

# A review on biomass torrefaction process and product properties for energy applications

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## Abstract

Torrefaction of biomass can be described as a mild form of pyrolysis at temperatures typically ranging between 200 and 300°C in an inert and reduced environment. Common biomass reactions during torrefaction include devolatilization, depolymerization, and carbonization of hemicellulose, lignin, and cellulose. The torrefaction process produces a brown to black uniform solid product, as well as condensable (water, organics, and lipids) and noncondensable gases (CO<sub>2</sub>, CO, and CH<sub>4</sub>). Typically during torrefaction, 70% of the mass is retained as a solid product, containing 90% of the initial energy content, while 30% of the lost mass is converted into condensable and noncondensable products. The system's energy efficiency can be improved by reintroducing the material lost during torrefaction as a source of heat. Torrefaction of biomass improves its physical properties like grindability; particle shape, size, and distribution; pelletability; and proximate and ultimate composition like moisture, carbon and hydrogen content, and calorific value. Compared to raw biomass, the carbon content and calorific value of torrefied biomass increases by 15–25% wt, while the moisture content decreases to <3% (w.b.). Torrefaction decreases the grinding energy by about 70%, and the ground torrefied biomass has improved sphericity, particle surface area, and particle size distribution. Torrefied biomass pelletization at temperatures of 225°C decreases the specific energy consumption and increases the capacity of the mill by a factor of 2. The loss of the OH functional group during torrefaction makes the material hydrophobic (i.e., loses the ability to attract water molecules) and more stable against chemical oxidation and microbial degradation. These improved properties make torrefied biomass particularly suitable for cofiring in power plants and as an upgraded feedstock for gasification.

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**KEYWORDS:** biomass torrefaction; torrefaction temperature and residence time; biomass reactions; off-gas composition; torrefied biomass physical, chemical, and storage properties

**ABBREVIATIONS:** CV, calorific value; GHG, greenhouse gas; TOP, torrefaction and pelletization

## Introduction

The world is currently challenged to reduce dependence on fossil fuels and achieve a sustainable, renewable energy supply. Energy produced from biomass is considered carbon-neutral because the carbon dioxide released during conversion is already part of the carbon cycle.<sup>1</sup> Increasing biomass use for energy can help reduce greenhouse gas (GHG) emissions and meet the targets established in the Kyoto Protocol.<sup>2</sup> Energy from biomass can be produced

from different thermochemical (combustion, gasification, and pyrolysis), biological (anaerobic digestion and fermentation), or chemical (esterification) processes, where direct combustion can provide a near-term energy solution.<sup>1</sup> The growing interest in biomass as a solid fuel includes combustion to produce steam for electrical power and commercial plant uses, as well as gasification to produce a combustible gas (large partial pressure of nitrogen and CO<sub>2</sub>, called producer gas) and syngas (carbon monoxide and hydrogen with low amounts of nitrogen and CO<sub>2</sub>). Still, the use of either producer gas or syngas in modern reciprocating or gas turbines, or to produce higher value chemicals and fuels, is limited due to biomass feedstock preparation, accumulation logistics, and economics.

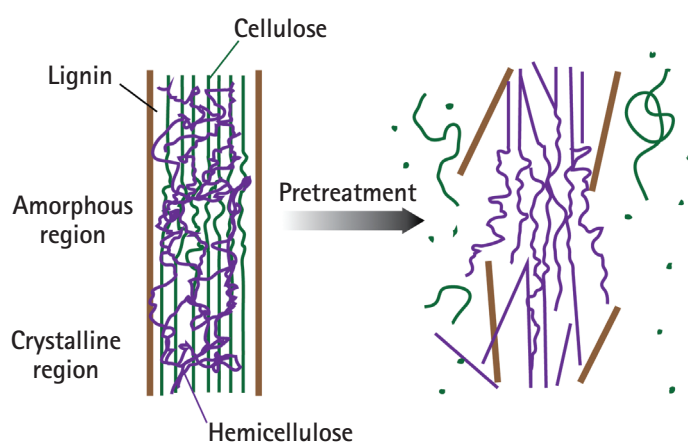
## Limitations of biomass as fuel

Some of the inherent problems with raw biomass materials compared to fossil fuel resources (low bulk density, high moisture content, hydrophilic nature, and low calorific value [CV]) render raw biomass difficult to use on a large scale.<sup>1</sup> These limitations greatly impact logistics and final energy efficiency. Due to its low energy density compared to fossil fuels, very high volumes of biomass are needed, which compounds problems associated with storage, transportation, and feed handling at cogeneration, thermochemical, and biochemical conversion plants.

High moisture in raw biomass is one of the primary challenges, as it reduces the efficiency of the process and increases fuel production costs.<sup>3</sup> High moisture content in biomass leads to natural decomposition, resulting in loss of quality and storage issues such as off-gas emissions. Another consequence of high moisture content is the uncertainty it causes in biomass's physical, chemical, and microbiological properties. Irregular biomass shapes constitute another issue, especially during feeding in a cofiring or gasification system. In addition, biomass has more oxygen than carbon and hydrogen, making it less suitable for thermochemical conversion processes. Considered collectively, these properties make raw biomass unacceptable for energy applications.

To overcome these challenges and make biomass suitable for energy applications, the material must be preprocessed. One of the commonly used preprocessing operations is grinding, which helps to achieve a consistent particle size; however, the moisture content of the biomass limits the performance of many grinders.<sup>3</sup> Furthermore, grinding can be very costly when smaller particle sizes are desired and, in some cases, impractical for biomass with high moisture content. High moisture content can also result in inconsistent particle sizes (especially when the particles are less than 2 mm), which may not react consistently, thereby reducing the efficiency and increasing the costs of the conversion process. Also, raw biomass is thermally unstable due to high moisture, which results in low CVs and inconsistent particle-size distribution issues when used in thermochemical processes such as gasification. This can lead to inconsistent products and the formation of condensable tars, which results in problems like gas-line blockage.<sup>4</sup>

A viable option is to pretreat the biomass before the end-use application. Pretreatment helps alter biomass's physical properties and chemical composition and makes it more suitable for conversion.<sup>5</sup> The pretreatment can be a chemical, thermal, or mechanical process, like ammonia fiber explosion, torrefaction, and steam explosion, respectively. These pretreatment processes help alter the amorphous and crystalline regions of the biomass and bring significant changes in structural and chemical compositions. *Figure 1*



**Figure 1. Pretreatment effect on lignocellulosic biomass<sup>5</sup>**

shows how the pretreatment of biomass makes the biomass easier to convert.<sup>5</sup>

Torrefaction, which is a thermal pretreatment process, is a viable technology that significantly alters the physical and chemical composition of the biomass. Torrefaction is defined as slowly heating biomass in an inert environment and temperature range of 200–300°C. This process improves the physical, chemical, and biochemical composition of the biomass, making it perform better for cofiring and gasification purposes. Many researchers have studied the effect of torrefaction process time and temperature on the physical and chemical composition.<sup>6–15</sup> However, a detailed literature review is lacking on the torrefaction process in terms of biomass reactions (such as depolymerization, devolatilization, and carbonization) and product properties. The primary focus of this research is to conduct a detailed literature review on biomass torrefaction, which includes (a) biomass reactions, including chemical and structural changes, (b) torrefaction product yields in terms of condensable, noncondensable, and solid product, and (c) the solid torrefied product's physical, chemical, and storage properties for energy applications.

### Biomass components

The plant cell wall is the tough, usually flexible but sometimes fairly rigid layer that provides structural support and protection from mechanical and thermal stresses. The major components of the primary cell wall are cellulose (carbohydrates), hemicelluloses, and pectin. The cellulose microfibrils are linked via hemicellulosic tethers to form the cellulose-hemicellulose network, which is embedded in the pectin matrix. The outer part of the primary cell wall is usually impregnated with cutin and wax, forming a permeability barrier known as the plant cuticle.<sup>16</sup>

Cells and tissues of the plant body play an important role in the growth of the plant. The structural complexity of the plant body results from variations in the form and function of the cells and also from differences in the manner of combination of cells into tissue and a tissue system. The three different types of plant tissues are (1) meristematic tissue, (2) dermal tissue, and (3) vascular tissue.<sup>17</sup>

Secondary cell walls contain a wide range of additional compounds that modify their mechanical properties and permeability. The polymers that make up the secondary cell wall include (1) cellulose, (2) xylan, a type of hemicellulose, (3) lignin, a complex phenolic polymer that penetrates the spaces in the cell wall between cellulose, hemicellulose, and pectin components and which drives out water and strengthens the wall, and (4) structural proteins (approximately 1–5%), which are found in most plant cell walls.<sup>16</sup> *Figure 2* shows the plant cell wall and lignocellulosic biomass composition.<sup>5</sup> *Table 1* shows the typical lignocellulosic content of some plant and woody biomass.<sup>12,18</sup>

### Torrefaction process overview

Torrefaction is a thermal pretreatment technology. It is also defined as isothermal pyrolysis of biomass occurring in temperature ranges of 200–300°C and performed at atmospheric pressure in the absence of

