Current Trends in the Production and Applications of Torrefied Wood/Biomass - A Review

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Trends in the production and applications of torrefied wood/biomass are reviewed in this article. The thermochemical conversion of biomass is a promising technology because biomass is an environmentally friendly fuel that produces substantially lower CO₂ emissions compared to fossil fuel. Torrefaction is the thermal treatment of biomass at temperatures from 200 to 300 °C in the absence of air or oxygen to liberate water and release volatile organic compounds, primarily through the decomposition of the hemicelluloses. Torrefied biomass has a higher heating value, is more hydrophobic, resists rotting, and has a prolonged storage time. The different torrefaction technologies and reactors are described. An overview of the applications of torrefied biomass, the economic status, and future prospects of torrefaction technology are presented and discussed. Currently, torrefaction demonstration plants have technical problems that have delayed their commercial operation. Torrefaction reactors still require optimization to economically meet end-use requirements and attain product standardization for the market. Several characteristics of torrefaction need to be demonstrated or scaled up for successful commercialization.

Keywords: Torrefaction; Torrefied wood/biomass; Torrefaction technologies; Torrefaction reactors

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INTRODUCTION

Biomass, which can be defined as lignocellulosic material from plants, has been recognized as the fourth largest energy source in the world; it is an important source for both renewable fuels and valuable chemicals (Saxena *et al.* 2008). A primary use of biomass is for power generation. It can be used directly as solid fuel or processed into gaseous or liquid fuels (Briens *et al.* 2008). There are many biochemical and thermochemical processes available to convert biomass to different fuels and chemicals.

Biomass is renewable, since new biomass can be grown to replace that used for energy. This growth removes CO_2 from the atmosphere, neutralizing the CO_2 emission generated when converting biomass to energy. However, several problems and challenges are unavoidably encountered during biomass utilization because of the diversity of its physical and chemical compositions, which depend on the origin of the raw material.

When biomass is used as feedstock for power generation, it often exhibits undesirable properties. Some types of biomass have high ash content, which leads to the agglomeration of the bed material inside the boiler as well as fouling the surface of heat transfer tubes in combustion chambers (Oehman *et al.* 2005; Pronobis 2006; Romeo and Gareta 2009). Raw biomass generally has low calorific value because of its high moisture and oxygen contents (Pimchuai *et al.* 2010; Chen and Kuo 2011).

Due to rigidity, mechanical strength, poor flow and fluidization properties, biomass requires high grinding energy. It is also difficult to feed into boilers (van der Stelt *et al.* 2011; Li *et al.* 2012; Ohliger *et al.* 2013). Other challenges to biomass use include the large land surface required to grow it (Higman and van der Burgt 2008) and high costs for collection and transportation (Biagini *et al.* 2005). After drying, biomass can regain moisture and may rot during storage (Bergman 2013). Biomass is hygroscopic and forms a considerable quantity of soot during combustion.

To enhance biomass utilization efficiency and limit the challenges mentioned above, a torrefaction pretreatment is beneficial (Mosier *et al.* 2005; Zwart *et al.* 2006; Acharjee *et al.* 2011; van der Stelt *et al.* 2011). Torrefaction technology and its applications have advanced significantly over the last decade (Stamm 1956; Kamdem *et al.* 2002; Tjeerdsma and Militz 2005; Stanzl-Tschegg *et al.* 2009; Chen *et al.* 2011; Phanphanich and Mani 2011; Agar and Wihersaari 2012a; Dhungana *et al.* 2012; Huang *et al.* 2012; Syu and Chiueh 2012; Makarov *et al.* 2013; Becer *et al.* 2013; Johnston 2013; Wilen *et al.* 2014; Halina *et al.* 2014). However, there are unresolved issues and an incomplete understanding of the scientific process of torrefaction.

This review discusses current trends in the production and applications of torrefied wood/biomass. First, the advantages of wet and dry torrefaction are discussed. Laboratory scale studies on torrefaction including mass and energy balances of wet lignocellulosic biomass torrefaction, torrefied wood/biomass gasification and characterization of torrefaction products as well as torrefaction kinetics are presented. An overview of current torrefaction technologies and reactors, advantages and disadvantages of these technologies then follow. In the fourth part of this review, applications of torrefied wood/biomass are described. These include: gasification, co-firing of torrefied biomass with coal, combined heat and power generation, standalone combustion, production of bio-based fuels and chemicals, heating blast furnaces and industrial applications. The final sections enumerate the economic status and future prospects of torrefaction technology.

The following excellent reviews on biomass torrefaction have been published: (Chew and Doshi 2011; van der Stelt *et al.* 2011; Koppejan *et al.* 2012; Batidzirai *et al.* 2013; Chen *et al.* 2015).

WHAT IS TORREFACTION?

Torrefaction is the thermal treatment of wood/biomass in the low-temperature range to achieve biomass energy balance optimization, to promote grindability, and to reduce the hygroscopic nature of biomass. This in turn reduces its susceptibility to biological decay (Kamdem *et al.* 2000; Almeida *et al.* 2010; Acharjee *et al.* 2011). The effect that torrefaction has on reducing the grinding energy needed is a primary consideration in many energy-producing applications. These include the co-firing of lignocellulosic materials in pulverized coal-fired power plants and other industrial kilns (*e.g.* cement, coke and steel industry kilns) (Phanphanich and Mani 2011; Koppejan *et al.* 2012). In addition to these impacts, irreversible material property changes such as reduction of strength, toughness, and abrasion can occur (Stamm 1956; Kamdem *et al.* 2002; Tjeerdsma and Militz 2005; Stanzl-Tschegg *et al.* 2009).

Torrefaction research was performed in France in the 1930s. Then, in the 1980s, the results of torrefaction experiments using two temperatures and two tropical wood samples at 270 to 275 °C were published (Bourgeois and Doat 1984). This research led to

the building of a continuous wood torrefaction plant in 1987. Torrefaction technologies can be divided into either the wet or dry process.

DRY TORREFACTION

Dry torrefaction is the thermal treatment of wood/biomass at temperatures of 200 to 300 °C in the absence of air or oxygen. The process results in the liberation of water and volatile organic compounds. This primarily occurs through the de-volatilization of the hemicelluloses. Dehydration and decarboxylation reactions occur during torrefaction. Cellulose and lignin in woody biomass are decomposed at temperatures above 300 °C (Chouchene *et al.* 2010). In spite of the fact that 30 wt.% of biomass can be lost during torrefaction, the torrefied product may retain up to 90% of the initial energy content (van der Stelt *et al.* 2011).

Dry torrefaction technology has been rapidly developed to the stage of market introduction and commercial operation. Several torrefaction installations have recently been built in Europe and North America. Market analyses have predicted that in 2020, torrefaction technology market will be about 130 million tons per year (Walton and Van Bommel 2010).

Once biomass has been torrefied, it has become a distinctly different material that has several advantages and disadvantages when compared to the original biomass. Figure 1 is an overview of an integrated torrefaction plant.



Fig. 1. Overview of an integrated torrefaction plant (Kiel et al. 2012)

Table 1. Logistics, Advantages, and Disadvantages of Handling Torrefied

 Wood/Biomass (Stelte 2013)

Advantages	Disadvantages/Challenges
The higher energy density of torrefied biomass	Dust and dirt are encountered during handling and
leads to effective transport	transport.
Reduced water retention force (increased	Self-ignition and spontaneous combustion at 150-
hydrophobicity)	170 °C can occur and requires caution.
Reduced biodegradability	Increased explosion hazard exists when compared
	to conventional biomass but probably not in
	comparison with coal.
Better grindability	Pelletization (pellets / briquettes) is more difficult.
Decreased handling, storage and transport cost;	Many fuel properties (e.g. degree of torrefaction,
New markets and trade flows as a commodity fuel	grindability, hydrophobic nature, resistance against
(product standards are needed)	biodegradation) and sustainability criteria have not
	been thoroughly defined or standardized.

Torrefaction can be used as a pretreatment method prior to fast pyrolysis of biomass to bio-oil. This pretreatment improves the quality of pyrolysis oil by lowering its water content and the proportion of low molecular weight compounds (Meng *et al.* 2012; Zheng *et al.* 2012). Torrefaction in general, is an effective method for reducing the water, acid, and oxygen contents of bio-oil when derived from fast pyrolysis of torrefied biomass. Removing oxygen raises the heating value and pH of bio-oil. Torrefaction-aided fast pyrolysis is a stepwise biomass pyrolysis through which the major biomass constituents are more selectively decomposed into a variety of chemicals at each stage. Products from each stage can be less complex and more stable than the products from direct fast pyrolysis, where all biomass constituents are decomposed synchronously at the same temperature (Czernik and Bridgwater 2004; Mohan *et al.* 2006). Torrefaction is influenced by the biomass chemical properties, treatment temperature, reaction time, and the apparatus used (Prins *et al.* 2006a; Chen *et al.* 2011). Meanwhile, the effects of torrefaction severity on the structure of torrefied biomass, its corresponding fast pyrolysis behavior and pyrolysis mechanism are currently not well understood (Zheng *et al.* 2013).

