a higher ratio of Ca/Mg, smaller dolomite grain size, and increasing the content of active metals such as iron. Gusta *et al.* (2009) reported that dolomite improve tar conversions and that iron content in dolomite played a vital role in promoting tar decomposition and the water gas reaction. They studied the gasification of wood biomass using dolomite from Canada, Australia, and Japan and found that the maximum tar conversion occurred when the iron content in dolomite reached the level of 0.9 wt. percent. Sutton *et al.* (2001) noted that with dolomite, dry tar reforming with CO₂ was more effective than steam reforming (Gasification reaction Eq. 8)



Husmann *et al.* (2016) experimented with the in-situ desulfurization of calcined and un-calcined dolomite in a bubbling fluidized bed gasifier. Results showed un-calcined dolomite to have twice the conversion (CaO to CaS) compared to calcined. Experiments by Lisy *et al.* (2012) showed that in-situ addition of dolomite to a fluidized bed resulted in a 60% reduction of tar; however; they confirmed that it was not possible to remove all of tar from the gas by primary methods. Kiel *et al.* (2004) reported that higher gasification temperature and longer residence time using dolomite resulted in lower amounts of water soluble tars and less water treatment required. They also reported the following on primary addition of dolomite:

- Only a few water soluble tars
- Less condensable tars
- Less contaminants in fuel gas
- Lower propensity for aerosol and condensate formation
- Lower carbon content in ashes

Srinakruang *et al.* (2006) reported that dolomite, as a tar catalyst, was more resistant to sulfur and coking when nickel was applied to it. Guan *et al.* (2014) reported metal doping on dolomite and olivine promoted their catalytic activity toward tar cracking. They reported that the addition of Ni to dolomite increased the tar conversion (650 °C) from 43 to 84% and the carbon deposition on the substrate was negligible. They also reported that Ni doped on calcined olivine showed the following:

- Toluene conversion of about 85% (750 °C) where olivine alone had very little activity
- Good selectivity to H₂, CO, and CO₂
- Naphthalene conversion by almost 2 times higher than olivine itself

Deactivation of dolomite by carbon deposition can be solved by steam reforming of carbon deposited on dolomite's surface (Gasification reaction, Eq. 9 below).



Olivine is a magnesium iron silicate (Mg,Fe)₂SiO₄ mineral that is being explored as an active material for catalytic cracking of tar compounds during biomass gasification. Its structure consists of silicate, in which magnesium and iron cations are located in the

silicate tetrahedra. Olivine's mechanical strength is comparable to sand even at very high temperatures. Compared to dolomite, olivine has slightly lower tar reduction and generates less particulate; however, it has higher resistance to abrasion (Table 17) and carbon deposition (Rapagna *et al.* 2000; Corella *et al.* 2004; Rauch *et al.* 2004; Virginie *et al.* 2012; Kaminska-Pietrzak *et al.* 2013). Rauch *et al.* (2004) reported that olivine showed attrition resistance and catalytic activity for tar reforming using a dual fluidized bed reactor. Swierczynski *et al.* (2006) presented experiments showing that iron present in olivine was a big factor in its catalytic activity for tar reduction. Shen and Yoshikawa (2013) reported that olivine's activity or activation depends on the content of iron oxide.

Table 17. Advantages and Disadvantages of Catalysts

Catalyst	Advantages	Disadvantages	References
Dolomite	Inexpensive, abundant, high tar conversion (~95%)	Fragile material and quickly erodes	Vivanpatarakij <i>et al.</i> 2014; Lahti and Romar 2010.; Shen and Yoshikawa 2013
Olivine	Inexpensive, high attrition resistance	Lower catalytic activity than dolomite	Lahti and Romar 2010; Shen and Yoshikawa 2013
Activated Alumina	High tar conversion comparable to dolomite	Rapid deactivation by coke	Lahti and Romar 2010
Transition Metals	Able to attain complete tar reduction at ~900 °C, increase the yield of H ₂ and CO, Ni-based catalyst 8-10 times more active than dolomite	Rapid deactivation because of sulfur and high tar content, relatively expensive	Lahti and Romar 2010; Vivanpatarakij <i>et al.</i> 2014
Iron Ores	Inexpensive and Abundant	Rapidly deactivated in absence of hydrogen and lower catalytic activity than dolomite	Lahti and Romar 2010
Char	Inexpensive, natural production, high tar conversion comparable to dolomite	Consumption because of gasification reactions, properties depends on biomass and gasification process	Lahti and Romar 2010; Al-Dury 2009

Rabou *et al.* (2009) stated that reduction of tars in all tar classes can be accomplished by adding dolomite or olivine to the gasifier bed material. The experiments of Rapagna *et al.* (2000) showed that when olivine was used in a FB gasifier, with steam as the gasifying agent, there was good performance for tar destruction. They stated that the role of iron in olivine was a positive factor for decomposition of tar. In addition, they showed an increase in producer gas for H₂, CO, and CO₂; however, methane remained the same and was not reformed. Another positive point in this experiment was that olivine showed good stability with negligible fines.

In a pilot plant experiment based on CFB and BFB gasifier, Corella *et al.* (2004) found that dolomite generated 4 to 6 times more particulates in the producer gas than

olivine. Devi's (2005) experiments showed that pre-treatment of olivine with air at 900 °C showed a marked improvement for tar removal. She noted the following during her experiments:

- During pre-treatment, olivine changed color from a pale green to brown-red indicating a change in oxidation state of iron from Fe²⁺ to Fe³⁺
- Fe migrated toward surface with higher treatment times
- Higher catalytic activity was found when Fe was at the olivine surface, and Fe³⁺ phases after pre-treatment
- The material was found to be highly attrition resistant

Rapagna *et al.* (2000) studied the performance of olivine, dolomite, and sand as a primary method for tar reduction in a bubbling fluidized bed lab scale gasifier. When comparing dolomite and olivine to sand, they observed the following:

- Gas yield was increased by more than 50%
- Tar was reduced by 20 times
- Char was reduced by 30%
- Olivine showed a negligible production of fines in the fluidized bed

Another class of naturally occurring earth metals that have shown promise for lignin depolymerization is the hydrotalcites (Mg₆Al₂CO₃(OH)₁₆·4H₂O). Kruger *et al.* (2016) demonstrated that using hydrotalcite on a lignin model dimer (2-phenoxy-1-phenethanol) yielded phenol and acetophenone. While the catalyst was not active for C-C bond cleavage on lignin model and also showed no effect on dimers with an alpha-OH group, it did demonstrate potential for selective depolymerization in a heterogenous system of β-0-4 groups on lignin (Fig. 27).

