

Torrefaction for entrained-flow gasification of biomass

P.C.A. Bergman

A.R. Boersma

J.H.A. Kiel

M.J. Prins

K.J. Ptasinski

F.J.J.G. Janssen

Revisions	
A	
B	
Made by:	
P.C.A. Bergman	Approved & Issued:
Checked by:	
J.H.A. Kiel	H.J. Veringa
	ECN Biomass

Contact

For more information, please contact:

Patrick C.A. Bergman M.Sc., MTD

Energy research Centre of the Netherlands (ECN)

ECN Biomass

P.O. Box 1

1755 ZG Petten

The Netherlands

Phone: +31-224-568289

Fax: +31-224-568487

Email: bergman@ecn.nl

Web: www.ecn.nl/biomass (*non-confidential ECN reports can be downloaded from this site*)

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Acknowledgement/Preface

Biomass, in particular wood, has historically been an important energy source for fires, ovens and stoves. In the industrialization period of the late 19th century, coal displaced biomass because of its high energy density (28 vs. 18 MJ/kg) and because it is available in large quantities at low cost. At the beginning of the 20th century, oil (which was discovered in the U.S. in 1859) covered only 4% of the world's energy demand. Decades later it became the most important energy source. Currently, oil covers about 40% of the world's energy demand and 96% of the transportation fuels are produced from oil.

With the world energy demand projected to rise by about 40% from now to 2020, it is possible that oil production will not increase accordingly. Natural gas, which covers almost 25% of the world's energy demand today, may overtake oil as the most important energy source by 2025. This trend is also supported by environmental concerns such as global warming which have resulted in calls for increased use of natural gas. Natural gas gives off only one half as much carbon dioxide (CO₂) per unit of energy produced as does coal, and 25% less than oil. Worldwide supplies of natural gas are reasonably widespread and should last for 60 years at current rates of production. Eventually, fossil fuel reserves will dwindle. Looking beyond the era of natural gas, coal may become increasingly used, but this requires CO₂ sequestration. Preferably, the world should move towards more sustainable energy sources such as wind energy, solar energy and energy from biomass.

Annually, photosynthesis stores 5-8 times more energy in biomass than man currently consumes from all sources. Biomass, currently the fourth largest energy source in the world, could therefore in principle become the main energy source. However, many challenges remain to be solved before biomass can be used on a much larger scale as a sustainable energy source. Some of these challenges are related to biomass production, e.g. land management, competition with food production, etc., but challenges also exist in the handling of biomass as a fuel. The relatively low energy density of biomass, in combination with its high moisture content, makes transport of biomass from production sites to power stations or future bio-refineries costly. Biomass is very fibrous and tough. The production of very small biomass fuel particles is therefore a rather difficult and energy consuming task, which complicates a number of applications in gasification and combustion.

The research on torrefaction carried out in collaboration between the Technical University of Eindhoven (TU/e) and the Energy research Centre of the Netherlands (ECN), which is presented in this report, presents solutions to some of these challenges. Such a contribution may extend the lifetime of our fossil fuels resources and alleviate global warming problems. Although the research was focussed on the application of torrefaction for entrained-flow gasification, the project team recognises that the outcomes can also be valuable for other applications, e.g., as a pre-treatment technology in the co-firing of biomass in power stations, the production of densified biomass fuels (e.g. pellets), and generally biomass fuel production chains.

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Patrick Bergman

Mark Prins

Abstract

A major technical obstacle in entrained-flow gasification of biomass concerns the size reduction and the subsequent pneumatic transport of the biomass powder. The fibrous structure of fresh biomass makes it very difficult and costly to reduce its particle size down to below 500 microns. Torrefaction, a thermal treatment of biomass in the temperature range of 200 °C to 300 °C in absence of oxygen, is capable of enhance the size reduction characteristics. Torrefaction partially destructs the fibrous structure of biomass and is therefore an interesting pre-treatment option for this application. However, the influence of the torrefaction process conditions and used biomass on the grindability and pneumatic transport properties of biomass is nowhere quantified, as well as the responsible decomposition mechanisms and its kinetics. This work quantifies these relations with the aim to produce design data for entrained-flow gasification based bioenergy conversion chains.

An experimental torrefaction programme has been conducted in multiple reactors on both laboratory and bench scale, varying from 5 cc to 20 l batch wise capacity. In these facilities, intensive parametric testing has been carried out to provide insight in the thermochemical decomposition mechanisms during torrefaction. Subsequently, the produced torrefied biomass has been used to effectuate size reduction and fluidisation experiments to investigate its grindability and fluidisation behaviour. The size reduction experiments have been carried out with a cutting mill, while a cold-flow bubbling fluidised bed has been used to characterise the fluidisation behaviour of (torrefied) biomass.

This work reveals the influence of the torrefaction temperature and residence time, feed particle size, and type of biomass on the main characteristics of product quality, size reduction (power consumption and capacity of a grinding device), and fluidisation (Geldart classification as a function of particle properties). Furthermore, possible mechanisms responsible for the observed changes in grindability and fluidisation behaviour are proposed. Torrefaction leads to a very substantial improvement of the grindability and fluidisation behaviour. It therefore provides a solution to the problems concerned with entrained-flow gasification related to size reduction of biomass and the subsequent pneumatic transport of the powder.

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Summary

Desk studies have identified entrained-flow gasification as a promising option for the large-scale production of syngas from biomass. This biosyngas then is a versatile feedstock for the production of transportation fuels, chemicals and electricity. However, an entrained-flow gasifier requires sub-millimetre sized feedstock particles and to reduce biomass to this size is known to be difficult and expensive because of the fibrous structure and the tenacity of many types of biomass, woody biomass in particular. Torrefaction may be an attractive biomass pre-treatment process, as it may largely improve the size reduction behaviour. Torrefaction essentially is a thermochemical pre-treatment at a temperature level of 200-300°C in the absence of oxygen. It not only may improve the milling characteristics, but also may have a positive impact on transport and storage due to the hydrophobic nature of the torrefied biomass. As there was a lack of data and mechanistic knowledge on the chain of torrefaction – size reduction – particle feeding, the objective of the present work was to gain this knowledge and to generate design data with respect to this chain.

On the basis of an extensive set of lab- and bench-scale torrefaction experiments, it is believed that hemicellulose decomposition together with the depolymerisation of cellulose are the most important mechanisms reducing the fibrous structure and tenacity of biomass. Hemicellulose binds the cellulose fibres present in cell walls of plants. Destruction of this polymer leaves disoriented fibres and their mutual coherence disappears. Cellulose depolymerisation, subsequently, decreases the length of the fibres. These mechanisms improve the overall characteristics of size reduction strongly. The energy requirements can be reduced with 50-85% depending on the applied torrefaction conditions. The capacity can be increased with a factor of 2-6.5. Strikingly, these improvements have been observed for all evaluated woody biomass types (willow, larch, and beech).

Because of the shortening of the fibres, the particles resulting from the size reduction process become more spherical (i.e., decreased length-to-diameter ratio), which improves the fluidisation behaviour. In a conventional feeding system of a dry-feed entrained-flow gasifier, fluidisation needs to proceed in the smooth regime, which requires an A powder according to the well-known Geldart classification. The preparation of such a powder is considered only possible using torrefied biomass. A Geldart A powder is obtained for torrefied willow in the size range of approx. 30-400 µm. Fluidisation tests proved indeed that such a powder (willow torrefied at 270 °C, 30 min reaction time) can be fluidised smoothly, but only in a narrow range of fluidisation velocities. It is believed that further shortening of the cellulose fibres can widen this range. This may be possible through optimisation of the torrefaction conditions (i.e., further increase of temperature in the range of 270 to 300 °C).

The results on torrefaction reveal that the process produces a dry, more hydrophobic product with increased energy density. The observed order of reactivity for the evaluated biomass types is: larch < willow/beech < straw. The differences in reactivity are likely to be related to the differences in hemicellulose content between these biomass types: A higher hemicellulose content leads to higher torrefaction reactivity. In an operating window of 8 – 30 min reaction time and at 230 to 270 °C, the solid mass yield is in the range of 78% to 95% and decreases gradually with temperature. The energy retained in the solid product ranges from 83% to 97% (LHV_{daf}) and is typically 90%. On average, the energy yield also decreases with temperature, but unfortunately this cannot be statistically justified due to a relative large inaccuracy in the measurement of heating values ($\pm 1.5\%$). It is argued that mainly a higher dehydration with increased temperature explains the interrelation between both yields. Increasing the torrefaction temperature from 250 to 270°C reduces the required reaction time from 15-30 min to 8-15 min.

In conclusion, applying torrefaction as a biomass pre-treatment process indeed may be expected to contribute largely to the technical and economic feasibility of entrained-flow biomass gasification. Prove for this should come from a techno-economic evaluation for which this work

provides important input data. Further research focusing on torrefaction in the range of 270 – 300 °C is recommended. Operation at such temperatures shortens the required reaction time and may further improve the fluidisation properties of torrefied wood.

1. Introduction

1.1 Problem formulation

Desk studies have identified entrained-flow gasification as a promising option for the large-scale production of syngas from biomass. This biosyngas then is a versatile feedstock for the production of transportation fuels, chemicals and electricity. However, an entrained-flow gasifier requires (sub-)millimetre size feedstock particles and to reduce biomass to this size is known to be difficult and expensive due to the fibrous structure and the tenacity of many types of biomass, woody biomass in particular.

This led to the idea of applying torrefaction as a biomass pre-treatment step. Torrefaction is a thermal treatment at a temperature of 200 to 300°C; it is operated at near atmospheric pressure and in the absence of oxygen. This mild thermal treatment not only destructs the fibrous structure and tenacity of the biomass (wood), but is also known to increase the calorific value and to invert the hydrophilic nature. During the process, the biomass partly devolatilises which leads to a decrease in mass, but the initial energy content of the biomass is mainly preserved in the solid product (fuel). The latter is of great importance to the overall energy efficiency of the biomass-to-biosyngas conversion chain.

Research done on torrefaction has mainly focussed on applications different from the one foreseen in this work. In many cases, research has revealed the influence of torrefaction on the chemical changes of biomass represented by the proximate and ultimate composition, mass and energy yields, added with some focus on composition of volatile reaction products. The positive effects of torrefaction on for instance friability are nearly always mentioned, but have never been quantified in publicly available documentation. Hence, the available knowledge base does not allow a proper techno-economic evaluation of a torrefaction-based biosyngas production chain based on entrained-flow gasification. The effects of torrefaction on subsequent size reduction and pneumatic feeding should be explored and quantified. Furthermore, these effects should be linked to the mechanisms responsible for the changes in biomass properties to enable a better understanding and optimisation of the torrefaction process.

1.2 Project objective

The objective of the presented work was to improve the knowledge base on (the mechanisms of) torrefaction and to generate design data with respect to the combination of torrefaction, size reduction and pneumatic particle feeding. More knowledge was to be gained on the decomposition mechanisms of torrefaction and how these relate to improvements in size reduction and pneumatic feeding of the biomass. The generation of design data concerned the processes of size reduction and pneumatic feeding in relation to the torrefaction operating conditions.

With respect to the feeding system, pneumatic feeding as applied in existing dry-feed coal-fired entrained-flow gasifiers was taken as a reference. Although it was realised that a 100% biomass-fired entrained-flow gasifier might be equipped with a dedicated feeding system, this was beyond the scope of this study. This also goes for the influence of torrefaction on the entrained-flow gasification process itself and the techno-economic evaluation of the overall biomass-to-biosyngas production chain.

1.3 This report

This report comprises three main Chapters. Chapter 2 provides an introduction to the torrefaction process and outlines some results from literature studies on the decomposition mechanisms that occur during the process. It also treats the basic cell structure of biomass and explains the role of the different polymeric constituents (cellulose, hemicellulose, and lignin)

and their relation to the mechanical properties of biomass. As the literature scrutinised did not provide a clear basis for definitions of the mass and energy yield, torrefaction temperature and torrefaction time, these parameters are discussed and definitions proposed as well.

Chapter 3 continues with the experimental results on torrefaction and focuses on the influence of biomass type, feed particle size, torrefaction temperature and reaction time on torrefaction characteristics such as mass and energy yield and volatile products. In addition, calorific value changes due to torrefaction are addressed to a limited extent as well.

Chapter 4 then treats results of size reduction- and fluidisation tests. The used torrefied biomass applied in these tests was produced during the torrefaction experiments described in Chapter 3. The influence of the varied torrefaction parameters (Chapter 3) on size reduction characteristics such as power consumption, mill capacity, and particle size distribution and shape are discussed, followed by the results of cold-flow experiments on fluidisation of torrefied biomass. Subsequently, an extensive discussion on the relation between torrefied biomass mechanical properties and decomposition mechanisms is held.

Finally, conclusions and recommendations for further research are presented in Chapter 5.