WET TORREFACTION

Wet torrefaction (also referred to as hydrothermal pretreatment), is the treatment of biomass in hydrothermal media or hot water at temperatures between 180 and 260 °C and pressures up to 4.6 MPa (Yan *et al.* 2009, 2010; Bach *et al.* 2013; Runge *et al.* 2013; Chen *et al.* 2012). Biomass is immersed in water at these conditions from 5 to 240 min (Lynam *et al.* 2011), resulting in the formation of solid fuel, aqueous compounds, and gases (Yan *et al.* 2009; Sasaki *et al.* 2003; Ando *et al.* 2000). The resulting solid product contains about 55 to 90% of the original mass and 80 to 95% of the fuel value of the original feedstock. Water soluble compounds, consisting primarily of monosaccharides, furfural derivatives, and organic acids, make up approximately 10% by mass of the by-products. Gaseous products make up the balance (Bobleter 1994; Petersen *et al.* 2009).

In wet torrefaction, the hemicellulose can be hydrolyzed and completely solubilized into the aqueous phase, while the lignin binding is disrupted. However, cellulose is almost

entirely preserved in this solid product. Nonetheless, the enzymatic digestibility of cellulose is enhanced because the cellulose in wet torrefied biomass is now more readily accessible to enzymes. Wet torrefaction is therefore an effective pretreatment technology for enhancing subsequent enzymatic hydrolysis of cellulose (Yu *et al.* 2011; Cybulska *et al.* 2012; Rohowsky *et al.* 2013). The term autohydrolysis is typically used in this context.

Wet-torrefied biomass has more fixed carbon (proximate analysis) and elemental carbon per unit of dry matter (ultimate analysis) than raw biomass. Thus, a higher weight fraction of biomass is transformed into a fuel with properties that resemble low-rank coal. With reduced equilibrium moisture content, the pretreated solid is more hydrophobic than the original biomass. Wet torrefied biomass can be easily stored to accommodate seasonal availability because it has far less propensity to absorb water, swell, or decompose. Wet-torrefied biomass is also very friable. Since it contains lignin, it can be pelletized for feeding to a thermochemical conversion process (Yan *et al.* 2009).

Wet torrefaction is similar to hydrothermal carbonization (Goto *et al.* 2004; Funke and Ziegler 2010; Parshetti *et al.* 2013; Liu *et al.* 2013; Hoekman *et al.* 2014), and it is sometimes discussed under the general term "hydrothermal conversion" (Knezevic *et al.* 2009; Wang *et al.* 2011; Kruse *et al.* 2013) or "hydrothermal treatment" (Karagoez *et al.* 2004; Nonaka *et al.* 2011; Murakami *et al.* 2012). In spite of the fact that wet torrefaction and hydrothermal carbonization have sometimes been used interchangeably, there is a significant difference between these terms. Wet torrefaction is primarily used for the production of upgraded solid fuels for energy applications only. In contrast, hydrothermal carbonization is applied to the production of charcoal that has much higher carbon content. This can be used not only as fuel but also as activated carbon, soil enhancers, or fertilizers, *etc.* Compared to dry torrefaction, (200 to 300 °C) the reaction temperature used for wet torrefaction is lower (180 to 260 °C). The pressure used is the saturated water vapor pressure, generated at the temperature applied.

ASSESSMENT OF DRY AND WET TORREFACTION

There are differences in the chemical structures of dry and wet torrefied biomass. These differences often give rise to subsequent divergent pyrolysis behavior observed in these two types of pretreated biomass. After wet torrefaction, the wet hydrophobic solid product can be effectively dried mechanically and/or by natural dewatering. These options are attractive and significantly reduce the energy requirements for the post-drying step. Valuable organic compounds such as acetic acid, formic acid, lactic acid, glycolic acid, levulinic acid, phenol, furfural, HMF, and sugars are found in the aqueous phase products of wet torrefaction, accounting for up to approximately 10 wt% of the feedstock (Yan *et al.* 2010; Hoekman *et al.* 2011). These water-soluble organic fractions might potentially be separated as valuable by-products to further improve wet torrefaction economics.

The significant reduction in ash content of fuel made by wet biomass torrefaction suggests that the procedure can be employed in the production of "cleaner" biomass solid fuels as well. Regression analyses and numerical prediction showed that wet torrefaction can produce solid fuel with greater heating value, higher energy yield, and better hydrophobicity at much lower processing temperatures and holding times than dry torrefaction (Bach *et al.* 2013). Wet torrefaction leads to easier pelletization than dry torrefaction because wet torrefied biomass does not require water addition to improve the pelletability and binding capacity (Reza *et al.* 2012).

The yields and solid fuel quality obtained from wet torrefaction have been reported to be better than those from dry torrefaction. At 200 °C, for example, wet torrefaction of loblolly pine can give mass and energy yields that are as high as 88.7% and 95% respectively, compared to 83.8% and 89.7% respectively, for dry torrefaction at 250 °C with the same holding time (Yan *et al.* 2009). In addition to the solid fuel, some water, CO₂, small amounts of CO, H₂, hydrocarbons, and dissolved organic and inorganic compounds are released from biomass during wet torrefaction (Erlach *et al.* 2012). Another advantage of wet torrefaction is its ability to dissolve and extract inorganic components from solid biomass fuels. In spite of the numerous advantages of wet over dry torrefaction, relatively few studies on wet torrefaction have been reported in the literature, compared to an increasing number of recent studies on dry torrefaction.

OXIDATIVE TORREFACTION

Oxidative torrefaction involves the torrefaction of biomass in an oxidative environment. In this process, there is a reduction in operating costs as well as N_2 consumption by employing air as the carrier gas. Wang and co-workers (2013) investigated the oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. The properties of torrefied sawdust and its pellets, including density, energy consumption for pelletization, higher heating value, and energy yield in oxidative environments were similar to those of the biomass torrefied in inert atmospheres. The use of oxygen-laden combustion flue gases as carrier gases in torrefaction was beneficial, avoiding the need for inert gasses application and additional thermal energy input.

Chen and co-workers (2013) determined the reaction characteristics of biomass torrefaction in inert and oxidative atmospheres at various superficial velocities. The reaction was controlled by heat and mass transfer in biomass torrefied in nitrogen. However, for that torrefied in air, surface oxidation was the dominant mechanism in the torrefaction process. The surface oxidation intensified the internal heat and mass transfer rates when temperature and superficial velocity were raised, resulting in a significant drop in solid and energy yields.

OVERVIEW OF LABORATORY SCALE STUDIES ON TORREFACTION

Mass and Energy Balances of Lignocellulosic Biomass Wet Torrefaction

Many studies have examined wood/biomass torrefaction. Mass and energy balances are of significant importance for the economic design and optimization of torrefaction technology. A particularly interesting study was carried out on the wet torrefaction of loblolly pine in the temperature range of 200 to 260 °C and at saturated vapor pressures of (225 to 680 psi) in a Parr reactor (Yan *et al.* 2010). Researchers reported that: a) gases accounted for 9 to 20% of the product and the quantity produced rose with increasing temperature, b) temperature also significantly affected mass yields and characteristics of the pretreated solid according to ultimate analyses and fuel-value measurements, c) organic acids were produced and accounted for 2 to 9% of the raw biomass, d) the quantity of precipitates dropped with increased temperature from 14% at 200 °C to 9% at 260 °C. The mass balances for wet torrefaction are shown in Table 2 for three temperatures.

Table 2.	Mass	Distributions	in the W	/et Tor	refaction	of Loblolly	^a Pine (`	Yan e	ət al.
2010)						-			

	Mass (g)	in		Mass (g)	out		
Temperature	Wood	Water	Torrefied	Acetic acid	^b Precipitates	Water	Gas
(°C)			wood				
200	1.00	4.93	0.83	0.01 (0.00)	0.14 (0.01)	4.86	0.09
		(0.06)	(0.00)			(0.04)	(0.01)
230	1.00	4.98	0.75	0.03 (0.00)	0.10 (0.01)	4.99	0.12
		(0.03)	(0.01)			(0.07)	(0.04)
260	1.00	4.99	0.63	0.06 (0.00)	0.09 (0.0)	5.01	0.20
		(0.02)	(0.02)			(0.08)	(0.10)

^a Reactants and products are given per the mass of dry wood. Uncertainty is shown in parentheses.

^b Precipitate compositions in the aqueous product stream are summarized in Fig. 2. As the wet torrefaction temperature was raised, the overall quantity of monosaccharides found in the aqueous output stream decreased due to their conversion to 5- hydroxymethylfurfural (5-HMF).



Fig. 2. Composition of precipitates in the aqueous output stream from loblolly pine wet torrefaction at various temperatures. Each mass fraction is reported as a fraction of the dry biomass feed (Yan *et al.* 2010).

The enthalpy and heat of reaction of loblolly pine wet torrefaction were also determined. The heat of formation was accurately measured with a calorimetric bomb, while the heat of reaction was determined by the difference of the heats of formation of the products and reactants at each temperature (Yan *et al.* 2010). The magnitude of the heat of

reaction was less than 2% of the heat of combustion for the untreated biomass. The reaction seemed to become less endothermic with an increase in temperature (Table 3).

	Enthalp (kJ g ⁻¹)	y in	Enthalpy out (kJ g ⁻¹)			Heat of reaction (kJ g ⁻¹)		
Temperature (°C)	Wood	Water	Torrefied wood	Acetic acid	Precipitates	Water	Gas	
200	-4.92	-74.64	-3.65	-0.08	-0.94	-73.56	-0.77	0.56
	(0.52)	(0.89)	(0.47))	(0.00)	(0.08)	(0.59)	(0.13)	(0.72)
230	-4.82	-74.64	-2.63	-0.19	-0.29	-74.78	-1.04	0.53
	(0.52)	(0.42)	(0.45)	(0.00)	(0.03)	(1.08)	(0.36)	(0.75)
260	-4.72	-74.12	-1.65	-0.42	-0.25	-74.41	-1.86	0.25
	(0.52)	(0.22)	(0.45)	(0.00)	(0.00)	(1.21)	(0.87)	(0.92)

Table 3. Enthalpy and Heat of Reaction in the Wet Torrefaction of Loblolly ^aPine (Yan *et al.* 2010).