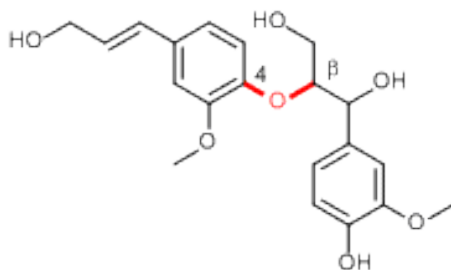


Fig. 27. Beta-0-4 linkage in lignin

Activated alumina

Activated alumina (aluminum oxide-Al₂O₃) is produced by dehydroxylating aluminum hydroxide, and this gives it the porous structure that makes it an excellent adsorbent for arsenic, fluoride, sulfur, and selenium and has shown catalytic activity for tar decomposition.

Simell *et al.* (1992) studied activated alumina for decomposition of tar in a tube reactor at a temperature range of 700 to 900 °C and found that it had nearly the same catalytic activity as dolomite. Research by Filippis *et al.* (2015) showed that aluminum oxide placed in a secondary fixed bed reactor (800 °C) was capable of tar removal of more than 50% and reduction of particulates by 80%. They noted that Al₂O₃ spheres (5 mm in diameter) had high porosity and were very resistant to high temperature. The experiment consisted of a medium industrial scale plant (250 kW_i) that fed olive husk to an updraft

reactor where syngas, tar, and particulates exit from the top of the reactor at 550 °C. The producer gas was then sent to a second reactor (Al_2O_3 , 800 °C) where endothermic tar cracking and reforming occurred. Air was injected into the secondary reactor to keep it at a constant temperature of 800 °C. The syngas was cooled from 800 °C to 350 °C by heating the gasifying air, and it proceeded through a cyclone where more particulates were removed. For additional cleaning of residual tar, the syngas is sent to a water direct contact heat exchanger. Next, the syngas is sent to an equalization tank, where it can be used to maintain a constant flow of syngas, at 50 °C, to an internal combustion engine coupled to an electric generator producing 60 kW_e.

Other tar-reforming catalysts include acid catalysts such as zeolites, which is a hydrated microporous aluminosilicate mineral. Y-zeolites have a ratio of silica to alumina of 3 or higher, and this high ratio aids in the catalytic cracking of high boiling fractions in petroleum crude (Holderich *et al.* 1988). Other forms of zeolite have been used in adsorption of CO₂ from gas streams and in purification of air. Because of the high content of silica, this catalyst is very stable and can be restored numerous times after catalytic reactions. Zeolites exhibit the following:

- High surface area
- High adsorption capacity
- Strong tolerance toward nitrogen and sulfur compounds
- Well define pore structure
- Easy to regenerate
- Excellent thermal stability
- Low price

Y-zeolite was found to remove about 100% tars from fuel gases at a temperature of 550 °C (Dung *et al.* 2013). Zeolite catalysts have been used in the following areas:

- Petrochemical Industry for fluid catalytic cracking of heavy crude oils
- Nuclear Industry for controlling leaks of radioactive material
- Chemical Industry for production of gasoline from methanol
- Organic synthesis including electrophilic and nucleophilic substitution reactions, isomerization of double bonds, and addition, elimination, and hydrogenation reactions

Jenkins (2016) reported on a two-component catalyst system that could take MSW and first generate alcohols from syngas and then convert these alcohols into aromatic hydrocarbons. The gasification process converted MSW first into syngas, and after gas cleaning the syngas was fed into a high-pressure reactor consisting of MoO₃ embedded inside zeolite. He noted that MoO₃ promoted syngas conversion into alcohols, *e.g.*, ethanol and propanol. Next, zeolite promoted alcohol conversion into aromatic compounds. Because of zeolite's pore size, the molecular weight distribution was from 78 to 160 g/mol, and this would produce compounds such as toluene, xylenes, and trimethyl benzene.

Transition metals

The International Union of Pure and Applied Chemistry (IUPAC) has defined transition metals as elements that have partial filled d sub-shells or ones that can form cations with an incomplete d sub-shell. This grouping includes elements in the d block of the periodic table, and some scientists have included the f-block, which includes the lanthanide and actinide elements and have labeled this the inner transition metals.