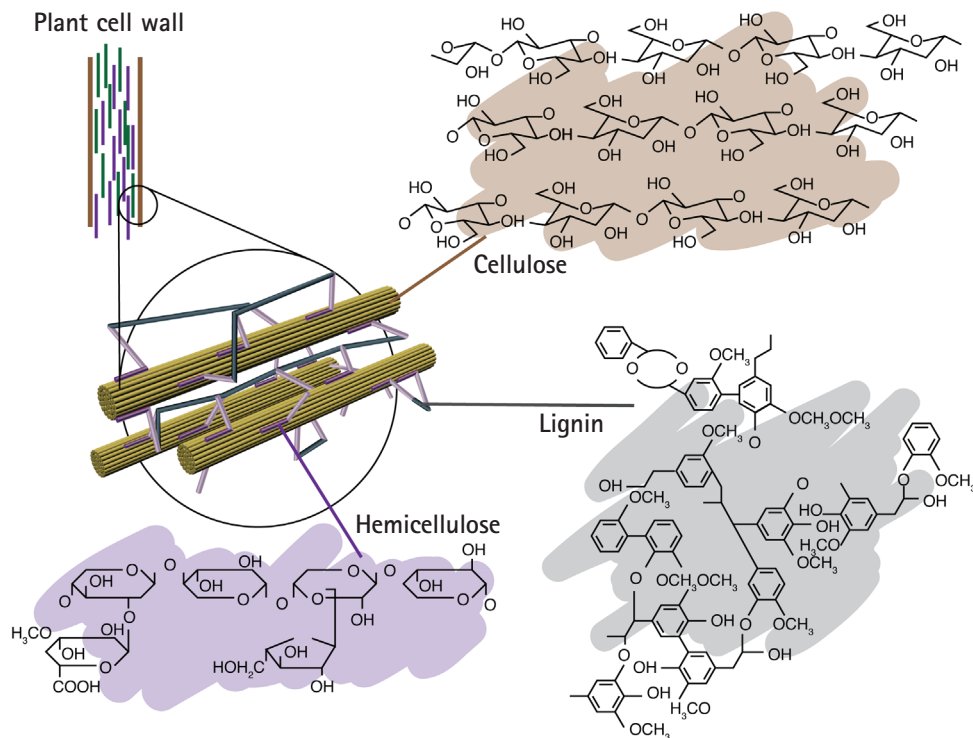


Figure 2. Plant cell wall and lignocellulosic biomass composition<sup>5</sup>

Table 1. Typical lignocellulosic content of some plant materials<sup>12,18</sup>

PLANT MATERIAL	LIGNOCELLULOSIC CONTENT (%)		
	HEMICELLULOSE	CELLULOSE	LIGNIN
Orchard grass (medium maturity)	40.0	32.0	4.7
Rice straw	27.2	34.0	14.2
Birch wood	25.7	40.0	15.7
Reed canary grass	29.7	42.6	7.6
Wheat straw	30.8	41.3	7.7
Willow	14.1	49.3	20.0

oxygen.<sup>6-7</sup> Biomass torrefaction has been recognized as a technically feasible method of converting raw biomass into a solid that is suitable for commercial and residential combustion and gasification applications, given that it has high energy density, is hydrophobic, compactable, and grindable, and has a lower oxygen-to-carbon (O/C) ratio.

During the initial heating of lignocellulosic materials, water due to chemical reactions is removed through a thermocondensation process. This happens at temperatures between 160 and 180°C and results in the formation of CO<sub>2</sub>.<sup>7</sup> At temperatures of 180–270°C, the

reaction is more exothermal, and the degradation of hemicellulose continues. At these temperatures, biomass begins to brown and give off additional moisture, CO<sub>2</sub>, and large amounts of acetic acid with some phenols that have low energy values.<sup>7</sup>

During torrefaction, the major decomposition reactions affect the hemicellulose. Lignin and cellulose also decompose in the range of temperatures at which torrefaction is normally carried out, but to a lesser degree.<sup>19-20</sup> Torrefied biomass retains most of its energy and simultaneously loses its hygroscopic properties. At about 280°C, the reaction is entirely exothermic, and gas production increases, resulting in the formation of carbon monoxide, hydrocarbons like phenols and cresols, and other heavier products. For torrefaction, process temperatures over 300°C are not recommended, as these may lead to extensive devolatilization of the biomass due to the initiation of the pyrolysis process.<sup>8</sup>

### Torrefaction process technique

Torrefaction is a thermochemical process involving the interaction of drying and incomplete pyrolysis. The different parameters that influence the torrefaction process are (a) reaction temperature, (b) heating rate, (c) absence of oxygen, (d) residence time, (e) ambient pressure, (d) flexible feedstock, (e) feedstock moisture, and (f) feedstock particle size. Biomass feedstock is typically predried to 10% or less moisture content prior to torrefaction. Particle size plays an important role in torrefaction in that it influences the reaction mechanisms, kinetics, and duration of the process, given a specific

heating rate. The chemical reactions that occur when reactive intermediates are trapped in a thick matrix differ from the situations in which products can escape and be swept away in a gas stream. The duration of the process is basically adjusted to produce friable, hydrophobic, and energy-rich enhanced biomass fuel.

#### Temperature effect on the biomass components

Understanding plant components and their composition will help in understanding the biomass degradation reactions during the thermal pretreatment process. Exposure of biomass to elevated temperatures results in thermal degradation of its structure, which is often accompanied by loss of mass. The degree of thermal degra-

ation depends on the duration of the heating and temperature.<sup>21-23</sup> The various components in the biomass perform unique functions within the plant structure and interact differently depending on thermal treatment time and temperature.

Drying process variables that can influence the structural and chemical compositional changes include biomass composition, particle size, processing temperature and time, heating rate, gas composition, pressure, and flow rate.<sup>9</sup> Figure 3 provides a modified version of Bergman et al's description of the torrefaction process.<sup>10</sup> The updated figure describes the structural changes, emissions due to bond cleavage, biomass reactions, and color changes at different temperature regimes ranging from 50–300°C.<sup>9,21-30</sup>

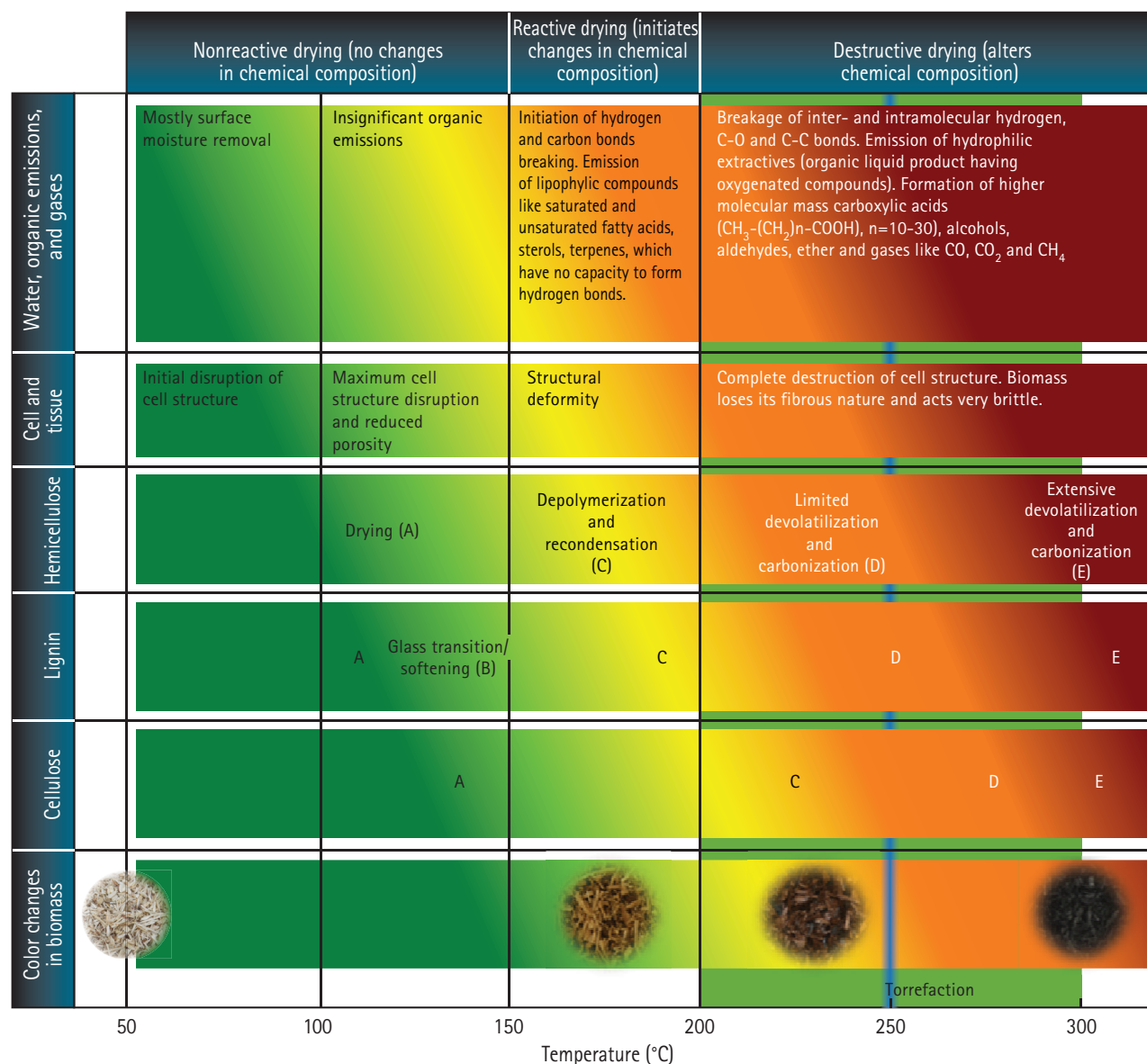


Figure 3. Structural, chemical, and color changes in biomass at different drying temperatures (modified version of Bergman et al's description of the torrefaction process<sup>10</sup>)

## RESEARCH

Based on *Figure 3*, at drying temperatures of 50–150°C (*A*), biomass loses moisture and shrinks. This also results in reduced porosity in the biomass, though the biomass may still have the ability to retain its structure if rewetted. This region is known as the nonreactive drying zone, where most of the chemical constituents of the biomass remain intact. At the higher end of these temperatures (i.e., 120–150°C) (*B*), the lignin softens and makes the material more suitable for densification, as the softened lignin acts as a binder. Temperature *Regime C* (i.e., 150–200°C), also called the reactive drying range, initiates the breakage of hydrogen and carbon bonds and results in the emission of lipophilic extractives and compounds due to thermal degradation of biomass solids. This temperature also results in structural deformity, from which biomass loses its ability to regain its original structure if rewetted. Also, according to Bergman and Kiel, depolymerization of hemicellulose results in shortened, condensed polymers with solid structures.<sup>10,31</sup> Increasing the temperature further, as shown in *Regime D*, also called destructive drying (200–300°C), results in carbonization and devolatilization.