^a All data were obtained on the basis of 1 g of biomass feedstock. Uncertainty (not further specified in the source work) is shown in parentheses. The errors associated with each variable may play a significant role in determining whether the reaction is endothermic or exothermic because the estimated heat of reaction is relatively small (0.25 kJ) compared to the energy in the reactants to the reaction temperatures. It is therefore necessary to conduct uncertainty analysis of the heat of reaction calculations.

An uncertainty analysis was also performed for the heat of reaction estimation. It showed that the effect of temperature on the heat of reaction was not significant (Fig. 3).



Fig. 3. Frequency distributions of the heats of reaction, during wet torrefaction of loblolly pine at three temperatures (Yan *et al.* 2010)

The effects of torrefaction on the chemical structures within torrefied wood derived from loblolly pine at different temperatures and times were examined (Ben and Ragauskas 2012). Solid-state cross-polarization/magic angle spinning (CP/MAS)¹³C, nuclear magnetic resonance (NMR) spectroscopy, and carbohydrate analysis were employed. The NMR results showed that the aryl-ether bonds in lignin were cleaved during torrefaction. The methyl carbons in hemicellulose acetyl groups were absent after torrefaction at 250 °C for 4 h. The torrefied wood had a higher heating value (HHV) that was greater than the original wood feed. The HHV (20.16 MJ kg⁻¹) of wood feed (dried at 75 °C, 48 h) was far lower than that of the torrefied wood, which was increased by 60% (32.34 MJ kg⁻¹) after torrefaction at 300 °C for 4 h (Table 4). This value is higher than for anthracite coal (31.84 MJ kg⁻¹) and Pittsburgh seam coal (31.75 MJ kg⁻¹), and much higher than Converse School-Sub C coal (21.67 MJ kg⁻¹), German Braunkohle lignite (25.10 MJ kg⁻¹), and Northumerland No. 81/2 Sem. Anth. Coal (24.73 MJ kg⁻¹) (Channiwala and Parikh 2002).

With an increased wood torrefaction time from 0.25 to 8 h, at 250 °C, the mass and energy yields decreased linearly from 94.97% to 64.36% and 99.79% to 79.12%, respectively (Ben and Ragauskas 2012). By contrast, the HHV increased from 21.22 to 24.78 MJ kg⁻¹ (Table 4). The mass yields of torrefied wood samples decreased significantly upon raising the torrefaction temperature from 250 to 300 °C. Less than 50 wt% of biomass remained after torrefaction at 300 °C (Ben and Ragauskas 2012). This magnitude is similar to other literature reports (Deng *et al.* 2009; Pimchuai *et al.* 2010; Chen and Kuo 2011).

T/ °C	Time (h)	Mass yield ^a (%)	HHV (MJ kg⁻¹)	Energy densification ratio ^ø	Energy yield ^c (%)
Original pine ^d	-	-	20.16	-	-
250	0.25	94.79	21.22	1.05	99.79
	0.50	86.19	21.87	1.08	93.48
	1.00	80.77	22.18	1.10	88.88
	2.00	75.46	22.61	1.12	84.62
	4.00	68.11	24.06	1.19	81.29
	6.00	66.19	24.40	1.21	80.11
	8.00	64.36	24.78	1.23	79.12
300	0.50	45.74	23.10	1.15	52.41
	1.00	40.36	-	-	-
	2.00	37.61	-	-	-
	4.00	36.65	32.34	1.60	58.79

Table 4. Influence of Temperatures and Residence Times on the Mass Yield,HHV, Energy Densification Ratio and Energy Yield of Torrefied Loblolly PineWood (Ben and Ragauskas 2012)

^a Mass yield = mass of dried torrefied wood/mass of dried wood \times 100%. ^b Energy densification ratio = HHV of dried torrefied wood/HHV of dried wood. ^c Energy yield = mass yield \times energy densification ratio. ^d The original loblolly pine wood sample was dried at 75 °C for 48 h before analysis of higher heating value.

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Torrefied Wood/Biomass Gasification

Torrefied wood/biomass gasification has been extensively studied, especially the resulting gas composition and heating values. Syngas composition can be influenced by several process parameters including feedstock composition, particle size, and gasification conditions: mainly temperature, steam to biomass ratio, pressure, and gasification reactor design (Gil *et al.* 1997; Kandiyoti *et al.* 2006; Higman and van der Burgt 2008; Pereira *et al.* 2012; El-Emam *et al.* 2012).

The influence of pressure and biomass feed composition on gasification product yields and composition during fluidized bed O₂/steam gasification was investigated (Berrueco *et al.* 2014). Two different biomass feedstocks: GROT (forest residues) and VW (virgin wood) were gasified. Three different torrefaction levels were applied: raw biomass, lightly torrefied (LT), and significantly torrefied (ST). A laboratory scale pressurized fluidized bed reactor was used. The main observed trend for both biomass feedstocks was that gas yield increased with increased pressure and torrefaction levels. Tar yield increased with the experimental pressure, and this occurred with a decrease in char yield. Also, raising the pressure shifted the gas composition towards higher CH₄ and CO₂ contents, while H₂ and CO levels decreased. VW-derived materials (VW-LT, VW-ST) yielded higher levels of H₂ and CO and lower levels of CH₄ than the corresponding forest residue (grot) feeds. As pressure and torrefaction level increased (more severe conditions), the differences between VW and forest residues became less relevant.

The gasification of wood pellets in a bubbling fluidized bed reactor at various temperatures, pressures and steam to biomass ratios (S/B) was reported (Mayerhofer *et al.* 2012). High temperatures (750 to 840 °C) promoted H₂ formation, while CH₄ and CO₂ content decreased. Additionally, higher S/B ratios shifted the gas composition to higher H₂ and CO₂ concentrations and lower CO and CH₄ contents in the gas produced. An increase in gasification pressure led to higher CH₄ content, due to the enhancement of methanation at high pressures. Raising pressure also resulted in a slight increase in H₂ content and lower CO/CO₂ ratios.

Torrefied wood and conventional wood gasification were compared (Prins *et al.* 2006a). Untorrefied willow was compared to torrefied willow at both 250 °C for 30 min and 300 °C for 10 min, respectively. These reaction times excluded the heating times required to go from 200 °C to the reaction temperature at 8.5 min and 17 min, respectively. Torrefaction raised the lower heating value (LHV) of willow from 17.6 to 19.4 and 21.0 MJ/kg, respectively (Table 5).

	Untorrefied willow	Torrefied willow (250 °C, 30 min)	Torrefied willow (300 °C, 10 min)
Carbon (%)	47.2	51.3	55.8
Hydrogen (%)	6.1	5.9	5.6
Oxygen (%)	45.1	40.9	36.2
Nitrogen (%)	0.3	0.4	0.5
Ash (%)	1.3	1.5	1.9
LHV(MJ/kg)	17.6	19.4	21.0

Table 5.	Composition	of Untorrefied a	and Torrefied	Willow (Prins et al.	2006a)
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Air-blown gasification of these untorrefied and torrefied wood feeds were conducted both at 950 °C in a circulating fluidized bed as well as at 1200 °C during oxygenblown gasification of torrefied wood in an entrained flow gasifier. Both gasification processes were run at atmospheric pressure. The overall exergetic efficiency of air-blown gasification of torrefied wood was lower than that of untorrefied wood because the volatiles produced in the torrefaction step were not utilized (Prins *et al.* 2006a).

The optimum gasification temperature of untorrefied wood is rather low (below 700 °C), and this feed is not an ideal fuel for gasifiers. Untorrefied wood becomes overoxidized in gasifiers because of its high O/C ratio and moisture content. It also produces low optimum gasification yields, leading to thermodynamic losses. Considering gasification of wood at 950 °C, there is a considerable amount of over-oxidation, which negatively influences the gasification efficiency. If wood is modified by torrefaction, its composition becomes more favorable so that it is over-oxidized less in the gasifier.

Figure 4 is a CHO illustration of untorrefied and torrefied wood produced at 250 and 300 °C which was then gasified at 950 °C (Prins *et al.* 2006a). The triangular CHOdiagram presents another reason for the increased gasification efficiency of torrefied wood. In this figure, the so-called carbon boundary line is shown at a temperature of 950 °C. In order to avoid the formation of solid carbon, this line has to be crossed. Excess oxygen is added to achieve complete gasification on the carbon boundary line where a thermodynamic optimum exists. C, H, and O are present in all the gasified products where I, IIa, and IIb represent their mole percentages in gasified untorrefied wood as well as wood, torrefied at 250 and 300 °C respectively.



Fig. 4. CHO diagram illustrating gasification of wood and torrefied wood (TW), where the torrefied wood was produced at 250 and 300 °C, then gasified at 950 °C (Prins *et al.* 2006a)

Gas yields and reaction kinetics during torrefied beech wood gasification were studied (Couhert *et al.* 2009). Beech wood was subjected to mild torrefaction (240 °C) and severe torrefaction (260 °C), using a specially designed crossed fixed bed reactor. A 2 s gasification at 1400 °C of the torrefied wood produced approximately the same quantities of CO₂, 7% more H₂, and 20% more CO than gasifying the untreated parent wood. Under these conditions, true equilibrium was reached. When gasification experiments were performed at a lower temperature, (1200 °C), the kinetics of torrefied wood gasification were comparable to that of the parent wood. However, the chars from torrefied wood were less reactive towards steam than the char from untreated wood.