Transition metals have been shown to have catalytic activity for cracking and reforming of tars (Kaminska-Pietrzak *et al.* 2013; Caraccio *et al.* 2014). Nickel catalysts have high catalytic activity and are often used in the petroleum industry for methane and naphtha reforming. However, support material plays a vital role in its resistance to sintering, poisoning, and carbon deposition. Vivanpatarakij *et al.* (2014) noted that 20% Ni loaded on an Al₂O₃ support had good stability and was effective at reforming tar using steam (steam to carbon ratio S/C of 5) and a reaction temperature of 650 °C. The surface area and pore volumes of Al₂O₃ allowed for heavy loading of Ni. Long *et al.* (2012) carried out experiments showing that magnesium nickel silicate (MNS) catalyst had high activity for converting methane, light hydrocarbons, and tar into syngas even in the presence of H₂S and/or NH₃. They concluded that MNS is a promising catalyst for conversion of biomass to power, liquid fuels, and valuable chemicals. Singh *et al.* (2014) reported that Han and Kim showed that Ni/dolomite (anticoking properties) in a secondary reactor had catalytic activity comparable to commercial steam reforming catalysts. Furusawa and Tsutsumi (2005) investigated the catalytic performance of Co/MgO and Ni/MgO for steam reforming of naphthalene and found that Co/MgO catalyst had higher activity than Ni/MgO. The main advantage of high temperature (900 °C) nickel-based catalysts is their ability to attain complete tar elimination. El-Rub *et al.* (2004) reported studies by Olivares that commercial nickel based catalyst are 8 to 10 times more active than calcined dolomites under the same conditions. Dayton (2002) reported 99% tar conversion with Ni catalyst operating in the range 750 to 850 °C with a dolomite guard bed that was used to reduce the initial tar lever from the gasifier. Courson *et al.* (2002) developed a nickel-based catalyst by infusion of nickel oxide into olivine and calcination at temperatures of 900 °C and above. Tests revealed the following:

- Olivine with its hardness and density proved to be an excellent support and link for nickel oxide.
- Nickel was the active phase of the catalyst in dry reforming of methane.
- No sintering or carbon deposits were observed on catalyst surface.
- No change in olivine structure or size of nickel deposits were observed.
- There were excellent results for catalytic gasification of biomass to CO and H₂.

Several authors have experimented with nanomaterial for catalytic efficiency because of its high surface area (Haruta and Date 2001; Yin *et al.* 2004; Li *et al.* 2008; Richardson *et al.* 2013; Shen and Yoshikawa 2013; Alshammari *et al.* 2016; Cui *et al.* 2016; Wang *et al.* 2016). Metal nanoparticles have been shown to have excellent catalytic performance due to their large surface area. Gold (Au) particles with diameters less than 10 nm have proven to be an active catalyst, while the catalytic activity decreases when the Au diameter increases. High catalytic activity was noted when Au was deposited as nanoparticles on metal oxides. An Au group 3.5 nm (3 atoms thick) is where Au loses its metallic nature, and some have suggested that this transition is the reason for its high catalytic activity (Haruta and Date 2001; Alshammari *et al.* 2016). Cui *et al.* (2016) designed ruthenium nanoparticles supported on a nitrogen (dicyanamide)-doped carbon material. The authors noted that this material had excellent activity for selective hydrogenation of arenes and in the transformation of aromatic ethers to alicyclic compounds. In addition, it maintained the phenyl and benzyl C-O bonds, which opens a new approach for valorization of lignin compounds. Li *et al.* (2008) developed a nano-NiO/Y-Al₂O₃ catalyst for tar removal in a biomass gasification pyrolysis system to improve the quality of produced gases. Tests revealed that the nano-NiO/Y-Al₂O₃ catalyst had a

NiO load of over 12 weight percent and had a higher BET surface area than commercial nickel-based catalysts. Experiments showed tar removal efficiency of 99% for catalytic pyrolysis at 800 °C with gas yields increasing significantly. For example, after the addition of nano catalyst, the percentage of CO₂ and CH₄ decreased, while H₂ and CO increased considerably. Shen and Yoshikawa (2013) noted that Corella's group tested several commercial nickel-based catalysts and compared product yields and gas composition to nano-NiO/Y-Al₂O₃ (Table 18). The results showed a definite improvement in gas quality for the prepared nano-NiO/Y-Al₂O₃. It had a higher H₂ and CO content and lower percentage of CO₂ compared to the commercial Ni-based catalyst. Richardson *et al.* (2013) experimented with applying a vacuum during impregnation of nickel and lignocellulosic matrix. This formed a strong interaction such that Ni⁰ nanoparticles were formed *in situ* during pyrolysis at temperatures below 500 °C. These nano-nickel particles exhibited catalytic properties for PAH compounds, and this reveals a promising strategy for cleaning producer gas. The experiments of Yin *et al.* (2004) showed that nanocomposite (impregnation of carbon nanotube (CNT) with Mg(NO₃)₂·6H₂O in ethanol solution followed by calcination) MgO-CNTs is thermally more stable and less reactive toward H₂ than pure CNT.

Table 18. Product Yield and Gas Composition from Pyrolyzing Sawdust with and without Catalyst (Shen and Yoshikawa 2013)

Conditions	Product yields (wt%,daf*)				Gas composition (vol%)						
	Gas	Tar	H ₂ O	Char	H ₂	CO	CO ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	
Primary pyrolysis without catalyst at 800 °C	62.9	18.2	7.1	11.8	18.8	22.3	39.3	16.5	2.6	0.5	
Catalytic pyrolysis with NiO/Y-Al ₂ O ₃ catalyst											
600 °C	77.8	1.9	8.4	11.9	42.3	22.5	27.6	6.1	1.1	0.4	
700 °C	80.9	0.8	6.5	11.8	45.1	33.6	16.7	3.7	0.7	0.2	
800 °C	85.2	0.2	3.0	11.6	49.2	42.2	5.9	2.1	0.5	0.1	
Catalytic pyrolysis with commercial catalyst											
600 °C	71.4	7.6	9.2	11.8	37.0	21.6	30.9	8.7	1.4	0.4	
700 °C	78.1	3.3	6.8	11.8	42.6	27.8	22.5	5.8	1.0	0.3	
800 °C	82.5	1.6	4.2	11.7	45.5	36.1	14.2	3.4	0.7	0.1	

*daf = dry ash free

Other expensive transition metals that have been researched include: cobalt (Co), platinum (Pt), ruthenium (Ru), palladium (Pd), and rhodium (Rh).