2. Torrefaction of biomass

2.1 Introduction

Torrefaction is a thermochemical treatment method in the first place earmarked by an operating temperature within the range of 200 to 300 °C. It is carried out under atmospheric conditions and in the absence of oxygen. The name torrefaction is adopted from the roasting of coffee beans, which is, however, done at lower temperature and does allow the presence of oxygen. Nevertheless, the mechanical effects of torrefaction on biomass are supposed to be similar to its effect on coffee beans, which is their brittle structure afterwards. Torrefaction has many synonyms. Some examples are roasting, slow and mild pyrolysis, wood cooking and high-T drying. Especially the link with pyrolysis is easy to make as torrefaction covers part of the initial decomposition reactions of pyrolysis.

The main torrefaction product is the solid phase, which is – similar to pyrolysis – referred to as the charred residue (or char). In the field of torrefaction the solid product is also frequently called torrefied wood or torrefied biomass. Similar to pyrolysis, during torrefaction the chemical structure of biomass is altered. This leads to the formation of a variety of volatile (decomposition) products of which some are liquids at room temperature (condensables). By mass, important reaction products other than char are carbon dioxide, carbon monoxide, water, acetic acid and methanol (Bourgeois and Guyonnet, 1988). After condensation, liquid products manifest themselves as a yellowish liquid. All these non-solid reaction products contain relatively more oxygen compared to the untreated biomass. Hence the O/C ratio of torrefied biomass is lower than untreated biomass, resulting in an increase of the calorific value of the solid product.

Torrefaction of wood has attracted more interest recently. Pentananunt et al (1990) carried out torrefaction experiments at the Asian Institute of Technology in Bangkok. They compared combustion characteristics of torrefied wood produced after 2-3 hours of torrefaction and concluded that torrefied wood produces less smoke compared with untreated wood. In Brazil, a bench unit was used to determine the effect of raw material, temperature, and residence time on the properties of torrefied wood at the University of Campinas (Felfli et al., 1998). Torrefaction research is currently carried out at the National Renewable Energy Centre (NREL) in Golden, Colorado (Nimlos et al, 2003) and the Royal Institute of Technology (KTH) in Stockholm, Sweden (Pach et al, 2002).

2.2 Cell structure of biomass (lignocellulose)

Lignocellulose is another word for biomass that originates from plants. It generalises the structure of plants to the three main sugar-based polymeric structures; cellulose, hemicellulose and lignin. These three polymeric structures are mainly considered in most of the studies aiming for the understanding of decomposition mechanisms of woody and herbaceous biomass. In plant structures lignocellulose normally forms the most dominant group of constituents on a mass basis. Its main role is found in the cellular structure of plants and forms the foundation of cell walls and their mutual coherence. Lignocellulose provides mechanical strength and tenacity (toughness) to plant structures and so provides body and the opportunity to grow in height for optimal photosynthesis.

A typical plant cell is structured as illustrated by Figure 2.1. A single cell is typically described by a primary and a secondary wall. Subsequently, three individual layers describe the secondary wall. Individual cells are connected through a gluey layer called the middle lamella.

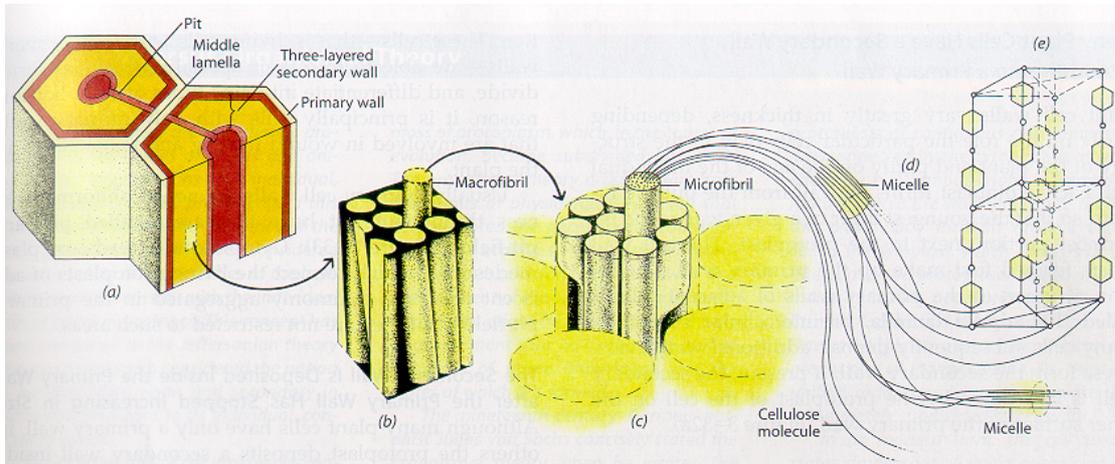


Figure 2.1 Detailed impression of the structure of a cell wall. (a) part of the cell wall and middle lamella, primary wall and secondary cell wall, (b) macrofibril mutual structure, (c) microfibril structure, (d) individual cellulose polymers including micelles, and (e) mutual coherence of individual cellulose polymers on a micro level (taken from: Raven and Eichhorn, 1999)

The second layer of the secondary wall is the thickest one and is built from vertically oriented macrofibrils. The macrofibril is on its turn composed from microfibrils, which predominantly consist of evenly oriented cellulose molecules of certain length. The cellulose chains comprise amorphous parts, but also crystalline parts whereby subsequent cellulose molecules are connected.

The polymeric composition of the different walls and layers varies strongly and each wall has different tasks. Figure 2.2 illustrates how the polymeric composition varies throughout the cell wall. The middle lamella predominantly contains lignin. Lignin acts as a binding agent and can be considered a glue to bind adjacent cells. Whilst the lignin fraction decreases cell inwards, the fraction of (hemi)cellulose increases. Cellulose meets a maximum content in the S_2 of the secondary layer and hemicellulose in S_3 .

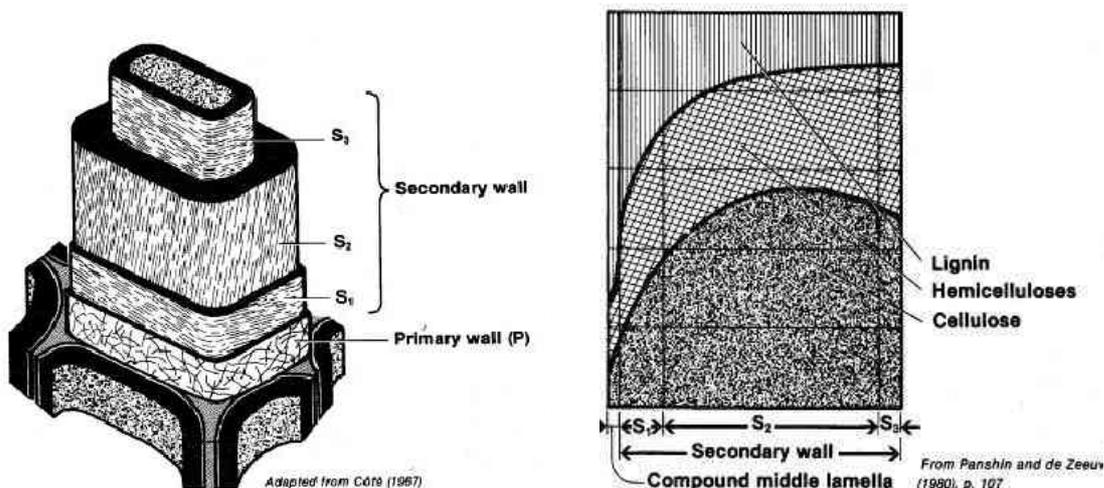


Figure 2.2 Distribution of lignocellulose within the three layered secondary wall (taken from Haygreen and Bowyer, 1987)

The three-layered secondary cell wall mainly consists of cellulose and is very well organised by nature. The cellulose macrofibrils are embedded in a matrix of (disoriented) hemicellulose that bonds the macrofibrils mechanically, but also through hydrogen bonding. The cell wall has a

repetitive pattern in which hemicellulose binds microfibrils of a cell wall and lignin binds adjacent cells. The function of hemicellulose is often well illustrated by comparing its function to concrete in reinforced concrete. Without the concrete the iron rods lose their mutual coherence and orientation.

Each layer of the three-layered cell wall has a different fibre orientation. The main body of the cells (S_2) is a vertical oriented structure of fibres kept in a compact form by an outer husk (S_1) and annular (inner) husk (S_3) both with near perpendicular fibre orientation. The wood structure consists of many of these cellular units 'glued' together by the lignin-rich primary walls. The anisotropic nature of wood, the fibrous structure, is caused due to the differences in thickness and orientation of the different layers. The way cell walls are mechanically organised is copied multiple times from nature because of the high strength and tenacity it provides.

Every type of green biomass has its own typical lignocellulose composition. Table 2.1 summarises the lignocellulose composition of biomass species used in the experimental programme of this work. Woody types of biomass are commonly divided into coniferous (larch) and deciduous (beech, willow) categories. Next to that a group of herbaceous species (straw) is commonly defined.

Table 2.1 *Lignocellulose composition of different biomass types used in this work and typical polymeric composition of deciduous and coniferous wood types (Holzatlas, 1974)*

Biomass	Lignin	Cellulose	Hemicellulose
Willow	25%	50%	19%
Larch	35%	26%	27%
Straw	14.2%	34%	27.2%
Beech	11.6-22.7%	33.7-46.4%	17.8-25.5%
Polymer		Deciduous	Conifer
Lignin (wt%)		18-25	25-35
Cellulose (wt%)		40-44	40-44
Hemicelluloses (wt%)		15-35	20-32
Composition hemicelluloses			
4-O methyl glucuronoxylan (wt%)		80-90	5-15
4-O methyl glucuronoarabinoxylan (wt%)		<1	15-30
Glucomannan (wt%)		1-5	60-70
Galactoglucomannan (wt%)		<1	1-5
Arabinogalactan (wt%)		<1	15-30
Other galactose polysaccharides (wt%)		<1	<1
Pectin (wt%)		1-5	1-5

Coniferous wood is typically high in lignin content, compared to deciduous wood and especially compared to herbaceous species. A big difference between deciduous and coniferous wood is found in their composition of the hemicellulose fractions. Whereas deciduous wood predominantly consists of xylan-based hemicellulose, coniferous wood predominantly consists of mannan-based hemicellulose. Chapter 2.3, discusses their different decomposition behaviour during torrefaction.

2.3 Decomposition mechanisms during torrefaction

From the three main polymeric constituents of biomass, cellulose has received most attention considering the thermal decomposition of biomass. Especially since the cellulose fraction is large. Therefore, in pyrolysis research cellulose decomposition is very important, but as Figure 2.3 illustrates, cellulose decomposition is not the most relevant constituent in the temperature range of torrefaction (200 – 300 °C). During torrefaction, mass loss will predominantly come from the decomposition (devolatilisation) of particularly hemicellulose and some of lignin. Xylan-based hemicellulose generally has its peaking rate in decomposition around 250 to 280 °C. Lignin decomposition proceeds slower, but shows a gradual increase of decomposition rate starting from temperatures of about 200 °C or even lower. Note, however, that the thermal decomposition behaviour of the individual polymers of wood (and in general biomass) may be different from their strongly interacted structure in wood itself. Indications for this can be extracted from Figure 2.3, as wood on mass basis starts to decompose at a temperature higher than 200 °C.

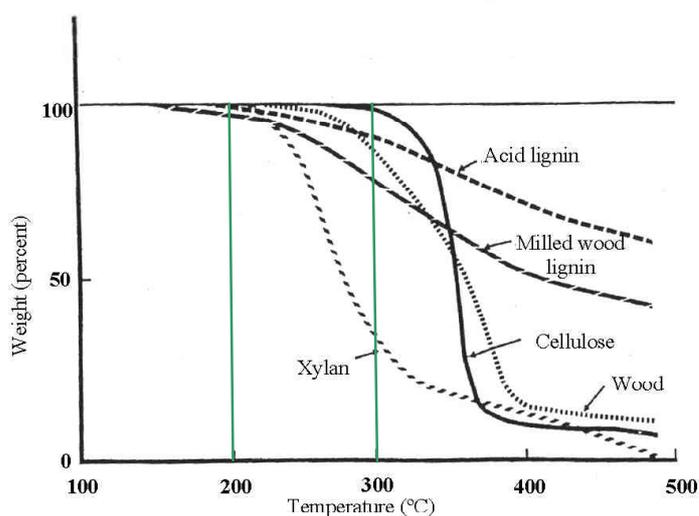


Figure 2.3 *Thermogravimetry of cotton wood and its constituents (taken from Shafizadeh and McGinnis, 1971). The green lines are added to indicate the torrefaction temperature regime*

Hemicellulose decomposition can be well described by a two-step mechanism as was found by Di Blasi and Lanzetta (1997). The first reactions usually taking place below 250°C (first step) are depolymerisation reactions leading to altered and rearranged polysugar structures. The decomposition of these oligosaccharides and monosaccharides at higher temperatures (250-300 °C) results in the formation of chars, CO, CO₂ and water. The formation of light volatiles like carbonyl compounds result from the fragmentation of the carbon skeleton.