Characterization of Torrefaction Products

Torrefaction products have been examined extensively (Felfli *et al.* 1998; Gaur and Reed 1998; Pach *et al.* 2002; Nimlos *et al.* 2003; Tumuluru *et al.* 2012; Hilten *et al.* 2013; Lin *et al.* 2013; Saleh *et al.* 2013; Keipi *et al.* 2014). The volatile species released during torrefaction of deciduous and coniferous wood at 270 °C have been analyzed (Prins *et al.* 2006b). Deciduous xylan-containing wood (beech and willow) and straw are more reactive during torrefaction than coniferous wood (larch). The solid mass conserved in the torrefied deciduous wood ranged from 73 to 83% (depending on residence time) versus 90% for the coniferous wood. The difference in the volatile species released during torrefaction of deciduous wood originated from the difference in their hemicellulose structures. Deciduous wood contains mostly the acetoxy- and methoxy-substituted xylose units of their hemicelluloses. These groups generated more acetic acid and methanol volatile products than coniferous wood.

The effect of varying torrefaction temperature on spruce wood and bagasse from 260 to 300 °C in an auger reactor was investigated at a 10 min residence time (Chang *et al.* 2012). The treatment temperature and original biomass chemical composition significantly influenced the solid/liquid/gas product distributions (Fig. 5).





The concentration of carboxyl or carboxylic acid groups in torrefied spruce wood was determined, using both methylene blue sorption and potentiometric titration, after torrefaction for 30 min at temperatures of 180, 200, 220, 240, 260, and 300 °C (Shoulaifar *et al.* 2012). They also determined the equilibrium moisture content of the torrefied samples along with dehydration reactions. The degradation of carboxylic acids is a key reaction that reduces hydrophilicity of torrefied biomass. This occurs primarily by decarboxylation, which increases as torrefaction severity increases. The equilibrium moisture content also decreased with increase in torrefaction temperature and a drop in carboxyl content.

The influence of torrefaction on different biomass sources was investigated by (Arnsfeld *et al.* 2014). Torrefaction at about 300 °C lowered the amount of oxygen in biomass significantly. Furthermore, the values of the ultimate content and proximate analysis after torrefaction depended strongly on the biomass origin. Integrated versus external torrefaction via thermodynamic modeling were analyzed and compared (Clausen 2014). The biomass to syngas efficiency increased from 63% to 86% (LHV - dry) by switching from external to integrated torrefaction at 300 °C. Integrated torrefaction at 250 °C and gasification without torrefaction yielded biomass to syngas efficiencies of 81% and 76% respectively.

Fast Pyrolysis of Torrefied Biomass for Bio-oil Production

Torrefaction of corncobs was carried out as a pretreatment before fast pyrolysis to generate bio-oil. Corncob torrefaction was conducted in an auger reactor at 250, 275, and 300 °C, and at 10, 20, and 60 min residence times for each temperature (Zheng *et al.* 2013). These torrefied corncobs were then fast-pyrolyzed in a bubbling fluidized bed reactor at 470 °C to generate bio-oil. Using solid state ¹³C NMR and FTIR, the structural changes of the torrefied corncobs were probed before fast pyrolysis. Employing torrefaction prior to fast pyrolysis improved the quality of the resulting bio-oil. When torrefaction severity was elevated, the heating value of bio-oil was increased and its acidity was lowered due, in part, to a drop in water content. However, the bio-oil yield decreased significantly. The decrease in bio-oil yield likely resulted from the crosslinking and charring of corncobs during torrefaction. Such pretreatment changes would require more fragmentation to occur when generating bio-oil in the fast pyrolysis step. This slows vaporization allows more time for solid phase condensation reactions to advance, producing more char.

Figure 6 illustrates, in a simple scheme, the effect of torrefaction on the subsequent fast pyrolysis mechanism of cellulose. The left side of Fig. 6 illustrates the thermal fragmentation of raw cellulose during fast pyrolysis. Fragmentation to lower weight polymers and oligomers of glucose occurs, while dehydration-cyclization simultaneously occurs to give anhydrosaccharides. Where fragmentation occurs all the way to the monosaccharide level, levoglucosan is produced. Further fragmentation to 5-hydroxymethylfurfural, hydroxyacetone, hydroxyacetaldehyde and other products occurs. Competing with decomposition to vaporizable molecules, larger cellulose fragments both partially dehydrate and crosslink. These larger solid phase species are unable to vaporize and instead, dehydrate and partially carbonize to char. On the right side of Fig. 6, the dehydration process is underway during the lower temperatures of torrefaction. Sufficient thermal energy is not available to cause extensive fragmentation to lower molecular weight oligomers, glucose, levoglucosan, and further decomposition products. Thus, bio-oil is not produced but some of the cellulose begins to crosslink and condense. After torrefaction, the 425 to 500 °C temperatures used in fast pyrolysis generate smaller amounts of volatiles as further crosslinking and char formation occur instead.



Fig. 6. Effects of torrefaction on the fast pyrolytic decomposition of cellulose (Chaiwat *et al.* 2008). Figures used by permission of copyright holder.

KINETICS OF TORREFACTION

Several attempts at correlating torrefaction properties with process conditions have been made in order to gain insight into this process. Most of the current torrefaction studies focus on the biomass property changes in batch-scale reactors. The degree of torrefaction is calculated based on the measured weight loss (Arias *et al.* 2008; Shang *et al.* 2012). In large-scale production facilities, torrefaction is usually performed continuously within a closed collector. This creates an inert atmosphere that makes process control more challenging. In order to improve the process control in continuous torrefaction reactors, mathematical models that accurately describe the torrefaction reaction under different heating rates need to be developed.

The weight loss kinetics of deciduous and coniferous wood types was studied (Prins *et al.* 2006c). The kinetics of torrefaction reactions in the temperature range of 230 to 300 $^{\circ}$ C were described accurately by a two-step mechanism, with the first step being much faster than the second step. The first step was hemicellulose decomposition, while the second step represented cellulose decomposition. The solid yields for the first step were higher by 70 to 88% than for the second step.

Linear regression mass loss was used to predict changes in fixed carbon (and thereby volatile matter) as well as the gross calorific value (and thereby energy yield) for three species of eucalyptus wood and bark (Almeida *et al.* 2010). Temperature and feedstock moisture were correlated as independent variables to predict mass loss and energy yield with a quadratic surface methodology for corn stover (Medic *et al.* 2012). A response surface methodology was used to correlate torrefaction severity (time and temperature) with weight loss, energy value, and energy yield for mixed softwoods (Lee *et al.* 2012). All three empirical data correlations performed well for their respective feedstocks. However, these empirical data did not offer a prediction for the behavior expected for additional feedstocks. These studies were purely empirical and not based on any fundamental understanding. Nonetheless, it is necessary for new empirical data to be modeled to adjust correlations for additional feedstock use.

Combustion kinetic studies of dry torrefied woody biomass materials using multiple pseudo-component models have been reported (Brostroem *et al.* 2012; Tapasvi *et al.* 2013). Brostroem *et al.* used a global kinetic model, while Tapasvi *et al.* employed a distributed activation energy model. Both studies showed that the degree of feed torrefaction had little effect on the combustion kinetic parameters of the torrefied biomass regardless of the torrefaction conditions. However, Brostroem *et al.* reported that hemicellulose, cellulose, and lignin activation energy values were constant at 100.6, 213.1 and 121.3 kJ/mol, respectively. This was true for both raw and dry-torrefied spruce. Tapasvi *et al.* reported that the activation energy values for the cellulose, non-cellulosic fractions, and char remained constant at 135, 160, and 153 kJ/mol respectively, for various types of feedstock and their degree of torrefaction.

A torrefaction model for wood chips in a pilot-scale continuous reactor with a twostep series, first-order reaction model was developed to study the two-step kinetics of wood chip torrefaction in a TGA setup (Shang *et al.* 2014). The first step was much faster than the second step. This study took into account the mass loss during the heating period in calculating the kinetic parameters, unlike other studies, that were based on kinetic parameters obtained from the isothermal part of torrefaction. These other approaches neglected sample degradation during the heating period. Shang *et al.*'s model was useful in predicting the HHV of wood chips torrefied in a continuous pilot scale reactor.

A simple first-order kinetic model was applied to estimate the activation energy and pre-exponential factor of both raw and dry-torrefied eucalyptus samples in a two-stage combustion process (devolatilization followed by combustion) (Arias *et al.* 2008). Both the activation energy and pre-exponential factor increased in stage 1 and decreased in stage 2 after dry torrefaction. Nonetheless, the model was based on an empirical method, which was not validated because the model itself could neither reproduce simulated curves nor give any information about the fit quality between the predicted and experimental data.

The fuel properties of typical Norwegian birch (hardwood) and spruce (softwood) were assessed after both dry and wet torrefaction (Bach *et al.* 2014). TGA experiments were employed. The thermal degradation kinetics under dry torrefaction conditions were investigated and the torrefaction kinetic parameters were determined. A two-step kinetic model was employed to simulate the recorded mass loss curves. In the first step, decomposition of the initial biomass to form an intermediate solid and volatiles exhibited a higher rate than the second step.