Iron compounds

Iron has been known to have a positive influence on the decomposition of tar compounds (Simell *et al.* 1992; Rapagna *et al.* 2000; Caglayan 2006; Swierczynski *et al.* 2006; Li and Suzuki 2009; Hanaoka *et al.* 2012; Nordgreen *et al.* 2012; Virginie *et al.* 2012; Shen and Yoshikawa 2013; Rapagna *et al.* 2014; David 2015). Salts of alkali metals and iron have been reported to not only catalyze gasification reactions but also serve as a heat exchanger and provide heat for the required system (Caglayan 2006). Nordgreen *et al.* (2012) conducted experiments showing that metallic iron stationed in a separate catalytic bed reactor had greater capacity for total tar decomposition (60%) in the product gas

compared to iron in the oxidized state (18%). Simell *et al.* (1992) noted that the activity of dolomite was increased by the presence of iron. Li and Suzuki (2009) reported tar decomposition from 40% to over 90% by addition of iron oxides to dolomite.

Hanaoka *et al.* (2012) used a Fe-supported activated carbon to remove PAHs, H₂S, COS, and particles. David (2015) reported that ilmenite (titanium iron oxide-FeTiO₃) had tar decomposition activity during steam reforming. He concluded that the Fe-containing species in ilmenite was highly dispersed and this contributed to its high activity. He also noted that the titanium oxide functions as a support that could inhibit sintering and agglomeration.

Ferrous compounds have proven to be very effective in the removal of ammonia at high temperatures; however, calcareous and ferrous compounds can increase the ammonia concentration at low temperatures. This reaction takes place by converting part of the organic nitrogen into ammonia if the gas has sufficient volume of tar (Leppalahti *et al.* 1992). Virginie *et al.* (2012) evaluated the efficiency of Fe/olivine in a fluidized bed reactor as a primary catalyst and found that there was a dual effect on tar decomposition. First, it acts as a catalyst for tar and hydrocarbon reforming, and lastly it acts as an oxygen carrier that transfers oxygen from the combustor to the gasifier. They demonstrated that the Fe/olivine catalyst structure was preserved even with a large number of redox cycles. The slight amount of carbon build-up on the Fe/olivine surface was easily oxidized in the combustion zone.

Char

Char is a carbon material that is formed by heated organic compounds that are partially burned or heated with limited air (incomplete combustion). Char has excellent structural properties and catalytic activity for tar removal due to its porous structure, surface area, and mineral content (Fjellerup *et al.* 2005; Kirubakaran *et al.* 2009; Paethanom *et al.* 2011; Rapagna *et al.* 2014; David 2015; Liu *et al.* 2016). David (2015) reported that the structural properties of char were favorable for dispersion of nano-Fe catalyst. These nano-Fe clusters were found to have high catalytic activity for tar reforming at temperatures of 800 °C or greater. Fjellerup *et al.* (2005) reported that tar cracking can be accomplished by tar being absorbed on the surface of porous char, which then increases the residence time resulting in depolymerization. Liu *et al.* (2016) stated that there were three methods for preparing char-supported catalysts. They include:

- Mechanically mixing metal ions with bio-char that can cause metal particles to stay on the outer surface of the char support
- Pyrolysis of metal ions by impregnating with biomass
- Impregnating bio-char

Liu *et al.* (2016) considered pyrolysis of metal ions by impregnating with biomass to be the most efficient approach for tar reforming. This tar reforming efficiency was due to metal nanoparticles being formed inside the support *via* impregnation and pyrolysis. Rapagna *et al.* (2014) carried out experiments indicating that char and olivine dust particles that collected on a ceramic filter in the freeboard were capable of catalyzing the steam reforming of tar compounds produced during biomass devolatilization.

Because of their highly porous structure, activated carbon products can be used as a catalyst support system for metal ions and as a transport media for PAH molecules. This combination would result in tar molecules being trapped in the AC's internal surface with PAH molecules being reduced to smaller chain hydrocarbons.

Rabou *et al.* (2009) set up an experiment by filling a reactor tube with active material (ash) sandwiched between pebbles and heated to 750 to 900 °C. A side stream of producer gas from a BFB gasifier was added to the reactor tube. Experimental work showed the following:

- Ash from paper sludge and chicken manure showed tar cracking activity.
- Char from biomass fuels with low ash content showed some tar cracking activity.

Carlsson (2008) found that the main part of ash from biomass (wood chips) comprises Ca, K, Si, Mg, Mn, Al, Fe, P, Na, and Zn. The alkali and alkaline earth metals (AAEM) that are in wood ash, have been shown to have catalytic activity toward tar reduction by thermal depolymerization.

Al-Dury (2009) used a FB gasifier at 800 °C (biomass was wood chips) and a catalytic filter temperature of 400 °C to test the catalytic activity for tar reduction for active carbon, coal char and black coke. Steam oxygen mixtures were used as gasification agents. In his experiments, all three catalysts (active carbon, coal char, and black coke) showed an approximate tar removal efficiency between 95 and 100%. He concluded that the large surface area and average particle size of carbon had a large influence on tar removal.

Catalytic activity of alkaline and alkali metals have been noted for their reduction in tar during reforming of hydrocarbons (Kaminska-Pietrzak *et al.* 2013). Kirubakaran *et al.* (2009) reported that produced char may react with water vapors to create CO and H₂ in the presence of catalytic ash. They also stated that reactions take place when carbon, hydrogen and oxygen molecules are chemisorbed on the ash matrix. Sutton *et al.* (2001) reported that alkali metals that are in ash are effective at tar removal when mixed with biomass.