These temperatures represent the torrefaction process limits, which result in the disruption of most inter- and intramolecular hydrogen bonds and C–C and C–O bonds, resulting in the formation of hydrophilic extractives, carboxylic acids, alcohols, aldehydes, ether, and gases like CO, CO<sub>2</sub>, and CH<sub>4</sub>. At these temperatures, cell structure is completely destroyed as the biomass loses its fibrous nature and becomes brittle. Bergman reports further that increasing the temperature to >300°C results in extensive devolatilization and carbonization of the polymers.<sup>10,32</sup> The blue line in *Figure 3* indicates that at temperatures lower than 250°C, the mass loss is at a minimum, as main biomass decomposition results from limited devolatilization and carbonization of the hemicellulose. At temperatures >250°C, the hemicellulose decomposes extensively into volatiles and a char-like solid product. Lignin and cellulose show limited devolatilization and carbonization.

Color change in the raw material can be a good means of describing the degree of torrefaction. The color changes in the biomass at

different temperature regimes indicate that the biomass turns brown to black at 150–300°C, which can be mainly attributed to chemical compositional changes. Lam et al quantified the severity of steam treatment based on color coordinates (such as *L*, *a*, and *b* values, which indicate lightness, redness/greenness, and yellowness/blueness, respectively) in their study.<sup>33</sup> The same authors also developed multilinear regression models to describe the chemical compositional changes like carbon and hydrogen based on color changes in steam-exploded wood pellets.<sup>33</sup> In addition, color measurement can be a good indicator for identifying impurities like bark, ash, or any other foreign material present in the biomass. For example, in the coffee bean roasting process, the change in the color is used as an indicator to define the changes in chemical composition.<sup>34</sup> Typical thermal treatment process variables (mass and energy yields at different temperature regimes) are given in *Table 2*.

During torrefaction at 200–300°C, mass loss predominantly results from the loss of moisture and decomposition (devolatilization), particularly hemicellulose and some lignin. Xylan-based hemicellulose generally decomposes around 250–280°C. Lignin decomposition proceeds more slowly, but gradually increases starting at about 200°C.<sup>11</sup> However, the thermal decomposition behavior of individual biomass polymers may be different from the strongly integrated structure of whole biomass. *Figure 4* indicates the typical weight loss in cottonwood as a function of temperature.<sup>35</sup> The figure clearly shows that the weight loss and degradation of biochemical composition typically starts at temperatures higher than 200°C.

### Biomass reactions

**Cell and tissue:** Changes in biomass cells and tissues, which lead to structural changes, typically happen at drying temperatures of 50–150°C. Terziev observed that different thermal treatments have a distinct effect on wood microstructure and properties.<sup>36</sup> Some studies on drying wood in a 100–150°C temperature range indicated significant cell wall shrinkage and a pore size volume decrease, which is attributed to moisture loss.<sup>37</sup> The drying damage manifests as irregu-

**Table 2. Thermal treatment process variables for different temperature regimes**

TEMPERATURE (°C)	TIME (min)	PROCESS REACTIONS	HEATING RATE (°C/min)	DRYING ENVIRONMENT AND PRESSURE	MASS YIELD (%)	ENERGY YIELD (%)
50–150	30–120	Nonreactive drying (moisture removal and structural changes)	<50	Air and ambient pressure	~90–95	Not significant
150–200	30–120	Reactive drying (moisture removal and structural damage due to cell wall collapse)	<50	Air and ambient pressure	~90	Needs to be researched
200–300	<30	Destructive drying > Devolatilization and carbonization of hemicellulose > Depolymerization and devolatilization/softening of lignin > Depolymerization and devolatilization of cellulose	<50	Inert environment and ambient pressure	~70	~90

larly distributed micro-cracks within the biomass cell wall. Three mechanisms result in structural changes to the biomass due to drying. First, initially elevated temperatures induce thermal degradation of the biomass components, which results in formation of cavities within the cell.<sup>21–22,38</sup> Second, the pore wall starts to collapse because water has been removed. This will result in closure of the pore wall due to irreversible hydrogen bonding.<sup>39–40</sup> Third, the anisotropic drying shrinkage of cell wall layers results in drying stresses, which can damage wood's cell walls.<sup>41–43</sup>

Kauman explained that total cell wall collapse during drying can be due to liquid tension collapse and stress collapse, which lead to biomass shrinkage.<sup>44</sup> It has been reported that the collapse intensity increases with increased temperature during drying.<sup>45–48</sup> Borrega and Kärenlampi stated that exposure of wood to temperatures of >150°C during drying may cause thermal degradation of its structure, often accompanied by loss of mass.<sup>38</sup> The degree of structural damage depends on tree species as well as process parameters, such as duration of treatment, temperature, and relative humidity.<sup>21–23</sup> All structural changes observed in the biomass due to moisture loss influence the biomass's mechanical properties, like bulk density and grindability.

**Hemicellulose:** Hemicellulose is a branched polymer (also a polysaccharide) that consists of shorter chains (500–3000 sugar units) as opposed to the 7000–15000 glucose molecules per unbranched polymer observed in cellulose, as shown in *Figure 2*. Hemicellulose accounts for about 25–35 wt% of biomass. The polysugars that form hemicelluloses vary differently among woods and much more among plants. In the case of deciduous wood, the hemicellulose fraction is very different. Deciduous wood contains 80–90% of 4-O-methylglucuronoxylan (referred to as xylan), whereas coniferous wood (most softwood) contains 60–70% of glucomannan and 15–30 wt% of arabinogalactan.<sup>18</sup>

Hemicellulose undergoes major decomposition reactions at torrefaction temperatures of 200–300°C, resulting in different

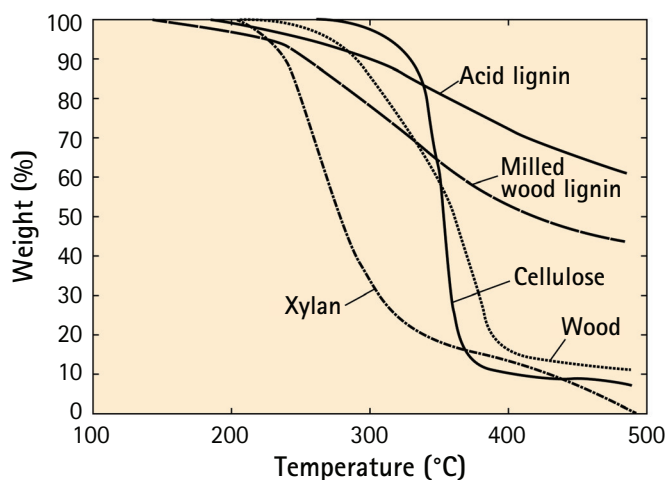
condensable and noncondensable products. Thermal degradation of hemicellulose initiates at 150°C, with the majority of weight loss occurring above 200°C, depending on the chemical nature of the hemicellulose and the relationship with lignin within the cell.<sup>18,49</sup> Compared to cellulose, hemicellulose generally evolves as light volatiles, producing fewer tars and less char. Many researchers have noted that major hemicellulose decomposition reactions occur at temperatures between 220°C and 280°C.<sup>9</sup> Native hemicellulose is partly depolymerized by hydrolysis and/or thermal chain scission to provide “reacting” hemicellulose. This intermediate is decomposed by acid and radical reactions to yield many substances (e.g., furfural) that recombine to form torrefied hemicellulose. Water and acids form during the above reactions and are released into the reaction environment.<sup>50</sup> Some of this water may be reused to depolymerize hemicellulose or to release acids from the hemicellulose by hydrolysis of acetate groups. These radical reactions can also result in the formation of acids.

**Cellulose:** Cellulose is a high-molecular-weight polymer (molecular weight of  $10^6$  and higher) that makes up the fibers in wood and other biomass. The multiple hydroxyl groups on the glucose residues from one chain form hydrogen bonds with oxygen molecules on the same or a neighboring chain. These chains are firmly held together side by side, resulting in the formation of microfibrils with high tensile strength. This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate matrix, conferring rigidity to plant cells. Cellulose strands with hydrogen bonds (dashed within and between cellulose molecules) are shown in *Figure 2*.

Cellulose degradation occurs between 240 and 350°C, resulting in anhydrous cellulose and levoglucosan.<sup>18</sup> The crystalline structure resists thermal depolymerization better than do unstructured hemicelluloses. Amorphous regions in the cellulose contain waters of hydration and hold free water within the plant. When heated rapidly, this water is converted to steam, which can further rupture the cellulose structure.