The determination of kinetic constants is often difficult. Kinetics derived from TGA experiments involve conditions that are dramatically different from those in torrefaction reactors. The TGA temperature ramp rates are very slow, and the particle size of the

samples is much smaller (Narayan and Antal 1996). Most fast pyrolysis reactors operate with a fixed heat source temperature, whereas the actual temperatures reached by the reacting samples are higher than those calculated for TGA studies. If several elementary reaction processes with different activation energies are involved, then the controlling chemical processes in TGA studies may differ markedly from torrefaction processes (Lede and Villermaux 1993; Lede 1996, 2010; Lede and Authier 2011).

Recent kinetic and mechanistic literature on thermal reactions, particularly the use of thermal analysis (TA), was evaluated (Galwey 2004). Major problems with kinetic studies based on thermal analysis experiments were described. Ambiguities exist in the definition of the essential terms ("mechanism", "rate constant," and "activation energy"). Also, a lack of order in the results was identified. The lack of physical meaning for the calculated Arrhenius parameters was noted, and the impossibility of finding a real kinetic mechanism from thermal analysis data alone was emphasized. Galwey concluded that supplementary tests (X-ray analysis, microscopy, *etc.*) are required.

The main bottleneck in using kinetic models expressed with calculated Arrhenius parameters to determine thermal decomposition pathways remains unsolved. "If we are to interpret them in terms of the transition-state theory, they are not applicable to solid state reactions" (Vyazovkin and Wight 1997). Because of the stable and tightly packed array-structure of samples in solid state reactions, the Maxwell-Boltzmann's energy distribution functions are not suitable. However, other energy distribution functions such as the Fermi-Dirac function for electrons and the Bose-Einstein function for photons can be applied (Vyazovkin and Wight 1997). In this case, E_a refers to the activation enthalpy and A refers to the frequency of lattice vibrations. Another major issue with these approaches is the empirical nature of the kinetic models tested (White *et al.* 2011).

In order to identify realistic solids' degradation mechanisms, further investigations are required because thermal changes (including chemical changes) are often more complex than is recognized. The origins of modern thermal analysis kinetics are located in a specialized branch of chemistry that is concerned with the thermal decomposition of solids, known as "crystolysis reactions" (Galwey 2004). The theory applied in cases that were evaluated was based on geometric models that are applicable to heterogeneous reactions in crystals, where the stoichiometries were regarded as already well established. For solid state thermal degradation kinetic studies employing thermal analysis methods, the calculated values of the Arrhenius parameters describe a given step of the process in a general manner. Arrhenius parameter values have a different physical meaning for reactions in crystals than for gas or liquid phase transformations.

The torrefaction technologies available today are basically designed and tested for biomass. Further research in the area of kinetic modelling for large scale reactor design and also for the optimization of product characteristics is absolutely necessary. The choice of torrefaction technology is exceptionally difficult because of the absence of practical comparative assessment of different types of reactors.

TORREFACTION TECHNOLOGIES

Most torrefaction technologies now being developed are based on already existing reactor concepts designed for other purposes such as drying or pyrolysis. These technologies are being modified for torrefaction. The reactors being developed in most cases are established technologies that developers are familiar with. They are simply being optimized for torrefaction applications. Some torrefaction technologies are capable of processing feedstock with small particles such as sawdust, while others are capable of processing large particles. Only a few can handle a large spectrum of particle sizes.

Many torrefaction technology developers are companies with extensive backgrounds in biomass processing and conversion technologies including carbonization and drying. This is an indication that technology selection needs to be based on feedstock characteristics. Alternatively, the feedstock needs to be pre-processed before torrefaction, using size reduction equipment such as scalpers for handling over-sized material or sieves for extraction of particles of smaller materials. These considerations all influence the capital and operating costs of a torrefaction plant. All of these technologies have their advantages and disadvantages. No single technique is fundamentally superior to the other. Since each reactor has unique characteristics and is well suited to handle specific types of biomass, proper reactor selection is important for specific biomass properties and application.

Torrefaction technology (Reactor type)	Company (Developer)
Fixed bed reactor	Parker Autoclave Engineers (US)
	New Earth Eco Technology (US)
	CDS (UK)
Rotary drum reactor	Torr-coal (NL)
	BIO3D (FR)
	EBES AG (AT)
	4Energy Invest (BE)
	BioEndev/EPTS (SWE)
	Atmosclear S.A. (CH)
Screw type reactor	Picheney Rotary
	BTG (NL)
	Biolake (NL)
	FoxCoal (NL)
	Agritech (US)
Multiple Hearth furnace	CMI-NESA (BE)
	Wyssmont (US) Multiple plate
	Integro Earth Fuels LLC (US)
Torbed (Rotating fluidized bed) reactor	Toppel (NL) Entrained
	Torftech Group (UK)
Microwave reactor	Rotawave Ltd (UK)
	CanBiocoal (UK)
	Airex (CAN)
	Torrefaction Systems (US)
Compact moving bed reactor	ECN (NL)
	Thermya (FR)
	Buhler (GER)
Belt dryer	Strampoy Green Investment (NL)
	New Earth Eco Technology (US)
	Agri-Tech producers LLC/RTF (US)
	4 EnergyInvest-AmelBiocoal(BE)

Table 6. Torrefaction Reactor Technologies and the Companies that haveDeveloped them

Key: AT-Austria, BE-Belgium, CA-Canada, CH-Switzerland, FR-France, IT-Italy, NL-Netherlands, GER-Germany, S-Spain, SWE-Sweden, UK-United Kingdom, US-United States of America. Sources: Kleinschmidt 2010; Beekes and Cremers 2012b; Kleinschmidt 2011; Nordin 2012; Melin 2011; Torrefaction of biomass 2012; and the respective company websites.

Current torrefaction technology can be categorized into two groups based on heating: 1) methods in which the biomass is heated directly, and 2) those in which it is heated indirectly. Those employing direct heating utilize a non-oxygen gas loop with a heat exchanger in a moving bed, drum, vibrating belt, or multiple hearth furnaces. Direct heating can also employ a low-oxygen gas loop linked to a burner in a tunnel, moving bed, or a torbed. Processes that are heated indirectly use an auger or a drum. Of these eight technology types, only a few are able to produce more than five tons/h of torrefied wood/biomass. Table 6 provides an overview of the eight most important torrefaction reaction technologies and the companies that have developed them. The following eight reactors are briefly described.

Fixed Bed Reactor

In a fixed bed down-flow reactor, the raw solid biomass is fed to the top of the reactor. The biomass undergoes drying and torrefaction, exiting at the bottom of the reactor. Neutral (oxygen free) hot gases enter the bottom of the column and travel upwards. The loaded gases exit at the top of the reactor. A condenser extracts water vapor and other condensable substances from the gas.



Fig. 7a. Fixed bed reactor (http://www.autoclaveengineers.com)



Fig. 7b. Schematics of a fixed bed reactor

The dry gas is combusted in a burner to generate hot gases for recirculation through the reactor. Excess gas is filtered and released to the environment during operation. In a fixed bed reactor, the biomass particles remain stationary (Dhungana *et al.* 2012).

Rotary Drum Reactor

The rotary drum is a proven technology for various applications (Koppejan *et al.* 2012). The rotary drum is heated directly or indirectly, using a superheated stream of flue gas resulting from the combustion of volatiles. The rotary drum of an indirectly heated reactor tumbles the biomass in an inert gaseous environment where heat is transferred from the hot drum wall to the biomass particles. In torrefaction applications, the process can be controlled by varying the torrefaction temperature, the rotational velocity, and the length and angle of the drum. If the rotational velocity is low, biomass will be carbonized instead of being torrefied. However, if the rotational velocity is too high, biomass will have low product quality because of partial torrefaction (Beekes and Cremers 2012b). As the drum rotates, biomass in the bed mixes homogeneously and heat is distributed between biomass particles. Because the scalability of the rotary drum is limited, a modular setup is required for higher capacities.



Fig. 8a. Rotary drum reactor (Thamer 2013)



Fig. 8b. Schematics of a rotary drum reactor

Screw Reactor

The screw torrefaction reactor is stationary. It could be vertical, horizontal, or inclined with a circular or rectangular cross-section. In this reactor, a rotating screw churns and moves the biomass through the reactor to enhance heat transfer between the wall and the bulk of the biomass. It also moves the biomass along its length at the same time (Dhungana *et al.* 2012). A screw reactor is often heated indirectly, using a heat transfer medium inside the hollow wall. Since the hot outer wall heats the biomass indirectly, there is no direct contact with an oxygen-laden heating medium. Some designs may have holes in the shaft for the volatiles to escape. Biomass may also be heated by applying heat to the screw itself *via* circulating hot fluid within its hollow structure. For torrefied biomass to achieve a good product quality, biomass with very low bulk density and high moisture content requires pre-treatment before feeding into the screw reactor (Beekes and Cremers 2012b).



Fig. 9a. Screw reactor (www.syncoal.com)



Fig. 9b. Schematics of a screw reactor

Multiple Hearth Furnace (MHF)

The multiple hearth furnace consists of a series of circular hearths placed one above the other and enclosed in a refractory-lined steel shell. Hot gases are input to the hearth to heat the biomass during torrefaction. Biomass is stirred and moved in a spiral path across each hearth by a vertical rotating shaft that goes through the center of the furnace, carrying arms with rabble blades (Lonardi *et al.* 2008). Biomass is fed to the top hearth, passing across it and then, through drop holes to the hearth below. Biomass passes continuously over and across each hearth to the bottom of the furnace, where the product is discharged through one or more ports.