Other catalyst systems that are currently being researched are ceramic candle filters that contain nickel-based catalyst in support body and filter elements coated with CeO₂, CaO-Al₂O₃, and MgO (Shen and Yoshikawa 2013)

Removal of Particulates

Particulates from biomass gasification or pyrolysis have been defined as solid phase matter entrained in the gas stream as it exits the gasifier, and typically this includes inorganic ash, char, or material from the gasifier bed (sand, dolomite, olivine, *etc.*). Particle concentrations are normally measured in grains/dry std. ft³ or mg/dry std. m³ or mg/normal m³. The quantity of particulate matter in the producer gas often depends on gas velocity, particle size, particle density, feedstock, and gasifier design (McGowan 2016). The gasifiers that present the most problems during gasification for particulates include bubbling fluidized bed and circulating fluidized bed. This is due to turbulent conditions inside of the BFB and CFB gasifiers, which necessitates particulate clean-up of high particulate concentration before going to downstream equipment. Particulate removal is important due to environmental (particles in atmosphere influence climate change), health (micron size particles can effect lung alveoli), prevention of abrasion, and damaging downstream equipment. Also, most states and cities have limits on particulate emissions.

Due to cooling and heating of producer gas, cleaning of particulates and tars using filtration and scrubbing has a low efficiency of 25% (Rapagna *et al.* 2009a). To improve efficiency, current work for gas cleaning involves hot gas conditioning, where the raw gas is treated at high temperatures (800 to 850 °C) using a catalyst to depolymerize tar compounds and ceramic filters for removal of particulates and volatile alkali metals (Rapagna *et al.* 2009a,b; Coll *et al.* 2011).

Particulate removal procedures can be combined with tar removal and often use cyclones, rotating particle separator, barrier filters, electrostatic filters, and wet scrubbers. McGowan noted that cyclones, fabric filters, and electrostatic precipitators can be used for removal of dry particulate matter from gas streams. Laurence and Ashenafi (2012) reported that cyclones, fabric filter, ceramic filters, granular bed filters, and dry and wet electrostatic precipitators are frequently used for particulate removal. They noted that the operating temperature should be above the tar dew point (375 to 400 °C) and that dry ESP are not recommended for biomass syngas cleaning because of condensation of high molecular weight PAH compounds. In addition, high carbon content can cause an increase in electric conduction and reduced removal of particles. For high temperature gas cleaning they recommended a combination of cyclones with either ceramic or sand bed filters. Ceramic filters are much more effective than ESPs when PM_{2.5}, and very low levels of PM need to be removed. Ceramic filters when compared to ESPs can handle much higher inlet loads, have lower maintenance demand, less corrosion problems, lower energy usage, and do not have the selective removal limitations of ESP. With the capability of forming filter cake (limestone, trona, *etc.*) on the filter surface, one can remove more efficaciously pollutants such as HCl, SO₂, NO_x, dioxin, and particulates. In the past few years, ceramic filters have been used by our military for destruction of munitions.

Prabhansu *et al.* (2015) reported on a sintered metal barrier filter that could remove close to 100% of particulate matter at temperatures of 1000 °C. Their metallic filters were constructed by taking metallic powder (iron aluminide) and heating in a mould to temperatures where the metallic powder begins to fuse together.

Another unique method for hot gas conditioning was reported by Foscolo and Bocci (2012). They stated that catalytically active filter elements inside the freeboard of a compact gasifier will accomplish the following:

- Reduce tar, particulates and reform methane by providing a catalytically active filter element
- Reduce investment and operational costs
- Reduce space
- Reduce thermal losses

Foscolo and Bocci (2012) reported the following results on hot gas cleaning using filter candles from the Gussing plant:

- Greater than 95% tar reduction
- 100% solid separation secondary removal
- No energy losses
- High temperature favorable for gas turbine, fuel cell, and gas synthesis
- Water content as raw product gas at high temperature >800 °C

Rapagna *et al.* (2009a,b) also experimented with installing in the freeboard of a gasifier a bundle of catalytic ceramic candles that function at gasification temperatures of 800 to 850 °C. The catalytic ceramic filter candle was provided by Pall Filtersystems GmbH Werk Schumacher. A significant improvement of all parameters was obtained by using catalytic filter candles in the freeboard. Parameters included gas yield, tar content, water gas shift, char residue, carbon conversion, particulates, filtration velocity, and water conversion. Rapagna *et al.* (2009b) concluded that catalytic hot gas filters in the freeboard of a gasifier can reduce particulates and increase gas yield and hydrogen concentration by

reducing tar content in the raw syngas. Catalytic candles that are being tested include (Simeone *et al.* 2010; Foscolo and Bocci 2012):

- Silicon Carbide (SiC) porous structure with mullite (refractory material $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) outer membrane impregnated with Ni supported on $\text{MgO}\text{-Al}_2\text{O}_3$. Integration of a Ni based catalyst layer allows for particle filtration and tar cracking.
- Al_2O_3 based grain-sintered filter element coated with a mullite outer membrane impregnated with Ni supported on $\text{MgO}\text{-Al}_2\text{O}_3$
- Ceramic foam with surface area impregnated with Cu and Fe for water gas shift

A rotational particle separator (RPS) (Fig. 28) can remove micron size particles by centrifugal separation. The core of the RPS element is a rotating cylindrical body, which has multitude of axially oriented channels (typically 1 mm in diameter), (a) & (b). After entering the channels of the rotating body, large particles go to the outside wall (c) of the RPS element and leave by the first outlet. Gas and fine particles will then enter the rotational filter element. Purified gas will leave the channels as a separate stream, while the particles are collected on the walls and are removed by applying pressure pulses or by flowing of the film (Brouwers 2002; Brouwers *et al.* 2012). Brouwers (2002) stated that "compared to conventional cyclones, the RPS is an order of magnitude smaller in size at equal separation performance, while at equal size it separates particles ten times smaller".