Up to 250 °C, thermal decomposition of cellulose is hardly accompanied with a serious mass loss. The most important mechanism occurring is found to be depolymerisation. Depolymerisation of cellulose has been observed at even 70 °C (Golova, 1971). From the work of Shafizadeh *et al.* (1983) it is known that depolymerisation of wood is already occurring at significant rates at 150 °C. At 190 °C, the rate of depolymerisation is already seriously fast. Gaur and Reed (1998) mention that cellulose decomposition involving mass loss starts at 250°C. A variety of permanent gases, condensable liquids and char are formed during this step.

Thermal degradation of lignin takes place over a wide temperature range. At temperatures below 200°C, some thermal softening has been observed resulting in a small weight loss of a few percent. Char formation and the release of volatiles result from a devolatilisation process in

the temperature region of 240-600°C. Since the composition of lignin is different for hardwood and softwood, different kinetics are expected. Müller-Hagedorn *et al.* (2003) concludes that coniferous lignin is thermally more stable than deciduous lignin.

2.4 Torrefaction process definitions

In biomass energy applications, torrefaction aims for the production of a fuel having improved properties compared to the original biomass feed. However, this should be achieved without losing too much chemical energy to volatile products during the process. Hence, the mass yield and energy yield are considered to be crucial parameters. In the open literature much focus is spent on the mass and energy yield of the torrefaction as a function of residence time and torrefaction temperature (see e.g. Pach *et al.*, 2002). It is often unclear which definitions are used to calculate both yields and how the torrefaction temperature and time are defined. In this work these definitions are carefully formulated.

2.4.1 Mass and energy yield

In considering the macro composition of biomass, it can be expressed as physically bound water, organics and ash. The organic part of the biomass contains all the (reactive) chemical energy and during torrefaction part of this energy is removed in the form of reaction products. Therefore, the definition of the mass and energy yield are expressed on the basis on the organic part of the biomass, thus on dry and ash-free basis (daf):

$$h_M = \left(\frac{m_{char}}{m_{feed}} \right)_{daf} \quad (1)$$

and

$$h_E = h_M \left(\frac{LHV_{char}}{LHV_{feed}} \right)_{daf} \quad (2)$$

Use is made of the lower heating value (LHV), although the higher heating value can be used as well. However, the LHV value of biomass represents the amount of usable energy to be utilised effectively from the biomass and is generally used in the evaluation of many applications.

2.4.2 Torrefaction temperature and torrefaction time (reaction time)

Difficulties in interpreting the torrefaction process may arise from the definition of the torrefaction time. The term residence time is frequently used, but it only expresses the hold-up time of biomass in a torrefaction reactor. It does not tell how long actual torrefaction takes place, since part of the residence time is 'lost' due to heating of the biomass possibly in combination with drying. Misunderstanding about the torrefaction time automatically leads to inaccuracies in relating product quality to torrefaction operating conditions. To overcome this problem, the use of (reactor) residence time has been abandoned and instead the definition of reaction time is introduced.

When biomass is processed in a torrefaction reactor, it passes several stages with each having its own time-temperature characteristics. This is illustrated in Figure 2.4 for a typical batch operation. When moist biomass of ambient temperature is fed into a batch torrefaction reactor, the biomass is first heated to a temperature at which the biomass is dried. Then the temperature further increases until the desired torrefaction temperature is reached. This temperature is maintained until the reactor is cooled again.

The temperature window of torrefaction is generally considered to range from about 200 °C to 300 °C. (illustrated by the green horizontal lines in Figure 2.4). Only in this temperature window the torrefaction decomposition reactions occur. In this temperature window three time-temperature phases are recognised. First the biomass is heated from 200 °C to the desired

torrefaction temperature (T_{tor}) in period $t_{tor,h}$. Then the temperature is hold for period t_{tor} at the torrefaction temperature, until cooling during period $t_{tor,c}$. During t_{tor} the decomposition reactions will contribute predominantly, but this will depend on the time contribution of the heating and cooling period.

The reaction time has been defined as the sum of $t_{tor,h}+t_{tor}$ and thus leaving out the cooling time $t_{tor,c}$. The heating period is important, as during this period the most thermally labile parts of the feed biomass will rapidly start to decompose. In contrast to the cooling period when the solid product is much more thermally stable as the highest reactive parts already reacted. It is therefore expected that the decomposition reactions will stop as soon as the temperature is decreased. Hence the cooling period hardly contributes to the decomposition of the biomass.

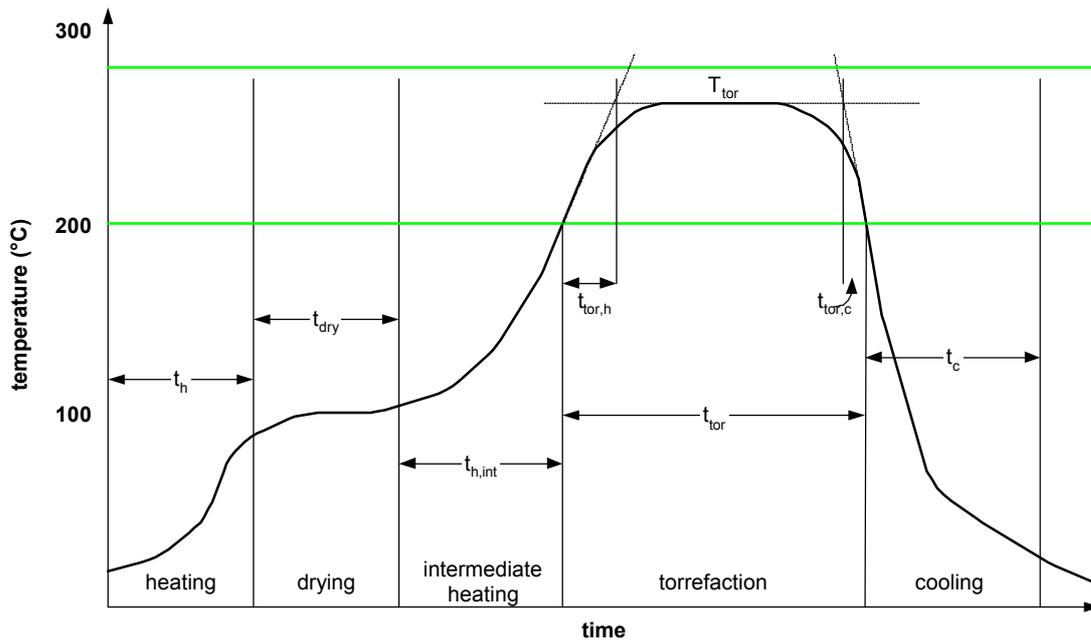


Figure 2.4 *Stages in the heating of moist biomass from 'ambient' temperature to the desired torrefaction temperature and the subsequent cooling of the torrefied product. Temperature-time profile is considered typical for a torrefaction batch process. Explanation: t_h = heating time to drying, t_{dry} = drying time, $t_{h,int}$ = intermediate heating time from drying to torrefaction, t_{tor} = reaction time at desired torrefaction temperature, $t_{tor,h}$ = heating time torrefaction from 200°C to desired torrefaction temperature (T_{tor}), $t_{tor,c}$ = cooling time from the desired T_{tor} to 200°C, t_c = cooling time to ambient temperature*

By using this approach, it is also possible to define the heating rate of the biomass that is really relevant to the process. On average this is $(T_{tor}-200\text{ °C})/t_{tor,h}$, which will normally not exceed 50 °C/min. Hence the particle heating rate is considered to be a less relevant parameter in torrefaction, as the torrefaction reactions are relatively slow. Note that Figure 2.4 is quite illustrative in what kind of error could be faced when the reactor residence time is mistaken with the reaction time of torrefaction.

In presenting and discussing the results (coming Chapter), use is made of a coding system by which is referred to a particular experiment. The coding represents the reaction coordinates of the pertinent experiment:

Reaction co-ordinate = (Biomass type, temperature [°C], reaction time [min], particle size [mm])

Typical examples of usage:

- (W,230,30,0-10) means: willow torrefied at 230 °C and 30 min reaction time using 0-10 mm sized particles.
- Willow (230,30,0-10): similar as first example.
- Willow (230,30): again similar as first example. Particle size is only mentioned when it differs from the reference size of 0-10 mm.

3. Torrefaction experiments

3.1 Facilities and experiments

An extensive experimental programme was conducted on biomass torrefaction using several experimental facilities. Table 3.1 provides an overview of these facilities. In general each facility was deployed for different aspects of the work. TGA was used to investigate the mass loss (*viz.* solid yield) curves as a function of torrefaction temperature and time for the different used biomass types. The bench-scale reactor available at the TU/e was used to study the mass and energy yield as a function of biomass type, torrefaction temperature and time. This facility was mainly used to perform accurate parametric studies in which also the composition of volatile products was analysed. The batch reactor present at ECN was used to study similar aspects. Its size allowed also particle size variations and the production of larger batches (3-6 kg) sufficient to perform size reduction and fluidisation experiments.

The control of the dynamic batch torrefaction process was found to be more difficult for the batch reactor compared to the bench-scale reactor, due to scale of operation (intrinsic time constants are larger) and heating effects. Therefore, a larger spread in the final reaction time and torrefaction temperature could not be avoided. The discussion on the results from the parametric studies was mainly based on the bench-scale reactor experiments.

Table 3.1 *Overview of used experimental facilities*

Experimental subject	Facility	Characteristics	Project partner
Torrefaction	TGA	Perkin Elmer Pyris 6 TGA with auto sampler Sample weights varied from 2-10 mg Nitrogen purge gas at a flow rate of 20 ml/min Heating rates from 10-100 K/min	TU/e
	Bench- scale reactor	Cylindrical 1 inch x 10 cm (± 50 ml) Heating mode: indirectly by electrically heated mantle Production capacity of 5 to 10 g per batch Permanent gases removed by argon purge gas, collected in gasbag and analysed by MICRO-GC (off-line) Liquid product collected in cold trap at -5°C Solid analysis by proximate/ultimate analysis Liquid analysis by HPLC using Chrompack organic acids column	TU/e
	Batch reactor	Cylindrical 90 cm x 18 cm (± 20 ltr) Heating mode: indirectly through vessel wall by electrical heating elements, and directly using a hot nitrogen flow Production capacity of 3 to 6 kg per batch Permanent gases analysis by MICRO-GC (on-line) Liquid product sampling using water filled impinger bottles Solid analysis by proximate/ultimate analysis Liquid analysis by GC-FID and GC-MS (off-line)	ECN
Size reduction	Retch SM 2000 heavy cutting mill	1.5 kW electric motor, manually operated particle feeding system Data acquisition of power rate, production capacity (mass balance) Variable bottom sieve (manually) for controlling particle size	ECN
Fluidisation	Cold-flow BFB	2D 3 cm x 10 cm x 20 cm particle bed Carrier gas: air, atmospheric, ambient temperature	ECN

In the experimental programme, the focus was set to biomass feedstock parameters and to reactor parameters. Most important feedstock parameters were considered to be biomass type and biomass particle size. In investigating the effect of biomass type, the general classification

of softwood, hardwood and herbaceous was followed. Experiments were carried out using willow and beech (hardwood), larch (softwood), and straw (herbaceous). The TGA studies also included experiments using xylan and cellulose. Willow was taken as the reference biomass and hence most experiments were conducted using this biomass. An overview of properties of the applied biomass types is found in Table 3.2.

Table 3.2 *Properties of biomass types used in experiments (elemental composition in wt. %)*

Biomass	MC (% wt.)	Size bin (mm)	Shape	C (% wt.)	H	N	O	Ash	LHV _{daf} (MJ/kg)
Willow	8.6	< 10	Cylindrical, (including bark)	47.2	6.1	0.34	44.8	1.6	17.7
		10 – 30							
		30 – 50							
Beech	8.1	2 – 16	Flat chips, debarked	47.2	6.0	0.40	45.2	1.2	17.0
Larch	9.8	10	Cubic, debarked	48.8	6.1	0.10	44.9	0.1	18.2
Straw	10.7	powder		44.3	5.8	0.40	42.4	7.1	16.1

To see the effect of feed particle size, experiments were carried out using the three willow size fractions. A feed particle size of 0-10 mm was used as reference, as these smaller particles could be used in all facilities (at ECN, as well as at TU/e).

The torrefaction temperature and reaction time were considered to be the most influential parameters. Other variables like heating rate, gas composition in the reactor, but also hydrodynamic aspects (mass and heat transfer) were not addressed. In following part of the open literature (see also Section 2.3), the strongest improvements in biomass properties were expected in the higher temperature region (250-300 °C), rather than in the lower temperature region (200-250 °C). Therefore most of the experiments were carried out above 250 °C.

The reference reaction time was set at 30 min and variations were mostly applied in the range of 8 to 30 min (especially when considering the batch reactor experiments). Experiments at longer reaction time (> 30 min reaction time) were mostly done using the bench-scale reactor. Not many experiments at longer reaction time were carried out, as it is believed that a long reaction time hampers the commercial attractiveness of torrefaction.

3.2 Results

3.2.1 Thermogravimetric experiments (solid yield)

Figure 3.1 depicts the mass loss curves of the different biomass types at 250 °C and 270 °C. The results were obtained from TGA. Different mass loss curves can be observed for the examined biomass types. With increasing order of mass loss in time:

Larch << willow/beech < straw, or

Coniferous wood << deciduous wood < herbaceous

The TGA results of cellulose reveal that the mass loss at 250 °C is limited to only a few percent even after a reaction time of ±45 min. At 270 °C this is approximately 5%. This is in contrast to hemicellulose (xylan), which is much more reactive resulting in a mass loss of ±30% at 250 °C and ±50% at 270 °C, both at 45 min reaction time. This is in agreement with trends in Figure 2.3.