Fig. 10a. Multiple hearth furnace (fgcgroupllc.com)



Fig. 10b. Schematics of a multiple hearth furnace

In some operations, combustion of charge-elements supplies the heat. In others, heat is provided by the combustion of auxiliary fuel in burners on certain hearths (direct firing), or in a separate combustion chamber (indirect firing) where the hot gases are fed by counter current flow from bottom to top of the furnace (fgcgroupllc.com).

A multiple hearth furnace offers operational flexibility, permitting a wide range of processing options and allowing for many structural variations to accommodate special operations. The residence time and temperature of the desired treatment can be closely controlled and also varied within wide limits. Fresh biomass can be loaded from the top or at any other hearth. Heat supply can be directed to the most effective area. Gases can escape from the top, bottom, and intermediate hearths, or any combination of these. The atmosphere can be oxidizing, reducing or neutral and can be varied in different parts of the furnace.

Torbed (Rotating Fluidized Bed) Reactor

In a torbed reactor, heat is carried *via* a gaseous medium that is blown in from the bottom of the bed with a high velocity (50 to 80 m/s) past stationary angled blades. The biomass particles inside the reactor acquire vertical and horizontal movements, resulting in toroidal swirls that rapidly heat the biomass particles in the reactor. This improves the heat and mass transfer among solids and gases, resulting in lower retention times and the production of a more homogeneous product (Beekes and Cremers 2012b). The relatively intense heat transfer enables torrefaction to be completed within a short residence time (around 80 s).

Intense heat transfer can also be used to operate the reactor in a controlled manner at elevated temperatures (up to 380 °C), resulting in a higher loss of volatiles from the biomass feed.



Fig. 11a. Torbed reactor (www.torftech.com)

bioresources.com



Fig. 11b. Schematics of a torbed reactor

Microwave Reactor

The microwave reactor employs microwave irradiation with electromagnetic waves, which can operate at a specific frequency in the range from 300 MHz to 300 GHz (Dhungana *et al.* 2012). The electric component of the electromagnetic microwave radiation causes heating by two main mechanisms: dipolar polarization and ionic conduction. Typical industrial microwave reactors usually operate at 2.45 GHz. The microwave irradiation produces efficient internal heating of biomass particles. The heating depends on the ability of the materials being heated to absorb the impinged microwaves and convert them into heat. The microwave reactor is different from the other reactors that utilize direct heating. In direct heating systems, by contrast, biomass is heated externally, such that heat from the heat carrier (gas, solid, liquid, or reactor wall) first contacts the surface of the biomass particles and moves by conduction into their center. This mode of heating is less efficient because biomass is a poor thermal conductor. Microwave heating occurs simultaneously throughout the sample.



Fig. 12. Microwave reactor (Thamer 2013)

Moving Bed Reactor

The moving bed reactor consists of an enclosed reactor vessel with the reactor length usually determined by the retention time that is required to produce the desired product. In torrefaction, the time required is 25 to 30 min (Beekes and Cremers 2012b). Biomass enters from the top of the vessel and moves downward gradually while torrefaction takes place. The heat for torrefaction is carried by a gaseous medium that enters from the bottom and flows counter to biomass to the top of the reactor. The torrefied product leaves the reactor from the bottom and is then cooled. Gaseous reaction products (volatiles) are removed from the top of the reactor.



Fig. 13a. Moving bed reactor (Thamer 2013)



Fig. 13b. Schematics of a moving bed reactor

Moving bed reactors use high quantities of biomass per unit of reactor volume compared to the torbed design. This is because the moving bed reactor utilizes the full reactor volume for torrefaction. When relatively small (<5 mm) biomass particles are processed, the pressure drop over the bed is relatively high because of the high feed volume fraction used. This can be avoided partially by sieving the biomass particles. Nonetheless, the formation of smaller particles at the bottom of the reactor cannot be avoided because pressure is highest in this area.

Belt Dryer

The belt dryer utilizes multiple porous belts placed on top of one another. It is a proven technology for biomass drying applications.



Fig. 14. Schematics of a belt dryer (www.biogreen-energy.com)

When biomass particles are transported using a moving porous belt, they are heated directly by a hot gaseous medium. Mixing of biomass particles is achieved by the particles falling from one belt onto the belt below. This results in the formation of a more homogeneous product. When the belt speed is controlled, the residence time can be controlled accurately. The belt dryer is more efficient than other reactors that may utilize a substantial spread in residence time, resulting in either charred particles or particles that are not properly torrefied from the same reactor (Koppejan *et al.* 2012).

Comparison of Torrefaction Reactor Performances

All the reactors described above have been developed and are employed basically for dry torrefaction. However, the reactor temperature may be markedly different from the temperature within the biomass being torrefied. Presently, torrefaction technology is taking its first careful steps towards commercialization. Torrefaction technology and product quality are still surrounded by uncertainties, as there is no universal best reactor technology because all torrefaction reactors have their advantages and disadvantages. However, proper technology can be selected for given biomass properties and applications. Comprehensive experimental observations comparing these reactors are still lacking. Nonetheless, a large part of the added value of torrefaction will be allocated before the power plant gate and can be calculated with the KEMA BioCase software (Beekes and Cremers 2012b). Table 7 is a summary, comparing the performances of torrefaction reactors. There is no available literature on torrefaction reactor design nor design sheets for estimating reactor capacity dimensions (Tumuluru *et al.* 2010).

Table 7. Comparison of the Performances of Torrefaction Reactor Concepts(Bergman and Kiel 2005; Dhungana 2011; Melin 2011; Beekes and Cremers2012b)

Reactor type	Advantages	Disadvantages
	Scalable technology	Slow temperature response
Fluidized bed reactor	Good heat transfer	Selects particle size
		Reduced interaction of bed solids with biomass
		Excessive biomass attrition
Rotary drum reactor	Proven technology for biomass drying	Poor temperature control
	Uniform heat transfer	Lower heat transfer rates
		Increase of dust due to friction
	Poor heat exchange because mixing of biomass is limited	between biomass and drum wall
	Various methods are available for controlling torrefaction process. It can	High cost and large space footprint
	employ both direct and indirect heating.	Limited upscaling ability. Maximum capacity is at 10–

	Ability to use any biomass particle size	12 t/h input, or 5 t/h torrefied product
	Relatively inexpensive reactor	
Screw type reactor	Proven technology	Poor heat exchange because mixing of biomass is limited
	Better biomass flow	I Inaqual tarrafaction on
	Ability to use any biomass particle size	biomass that touches the reactor wall is heated relatively more rapidly,
	Relatively cheap reactor	resulting in not spots
		Limited scaling potential as the ratio of screw surface area/biomass volume is less attractive with larger screws
Microwave reactor	High heat transfer and fast torrefaction	Electric energy is required for torrefaction
	Good temperature control	Heating of biomass interior is not uniform.
	Radiation based heat transfer instead of convection and conduction	Unproven technology for drying or torrefaction of biomass because the effects
	Heat transfer is less dependent on the size of the biomass particle	of rapid heating of biomass is unknown
	Ability to use large-size biomass particles	Requires integration with other conventional heaters to achieve uniform heating
	Modular	
Multiple Hearth reactor	Cood tomporature control	Heat domand is mot through
	Good temperature control	gas consumption making
	Good heat transfer	process less sustainable.
	Scalable technology (7 to 8 diameters are possible)	Gas combustion leads to the production of moisture in the flue gas. This gives a less
	Ability to use any biomass particle size	efficient combustion of the flue gas.
		Reactor has a large size.

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Torbed reactor	Scalable technology (to 25 t/h) Ability to precisely control product volatiles Low residence time (<100s) Large throughput due to fast heat transfer and low residence time No moving parts (low maintenance)	High temperature leads to a greater loss of volatiles.Volumetric reactor capacity is limited.High utility fuel demandRisk of tar formation due to relative higher loss
Compact (moving) bed reactor	Relatively simple and low cost reactor High heat transfer High reactor capacity makes it able to support large biomass throughput No moving reactor parts Can process biomass with lower density without large disadvantages	Presence of dust particles causes high pressure drops, which can result in automatic reactor shut down Limited biomass size and type due to pressure drop Temperature distribution is not uniform, especially with indirect heating Possibility for channel formation between biomass particles causing unequal torrefaction Difficult temperature control Scale-up potential is unproven
Belt dryer	Proven technology for biomass drying industry Better temperature control Relatively low costs Easy control of residence time by varying belt speed Ability to take wide range of biomass sizes	Limited temperature control Limited upscaling potential since capacity is dependent on the surface area of the belt (other systems are volume dependent) The holes in the belt can become clogged with tar and dust, causing unequal torrefaction, leading to non- homogeneous torrefied product. System has numerous mechanical parts, increasing maintenance costs.