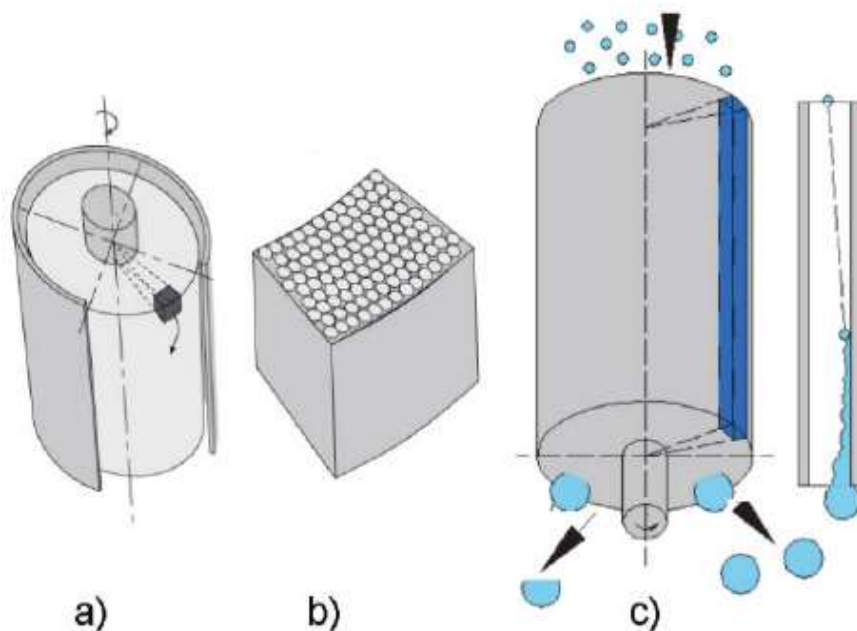


Fig. 28. Rotational particle separator (Source: Romico Companies, CEO J.J.H. Brouwers); figure used with permission of the copyright holder

Removal of Nitrogen Compounds

Nitrogen is a macronutrient that is found in wood (Douglas fir 0.06%, hemlock 0.10%, poplar 0.22%), with larger percentages found in energy crops, *e.g.*, sorghum stalks (1.40%), cotton stalks (1.20%), almond shells (1.16%), alfalfa straw (1.00%), switchgrass (0.74%), and wheat straw (0.61%) (Table 3). During gasification, nitrogen in the biomass or air is formed as ammonia, cyanides, nitrogen oxides, molecular nitrogen, and structures

of aromatic compounds, of which small quantities can be found in the non-reacted solids. The percentage of nitrogen compounds in the raw gas is dependent upon the quantitative amount of nitrogen in the biomass and upon the gasification operating conditions with ammonia (NH_3) being the major component followed by hydrogen cyanide (HCN) in biomass gasification. Ammonia can be decomposed on Fe, Ni, and Ru based catalyst (Yin *et al.* 2004; Asadullah 2013). Nickel monolith ($\text{Ni}/\text{Al}_2\text{O}_3$) gave 100% conversion of ammonia at 900 °C with fuel composition being 4400 ppm NH_3 in 11% CO, 14% CO_2 , 5% CH_4 , 10% H_2 , 12% H_2O , 0-500 ppm H_2S , 3200 ppm toluene, and N_2 as the balance (Xu *et al.* 2010; Prabhansu *et al.* 2015).

Yin *et al.* (2004) experimented with magnesia-carbon nanotubes (MgO-CNTs) composites for ammonia destruction. These composites were formed by impregnation of CNT with $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in ethanol solution followed by calcination. This resulted in a nanocomposite with Ru catalyst that gave higher dispersion and higher catalytic activity for ammonia decomposition as compared to other supports for Ru. Leppalahti and Koljonen (1995) and Kumar *et al.* (2009) carried out experiments that showed that hot gas cleaning of ammonia could be performed at high temperatures using dolomite, nickel based catalyst, and iron based catalysts.

Under pyrolysis conditions (oxygen starved conditions), fuel-bound nitrogen can be reduced to molecular nitrogen (N_2) with much smaller amounts of ammonia, and this procedure is used as a control method for reduction of NO_x . The US EPA regulates NO_x because it can cause irritation to eyes and throat, nausea, headache and it can form ground level ozone by reacting with organic vapors in presence of sunlight. The NO_x level can be controlled by oxygen amount, flame geometry, mixing, temperature, time, and nitrogen amount. Cement and lime kilns produce some of the highest levels of NO_x (2,000 ppm at 2,000 °F, which equals 1093 °C), while a standard burner as in package boilers contain only 100 to 200 ppm of NO_x (McGowan 2016).

Removal of Sulfur Compounds

Sulfur content in most biomass feedstock is low, with wood typically less than 0.1%, *e.g.* black locust (0.01%), Douglas fir (0.02%), ponderosa pine (0.03%), poplar (0.05%), and hemlock-western (0.10) (Table 3). However, some herbaceous crops can contain higher amounts of sulfur, such as sorghum stalks (0.20%), corn grain (0.14%), and wheat straw (0.11%) (Table 3).

For most applications, the sulfur content is low enough to meet requirements. However, for methanol synthesis, fuel cells, and some tar catalysts, low levels of sulfur can deactivate catalysts. The primary sulfur compounds in exit gases from coal combustion and gasification are SO_2 (Fig. 29A) and H_2S (Fig. 29B), respectively. However, for biomass gasification, the main sulfur compound is H_2S , with small amounts of carbonyl sulfide (Fig. 29C), carbon disulfide (Fig. 29D), and thiophenes (Fig. 29E) (Meng *et al.* 2010).

Due to their low cost and wide availability, dolomite, limestone and CaO are used for SO_2 and H_2S removal (Vamvuka *et al.* 2004; Basu 2006; Kumar *et al.* 2009; Meng *et al.* 2010; Zhang *et al.* 2012; Husmann *et al.* 2016). Limestone and dolomite are the main compounds used for *in situ* capture of sulfur, while metal oxides are the most popular for downstream sulfur capture.