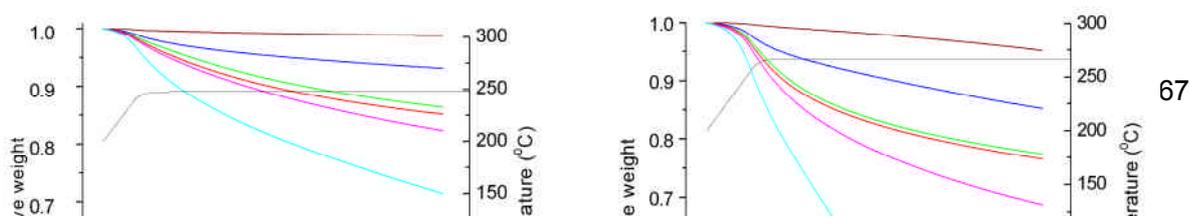


Figure 3.1 *TGA results for the different biomasses and biomass polymeric constituents (xylan and cellulose) at 250°C and 270°C. The grey line indicates the sample temperature. Note that the reaction time starts at about 1200 sec and reaches the final temperature after approximately 1500 resp. 1650 seconds*

An S-shaped mass loss curve can be observed for all biomass types, which implies a second order relationship between mass loss in time. Devolatilisation is initiated, as soon the temperature of the biomass is above 200 °C and its rate increases fast until the desired torrefaction temperature is reached. Then the rate of mass loss starts to decrease again in time (but it does not stop after 4000 sec). The rate of mass loss during the heating period ($t_{\text{tor,h}}$) from 200 °C to the torrefaction temperature emphasises the importance of the time period, $t_{\text{tor,h}}$ (see Section 2.4.2) in relation to the total reaction time ($t_{\text{tor,h}}+t_{\text{tor}}$) especially when the reaction time is short. It also emphasises that biomass can be decomposed significantly after short periods of time.

3.2.2 Solid yield (batch reactor results)

The solid yield as a function of torrefaction and feed parameters was experimentally evaluated in both the 3-6 kg batch reactor and the 5-10 gram bench-scale reactor. Figure 3.2 and Figure 3.4 represent the experimental results respectively. From these results the influence of biomass type, particle size (willow), torrefaction temperature and reaction time can be evaluated.

Figure 3.4 reveals a similar order of reactivity between the different biomass types as was observed in the TGA experiments. At 250 °C, the solid yield of larch exceeds 95%, whilst that of willow and beech is in the range of 86-90% and of straw 85%. Note, however, that only a few experiments were carried out using straw and larch so that this interpretation cannot be statistically substantiated.

A distinct dependency of the solid yield on the torrefaction temperature can be observed in Figure 3.4. Within the examined range, a temperature increase leads to decreased solid yield. Above 250 °C, the solid yield drops exponentially. This can also be observed in Figure 3.2 by taking the lump of the experiments performed on beech and willow (deciduous wood).

Increased reaction time (Figure 3.4) results in decreased solids yield, although the process seems not so sensitive towards this parameter when compared to temperature. Fast decomposition rates during the initial stage of torrefaction (*viz.* during $t_{\text{tor,h}}$, see Figure 2.4 in Section 2.4) may partly explain why the influence of reaction time is not distinct in Figure 3.2. Willow (245,10) is very comparable to willow (230,30) and willow (254,24) follows the general trend of the solids yield of willow with temperature. Figure 3.2 also includes the results of the experiments wherein willow of different size-bins were used (*viz.*, 0-10, 10-30, 30-50 mm). The observed solid yields are rather similar despite the size differences and the minor differences that exist are inconsistent.

3.2.3 Energy yield

Figure 3.3 represents the energy yields found for the batch reactor experiments and Figure 3.5 represents the energy yield results obtained from experiments using the bench-scale reactor. The energy yield is calculated using (2), which is given in Section 2.4.1. To calculate the energy yield, both the lower heating value of biomass and torrefied biomass were to be estimated from the higher heating value (HHV). The HHV is determined by using an adiabatic bomb calorimeter. The inaccuracy of such measurement is approximately 240 J/g, which is up to 1.5% in HHV on relative basis (95% confidence). These errors have to be added up in the case of the energy yield calculation, meaning that the calculated energy yield has a relative inaccuracy of $\pm 3\%$, only caused by the measurement of the calorific value. Consequently, this inaccuracy complicates the interpretation of the results, as the observed spread in energy yield is not large. Hence, substantial experimental data is required to make conclusions statistically justified.

The influence of biomass type on the energy yield is best observed in Figure 3.5. At 250 °C and 30 min reaction time the order with increasing energy yield is:

larch >> willow > beech > straw

For larch, practically all the chemical energy is retained in the solid product up to a temperature of 250 °C. The energy yield of willow is about 95% at (250,30). Beech and straw torrefaction proceeded with an energy yield of respectively 92% and 88% under same conditions. Figure 3.3 shows similar trends, but the observed energy yields are slightly lower. Only minor differences are observed between the energy yield of the differently sized willow fractions used in the experiments (see Figure 3.3). This is in line with the small differences found in solid yield (Figure 3.2). Again this emphasises the small influence of particle size under the maintained conditions.

Figure 3.5 most clearly reveals the decrease of the energy yield with increasing torrefaction temperature. Up to a temperature of 270 °C, all the experiments resulted in an energy yield exceeding 85% (both Figure 3.3 and Figure 3.5). The lowest energy yield was found for willow (300,15) and is 78%.

The effect of reaction time can be evaluated from willow (250,30) and willow (250,60). The differences in energy yield amount $\pm 3\%$ -points. A similar difference in energy yield can be observed between (270,30) and beech (270,15). The effect of reaction time seems to be small compared to temperature. In case of (W,250,30;W,250,60) the corresponding mass yields are respectively 92% and 83%, meaning only a few %-points of energy loss whilst the mass loss nearly doubles.

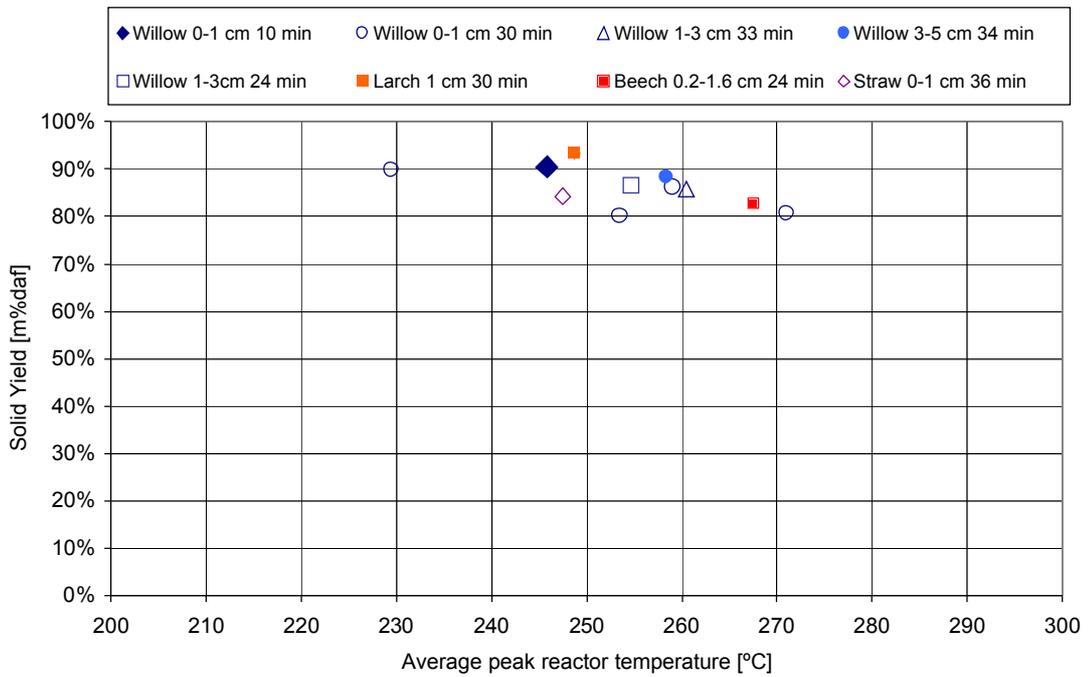


Figure 3.2 Solid yields obtained for various batch experiments carried out at ECN, wherein biomass type (willow, larch, beech, and straw), temperature, reaction time, and particle size are varied

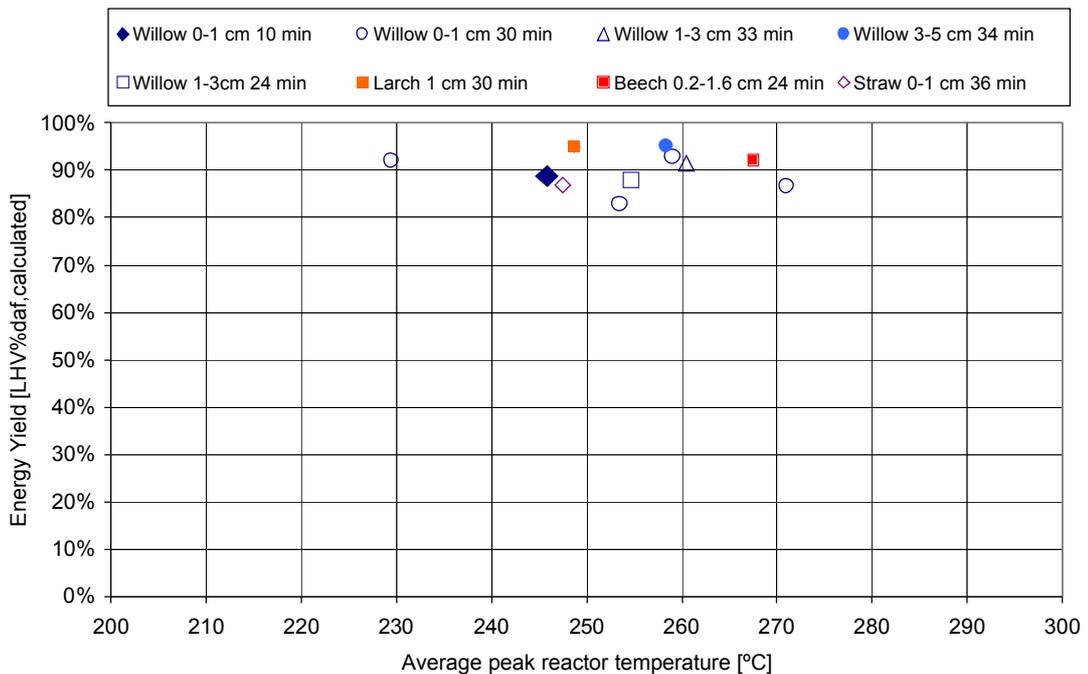


Figure 3.3 Energy yields obtained for various batch experiments carried out at ECN, wherein biomass type (willow, larch, beech, and straw), temperature, reaction time, and particle size are varied. The energy yields correspond with the solid yields given in Figure 3.2

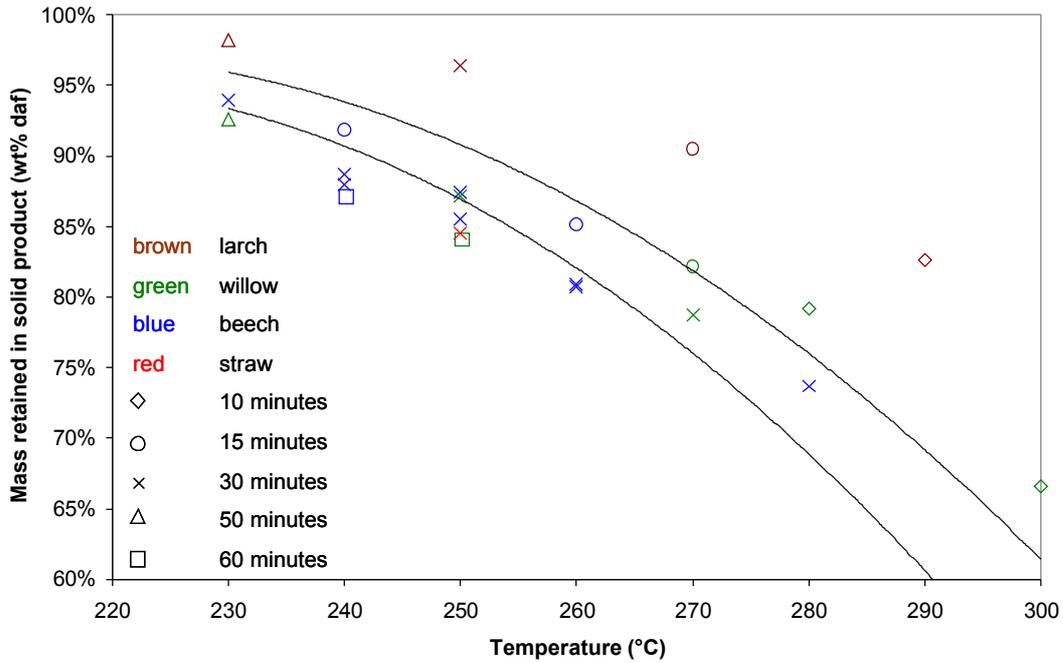


Figure 3.4 Solid yields obtained for various batch experiments carried out at TU/e, wherein biomass type (willow, larch, beech, and straw), temperature and reaction time are varied. Model lines from kinetic model for torrefaction of willow at 15 minutes (upper line) and 30 minutes (lower line) residence time