TECHNOLOGICAL VIABILITY OF TORREFACTION PLANTS

In order for a torrefaction process to be technologically viable, those involved in developing torrefaction technology and promoting a commercial application should consider the following criteria. Every torrefaction plant:

- 1. Must produce torrefied biomass that has sufficiently high heating value, low moisture content, high moisture resistance as well as a high transport and energy density in order to be a suitable clean coal substitute.
- 2. Must be capable of running continuously on a 24h/7d basis without releasing volatile organic compounds (VOC) as emissions.
- 3. Must have easy-to-operate process controls that require only a small crew of operators and minimum maintenance.
- 4. Must produce torrefied biomass, using pyrolysis residence times that are short enough to ensure adequate throughput and high yield.
- 5. Must be able to accept feedstock that is of standard industry sizes that do not need special pre-treatment such as pulverization or excess drying.
- 6. Must employ automated process controls in order to maintain temperatures within ranges that will foster complete mild pyrolysis of the woody biomass.
- 7. Must employ process controls that can adjust easily to various mixtures of woody biomass feeds without adversely impacting production efficiency or quality of the torrefied wood produced.
- 8. Must produce torrefied biomass that is uniform and that can also be pelletized or reformed into briquettes.
- 9. Should be designed to facilitate a scale-up to higher capacity levels at a later date. In other words, the cost of a torrefaction plant with the capacity of producing 10,000 metric tons per year of torrefied biomass should not double if a later scale-up to 20,000 metric tons per year is undertaken.

APPLICATIONS OF TORREFIED WOOD/BIOMASS

The most common applications of torrefied wood/biomass are: (1) adding to pulverized fuel combustion in coal-fired power stations and also in cement kilns, (2) use in dedicated combustion in small scale pellet burners and gasification in entrained flow gasifiers that normally operate on pulverized coal, (3) feed for combined heat and power generation, (4) a fuel for stand-alone combustion, (5) feedstock for the production of biobased fuels and chemicals, and (6) a source of heat generation and carbon for metal oxides reduction in blast furnaces. In general, torrefied biomass is very attractive for combustion and gasification applications due to its high fuel quality (Bergman and Kiel 2005). Other applications of torrefied wood/biomass are the production of high-quality smokeless solid fuels for industrial, commercial and domestic applications, as well as feedstock for fuel pellets, briquettes, and other densified biomass fuels. Torrefied biomass is a leading solid

fuel for advanced bioenergy applications. However, several issues need to be verified in all of these applications.

Gasification

Gasification with sub-stoichiometric amounts of oxygen converts carboncontaining materials such as coal, petroleum, coke (pet coke), biomass or waste into synthesis gas (syngas). Syngas of varying H₂/CO ratios may also contain CO₂, N₂, and H₂O, *etc.* Syngas can be burned in a turbine to produce electricity or further processed to manufacture chemicals, fertilizers, liquid fuels, substitute natural gas, or hydrogen. For over 60 years, gasification has been reliably used on a commercial scale worldwide for petroleum refining and also in the fertilizer and chemical industries. It has been used for over 35 years in the electric power industry. Currently, gasification is being used to convert municipal and hazardous waste into valuable products (http://www.gasification.org).

Gasification takes place at much higher temperatures than pyrolysis and torrefaction, with a deficiency of oxygen (Basu 2013). In addition to the thermal decomposition and partial oxidation of volatile components, the non-volatile carbon char that remains from pyrolysis can be converted to additional syngas. Steam may also be added to the gasifier to convert carbon *via* the water gas shift reaction to syngas. Gasification utilizes only a fraction of the oxygen that is required to burn biomass. Heat is supplied directly by partial feedstock oxidation. There are some 'gasifiers' that do not produce gas for end use but produce heat for cooking and heating.

The relatively low moisture content, good grindability, and attractive C/H/O ratios of torrefied wood/biomass have made torrefaction an important pretreatment technology for gasification. Particle size and moisture contents are critical factors for biomass gasifier operation. The gasification of torrefied biomass improves flow properties of the feedstock, increases levels of H₂ and CO in the resulting syngas, and enhances overall process efficiencies. Ease of grinding is especially beneficial for entrained flow gasifiers. Nonetheless, extensive knowledge and experience are not available on the options and limitations of the use of torrefied biomass for gasification. This is an area where systemic research and development would be valuable.

Co-firing of Torrefied Biomass with Coal

Coal is a complex matrix solid that consists primarily of carbon, hydrogen, oxygen, nitrogen, sulfur, and ash-producing inorganics. This compact, aged form of biomass contains combustibles, moisture, intrinsic mineral matter (originating from dissolved salts in water), and extrinsic ash (due to mixing with soil) (Shah *et al.* 2012). Co-firing refers to the simultaneous use of two or more fuels in the same furnace (De and Assadi 2009). Torrefied wood/biomass can be advantageously used in existing relatively old pulverized coal (PC)-fired power plants. Since these installations were not designed for biomass co-firing originally, significant capital expenditures for plant modifications can be saved when torrefied biomass is co-fired instead of regular wood pellets.

Pulverized coal combustion employs coal that is first ground into fine powder in coal mills. This is a common combustion technology. A mixture of air and pulverized coal is blown into the burners from the bottom of the boiler. Steam is generated to drive turbines and generate power (George *et al.* 2010). The combustion of additional solid fuels in pulverized coal burners requires that these co-fed fuels be ground into very fine particles. Thus, good grindability is a desirable property for a solid fuel that is co-fired with coal. Brittle torrefied biomass has far superior grinding characteristics than raw biomass.

Torrefied biomass can be co-fired with coal directly or indirectly. Direct co-firing involves direct feeding of biomass into the coal-firing system while indirect co-firing involves initial gasification of the biomass, followed by combustion of the product fuel gas in the boiler (McIlveen-Wright *et al.* 2010). Pulverized coal combustion technology is currently used in several coal-fired power plants, mainly in Europe and the USA (Saidur *et al.* 2011).

A high percentage of electricity produced today comes from coal. Topell Energy (www.topellenergy.com) believes that a significant contribution of the future renewable energy mix will come from replacing fossil coal used for electricity production with biomass. This could cause a sizeable leap forward in the decarbonization of energy production. By replacing a fraction of the coal burned for power generation with biomass, the net release of new CO₂ to the atmosphere may be reduced. This is because the replacement biomass growth removes most of the CO₂ generated by the original biomass combusted. This may be an alternative to natural gas for lowering CO₂ emissions if natural gas prices rise in the future. Leveraging the enormous installed base of current coal-fueled power production assets and invested capital allows torrefaction to represent an affordable and fast substitution of fossil coal by biomass.

The financial advantages of torrefied biomass fuel with characteristics similar to the main fuel has been made less obvious because the new coal-fired power plants that are currently planned or in the construction phase are designed for high lignocellulosic biomass co-firing ratios. However, the use of torrefied biomass may lead to even higher co-firing ratios in new PC boilers than was originally envisaged for biomass co-firing. Torrefied biomass is a much better replacement because of its similarity in terms of grindability and combustion. The financial drivers for co-firing of torrefied biomass will therefore mainly be determined by the market value of CO₂ and the replacement value of coal.

Combined Heat and Power Generation

Cogeneration or combined heat and power (CHP) refers to the simultaneous generation of multiple forms of useful energy (usually mechanical and thermal) in a single integrated system. About 35% of the fuel energy potential contained in conventional electricity generation systems is converted on average into electricity. The rest is lost as waste heat. Since CHP systems use both electricity and heat, they can attain an efficiency as high as 90% (Zafar 2015). CHP generation represents a more efficient use of fuel because the heat generated as a by-product of electricity is not discarded. Direct heating is another option where the main purpose is to produce heat with electricity as a potential by-product. CHP systems consist of a variety of individual components such as: the prime mover (heat engine), generator, heat recovery system, and electrical interconnection that are configured into an integrated system. Prime movers for CHP units include reciprocating engines, combustion or gas turbines, steam turbines, micro turbines, and fuel cells (Zafar 2015). Furthermore, the much reduced biological decay and improved hydrophobic characteristics of torrefied biomass allow storage concepts for small CHP facilities.

Stand-alone Combustion

Installations for stand-alone combustion are typically based on a grate furnace or fluidized bed furnace but lack the pulverizer used in PC plants. This feature makes them much more flexible in terms of the fuel characteristics that result from torrefaction (fuel particle size, physical appearance and grindability). The range of fuels that can be used in dedicated plants is mostly limited by their chemical composition (which is not influenced by torrefaction). Therefore, there is no reason to combine torrefaction with dedicated combustion. However, the application of relatively small scale pellet boilers that are used for space heating may be an exception.

Bio-based Fuels and Chemicals

Currently, the production of most fuels and chemicals remains based on fossil fuel and natural gas. Technically, many industrial materials made from fossil resources can also be synthesized from bio-based resources (www.topellenergy.com). The current global biobased chemical and polymer production excluding biofuels is estimated to be around 50 million tons. Nonetheless, the majority of organic chemicals and polymers (330 million tons) continue to be derived from fossil-based feedstocks (Raschka and Carus 2012). This is either because the cost of production of bio-based chemicals and polymers exceeds the cost of fossil fuel based production or proven industrial scale production processes are not yet in existence. However, alternative synthetic routes to many chemicals from bio-based feedstocks are being rapidly developed. The recent development of shale-derived natural gas in North America is driving a huge expansion of polymer, fuel and chemical production. This will compete with bio-based chemical development.

Torrefied biomass is suitable for syngas production. Syngas can be catalytically or enzymatically converted into high-value bio-based fuels and chemicals, most notably via Fischer Tropsch chemistry. Syngas can be used to produce power or be converted by catalytic processes to chemicals and fuels. Retrievable products include methanol, ethanol, dimethyl ether, butanol, hydrogen, ammonia and Fischer Tropsch diesel. Other chemicals, polymers and plastics can also be produced from these products. Furthermore, syngas itself can be further processed by fermentation into longer chain chemicals such as oleochemicals, polymers, and many other products (www.topellenergy.com).