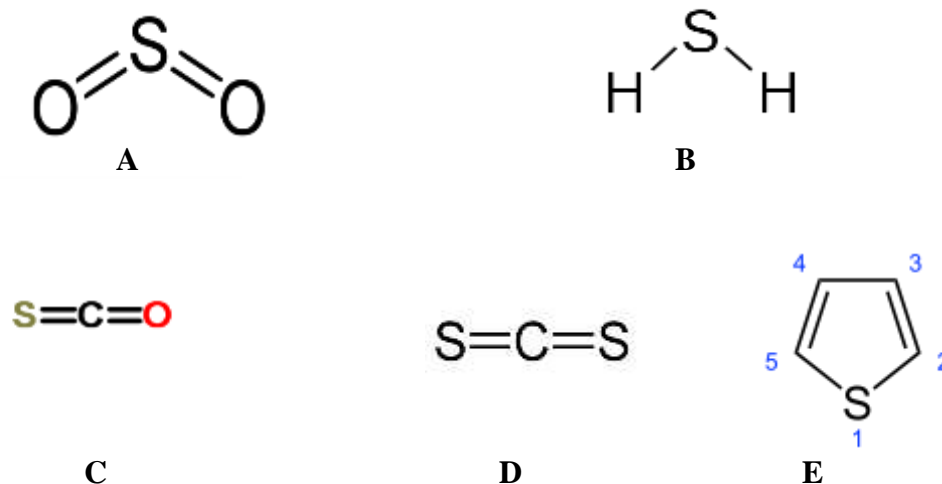
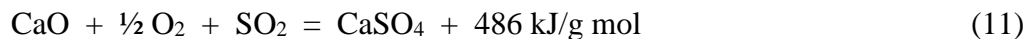


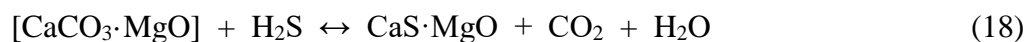
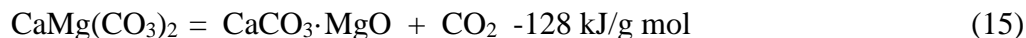
Fig. 29. Sulfur-containing gas compounds often present in exhaust from combustion of coal

Vamvuka *et al.* (2004) noted that calcination is important for SO₂ removal and that cleaning in the range 600 to 900 °C and regeneration of sorbents is the best process for H₂S removal from hot gases. Basu (2006) stated that the chemical reactions shown below are important for capture of SO₂ in FBs that typically operate at 800 to 900 °C. He noted that sulfur can be oxidized to sulfur dioxide (Eq. 10), which can then react with CaO, forming calcium sulfate (Eq. 11). Small amounts of sulfur dioxide can react with oxygen inside the gasifier forming sulfur trioxide (Eq. 12). This reaction depends on temperature, excess air, residence time, and whether there are any catalytic surfaces inside the gasifier. Lastly, the sulfur trioxide can come in contact with moisture in the flue gas forming sulfuric acid, which can then condense on cold surfaces causing corrosion problems (Eq. 13).

Dolomite and limestone are sorbents that can be used for reduction of sulfur dioxide (Eq. 14). Reactions 15 and 16 show how partial calcined dolomite could react with calcium carbonate. Because magnesium oxide reacts very slowly with sulfur dioxide at temperatures between 540 and 980 °C, there is very little interaction with sulfur. During calcination, the released CO₂ creates pores from the interior of the rock and this allows SO₂ to enter and react with CaCO₃. Reactions 17 and 18 describe the primary sulfidation reaction between calcined dolomite and half-calcined dolomite and hydrogen sulfide, resulting in calcium sulfide (Ay *et al.* 2012; Abbasian *et al.* 2017). As a byproduct, CaS (powder material) can be used in paints, varnishes, insecticides, and lubricants.

Zinc oxide (ZnO) can also be used for removal of sulfur in hydrogen sulfide (Eq. 19) due to its greater sulfidation thermodynamics (Lew *et al.* 1992; Hassan *et al.* 2008). Tests reveal that the catalyst has over 99% efficiency for sulfur removal; however, vaporization of elemental zinc at temperatures over 600 °C (Table 11) is a major disadvantage for hot gas conditioning.





Removal of Halogens and Their Acids

McGowan (2016) reported that acid gas (HCl, SO₂) removal can be accomplished by using two approaches. The first approach is to inject powdered lime or sodium based reagent upstream of an ESP or fabric filters. The second approach is to spray lime slurry into a spray drying tower. These compounds adsorb and react with acid gases producing solid particles. Simell *et al.* (2014) described how HCl in gasification gas can react with calcium or alkali metals and the solid chlorides can be removed by filtration. Prabhansu *et al.* (2015) reported that sodium rich compounds like nahcolite (NaHCO₃), trona (Na₂CO₃·NaHCO₃·2H₂O), and sodium carbonate (Na₂CO₃) are used for high temperature removal of halogens such as HCl. Other compounds used for removal of halogens include calcium hydroxide (Ca(OH)₂), magnesium hydroxide (Mg(OH)₂) and their calcined form CaO and MgO, and limestone.

Removal of Alkali Metals

From Table 3, one can see that some biomass feedstock can contain significant amounts of ash, *e.g.*, rice hulls (18.34%), cotton stalk (17.30%), sorghum stalks (12.50%), and wheat straw (11.40%). Kumar *et al.* (2009) reported that significant amounts of alkali compounds are in biomass including CaO, K₂O, P₂O₅, MgO, Na₂O, SiO₂, and SO₃. Stevens (2001) described how the chemical composition of ash is what determines the physical properties including softening, vaporization points, and melting points. With potassium content being high in rapid growing biomass feedstock and with the presence of sodium, eutectic mixtures of both can create a lower vaporization temperature, which creates problems in gas cleanup. These alkali compounds can vaporize at 700 °C and if not removed, condensation can begin around 650 °C or even higher with deposits on cooler surfaces such as heat exchangers and turbine blades, *i.e.*, deposition with rapid imbalance and corrosion problems.