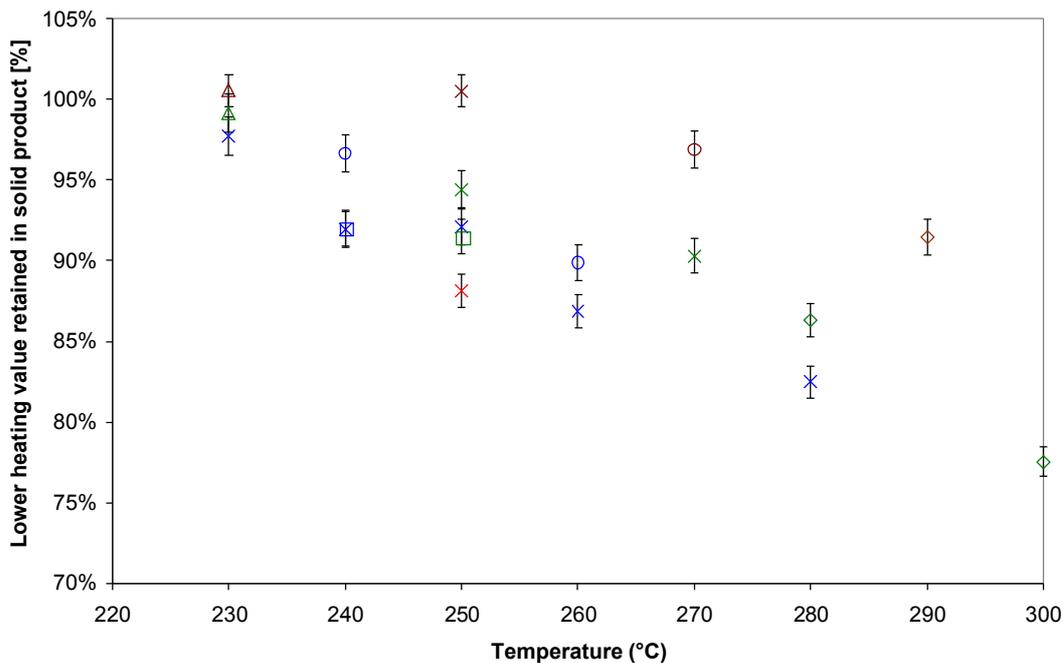


Figure 3.5 Energy yields obtained for various batch experiments carried out at TU/e, wherein biomass type (willow, larch, beech, and straw), temperature and reaction time are varied. The energy yields correspond with the solid yields given in Figure 3.4

3.2.4 Gas and liquid yields

The volatiles consist of a condensable fraction and a non-condensable fraction. For both fractions, the amount formed increases with torrefaction temperature. Figure 3.6 and Figure 3.7 show the yields of condensable products (weight formed divided by the dry- and ash-free weight of wood) for respectively willow and larch at varying experimental conditions.

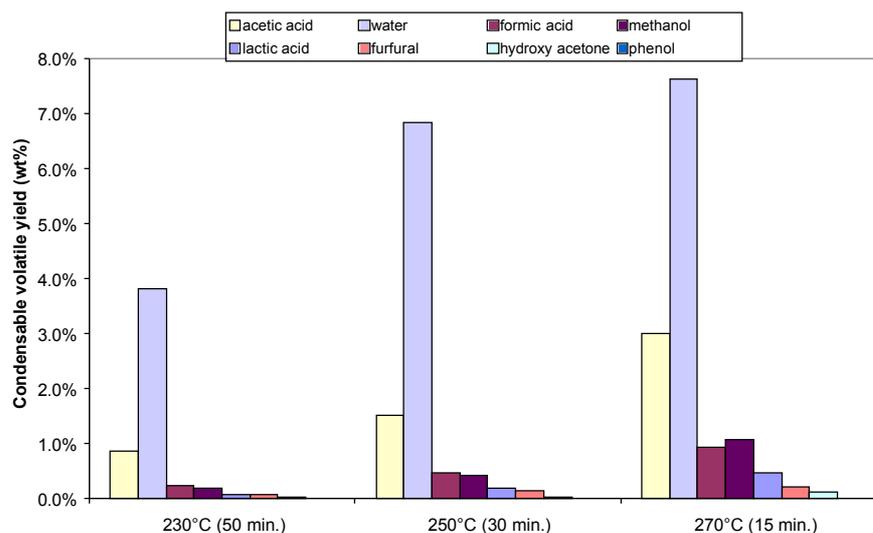


Figure 3.6 Product yields of condensable volatiles formed in torrefaction of willow at different conditions

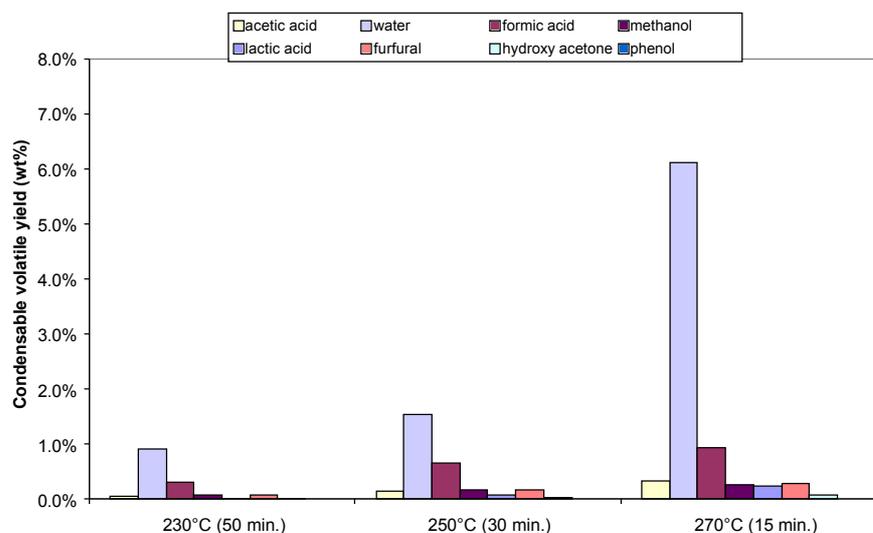


Figure 3.7 Product yields of condensable volatiles formed in torrefaction of larch at different conditions

Acetic acid and water are the main liquid torrefaction products of willow, while smaller quantities of methanol, formic acid, lactic acid, furfural, hydroxyl acetone and traces of phenol are found. Šimkovic, Varhegyi and Antal (1988) used TG/MS to study thermal decomposition of xylan and also observed these compounds. Thus, the identified products likely originate from the decomposition of the hemicellulose fraction. The difference in product distribution between larch and willow may be explained from differences in hemicellulose composition. The hemicellulose of deciduous woods has acetoxy- and methoxy-groups attached to the polysugars (in particular to xylose units), which form acetic acid and methanol when the wood is heated to temperatures around 200°C (White and Dietenberger, 2001). The amount of acetic acid formed

from willow increases with temperature: the amount of acetic acid formed is as much as 3% at 270°C. For larch wood, the yield of condensable products is much smaller, in agreement with the observed lower weight loss. This weight loss of larch is mainly due to water and the main acid formed is formic acid.

The composition of the non-condensable volatile product obtained from torrefaction is depicted in Figure 3.8 for larch and willow at various conditions. The amount of non-condensable volatiles is again higher for willow than for larch, which further exemplifies the higher degree of devolatilisation for deciduous, xylan-containing wood. The main permanent gases formed are carbon dioxide and carbon monoxide. Traces of hydrogen and methane are detected as well. The formation of carbon dioxide may be explained by decarboxylation of acid groups in the wood. However, the formation of carbon monoxide cannot be explained by dehydration or decarboxylation reactions. The increased carbon monoxide formation is reported in literature (White and Diertenberger, 2001) as the reaction of carbon dioxide and steam with porous char to carbon monoxide with increasing temperature. Mineral matter may catalyse such reactions, especially since the gases formed in the torrefaction experiment using straw contained a relatively higher amount of carbon monoxide than the experiments using wood (which contains much less mineral matter).

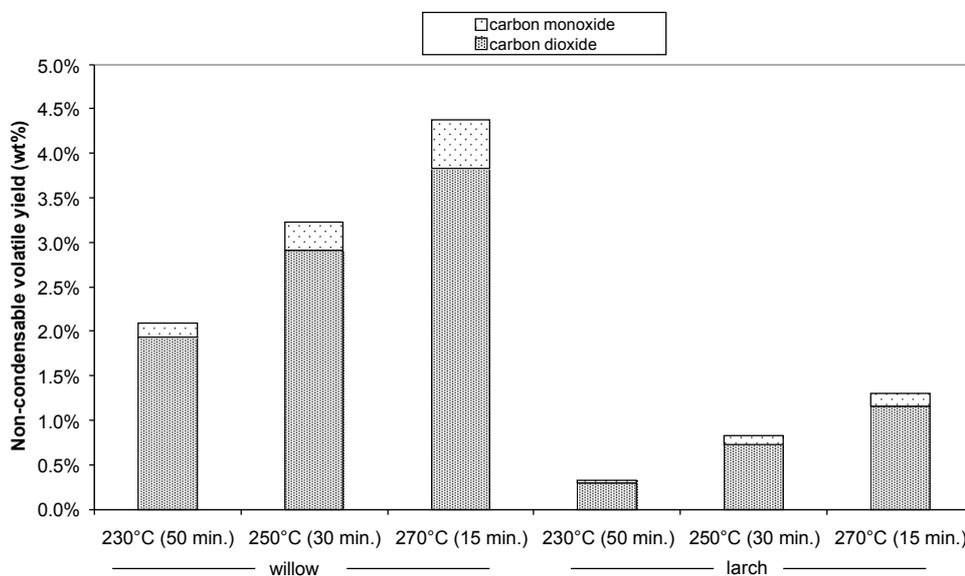


Figure 3.8 Product yields of non-condensable volatiles formed in torrefaction at different conditions, for willow and larch

3.2.5 Modelling of mass loss kinetics

Modelling of biomass decomposition was done to support the interpretation of the results. The modelling work of Di Blasi and Lanzetta (1997) on xylan decomposition was taken as a basis for determining the kinetics of decomposition of willow. The reaction model is based on a two-step mechanism and is given by Table 3.3. As hemicellulose is most reactive, the first decomposition step would mainly describe the rearrangements reactions of this polymer into new sugar structures (see also Section 2.3). The second step then would describe the further deterioration of these new structures into char. In both steps weight loss is a consequence of the formation of gaseous and liquid products.

In the model, component A represents willow involved in the decomposition reactions. Model component B represents the intermediate solid product formed out of A, and component C is the final char product from B. V_1 and V_2 represent the gaseous and liquid products from both reactions. An important part of the model was to determine the total reactive part of the biomass ($A_{t=0}$). This was done by TGA analysis wherein willow was torrefied up to 48 hours. The

resulting mass loss after this period was considered a measure for $A_{t=0}$. Remarkably, it is observed that after such a long period the decomposition reactions did not extinguish. Also, the remaining solid yield was too low to be only explained by the complete decomposition of hemicellulose alone. This was the case even after a temperature as low as 230 °C. Consequently, part of the cellulose and/or lignin must have reacted as well. Maybe catalysed by inorganic substances or by gases and liquids from the reactions itself.

Table 3.3 *Kinetic model derived for willow. Model is based on a two-step decomposition mechanism similar to the kinetic model for xylan decomposition proposed by Di Blasi and Lanzetta (1997)*

Kinetic model				
				$k = k_0 e^{\frac{E_{act}}{RT}}$
Model constants	k_1 (A→B)	k_{v2} (A→V ₁)	k_2 (B→C)	k_{v2} (B→C)
E_{act} (kJ/mol)	76.0	114.2	151.7	151.7
k_0 (kg/kg s)	$2.48 \cdot 10^4$	$3.23 \cdot 10^7$	$1.10 \cdot 10^{10}$	$1.59 \cdot 10^{10}$

Thus, the two-step modelling approach does not describe the decomposition of hemicellulose within the biomass, but also includes the decomposition behaviour of both cellulose and lignin. It is, however, unclear at which point the decomposition of these constituents of the biomass dominate the mass loss in the applied period of 48 hours. TGA analysis of cellulose demonstrated that its mass loss after 30 min reaction time at 270 °C is hardly a few percent, whilst xylan mass loss amounts about 30%. Hemicellulose will therefore be most responsible for mass loss in the relevant time scope (0 – 60 min reaction time), although the role of lignin was not evaluated.