Cellulose also undergoes polymer restructuring similar to hemicellulose through depolymerization reactions, but to a lesser extent. The water and acids released due to hemicellulose depolymerization can result in more cellulose degradation. This disordered cellulose is thermostable and contains furan, aliphatic, and keto groups.

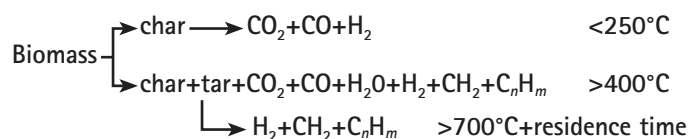
**Lignin:** Lignin is an amorphous, highly branched, cross-linked macromolecular polyphenolic resin with no exact structure. Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components. It is covalently linked to hemicellulose and thereby cross-links different plant polysaccharides, conferring mechanical strength to the cell wall and, by extension, to the plant as a whole. It is relatively hydrophobic and aromatic in nature. The degree of polymerization in nature is difficult to measure since it is fragmented during extraction and the molecule consists of various types of substructures that appear to repeat in a haphazard manner. An example of a lignin polymer is provided in *Figure 2*.



**Figure 4. Thermogravimetry of cottonwood and its constituents<sup>35</sup>**

## RESEARCH

Lignin decomposes when heated to 280–500°C, producing phenols via the cleavage of ether bonds and scissioning of carbon-carbon bonds.<sup>18,49</sup> Lignin is difficult to dehydrate and thus converts to char more than cellulose or hemicellulose. Evans et al showed that lignin releases some small phenolic fragments within the torrefaction temperature range.<sup>51</sup> Grafting torrefied hemicellulose onto cellulose and/or lignin may also be possible, indicating that all of the biomass polymers can participate in torrefaction.<sup>9</sup> The biomass decomposition reactions at different temperature regimes are given in *Figure 5*.<sup>28</sup>



**Figure 5. Biomass decomposition reactions at different temperature regimes<sup>28</sup>**

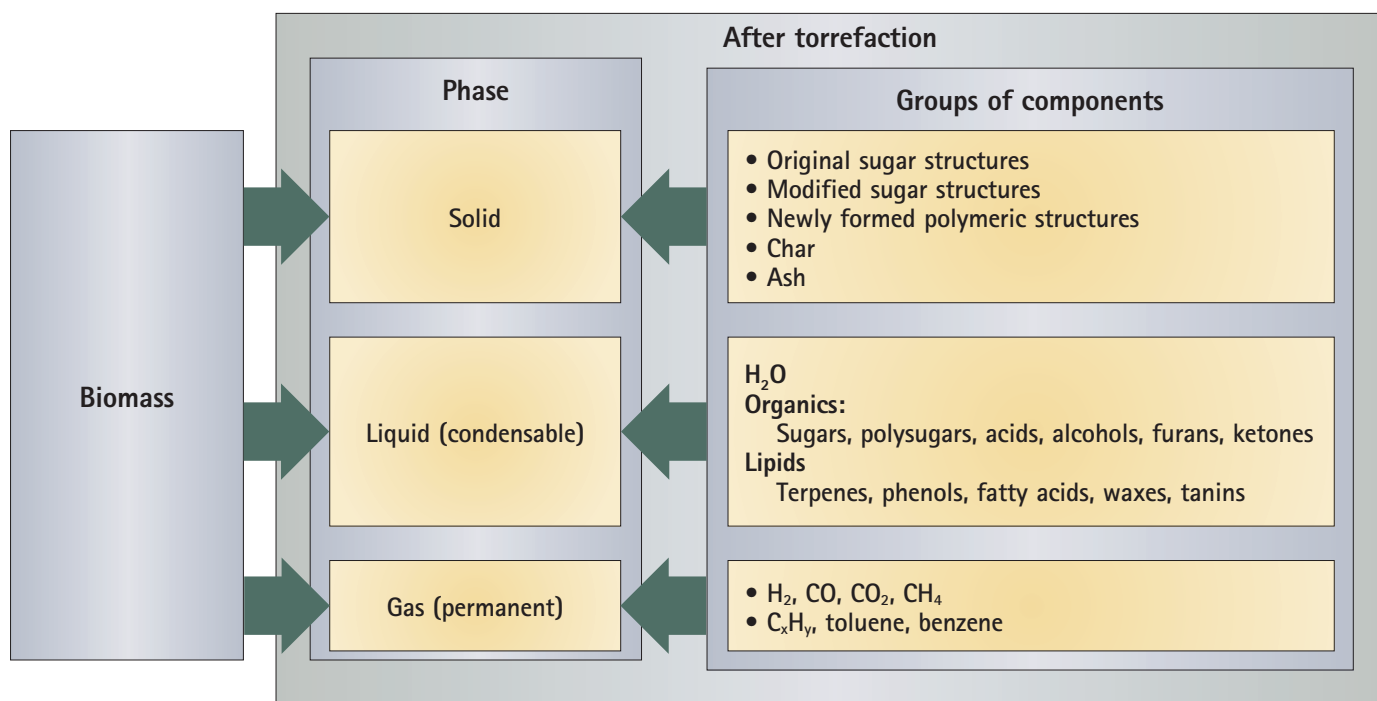
**Organic extractables:** Organic extractables include fats, waxes, alkaloids, proteins, phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils.<sup>18</sup> Again, these vary in amount and composition depending on the type of biomass. Hence, devolatilization behavior depends on the amount and location of the biomass extractables.

### Torrefaction products

During torrefaction, three different products are produced: (1) brown to black uniform solid biomass, which is used for bioenergy applications, (2) condensable volatile organic compounds comprising water, acetic acid, aldehydes, alcohols, and ketones, and (3) noncondensable gases like CO<sub>2</sub>, CO, and small amounts of methane. Release of these condensable and noncondensable products results in changes in the physical, chemical, and storage properties of biomass. Several studies have also investigated the physical properties and chemical composition of the liquids and gases released during torrefaction.<sup>11,14,52</sup> Bergman et al provide an overview of the torrefaction products, based on their states at room temperature, which can be solid, liquid, or gas, as shown in *Figure 6*.<sup>10</sup> The solid phase consists of a chaotic structure of the original sugars and reaction products. The gas phase includes gases that are considered permanent gases, and light aromatic components such as benzene and toluene.

The condensables, or liquids, can be further divided into four subgroups: (1) reaction water produced from thermal decomposition, (2) freely bound water that has been released through evaporation, (3) organics (in liquid form), which consist of organics produced during devolatilization and carbonization, and (4) lipids, which contain compounds such as waxes and fatty acids.

Condensable and noncondensable products are emitted from the biomass based on heating rate, torrefaction temperature and time, and biomass composition. The emission profiles of these products greatly depend on the moisture content in the biomass.



**Figure 6. Products formed during torrefaction of biomass<sup>10</sup>**

At high moisture content, some of the surfactants present in the biomass (oleic acid, fatty acids, and resin acids) help solubilize the monoterpenes in water and transport them through the wood matrix. At low moisture content, the emission of different compounds like terpenes is driven by vapor pressure and temperature. During torrefaction the raw material loses most of its moisture and other volatiles, which have a low heat value. Many researchers have worked on identifying gas composition in terms of quantity and quality.<sup>7,53</sup> The type and amount of gas released as off-gas during torrefaction depend on the raw material type (i.e., anatomical, molecular, and chemical composition) and torrefaction process conditions, including the process temperature and residence time.

### Mass and energy yield

A typical mass-and-energy distribution is shown in *Table 3*, which illustrates the preservation of mass and energy in the solid product. One can see that besides the solids, mostly water is produced during torrefaction, and the energy content of the volatiles is mainly preserved in the lipids and organics. Torrefaction operating conditions and biomass properties have a significant impact on the amount of solid residue remaining and the volatile and gaseous products produced during torrefaction. Thus, solid, volatiles, and gases analysis and results from different studies are not exactly the same.

Prins et al conducted several torrefaction mass balances experiments.<sup>14</sup> This data is reproduced in *Figure 7*, which shows a large difference in product distribution for different types of biomass. Larch has the largest yield of solid product and smallest gas and liquid yield, straw has higher gas and liquid fractions than woody biomass, and willow is between woody biomass and straw. It was also found that an increase in torrefaction temperature leads to a decrease in solid char yield and an increase in the volatile fractions, including liquid and noncondensable gases, which is a result of the competition between charring and devolatilization reactions that become more reactive at higher temperatures.