Blast Furnaces

A potential exists for substituting coal with torrefied biomass in blast furnaces because of the lack of alternative possibilities to reduce net CO₂ emissions. The main problems of torrefied biomass in a blast furnace are related to its alkali composition as well as high volatiles content. However, the steel industry is mainly interested in more highly carbonized biomass. Thus, the application of torrefied biomass in blast furnaces seems limited. It is possible to use torrefied biomass as a replacement for high-volatile bituminous coal but not low-volatile coals (Chen *et al.* 2012).

Industrial

Changes in the physical structure of biomass during torrefaction open new fields of possible biomass uses. Through torrefaction, water is driven out of biomass, hemicellulose de-polymerization takes place, and a stable physical state is achieved. The biomass might now be utilized as a commodity in industrial carbonization, polymer compounding, and other carbon related processes (www.topellenergy.com).

TECHNOLOGICAL AND ECONOMIC CHALLENGES OF TORREFACTION

In spite of global efforts to develop torrefaction technology, several technical and economic challenges need to be overcome before the technology is fully commercialized (Nordin 2012b).

The torrefaction process is not fully understood scientifically (Chen and Kuo 2010; Ratte *et al.* 2011; Melkior *et al.* 2012; Bates and Ghoniem 2012; Wannapeera and Worasuwannarak 2012; Peng *et al.* 2012). The detailed time-temperature profile of particles derived from different species in each type of reactor is not yet precisely correlated with the exact extent of dehydration and chemical decomposition of the feed. The effects of reaction conditions continue to be investigated. Since significant progress has been made, the next few years will represent a commercial demonstration phase for this technology (Van Essendelft *et al.* 2013).

Torrefaction reactors still require optimization to economically meet end-use requirements and to attain product standardization for the market. Certain characteristics of torrefaction need to be demonstrated or scaled up for commercialization purposes (Wild 2011; Jones *et al.* 2012; Agar and Wihersaari 2012b; Lu *et al.* 2012; Van Essendelft *et al.* 2013).

The hydrophobicity and grinding characteristics of torrefied biomass that were demonstrated in commercial scale tests are important for improving biomass handling when biomass is used as a substitution for coal. However, there is no scientific agreement on these characteristics (Bergman 2005; Peng *et al.* 2012; Agar and Wihersaari 2012a; Ruhul and Kumar 2012). Torrefied biomass pelletization employs binding that is accomplished by adding steam or hot water to the biomass (Bergman 2005; Ruhul and Kumar 2012; Tumuluru *et al.* 2012). Furthermore, torrefied pellets may require an additional binding material such as glycerin, dried distiller grains, or soybean meal for severely torrefied biomass with a high heating value (Boyd *et al.* 2011; Kiel 2011; Pirraglia *et al.* 2012). Severe torrefaction leads to a higher heating value but it is less cost-effective. On the other hand, light torrefaction does not adequately improve all the biomass characteristics sufficiently (Park *et al.* 2012).

The quantities of torrefied biomass that are currently consumed in demonstration and laboratory scale production levels are inadequate to test torrefaction products at a commercial scale (Ostermeijer 2011). Studies of the effects of varying process conditions (particle size, residence time, process temperature, and heating rate) and identification of optimum conditions for efficient and cost effective production of torrefied biomass are ongoing and inconclusive (Chen *et al.* 2012; Lee *et al.* 2012; Peng *et al.* 2012). Therefore, a need exists to identify the optimum torrefaction conditions through 'trial and error' matched to end-use requirements (Verhoeff *et al.* 2011).

The ability to accept a wider variety of heterogeneous biomass feedstocks rather than very clean woody biomass is of central importance for increasing the biomass resource base. Torrefaction to handle low-cost agricultural residues is especially important (Brouwers 2011) because agricultural residues have lower density and long fibers that ignite easily (Meijer 2011).

Inconsistency in biomass sizing results in uneven torrefaction (Boyd *et al.* 2011; Melin 2011). Substantial biomass particles size differences result in heat transfer delays and mass transfer differences that result in a diversity of the extent of torrefaction in the products. The presence of highly reactive dust, flammable gases and the need to operate in an oxygen-free environment, present significant safety challenges associated with spontaneous combustion, self-ignition and dust explosions of torrefied biomass (Boyd *et al.* 2011; Kiel 2011; Melin 2011; Kokko *et al.* 2012).

ECONOMIC STATUS AND FUTURE PROSPECTS OF TORREFACTION TECHNOLOGY

Torrefaction is still being developed as a biomass pretreatment technology. Several organizations are currently conducting research, demonstrations, and pilot schemes in order to improve torrefaction operational performance and to achieve commercial competitiveness (Kleinschmidt 2010; Batidzirai *et al.* 2013). Despite the fact that recent biomass-processing techniques are effective in biomass conversion, the production costs remain high for the development of cellulosic biofuels. Biomass torrefaction has a great potential to benefit both the supply chain and downstream processing units (Ciolkosz and Wallace 2011; Batidzirai *et al.* 2013).

Torrefaction investment costs are approximated using the factorial approach, where cost components are estimated using factors and percentages, based on the capital equipment costs (Peters *et al.* 2003; Ereev and Patel 2011; Knoope *et al.* 2013). The technical and economic advantages of torrefied pellets are now recognized by most of the larger power producers. Significant advantages are reaped from economies of scale. Operating conditions are perhaps the most important parameters affecting production cost (Uslu *et al.* 2008; Shah *et al.* 2012). However, moisture content is also important (Shah *et al.* 2012).

A review reported that very few studies have examined the techno-economic aspects of the torrefaction process from a supply chain perspective (Ciolkosz and Wallace 2011). Nonetheless, a torrefaction plant should adapt a production strategy geared both to the customer demand and to the supply chain (Svanberg and Halldorsson 2013). The torrefaction supply chain was evaluated and the assumption was made that centralized and de-centralized torrefaction plants have the same costs (Chiueh *et al.* 2012). The researchers pointed out that cost as a function of the level of centralization is an important future research area.

A techno-economical system model was developed (Svanberg *et al.* 2013) as an extension of the study performed by Chiueh and co-workers (2012). This model addressed how logistics and torrefaction production parameters affected (1) the optimal size of a torrefaction plant and (2) the total cost of supplying torrefied biomass to an end user. This study concluded that the torrefaction supply chain resulted in significant economies of scale-up to a plant size of about 150 to 200 kiloton of dry substance per year (kton_{DS}/year). However, the total supply chain costs accounted for 31.8 euros per megawatt hour, based on the lower heating value (\notin /MWhLHV). In this case, the supply system accounted for 59.5% of the total cost, the production cost accounted for 31.0% and the distribution system for only 9.48%. The quantity of available biomass, biomass premium, logistics, torrefaction mass yield, torrefaction plant, biomass moisture content, drying technology, and equipment were the key parameters that affected total cost.

Cost estimates for new technologies have high uncertainties because of unexpected implementation challenges and lack of previous scaling experience (Yeh and Rubin 2012). However, there is a need to include additional indirect costs for unforeseen contingencies. In spite of these uncertainties, the costs of major pieces of equipment are to a great extent known. Consequently, reasonably reliable production cost estimates can be obtained (Ereev and Patel 2011). The European market perspective for torrefied fuels was evaluated (Wilen *et al.* 2013). Researchers concluded that the torrefied pellet industry needs to have a wood-paying capability that is equivalent to prevailing wood prices. This is a required competition with other wood processing sectors. Figure 15 presents the cost of pulpwood

in 2012 at mills in Europe, which fell somewhere between 30 and 55 EUR/m³ sob (solid over bark).



Fig. 15. Pulpwood costs in selected regions, 2012 (Pöyry database) (Wilen 2013)

It is very likely that torrefaction production processes will improve and more plants will be built in the timeframe up to 2030. As cumulative installed capacity increases, the costs for installing a specific capacity will decrease (Junginger *et al.* 2010; Knoope *et al.* 2013). Clearly, however, several gaps still exist in the technical understanding of torrefaction.

CONCLUSIONS

1. The thermochemical conversion of biomass is attractive because biomass is an environmentally friendly fuel that produces substantially lower net CO_2 emissions than do fossil fuels. Torrefaction thermochemically upgrades cellulosic biomass into a more homogeneous fuel that can be utilized in many energy conversion processes. The main purpose of torrefaction is to modify feedstock properties to a more predictable and storable fuel for energy conversion without losing much of its original energy content. Some of the energy content of the dry biomass is lost as volatiles during torrefaction. However, acceptable overall efficiencies of approximately 90% can still be obtained. Energy from volatiles combustion is used to remove moisture from biomass. Both wet and dry torrefaction result in substantial losses of mass and a significant increase in energy densities.

2. Torrefaction significantly improves the suitability of biomass for co-firing in coalfired power plants and has the potential to enable higher co-firing percentages at reduced cost. Torrefaction technology has been demonstrated on a pilot scale, and the first initiatives are underway to demonstrate the technology at commercial scale (50,000 to 70,000 tons/year and above). The commercial development of torrefaction is now in its early phase. Torrefaction demonstration plants have had technical problems that have delayed their commercial operation. The torrefaction market is expected to move forward, but available public information is limited especially with regard to the technologies used and volumes of torrefied biomass produced.

3. One of the most important technical challenges facing large-scale implementation of torrefaction is the ability to densify the biomass into durable pellets or briquettes that can be handled without generating highly explosive dust. Other challenges are: the attainment of constant and well controlled product quality, scaling up the process, obtaining high system efficiencies through proper heat integration, and enabling a wide flexibility of input biomass. Optimal process conditions still need to be well researched and determined.

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