The values determined for the reaction constants k_0 and E_{act} given in Table 3.3 show that the first stage of decomposition is much faster compared to the second one. The first stage of decomposition is rather ‘explosive’ in the first 30 min reaction time. Within this period more than 45% of the reactive part of the biomass (A) is at 230 °C already converted into the intermediate reaction products (B). At 250 °C the conversion is about 75% and at 270 °C even exceeding 90%. In contrast to that, after 30 min reaction time at 270 °C hardly 1% of A is converted to char.

The effect of heating rate was investigated by varying the heating rate in the range of 10°C/min to 100 °C/min during the TGA experiments. This reduces the weight loss during the heating phase, which is accurately described by the model.

3.3 Discussion

In general the conducted experiments reveal that torrefaction can be applied with high biomass to solid energy yield ranging from 95-100% within the lower temperature region (<250 °C) and 83-95% within the higher temperature region (>250 °C). At a temperature exceeding 270 °C, the energy yield drops further, but can still be limited when the reaction time is kept short. Corresponding mass yields are consistently lower and range from 90-100% within the lower temperature region to 80% to 90% in the higher temperature range (up to 270 °C). The higher loss of mass compared to the loss of energy confirms that indeed energy is densified during

torrefaction. The main cause of this energy densification is found in the amount and composition of the volatile products. On mass basis, water (produced from dehydration reactions) and CO₂ (produced from decarboxylation reactions) are the dominating reaction products. These do not contribute to the calorific value of the biomass and hence mass is lost while the chemical energy is retained in the solid product.

The TGA experiments and analysis of volatile reaction products point out that hemicellulose is the most reactive polymeric constituent of biomass during torrefaction. Especially when compared to cellulose, which showed limited mass loss at short reaction time (< 30 min). Experiments using lignin were not carried out, but it is known from literature (Gaur and Reed, 1998) that its weight loss is limited below 300°C.

Distinct differences were found in the torrefaction of deciduous wood (beech and willow) and straw, when compared to coniferous wood (larch). In the first case, the mass conserved in the torrefied wood is lower; 73-83% (depending on reaction time) versus 90% at a temperature of 270°C. Much more volatiles are formed in the case of deciduous wood, such as acetic acid and methanol, which mainly originate from acetoxy- and methoxy-groups present as side chains in xylose units present in hemicellulose. These are not present in the hemicellulose fraction of coniferous wood. For deciduous wood and straw, also more non-condensable gases such as carbon dioxide and carbon monoxide are produced and the extent of dehydration is higher. Consequently, the increase in energy density of the solid product is much higher, up to 15% for deciduous wood versus up to 7% for coniferous wood at 270°C and 15 minutes reaction time. Torrefaction of willow at these conditions increases the lower heating value of the solid product from 17.7 MJ/kg to 20.7 MJ/kg, while still retaining 90% of the energy in the solid material.

Based on the above, it is believed that the found order of reactivity of the examined biomass types (larch << beech/willow < straw) is mainly determined by their mutual differences in hemicellulose content and composition (see also Table 2.1). Mainly this implies distinct torrefaction differences between coniferous and deciduous wood, but minor differences within the population of these two main classes. In addition, from deciduous wood acetic acid and methanol are produced as volatile products, so that energy is transferred from the solid phase to the volatiles. It is expected that this mainly explains the lower energy yield of deciduous wood compared to that of coniferous wood.

In discussing the effect of temperature and reaction time on the characteristics of torrefaction, the torrefaction temperature is more influential. Temperature determines the possible decomposition reactions and their kinetics. These are normally strongly non-linear. Hence, a relatively small increase of temperature will much more increase the rate of decomposition compared to a relatively large increase of reaction time. By varying particle size, it was expected to see the combined effects of differences in heating rates inside the particles, perhaps in combination with the effect of intra-particle reactions between reactive parts of the solid matrix and volatile products. In the case these phenomena would be significant, this should lead to higher solid yields and energy yields with increased particle size. As these were not observed, apparently these phenomena do not play a dominant role (under the applied conditions and in particular particle size).

A very important property is the increase in energy density of the torrefied wood compared to untreated wood. The lower heating value of the dry biomass was found to increase with temperature: for willow a 17% increase was observed at 270°C (from 17.7 to 20.7 MJ/kg on daf basis) and for beech an increase of almost 20% at 280°C (from 17.0 to 20.3 MJ/kg on daf basis). It is also expected to increase with reaction time, but in many cases such an increase could not be observed due to the error margin in the determination of lower heating values. For coniferous wood such as larch, a smaller but statistically relevant increase in energy density of up to 7% is observed. As has been argued earlier, the smaller weight loss due to the lower reactivity of softwood explains this. It must be remarked that the torrefied wood samples produced at temperatures above 250°C contained less than 0.1% moisture, whereas the untreated wood did contain moisture, e.g. for beech approximately 8.6%. If the lower heating value of untreated

wood is corrected for the heat of evaporation of present moisture, the actual increase brought about by torrefaction is up to 30% for deciduous wood types.

4. Size reduction and fluidisation experiments

4.1 Facilities and experiments

Size reduction experiments were performed on batches of torrefied biomass that were produced with the 3-6 kg batch reactor (see also Section 3.1). A heavy-duty cutting mill (1.5 kW_e) was deployed for these experiments (see also Table 3.1). An overview of the evaluated parameters in size reduction is provided by Table 4.1. As the production rate in energy production chains depends on energy flows rather than mass flows, the evaluated size reduction parameters are expressed in energy units. The power consumption is therefore expressed as kW_e per MW_{th} of processed biomass, instead of for instance in kJ/kg. Similarly, the mill capacity is expressed in kW_{th} of processed biomass, instead of expressed in some mass unit per unit of time.

Table 4.1 *Evaluated size reduction parameters and their relevance to the technical and economic feasibility*

Parameter	Unit	Relevance
Power consumption	kW _e /MW _{th}	Variable costs (utility consumption, production chain efficiency)
Mill capacity	kW _{th}	Capital investment (amortisation)
Particle size (distribution) and shape	mm, sphericity	Fluidisation quality

Fluidisation experiments were carried out for a limited number of torrefied biomass of different particle size bins. A small cold-flow fluidised bed (20 x 10 x 3 cm) was designed and built to carry out the experiments. Optical analysis of the powders was done to get an impression of the particle shape of torrefied willow compared to untreated willow. An optical microscope was used for this.

4.2 Results

4.2.1 Power consumption

Figure 3.1 provides typical results obtained for the power consumption versus the resulting particle size for the different types of (torrefied) biomass. Power consumption as a function of resulting particle size of the used cutting mill is called the power curve.

The power consumption for untreated biomass increases strongly with a decrease of the resulting particle size. Whereas the power consumption for resulting particle sizes of about 0.8 mm is in the range of 10 to 20 kW_e/MW_{th}, this increases to 50 to 65 kW_e/MW_{th} for a resulting particle size of approximately 0.2 mm. Assuming that the required electrical energy can be obtained from biomass with an efficiency of 40%, the parasitic energy demand of size reduction for 0.2 mm particle size (on average) is then approximately 12.5% up to even 16.3%. Some differences between the power curves of the fresh biomass exist, which may be the result of differences in mechanical properties, but may also be related to differences in feed size and shape (see also Table 3.2). The order of power consumption for the evaluated biomass types is:

willow > beech > larch

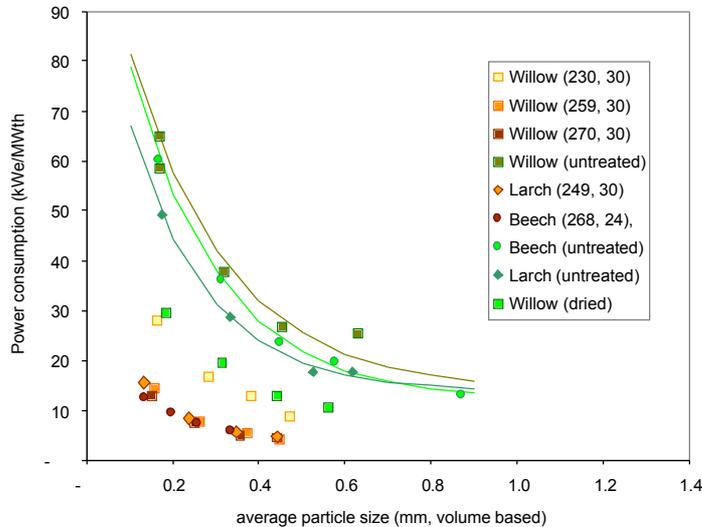


Figure 4.1 *Relation between power consumption and particle size (particle diameter) for fresh biomass and torrefied biomass. Moisture content of the fresh biomass was in the range of 10 – 13% on mass basis, except for the dried willow (< 1% wt.). Moisture content of the torrefied biomass ranged from 1.2 – 6.6% wt*

The power consumption is greatly reduced when the biomass is first torrefied. A reduction of 85% is maximally observed for torrefied willow (250,30). Strikingly, willow (261,30) and (271,30) lead to this same reduction. Consequently, the electricity required for grinding torrefied biomass would consume approximately 1.5% of its own energy content when particles of 0.2 mm average size are produced. This result is obtainable in the higher temperature region (250-280 °C). Willow torrefied at (230,30) leads to a decrease in power consumption of approximately 50% compared to untreated biomass. An increase of temperature in the range of 250 °C to 270 °C does not reduce the power consumption any further and neither does a decrease of the reaction time down to 8 min at 264 °C (willow). Above 250 °C, all evaluated biomass types follow the same power curve, despite the differences that were observed between their untreated precursors. The power curves of the three torrefied biomass types (willow, beech, larch) show considerable similarity when torrefied at 250 °C or higher temperature. Apparently, the original differences in shape, polymeric structure and other relevant properties leading to different (grinding) behaviour, seem to be filtered through torrefaction.

To isolate the influence of the chemical changes from physical changes due to drying, willow was completely dried and milled, see 'Willow (dried)' in Figure 4.1. The difference between 10-13% moisture content (mass basis) and bone-dry willow (<1% moist) is about 45% in power consumption. This is about half the improvement obtained when it is torrefied at a temperature above 250 °C and hence the other half is due to the chemical changes during torrefaction. The difference between bone-dry willow and (W,230,30) is rather small. This indicates that the decomposition reactions did not occur vigorously at this temperature.

Figure 4.1 represents results for torrefaction experiments carried out at a reaction time of 30 min. As these results imply that such a reaction time is sufficient to meet a maximum reduction in power consumption, two experiments were carried out at shorter reaction time (W,246,10;W,264,8). The power curve of (W,246,10) was found to be very similar to that of (W,230,30). The power curve of willow (264,8) is similar to (W,270,30), which demonstrates that the responsible decomposition mechanisms occur relatively fast and in the first stage of decomposition. This also indicates the importance of including the heating from 200 °C to final

torrefaction temperature, $T_{\text{tor,h}}$ (see also Section 2.4.2), in the definition of reaction time. This heating takes generally 3 to 5 min under the applied reactor conditions.

At a reaction time of 30 min, larger willow particles were torrefied to reveal the effect of particle size on the energy consumption. Two other size bins have been used next to 0-10 mm; 10 to 30 mm cut-size and 30 to 50 mm cut-size, in line with the torrefaction experiments discussed in Section 3.2. Again great similarity between the different size-fractions was observed. This can be expected, however, as the main influence of particle size deals with the heating rate of the subsequent particles, but only 8 min reaction time is already sufficient to have maximum benefit. Hence, 30 min reaction time is probably too long to observe particle size effects.

4.2.2 Mill capacity

Figure 4.2 represents the capacity characteristics of the used cutting mill corresponding with the power consumption results represented by Figure 4.1. In general the capacity increases with increased particle size in a typical (slightly) non-linear relationship between both. Relatively small differences are observed between the different untreated biomass types. The order of increased capacity observed is:

willow < beech < larch

The mill capacity for bone-dry willow was found to be about 2 times higher compared to willow with 10-13% moisture content.

With torrefaction a strong capacity increase of the size reduction process up to 6.5 times the capacity of untreated biomass is possible. This maximum is achieved at the highest temperature explored and any decrease of temperature leads to decreased capacity. This decrease is relatively small in the higher temperature region..