**Table 3. Mass and energy distribution of willow at 280°C for 17.5 min reaction time<sup>31</sup>**

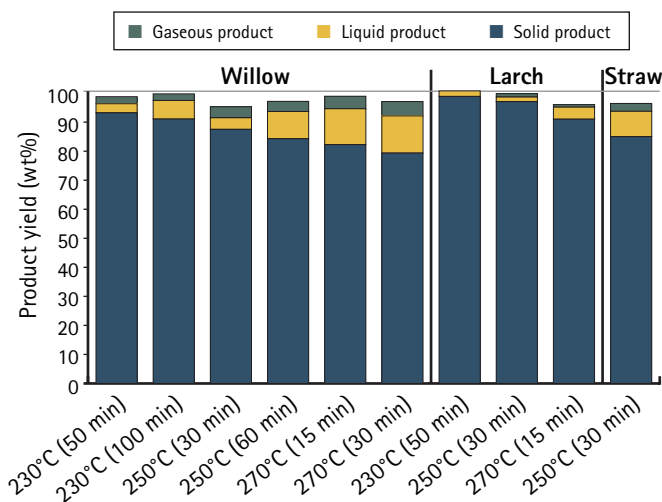
REACTION PRODUCTS	MASS YIELD	ENERGY YIELD (LOWER HEATING VALUE [LHV], daf) (%)
Solid	87.5	94.9
Lipids	1.4	3.4
Organics	1.7	1.6
Gases	1.4	0.1
Water	8.0	0.0

Note: (daf: dry and ash-free basis)

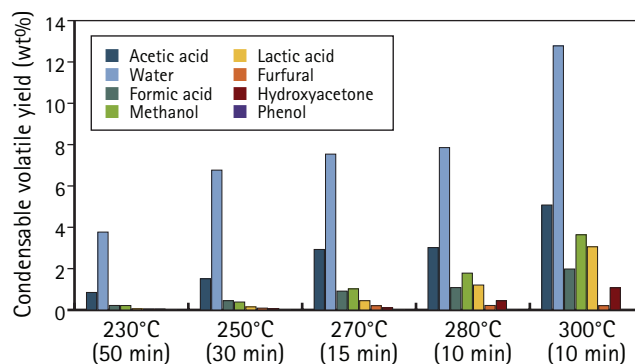
Comparing the conversion of agricultural residues (i.e., rice straw and rape stalk) to woody biomass from the literature, the solid-to-liquid conversion of the former is much higher than that of the latter under the same torrefaction conditions (i.e., temperature and residence time).<sup>10</sup> This is due to the higher volatile matter content in the agricultural residues and the decomposition of hemicellulose, the main fraction decomposed in the torrefaction temperature range. Bridgeman et al drew similar conclusions where the mass yield (dry ash-free) was 55.1, 61.5, and 72.0% for wheat straw, reed canary grass, and willow, respectively, at 290°C for 30 min.<sup>12</sup>

### Condensable products

Water is the main condensable product of torrefaction. It is released during drying when moisture evaporates and during dehydration reactions between organic molecules. Acetic acid is also a condensable torrefaction product that mainly originates from acetoxy- and methoxy-groups present as side chains in xylose units



**Figure 7. Overall mass balance of several torrefaction experiments<sup>14</sup>**



**Figure 8. Condensable volatiles yields during torrefaction<sup>14</sup>**



(part of the hemicellulose fraction). Prins et al proved that smaller quantities of formic acid, lactic acid, furfural, hydroxyl acetone, and traces of phenol are also present in the volatile component.<sup>14</sup> Yields of most of the condensable volatiles will increase with the torrefaction temperature, as is shown in *Figure 8*. As a result, more energy is transferred to the volatiles in the form of combustibles, such as methanol and acetic acid.

### Noncondensable products

The major gases formed during torrefaction are carbon dioxide and carbon monoxide with traces of other gases, as is shown in *Figure 9*.<sup>10,54</sup> Carbon monoxide is the main source of the noncondensable CV of torrefaction products.

The formation of CO<sub>2</sub> may be explained by decarboxylation of acid groups in wood and other herbaceous biomass. The formation of CO cannot be explained by dehydration or decarboxylation reactions. The increased CO formation is reported to be caused by the reaction of carbon dioxide and steam with porous char.<sup>55</sup> Traces of hydrogen and methane are also detected in noncondensable products. A gas composition comparison between wood and agricultural residues indicates that the latter is characterized by higher

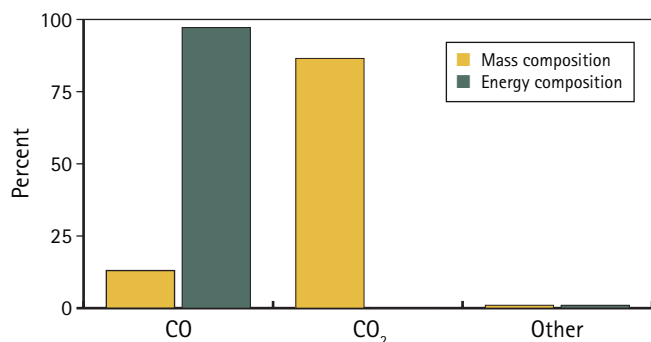


Figure 9. Main permanent gases compositions<sup>10,54</sup>

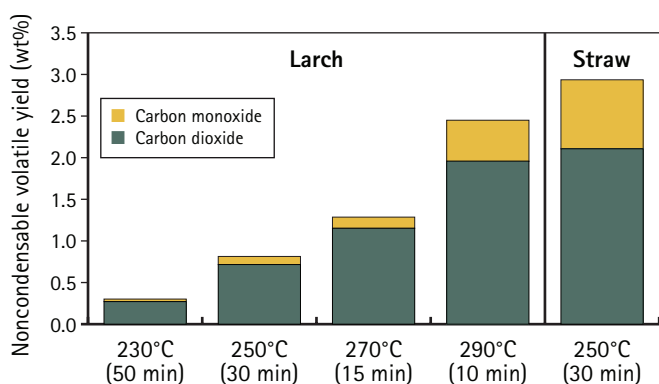


Figure 10. Noncondensable volatile yields for larch and straw<sup>14</sup>

CO<sub>2</sub> production.<sup>11,14,52</sup> In addition, a kinetic study on the generation of noncondensable gases shows that the gases are formed through parallel independent first-order reactions.<sup>13</sup>

The composition of the noncondensable volatiles produced during different torrefaction conditions is shown in *Figure 10*. The ratio of CO to CO<sub>2</sub> increased with temperature because cellulose and lignin decompose at higher temperatures.<sup>14</sup>

*Figure 11* shows the gas composition of the noncondensable products over time, which do not total 100% because only the main components (CO<sub>2</sub> and CO) are shown.<sup>14</sup> These results were obtained by torrefaction of larch and willow at 250°C for 5, 15, and 30 min. It was found that the ratio of CO<sub>2</sub> to CO decreases with time, in line with the theory that CO is formed in a secondary reaction.<sup>14</sup>

### Torrefaction process efficiency

The torrefaction process increases the energy density and improves the overall fuel properties of the torrefied product. However, torrefaction is an energy-intensive pretreatment operation due to the high temperatures used in the process. Reusing the excess heat generated in the process will have a significant impact on the overall efficiency of the system. Also, both the condensable and noncondensable volatiles have a significant impact on the energy efficiency of the process. To achieve high energy efficiency at low cost, innovative torrefaction technologies have been developed to capture excess heat and volatile energy; the Energy Research Center of the Netherlands' (ECN's) torrefaction process is one of the most mature, as is shown in *Figure 12*.<sup>10</sup>

The depicted process layout is based on the direct heating of biomass during torrefaction by means of recycled hot gas. The hot gas consists of the torrefaction gas and is re-pressurized to compensate for the pressure drop in the recycle loop. It heats the recycled gas to deliver the required heat demand in the torrefaction reactor. Combustion of the liberated torrefaction gas produces the necessary heat for torrefaction and pre-drying. A utility fuel can be used when the energy content of the torrefaction gas is insufficient

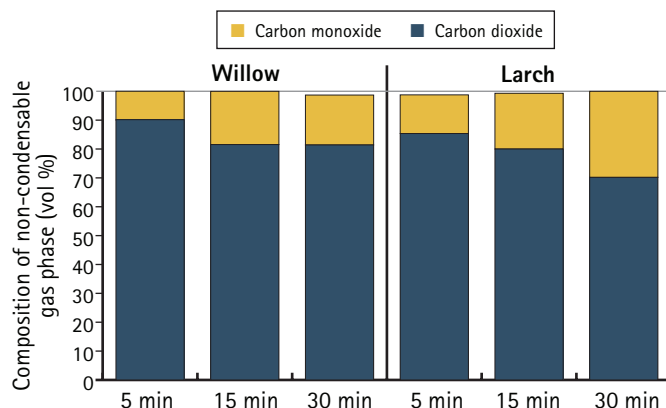


Figure 11. Change in gas composition over time for torrefaction at 250°C<sup>14</sup>

to thermally balance the torrefaction process and to provide stability and control of the combustion process. Bergman et al identified this process concept as the most promising for torrefaction, which achieves autothermal operation when the total heat demand of the process (drying and torrefaction) is balanced by the energy content of the torrefaction gas.<sup>10</sup> The torrefaction conditions (temperature and residence time) are the crucial variables to tune the thermal balance (i.e., the energy yield of torrefaction and hence the energy content of the torrefaction gas).

The torrefaction gas consists of a wide variety of combustible organic components. However, the main components of torrefaction gas are incombustible (water and CO<sub>2</sub>). The given product distribution in *Figures 6–8* shows that the torrefaction gas is rather wet. Even when completely dry biomass is torrefied, the torrefaction gas is expected to have a water content of over 50% wt and a CO<sub>2</sub>

content of about 10% wt, which makes up a total of 60% wt of incombustible components of the total emissions. The exact amount is determined by specific conditions and by the moisture content of the biomass feed.

Bergman et al<sup>10,11</sup> and Bergman<sup>32</sup> further examined the CV of the torrefaction gas experimentally, while mass-and-energy balance thermal-process efficiency, autothermal operation, and combustibility of the torrefaction gas were investigated by means of process simulations. In their studies, the yield of reaction water varied between 5 and 15% wt, resulting in a concentration of 50–80% wt in the torrefaction gas (excluding free water from the feedstock). The reaction water yield increased with residence time and temperature, while its concentration decreased. Consequently, the relative contribution of combustible products increases with increased temperature and residence time, as does the CV, which ranges from 5.3–16.2 MJ/Nm<sup>3</sup>.