Laurence and Ashenafi (2012) recommended removal of alkali vapors with a cyclone combined with dual layer sand bed filter and temperatures lower than 600 to 650 °C. Kumar *et al.* (2009) and Turn *et al.* (2001) reported that activated bauxite filter at 650 to 725 °C removed most of the Na and K compounds. Wolf *et al.* (2004) reported a reduction (<50 ppbv) of overall alkali concentration in a hot gas environment by using activated bauxite and bentonite (aluminum phyllosilicate clay). They reported that a 500 MW_e power plant would use approximately 100 kg/h of sorbent at a hot gas temperature of 700 °C. Activated bauxite has also been demonstrated to be an excellent adsorbent for sulfur recovery, HCl adsorption, vapor and liquid dehydration, COS, H₂O, and CO₂ adsorption, and Hg adsorption. Mineracao Curimbaba produces activated bauxite and listed its chemical composition as: Al₂O₃ (76.3%), Fe₂O₃ (11%), SiO₂ (9.62%), TiO₂ (1.41%), K₂O (0.33%), CaO (0.03%), others (1.29%).

Mercury Removal

Mercury from natural and anthropogenic sources has been emitted for centuries and has accumulated worldwide. Because of this widespread discharge, we find mercury in forest biomass. Laacouri *et al.* (2013) reported concentrations of Hg in leaf tissues at 54 ng/g and Meier (2013) reported approximately 1 ng/g for Hg in wood chips. Thy and Jenkins (2010) did a survey of Hg content on a few California biomass feedstocks and showed that the concentration was well below EPA toxicity level. They noted Hg levels for rice straw at 20 ppb, wheat straw 28 ppb, and wood chips at 32 ppb. Basu (2006) stated that the most common method for Hg capture was to inject activated carbon, bromine, or polysulfide into the combustion gas for absorption. Mercury in the solid form can then be captured downstream in equipment such as ESP or baghouse.

CONCLUSIONS

Biomass gasification is a thermochemical process that is considered a sustainable way of taking low value lignocellulose and converting it to fuel gas for power generation, fuel cell, chemicals, and fuel for cars and trucks. Studies have shown that biomass with higher lignin content and MSW containing plastics are excellent materials for production of high calorific gases through gasification or pyrolysis.

The following information is essential for biomass conversion to value added gases:

- Preprocessing must consist of particle size reduction for larger surface area, which creates faster rate of heat transfer.
- Biomass moisture reduction during preprocessing will improve the overall energy efficiency.
- Blending of energy crops (high ash content have low HHV) can be optimized.
- Gasifier design (downdraft) is important for low tar and high energy efficiency.
- Increasing temperature and residence time in gasifier enhances tar cracking.
- Catalytic hot gas conditioning provides greater process efficiency, lower environmental effect, and yields gas having a greater calorific value.
- Hot gas conditioning for particulate removal can proceed with cyclones (series), ceramic tubes, ceramic fibers, and granular bed filters.
- Calcined dolomite has proven to be an abundant, easy to dispose of, and inexpensive basic catalyst for tar removal and hydrogen production with promotion of water gas shift reaction.
- Calcined dolomite is also used as an inexpensive guard bed for extending the lifetime for nano-nickel catalyst.
- Iron in dolomite and in metallic state possess excellent activity for decomposition of tars in product gas.
- Use of trona and limestone in a gasifier can reduce sulfur and halogens in producer gas.
- Metal oxide sorbents are excellent for sulfur removal.
- Nano-nickel base catalyst (high BET surface area) that have been doped into ceramic tubes or fibers can decompose tars and ammonia.
- Adding promoters and support modifiers can improve catalyst lifetimes by decreases in deactivation caused by coke formation, sulfur and chlorine poisoning, and sintering.

- Reverse jet pulse or coupled pressure pulse can be used for de-dusting catalyst systems.
- Steam can be added to gasifier to assist in tar reduction.
- Steam can be added to dolomite reactor and ceramic tubes for water gas shift reaction, water gas (steam) reaction, and steam reforming reactions.

This research work has pointed to a general procedure that shows potential for taking biomass and converting it into value added gases by using the following sequence: pretreatment, downdraft gasifier (high temperatures), cyclones in series, calcined dolomite, sorbents, ceramic tube, gas analysis (MS), gas turbine, and power generator. Hot gas cleaning with high concentration of Fe in dolomite will aid in tar decomposition and reforming. In addition, some dolomites were discovered that showed higher than normal amounts of SiO₂, and this will improve stability and attrition of dolomite during high temperature conditioning.

Biomass gasifiers can range from >50 MW stationary units to skid mounted units <10 MW that are scalable and can be transported to biomass locations including farms, timber crops, agricultural areas, *etc.* The future looks great for biomass power either from co-firing (coal and biomass), combustion, or creating gases from pyrolysis or gasification. Co-firing (biomass and coal) is becoming a common method for generating electricity in Europe and is gaining traction in the United States due to reduction in the following:

- Fossil fuel consumption
- GHG
- SO_x, NO_x
- Flue gas opacity
- Landfills
- Heavy metals such as (Hg, As, Cd, Sb, Cr, Pb, radioactive isotopes U, Th, Sr)

Hvistendahl (2007) stated that “coal ash is more radioactive than nuclear waste”. Her reasoning was that burning all the carbon and other impurities produced large quantities of radiation. She noted over the past few decades, a series of studies have showed that fly ash, emitted by power plants, can carry 100 times more radiation than a nuclear power plant producing the same amount of energy. Other authors have stated that acid rain from sulfur dioxide and smog forming nitrous oxide pose a greater health risks than radiation. The biomass-based technologies outlined in the present review article can provide a way to decrease our dependency on coal, thus mitigating the cited environmental harm.

In 2016, the United States Energy Information Administration stated that approximately 19.69 million barrels of petroleum products were consumed per day. With technology rapidly advancing in biomass gasification, the future looks promising for renewable energy. Biomass power will only increase in volume in the future due to its abundance, carbon neutral, sustainability, energy security, rural job creation, domestic resource, and air quality improvements.

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