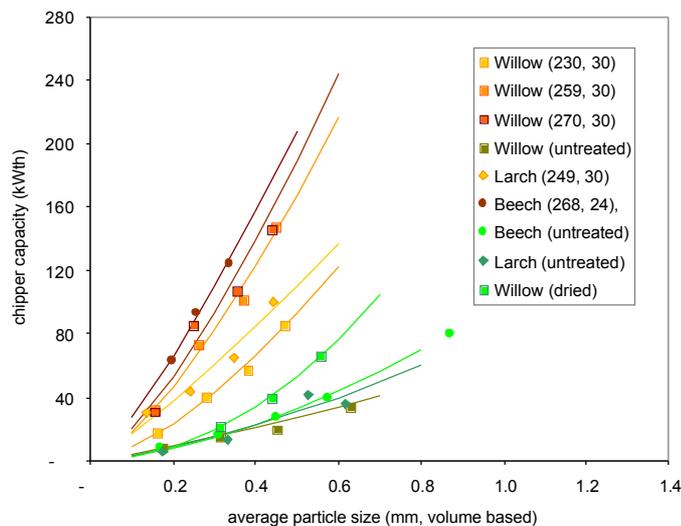


Figure 4.2 *Relation between the mill capacity and particle size (particle diameter) for fresh biomass and torrefied biomass. Moisture content of the fresh biomass was in the range of 10 – 13% on mass basis, except for the dried willow (< 1% wt.). Moisture content of the torrefied biomass ranged from 1.2 – 6.6% wt*

Only small differences are observed between the different biomasses that are also observed for the untreated biomass. Therewith the effect of temperature on capacity seems to be slightly different to its effect on power consumption. A small difference in mill capacity is observed between (B,268,24) and (W,270,30). As fresh beech also showed somewhat higher capacity compared to willow, this may be due to the differences in the original plant structure or to

differences in feed particle size and shape (see also Table 3.2). Larch that was torrefied under milder conditions (249,30) follows the trend of increasing capacity with increasing torrefaction temperature when compared to (W,230,30) and (W,259,30).

The capacity characteristics of (W,246,10) and (W,264,8) were both analysed to evaluate the effect of shorter reaction time. Willow torrefied at (246,10) exposed great similarity with willow torrefied at (230,30). Willow (264,8) proved that a similar capacity curve compared to (W,269,30) is obtainable after only a very short period of heating with a temperature peaking at 264 °C. The experiments done on larger willow particles at (260,30) (1-3 cm and 3-5 cm size bins, not shown in Figure 4.2) revealed that the influence of particle size on capacity is very insignificant. This was also found for untreated willow.

4.2.3 Particle size distribution and shape (product quality)

Typical particle size distributions obtained from the size reduction experiments are given in Figure 4.3 (willow). The results reveal the influence of torrefaction temperature for various particle size ranges, which were obtained by varying bottom sieves to have different cut-sizes.

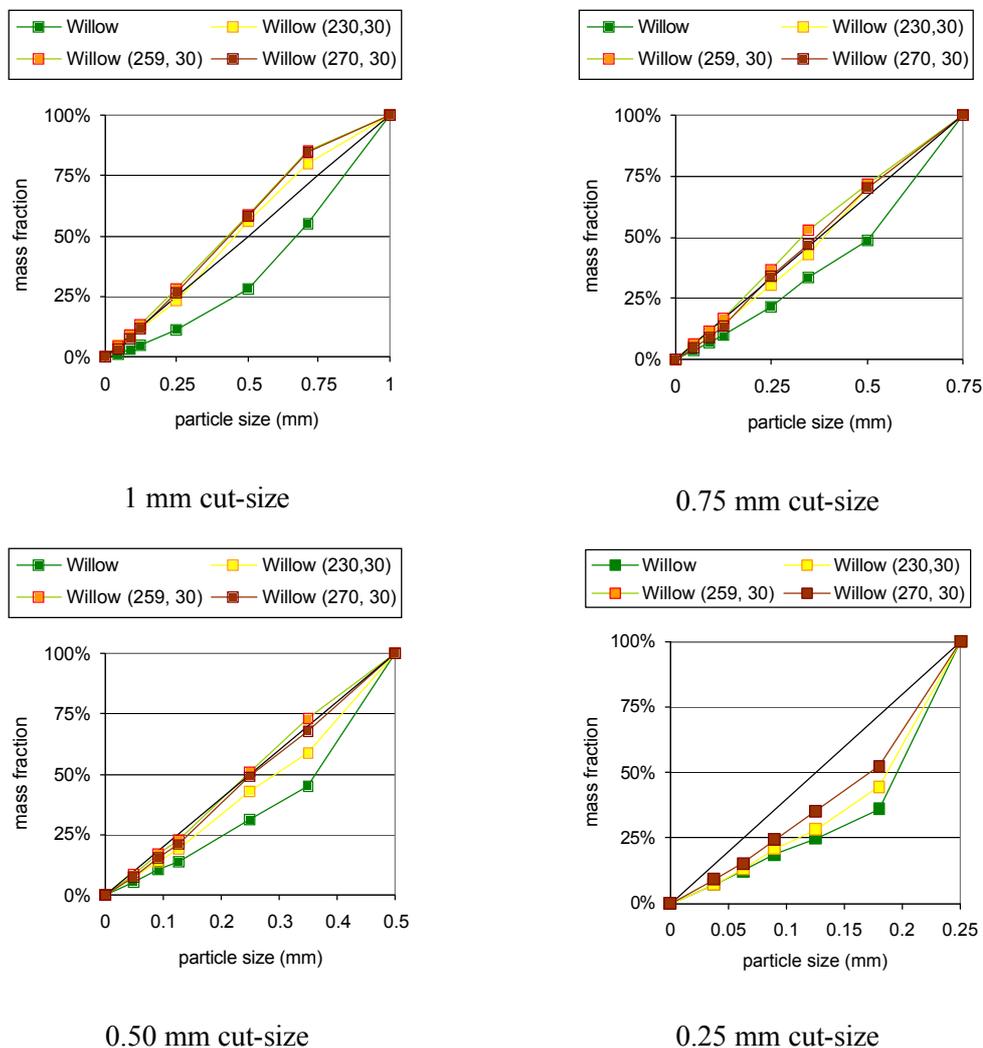


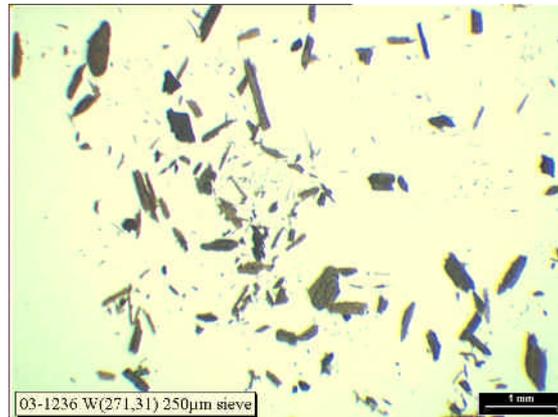
Figure 4.3 Particle size distributions (cumulative curves, wt%) of virgin willow (0 – 10 mm) and torrefied willow at approximately 30 min reaction time and different temperatures

Fresh biomass typically exhibit a power distribution¹ in particle size wherein the mean particle size is shifted from the $x=y$ -curve towards the maximum particle size possible (which is the cut-size of the applied bottom sieve). Such a distribution indicates that the feed particles are difficult to grind and is found for all applied bottom sieves. For torrefied willow a rectangular (or uniform) distribution¹ is found; the distribution curve reasonably matches the $x=y$ -curve, except for the smallest bottom sieve cut-size of 0.25 mm. Hence thinner particles are produced. The effect of torrefaction temperature is most clearly visible for the bottom sieve of 0.25 mm. Increased temperature shifts the particle size distribution from a power distribution to a rectangular distribution. This characteristic was found to be typical for willow and larch, regardless of the applied changes in feed particle size and reaction time. Only beech showed slightly different behaviour as for the larger cut-sizes relatively smaller particles were formed and a 0.25 mm cut-size bottom sieve still resulted in a rectangular distribution.

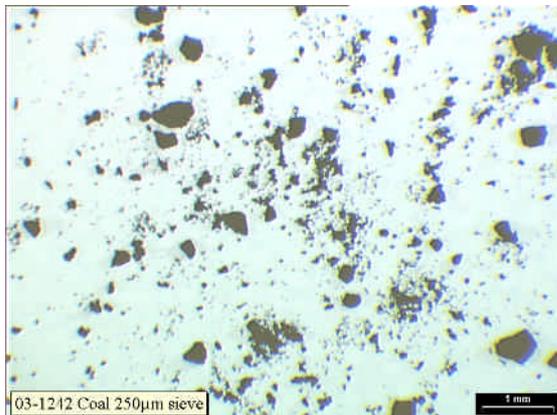
¹ A power distribution is a typical of distribution known from statistical analysis. An overview of typical statistical distributions can be obtained from www.xycoon.com.



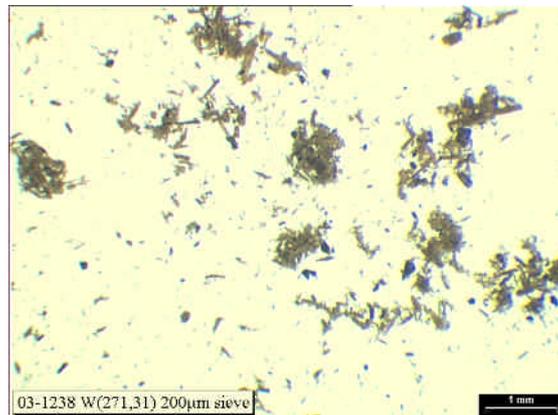
A: Fresh willow milled in the cutting mill with bottom sieve of 250 μm



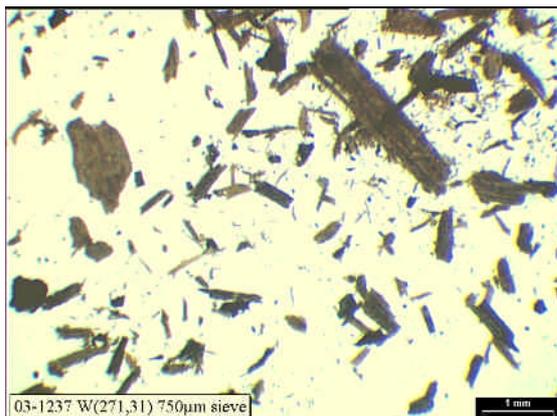
B: Willow (270,30) milled in the cutting mill with bottom sieve of 250 μm bottom sieve



C: Coal milled in the cutting mill with bottom sieve of 250 μm



D: Willow (270,30) 200 milled in a hammer mill with bottom sieve of 200 μm



E: Willow (270,30) 200 milled in a hammer mill with bottom sieve of 750 μm

Figure 4.4 Pictures of willow, torrefied willow and coal particles after size reduction

Figure 4.4 represents pictures made with an optical microscope reflecting the particle shape of fresh willow and torrefied willow (270,30), and illustratively also coal. For fresh willow, it can be observed that the particles a rather large Length to Diameter Ratio (LDR) caused by the fibrous and anisotropic nature of wood (see also Section 2.2). Although these particles are obtained using a 250 μm cut-size bottom sieve, the length of the particles is in general many times larger. Particles exceeding 1 mm in length are no exception. The diameter of the fresh willow particles is in many cases approximately the cut-size of the bottom sieve. Consequently,

the feed particles are more or less ‘scraped’ until the diameter of the resulting particles is small enough to be processed through the bottom sieve of the cutting mill. Consequently, in the interpretation and use of the data provided by Figure 4.1, Figure 4.2 and Figure 4.3 it is very important to recognise that ‘particle size’ represents the diameter of the particles rather than their length.

The effect of torrefaction (W,270,30) is in the first place that the particles become smaller, in length as in diameter. From the pictures made with the optical microscope, a trend of decreased LDR after torrefaction is observed. Apparently more spherical particles are produced. When larger bottom sieves are used in the cutting mill, particles become more spherical. This was found for fresh biomass, but more strongly for torrefied willow. An increase of torrefaction temperature results also in more spherical particles.

4.3 Fluidisation behaviour

The feeding of fuel powders relevant in this work is based on principles used in the entrained-flow gasification of coal, see Figure 4.5. The feeding system is essentially a fluidised bed operated in the smooth regime by using a fluidisation medium, which is normally nitrogen. By applying a pressure drop (DP) over the solids exit line solids are pneumatically conveyed to the entrained-flow gasifier. The operating pressure of the feeding system is tuned to the applied pressure in the entrained-flow gasifier. Typically this is about 20 bar.

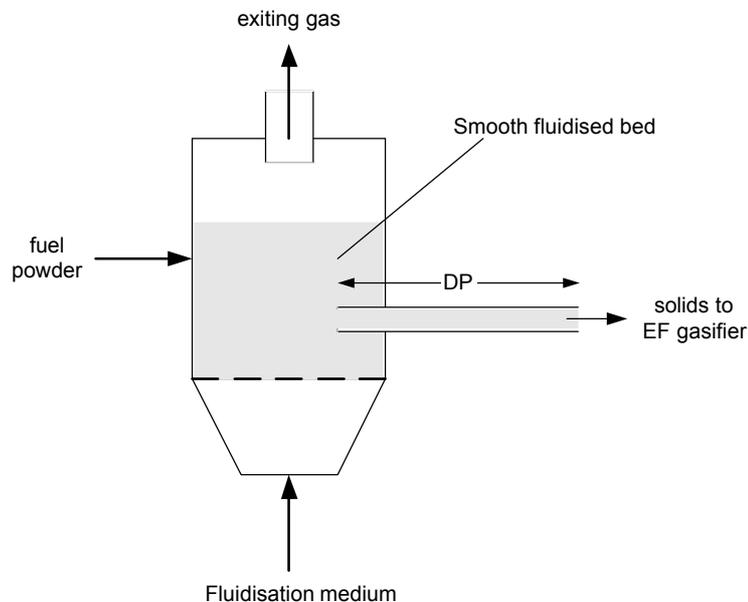


Figure 4.5 *Schematic representation of feeding system of coal powder fuelled EF gasifier*

The operation of the bed in the smooth fluidised mode can be considered the most crucial aspect. The bed of particles is aerated meaning that the bed has expanded but gas bubbles are not formed. The absence of gas bubbles provides a uniform and dense bed of solid particles, which creates a continuous and stable flow of fuel particles to the stationary flame present in the entrained-flow gasifier. The presence of gas bubbles – as in a bubbling fluidised bed – leads to unstable behaviour of the flame, which hampers the gasifier performance negatively. Additionally, operation in the smooth regime requires a minimum amount of fluidisation medium, which is important with respect to the quality of the syngas exiting the entrained-flow gasifier. Smooth operation of the fluidised bed requires fuel particles that according to the Geldart classification can be classified as **A** powder (Geldart **A**). Such a powder is characterised by a small mean diameter and/or a low particle density (Kunii and Levenspiel, 1991). Coal particles of typically 75 μm mean particle size belong to this group.