Despite the high water content of the torrefaction gas, the CV is relatively high. It can be compared to producer gas from air-blown biomass gasification (4–7 MJ/Nm<sup>3</sup>) and to syngas from an indirectly heated gasification process (15–20 MJ/Nm<sup>3</sup>). Based on this comparison, the torrefaction gas should be combustible and can play an important role in the torrefaction process.<sup>10,11,32</sup> Typical experimental results for torrefaction mass and energy yields and gas-phase composition for willow are given in *Figure 13*.

### Solid torrefied biomass properties

Torrefaction of biomass significantly changes its physical and chemical properties like moisture content, density, grindability, pelletability, hydrophobicity, CV, proximate and ultimate composition, and storage behaviors in terms of off-gassing, spontaneous combustion, and self heating.<sup>15</sup>

### Physical properties

#### Moisture content

Normally, feedstock moisture content ranges from 10–50%, but because torrefaction is a deep drying process, moisture content is reduced to 1–3% on a weight basis, depending on the torrefaction conditions.<sup>31</sup> Typically, torrefaction achieves an equilibrium moisture content of 3% and a reduction of mass by 20–30% (primarily by release of water, carbon oxides, and volatiles), while retaining 80–90% of the wood's original energy content.<sup>9</sup> Reduction in moisture during torrefaction provides three main benefits: (1) reduced moisture level for the conversion process, (2) reduced transportation costs associated with moving unwanted water, and (3) the prevention of biomass decomposition and moisture absorption during storage and transportation.

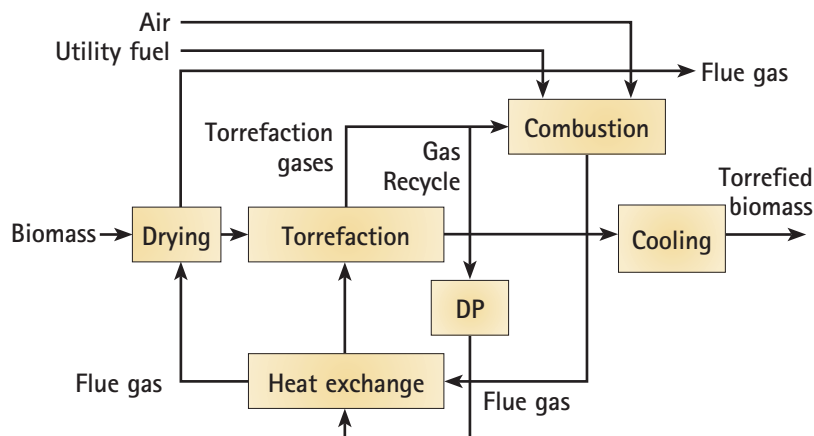


Figure 12. The envisaged conceptual structure of ECN's torrefaction process<sup>10</sup>

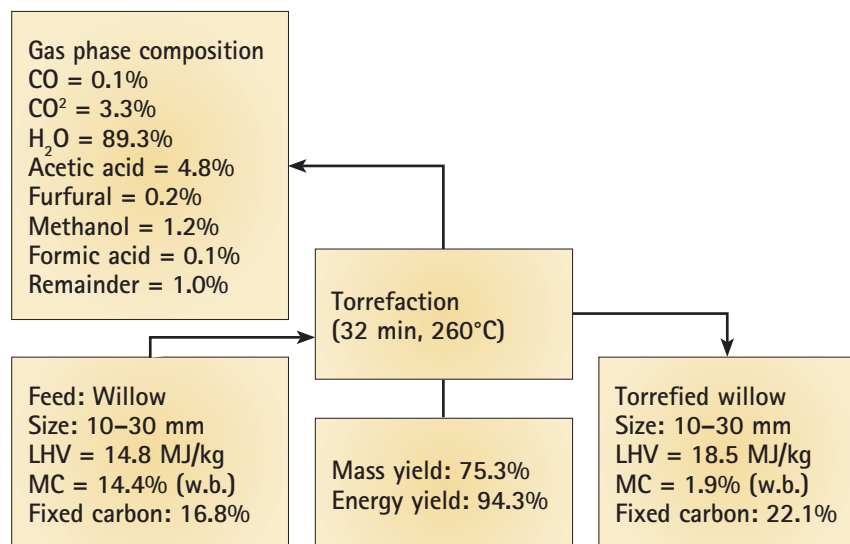


Figure 13. Typical experimental results of torrefaction of willow<sup>34</sup>

**Table 4. Bulk density (dry basis) of *Eucalyptus grandis* wood in three different treatments<sup>56</sup>**

TREATMENT	BULK DENSITY (g/cm <sup>3</sup> )	PERCENTAGE LOSS
Control*	0.85 <sup>a</sup>	—
220°C	0.83 <sup>a</sup>	2.35
250°C	0.79 <sup>b</sup>	7.06
280°C	0.73 <sup>c</sup>	14.12

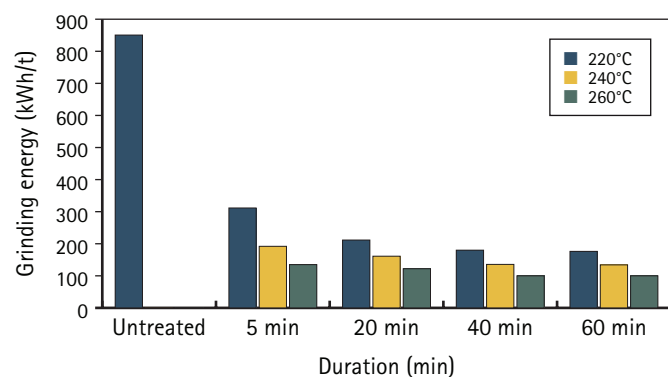
Note: Means followed by the same letter are statistically similar at the 5% probability level.  
\*Average moisture content of control treatment = 15%.

### Bulk and energy density

Mass loss in the form of solids, liquids, and gases during torrefaction cause the biomass to become more porous. This results in significantly reduced volumetric density, typically between 180 and 300 kg/m<sup>3</sup>, depending on initial biomass density and torrefaction conditions.<sup>31</sup> Oliveira-Rodrigues and Rousset's study on the effect of torrefaction on energy properties of *Eucalyptus grandis* wood indicated a bulk density loss of 14.12% when the wood was torrefied at 280°C for 30 min.<sup>56</sup> Table 4 shows the loss in bulk density for torrefaction temperatures ranging from 220–280°C.<sup>56</sup> In spite of reduced bulk density, the energy density increases. Bergman et al observed that the calorific density of pine woodchips increased from 11–20 MJ/kg.<sup>11</sup> Many researchers have observed that the energy density of both lignocellulosic and woody biomass increased significantly after torrefaction (>60%).

### Grindability

Biomass is highly fibrous and tenacious in nature; fibers form links between particles and make handling the raw ground samples difficult. During torrefaction, the biomass loses its tenacious nature,



**Figure 14. Grinding energy of beech as a function of torrefaction duration, obtained with a Retsch ZM1 ultracentrifugal mill equipped with a 500-mm grid<sup>58</sup>**

which is mainly associated with the breakdown of the hemicellulose matrix and depolymerization of the cellulose, resulting in decreased fiber length.<sup>10,31</sup> Particle length is also decreased, but not the diameter per se, resulting in better grindability, handling characteristics, and flowability through processing and transportation systems. Also during the torrefaction process, the biomass tends to shrink, become lightweight, flaky, and fragile, and lose its mechanical strength, making it easier to grind and pulverize.<sup>1</sup>

Bergman and Kiel conducted studies on the energy requirements for grinding raw and torrefied biomass like willow, woodcuttings, demolition wood, and coal using a heavy-duty cutting mill.<sup>31</sup> They concluded that power consumption reduces dramatically when biomass is first torrefied. This reduction ranges from 70–90%, based on the conditions under which the material is torrefied. Bergman and Kiel also found that the capacity of the mill increases by a factor of 7.5–15%.<sup>31</sup> The most important observation they made was that the size-reduction characteristics of torrefied biomass were similar to coal. Phanphanich and Sudhagar also observed a decrease in the grinding energy from 237.7–37.6 kWh/t, from raw to torrefied forest biomass at 300°C for 30 min.<sup>57</sup> Figure 14 gives the typical grinding energy reduction for torrefied wood.<sup>58</sup>

### Particle size distribution, sphericity, and particle surface area

Particle-size distribution curves, sphericity, and surface area are important parameters for understanding flowability and combustion behavior during cofiring. Many researchers observed that ground, torrefied biomass produced narrower, more uniform particle sizes compared to untreated biomass due to its brittle nature, which is similar to coal. Phanphanich and Sudhagar studied torrefied pine chips and logging residues and found that smaller particle sizes are produced compared to untreated biomass.<sup>57</sup> In addition, they observed that the particle distribution curve was skewed towards smaller particle sizes with increased torrefaction temperatures.<sup>57</sup>

Torrefaction also significantly influences the sphericity and particle surface area. Phanphanich and Sudhagar's results also indicated that sphericity and particle surface area increased as the torrefaction temperature was increased up to 300°C.<sup>57</sup> For ground, torrefied chips, they found that the sphericity increased from 0.48% to 0.62%, concluding that an increase in particle surface area or decrease in particle size of torrefied biomass can be desirable properties for efficient cofiring and combustion applications.<sup>57</sup> Also, the bulk and particle densities of ground torrefied biomass increase because the inter- and intraparticle voids generated after milling are reduced.<sup>59–60</sup> Research studies have indicated that ground torrefied material results in a powder with favorable size distribution and spherical particles, allowing torrefied powder to meet the smooth fluidization regime required for feeding it to entrained-flow processes (i.e., gasifier and pulverized coal).

### Pelletability

Variability in feedstock quality due to differences in the types of raw materials, tree species, climatic and seasonal variations,

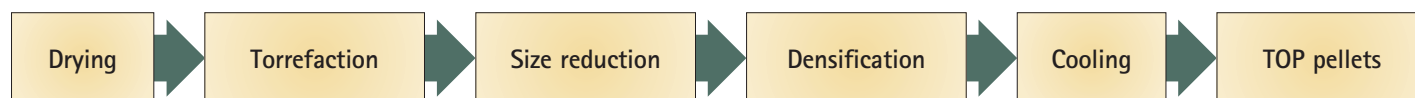


Figure 15. Flow diagram for production of torrefied wood pellets<sup>32</sup>

storage conditions, and time significantly influence the quality of biopellets.<sup>61</sup> Torrefying the biomass before pelletization, however, produces uniform feedstock with consistent quality.

Lignin in the biomass is considered to be the basic binding agent; thus, the pelletability of any biomass is evaluated based on lignin content. In general, higher amounts of lignin improve binding and reduce the severity of process conditions. The torrefaction process opens more lignin-active sites by breaking down the hemicellulose matrix and forming fatty unsaturated structures, which creates better binding. Densification following torrefaction has been considered by several researchers.<sup>9,11,32,62–63</sup> These studies indicate that, compared to raw biomass pelletization, the required pressure and energy consumption can be reduced by a factor of 2 when the material is densified at a temperature of 225°C. In addition, densification tests on torrefied biomass using a Pronto-Press indicated that the density of torrefied and pelletized material varied in the range of 750–850 kg/m<sup>3</sup> compared to conventional wood pellets, which are in the range of 520–640 kg/m<sup>3</sup>. The energy density and CV have also increased by approximately 70–80%, which is comparable to sub-bituminous coal.<sup>31</sup> Figure 15 shows the flow diagram for the TOP process that Bergman proposed.<sup>32</sup>

### Chemical compositional changes

Besides improving physical attributes, torrefaction also results in significant changes in proximate and ultimate composition of the biomass and makes it more suitable for fuel applications. Sadaka and Negi's<sup>15</sup> study on torrefaction of wheat straw, rice straw, and cotton gin waste at 200, 260, and 315°C for 60, 120, and 180 min, respectively, concluded that moisture content was reduced at the conditions (260°C for 120 min) for all three feedstocks by 70.5, 49.4, and 48.6%, and the heating value increased by 15.3, 16.9, and 6.3%, respectively. Zanzi et al, in their study on miscanthus torrefaction, made similar observations, where increasing temperature from 230 to 280°C and time from 1–3 h increased the carbon content and decreased the hydrogen, nitrogen, and oxygen content.<sup>7</sup> At 280°C, the carbon content increased to about 52% from an initial value of 43.5%, while hydrogen and nitrogen content decreased from 6.49 to 5.54% and 0.90 to 0.65%, respectively, for 2 h of torrefaction. In general, increased torrefaction temperatures result in increased carbon content and decreased hydrogen and oxygen content due to the formation of water, CO, and CO<sub>2</sub>.

This process also causes the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios to decrease with increasing torrefaction temperature and time, which results in less smoke and water-vapor formation and reduced energy loss during combustion

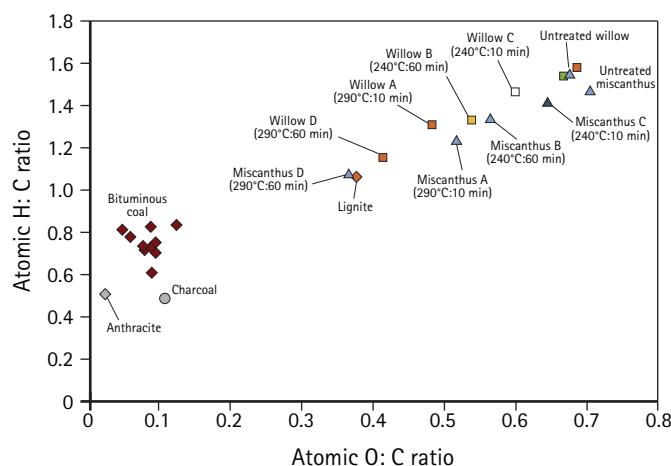


Figure 16. Van Krevelen diagram for torrefied willow and miscanthus<sup>64</sup>

and gasification processes. In torrefaction studies of reed canary grass and wheat straw torrefaction at 230, 250, 270, and 290°C for 30 min residence times, Bridgeman et al found that the moisture content decreases from an initial value of 4.7–0.8%.<sup>12</sup> They found that carbon increased 48.6–54.3%, while the hydrogen and nitrogen content decreased from 6.8–6.1% and 0.3–0.1%, respectively. In another study, Bridgeman et al made a Van Krevelen diagram for torrefied willow and miscanthus, as is shown in Figure 16.<sup>64</sup> It is clear that at higher temperatures and residence times, the atomic O/C and H/C ratios are closer to that of lignite coal. Table 5 shows the effect of different torrefaction temperatures on ultimate compositional changes in woody and herbaceous biomass.<sup>12</sup> Table 6 shows the physiochemical composition of pine and heat-treated pine at torrefaction temperatures from 240–290°C and indicates that as torrefaction temperature increases, fixed carbon increases and volatiles and moisture content decrease.<sup>65</sup>

### Calorific value

Biomass loses relatively more oxygen and hydrogen than carbon during torrefaction, which increases the calorific value of the product.<sup>6</sup> The net CV of torrefied biomass is 18–23 MJ/kg (lower heating value [LHV], dry) or 20–24 MJ/kg (higher heating value [HHV], dry).<sup>11,66</sup> The mass and energy in the torrefied biomass is preserved in the solid product for a long time, as the material does not degrade with time. Table 5 provides the ultimate analysis and elemental composition of torrefied woody and herbaceous biomass proper-

## RESEARCH

**Table 5. Ultimate analysis, moisture content, and HHV (dry ash free basis) of untreated and torrefied biomass<sup>12</sup>**

	RAW	TORREFACTION TEMPERATURE			
	0°K	503°K	523°K	543°K	563°K
<b>REED CANARY GRASS</b>					
C (%)	48.6	49.3	50.3	52.2	54.3
H (%)	6.8	6.5	6.3	6.0	6.1
N (%)	0.3	0.1	0.0	0.1	0.1
O (%)	37.3	N/A	37.0	37.3	36.3
Moisture (%)	4.7	2.5	1.9	1.3	1.2
CV (kJ/kg)	19,500	N/A	20000	20800	21800
<b>WHEAT STRAW</b>					
C (%)	47.3	48.7	49.6	51.9	5.6
H (%)	6.8	6.3	6.1	5.9	1.0
N (%)	0.8	0.7	0.9	0.8	27.6
O (%)	37.7	N/A	35.6	33.2	0.8
Moisture (%)	4.1	1.5	0.9	0.3	0.8
CV (kJ/kg)	18,900	19 400	19800	20700	22 600
<b>WILLOW</b>					
C (%)	49.9	50.7	51.7	53.4	54.7
H (%)	6.5	6.2	6.1	6.1	6.0
N (%)	0.2	0.2	0.2	0.2	0.1
O (%)	39.9	39.5	38.7	37.2	36.4
Moisture (%)	2.8	0.5	0.1	0.1	0.0
CV (kJ/kg)	20,000	20 600	20 600	21 400	21 900

**Table 6. Physiochemical analysis<sup>a</sup> of pine and heat-treated pine<sup>65</sup>**

T (°C) <sup>b</sup>	P <sup>c</sup>	240	250	260	270	290
Fixed carbon, %	20.64	23.55	25.59	25.69	29.38	35.39
Elementary analysis						
C, %	50.98	51.14	51.93	53.78	53.57	58.08
O, %	42.80	42.70	42.18	40.66	40.67	36.40
Pentosans, %	9.61	5.93	5.90	3.10	2.54	1.40
Lignin, %	22.84	24.90	28.72	33.44	39.23	53.47
Extractables, % <sup>d</sup>	14.67	8.19	14.09	19.35	16.49	17.98
Moisture, % <sup>e</sup>	10.80	5.66	4.08	3.96	3.76	3.88
Yield, %	—	86.2	81.8	75.7	66.4	48.8

<sup>a</sup>In each case, the mean result given was obtained from a minimum of four different experiments. <sup>b</sup>Torrefaction time: 30 min. <sup>c</sup>Native pine. <sup>d</sup>Neutral-solvent extractables (ethanol, benzene, boiling water). <sup>e</sup>Powder samples left at the laboratory atmosphere still had a constant humidity.

ties as compared to raw materials. Sadaka and Negi also observed that the highest heating value of 22.75 MJ/kg, or 9761 BTU/lb, was achievable at torrefaction conditions of 315°C and 3 h.<sup>15</sup>

## Storage aspects of torrefied biomass

### Off-gassing

Storage issues like off-gassing and self-heating may also be insignificant in torrefied biomass, as most of the solid, liquid, and gaseous products that are chemically and microbiologically active are removed during the torrefaction process. Kuang et al's<sup>67</sup> and Tumuluru et al's<sup>68</sup> studies on wood pellets concluded that high storage temperatures of 50°C can result in high CO and CO<sub>2</sub> emissions, and the concentrations of these off-gases can reach up to 1.5% and 6% for a 60-day storage period. These emissions were also found to be sensitive to relative humidity and product moisture content. The same researchers at the University of British Columbia conducted studies on off-gassing from torrefied woodchips and indicated that CO and CO<sub>2</sub> emissions were very low—nearly one-third that of regular woodchips at room temperature (20°C). This could be due to low moisture content and reduced volatile content, which could result in less reactivity with the storage environment.

### Hydrophobicity

In general, the uptake of water by raw biomass is due to the presence of OH groups. Torrefaction produces a hydrophobic product by destroying OH groups and causing the biomass to lose the capacity to form hydrogen bonds.<sup>69</sup> Due to these chemical rearrangement reactions, nonpolar unsaturated structures are formed, which preserve the biomass for a long time without biological degradation, similar to coal.<sup>31,70</sup>

Bergman determined the hydrophobicity of torrefied pellets by immersing them in water for 15 h.<sup>32</sup> Their hydrophobic nature was evaluated based on the state of the pellet after this period and by

gravimetric measurement to determine the degree of water uptake. Bergman's study indicated that raw pellets swelled rapidly and disintegrated into original particles.<sup>32</sup> Torrefied pellets produced under optimal conditions, however, did not disintegrate and showed little water uptake (7–20% on a mass basis). Bergman also concluded that torrefaction conditions play a vital role in the hydrophobic nature of biomass.<sup>32</sup> Sokhansanj et al compared the moisture uptake of the torrefied biomass to the untreated biomass and found a 25% decrease in water uptake when compared to the control, as shown in Figure 17.<sup>71</sup>

Biomass is porous, often moist, and prone to off-gassing and self-heating due to chemical oxidation and microbiological activity. In general, the biomass moisture content plays an important role in initiating chemical and microbial reactions. Moisture content coupled with high storage temperatures can cause severe off-gassing and self-heating from biomass-based fuels. Another important storage issue for ground torrefied biomass is its reactivity in powder form, which can result in fire during storage. It is preferred to store the torrefied biomass in an inert environment to avoid incidents of spontaneous combustion. In his laboratory-scale combustion studies of torrefied wood, Kiel found that it is highly reactive, similar to coal.<sup>53</sup>

Table 7 shows the product characteristics of torrefied biomass compared to coal and wood, revealing that torrefied wood closely resembles charcoal. The major difference between charcoal and torrefied wood is the volatile content. Volatiles are lost during charcoal production, which also means a possible loss of energy.<sup>72</sup> On the other hand, during torrefaction, most of the volatiles are retained. It is also recommended that every form of carbonization be avoided during torrefaction. As Table 7 shows, torrefied pellets have product characteristics, like handling, milling, and transport requirements, similar to coal.<sup>65</sup> Torrefied pellets allow for higher cofiring percentages up to 40% due to matching fuel properties with coal, and they can use the existing equipment setup for coal.

## Torrefied biomass applications

Pulverized fuel combustion in coal-fired power stations and entrained-flow gasification are particularly interesting product outlets for biomass. In both applications, biomass has to be fed to the reactor as a powder, which is difficult, costly, and achievable only at very low capacity in classical coal mills. Due to this limitation, wood pellets are currently the state-of-the-art for cofiring, as they consist of sufficiently small particles. Consequently, wood pellets also have some limitations in terms of energy content and moisture uptake during storage and transportation. Torrefied biomass, because it is energy-dense and hydrophobic in nature, can be a good replacement for wood pellets in cofiring and gasification plants. The high fuel quality of torrefied biomass makes it very attractive for combustion and gasification applications. Due to high calorific values, the thermal energies of the combustion and gasification system can be improved significantly.<sup>31</sup> However, data is lacking on milling, handling, storing, transporting, and combusting

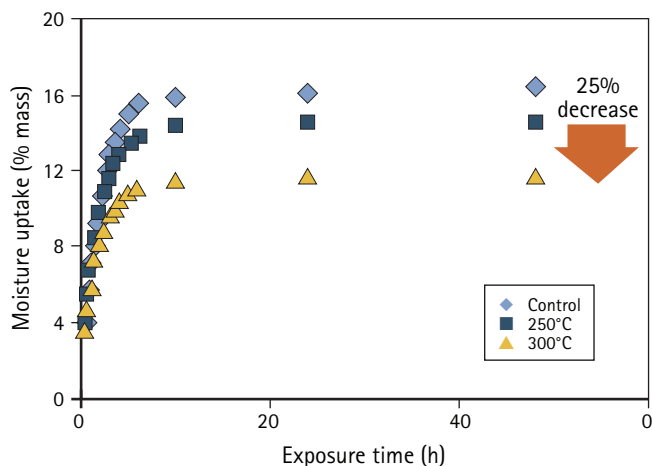


Figure 17. Moisture uptake by the torrefied wood pellets made from a 0.8 mm particle size<sup>71</sup>

Table 7. Indicative properties of different biomass and coal-based fuels<sup>72</sup>

	WOOD	WOOD PELLETS	TORREFIED PELLETS	CHARCOAL	COAL
Moisture content (% wt)	30–45	7–10	1–5	1–5	10–15
Calorific value (MJ/kg)	9–12	15–16	20–24	30–32	23–28
Volatiles (% db)	70–75	70–75	55–65	10–12	15–30
Fixed carbon (% bd)	20–25	20–25	28–35	85–87	50–55
Bulk density (kg/l)	0.2–0.25	0.55–0.75	0.75–0.85	~0.2	0.8–0.85
Volumetric energy density (GJ/m <sup>3</sup> )	2.0–3.0	7.5–10.4	15.0–18.7	6.0–6.4	18.4–23.8
Dust	Average	Limited	Limited	High	Limited
Hygroscopic properties	Hydrophilic	Hydrophilic	Hydrophobic	Hydrophobic	Hydrophobic
Biological degradation	Yes	Yes	No	No	No
Milling requirement	Special	Special	Classic	Classic	Classic
Handling requirements	Special	Easy	Easy	Easy	Easy
Product consistency	Limited	High	High	High	High
Transport cost	High	Average	Low	Average	Low

large amounts of torrefied biomass at a commercial scale. Common torrefied biomass applications include: (1) high-quality smokeless solid fuels for industrial, commercial, and domestic applications, (2) solid fuel for cofiring directly with pulverized coal at electric power plants, (3) an upgraded feedstock for fuel pellets, briquettes, and other densified biomass fuels, and (4) high-quality biomass solid fuel for advanced bioenergy application.

## Conclusions

Interest in research on torrefaction of biomass materials is growing. Its potential to improve the quality of both herbaceous and woody materials provides a path for using these resources in many energy applications. This review has provided insight into the limitations of raw biomass materials to meet the needs of energy providers and has discussed options for improving biomass resources for use in power and liquid-fuel production. Based on this review, nine areas of discussion are summarized below. These areas provide a brief understanding of the potential use of torrefaction as a means of improving the physical, chemical, and rheological characteristics of biomass materials. As with most biomass-upgrading options, however, torrefaction, and the subsequent densification processes, need to be evaluated for energy inputs to understand the logistical advantages and end use of the product.

1. Torrefied biomass, in general, defines a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring at the 200–300°C temperature range.
2. The most common torrefaction reactions include (a) devolatilization and carbonization of hemicelluloses, and (b) depolymerization and devolatilization of lignin and cellulose.

3. Torrefaction of the biomass helps in developing a uniform feedstock with minimum variability in moisture content.
4. Torrefaction of biomass improves (a) energy density, grindability, and pelletability index ratings, (b) ultimate and proximate composition by increasing the carbon content and CV and decreasing the moisture and oxygen content, and (c) biochemical composition by decomposing the hemicelluloses and softening the lignin, which results in better binding during pelletization.
5. Ground torrefied biomass has improved sphericity, particle surface area, and particle size distribution.
6. Densification of torrefied material reduces specific energy consumption and increases throughput by about a factor of 2 compared to raw or untreated biomass.
7. During torrefaction the biomass loses most of the low energy content of the material, like (a) solids, which include original sugar structures and other newly formed polymeric structures, and (b) liquids, which include condensables, like water, organics, and lipids, and (c) gases, which include H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>, C<sub>x</sub>H<sub>y</sub>, toluene, and benzene.
8. Torrefaction preserves the biomass for a long time without biological degradation due to the chemical rearrangement reactions and formation of nonpolar unsaturated structures.
9. Torrefied biomass has been successfully used as an upgraded solid fuel in electric power plants and gasification plants.

Not all aspects of torrefaction and its influence on other processing operations have been explored. Opportunities for future research can include:

- a. Optimizing torrefaction processes based on activation energies required to degrade the cellulose, hemicelluloses, and lignin.

- b. Understanding the torrefaction process at a molecular level by identifying different functional groups and energies associated with breaking the bonds.
- c. Understanding the spontaneous torrefaction process reactions using Fourier transform infrared (FTIR) and Raman spectroscopy.
- d. Understanding the severity of the torrefaction process based on color changes using the Hunter colorimeter.
- e. Studies on thermogravimetrics to establish the weight-loss kinetics.
- f. Studies on microstructural changes in biomass at different temperature regimes.
- g. Testing integrated processes such as torrefaction and densification.
- h. Calculating energies associated with condensable and noncondensable products produced during torrefaction and the ability to reuse them to improve the overall process efficiency.
- i. Understanding the storage behavior of torrefied biomass in terms of off-gassing and spontaneous combustion at different storage temperatures.

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