Two characteristic gas velocities bound the smooth regime. The gas velocity must exceed the minimum fluidisation velocity, u_{mf} , and needs to stay below the minimum velocity at which bubbles start to form, u_{mb} . In between these characteristic gas velocities, smooth and continuous expansion of the bed occurs. Only in this regime the bed is in smooth operation, below this velocity the state of aeration is too poor and above gas bubbles are formed. Only for Geldart **A** powders such a regime occurs. In the case of Geldart **B** powders, bubbles start to form when the gas velocity equals u_{mf} . Pressure has a significant effect on the ratio of u_{mb} over u_{mf} . An increase of 30% of this ratio can be expected when the pressure is increased in comparison with atmospheric operation (Kunii and Levenspiel, 1991).

Cold flow fluidisation experiments have been carried out on coal, untreated willow and torrefied willow to see if smooth fluidisation is possible. It was determined that smooth fluidisation of torrefied willow should be possible with spherical particles in the size range of 30 to 400 μm . Powders belonging to this particle size range were selected. The fluidisation quality was determined on the basis of visual observations of the existence of bed expansion without the formation of gas bubbles. The results from these tests are given in Table 4.2.

Table 4.2 *Fluidisation behaviour of coal, willow and torrefied willow*

Bed	d_p (mm)	Fluidisation Regime	Fluidisation quality
Coal	75 - 120	Smooth	++
Willow	200	Poor bubbling	- - -
(W,260,30)	170	bubbling	- -
(W,270,30)	160	bubbling	-
(W,270,30)	± 100	Smooth	+

Smooth fluidisation was observed for coal and for torrefied willow (270,30) with a mean particle size of approximately 100 μm . Smooth fluidisation of torrefied willow particles of mean particle size of 160 μm was not possible, as these particles were too large and non-spherical causing the hypothetical particle diameter (as if spherical) is plausibly exceeding 400 μm . The same conclusion was drawn for willow torrefied at (260,30). For untreated willow particles smooth fluidisation was found to be impossible, as the particles were not small and spherical enough (the 200 μm particles have a length of more than 1 mm). Even operation in the bubbling regime did not result in a stable bed (presence of bridges, dead zones) due to hooking of the needle shaped particles.

4.4 Discussion

Based on the results presented in this chapter, torrefaction exerts a strong and positive influence on the performance characteristics of biomass size reduction when considering the power consumption and capacity of the mill, but also on the particle size distribution and shape of the powder representing the product quality of the produced powder. In addition, the smooth fluidisation behaviour that was observed for willow (270,30) of 100 μm average particle size proves that the quality of the powder is sufficient for its feeding into an entrained-flow gasifier. The fluidisation experiments have shown that this is impossible for untreated biomass, due to their needle shape, which keeps the particles also too large to meet the smooth fluidisation regime. Nevertheless, further optimisation of the torrefaction conditions is recommended to further increase the powder quality for optimal feeding. The torrefaction temperature is considered the most important parameter in this respect. The higher this temperature, the more smaller and spherical particles can be obtained after size reduction. In this work 270 °C was the highest temperature explored and further optimisation should be focussed on the temperature range of 270-300 °C.

Based on both literature and experimental results of this work, it is believed that two decomposition mechanisms are mainly responsible for the observed improvements. These are hemicellulose (two-step) decomposition and cellulose depolymerisation. Hemicellulose is the most reactive polymer present in the polymeric structures of biomass. Many of the observations done in Section 3.2 could be explained on the basis of the decomposition of this polymer. It is believed that biomass its tenacity and strength is lost through the deterioration of hemicellulose, regarding the contribution it has towards the mechanical properties of biomass, see also Section 2.2. Hemicellulose forms a matrix of disoriented chain structures by which the highly structured cellulose fibres are oriented and interlinked. It may be expected that the (partial) destruction of this matrix into randomly organised sugar structures and volatiles results in a modified matrix that is no longer capable to support the cellulose fibres. Therefore the cellulose fibres are more easily detachable. Hence less energy is needed during size reduction and thinner particles can be produced.

The anisotropic nature of biomass is mainly caused by the orientation of the cellulose fibres in combination with their length. This is the main cause why the size reduction of biomass results in a powder of mostly needle shaped particles having a high length-to-diameter ratio. The depolymerisation of cellulose shortens the individual cellulose chains. As a result of the degree of polymerisation (micro) cracks are formed in the cellulose fibres. Therefore, the number of weak positions within the fibre structure is strongly increased in a random way. When a force is applied to such a damaged structure the process of breakage proceeds more random as well. Hence the anisotropic nature of biomass is less dominant in size reduction after torrefaction and shorter particles are produced.

The size reduction experiments that were carried out in this work indicate that the effect of torrefaction temperature on the power consumption of size reduction is strongly non-linear over 200 to 280 °C and that an important transition seems to be present at about 250 °C. The two-step mechanism by which hemicellulose decomposes (Di Blasi and Lanzetta, 1997) may explain this phenomenon. The modelling results (Section 3.2.5) showed that the first step of biomass decomposition into new sugar structures and volatiles (destruction of the hemicellulose matrix) proceeds relatively fast, whilst the second step of charring of formed sugar structures proceeds rather slowly. As only the first step significantly occurs below 250 °C and reaches completion fast at temperatures exceeding 250 °C, this step is held responsible for the improvements observed in power consumption. To have an indication of the conversion degree of biomass (A) in the first step, Table 4.3 provides an illustrative summary and couples the conversion rate and power consumption to temperature and residence time of torrefaction. The model derived for willow (Section 3.2.5) was used to estimate the conversion rate.

Table 4.3 *Conversion rate of A based on experimental conditions applied on willow torrefaction. The conversion rate is estimated using the derived model in Section 3.2.5*

Experiment / Conditions	Conversion rate of A (%)	Power consumption (kW _e /MW _{th}) (dp≈0.2 mm)
Bone-dried willow	0	26
(W,246,10)	20	23
(W,230,30)	45	24
(W,264,8)	60	10
(W,260,30)	75	10
(W,270,30)	90	10

Figure 4.6 illustrates the coupling of the two-step decomposition mechanism to the power consumption observations. The black curve represents the effect of the chemical changes due to torrefaction, supported by part of the results covered by Figure 4.1. Up to a temperature of 230

°C (willow), the physical and chemical changes that do occur during torrefaction lead to improved size reduction characteristics (e.g., power consumption) compared to the untreated biomass. However, the improvements are very similar to that of solely drying (bone-dry) of the biomass. Therefore it is stated that the needed chemical changes hardly occur below 230 °C and that the observed improvement at 230 °C (compared to untreated biomass) mainly comes from the removal of physically bound water. Once the first step of decomposition is sufficiently completed, apparently in the range of 45% to 60% conversion rate according to the modelling results presented in Table 4.3, the deterioration of the hemicellulose matrix is already in a stage that further decomposition at higher temperature does not result in a further decrease of power consumption. As the second step of decomposition is slow, its effect can be considered irrelevant in the examined operation window.

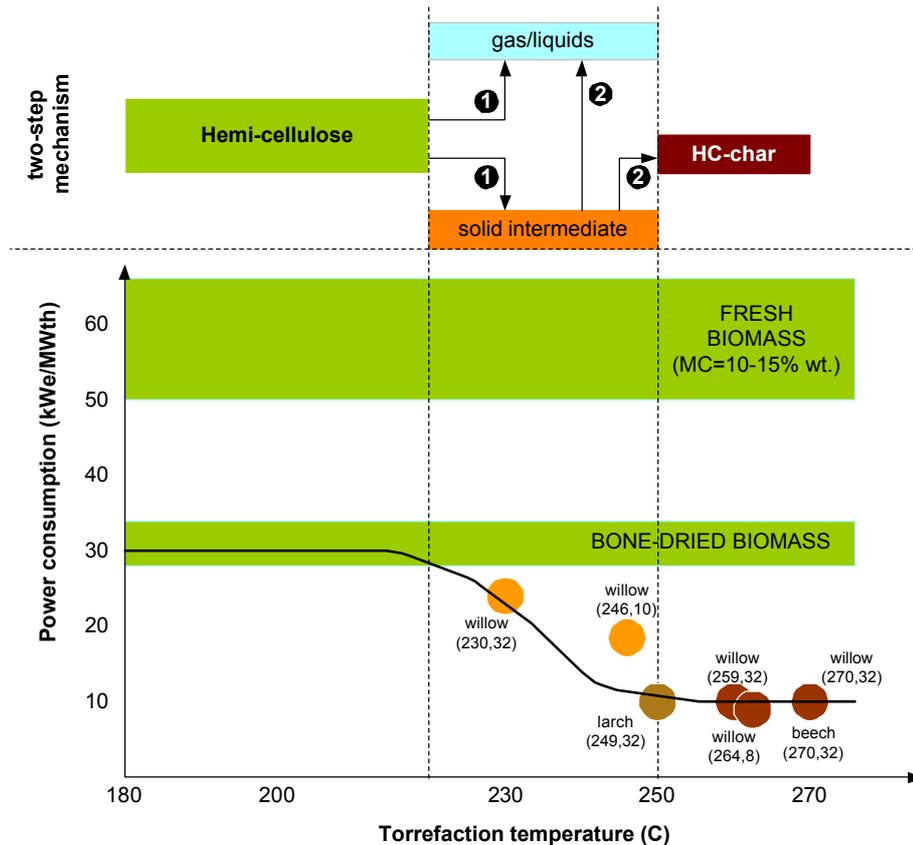


Figure 4.6 *Artist impression of the decomposition mechanisms of hemicellulose versus temperature and related to the reduction of the energy requirements of the size reduction process*

Although biomass can be found in a wide variety of species, they all are composed of the same polymers, which contribute in a similar way to the general properties of biomass such as tenacity and strength. It is therefore believed that the decomposition reactions during torrefaction have a similar effect on any biomass, despite the differences in (polymeric) composition and mechanical strength. This is considered to be the main cause why the evaluated biomass types show the same power consumption characteristics after torrefaction. From this angle, torrefaction acts as a thermal filter filtering original differences existing in untreated biomass to yield a fuel product with similar mechanical properties.

The independence of power consumption on the torrefaction temperature in the range of 250-270 °C was not found for the relation between capacity and the torrefaction temperature in this same temperature range. Instead an increase of capacity with an increase of temperature is observed. Though it is believed that hemicellulose decomposition significantly contributes to

the enhancement of the kinetics of particle breakdown, also cellulose depolymerisation will further enhance this kinetics. Above 250 °C the depolymerisation becomes exponentially more dominant. When the length of the particles is further reduced thereby, they are easier transported through the bottom sieve of the mill. Increased temperature therefore increases the capacity of the mill. Most probably, hemicellulose decomposition is the dominant mechanism up to 250 °C and cellulose depolymerisation becomes increasingly more important at higher temperatures.

The changes that torrefaction induces in the molecular structure of biomass (wood) not only lead to a less energy consuming process with higher capacity, the observations for particle size distribution and shape indicate that the mechanism of size reduction is different from that of fresh wood. Figure 4.7 proposes schematically how torrefaction may have changed the mechanism of particle breakdown due to hemicellulose decomposition and cellulose depolymerisation. In this 'artist impression' a small part of a cell wall is depicted schematically. The fat solid lines represent the macrofibrils and the more randomly oriented orange-red lines represent the hemicellulose. The red parts symbolise the attachment of hemicellulose to the macrofibrils (hydrogen bonding), the orange parts symbolise interweavement of hemicellulose and cellulose. Three pathways are shown; breakdown of untreated biomass, and the breakdown of torrefied biomass in the lower (230-250 °C) and higher temperature region (250-270 °C). Note that the effect of torrefaction on the biomass structure is made visible by a decrease of interweavement and shortening of the macrofibrils. These effects are more strongly within the higher temperature region.

When untreated biomass is grinded, the state of stress being induced on feed particles leads to breakdown of the particles along the fibre orientation. The exerted stress breaks up the hemicellulose along the line of fracture rather than breaking up the cellulose fibres themselves. Hence the formation of needle shaped particles. When the same stress is applied to torrefied biomass, a similar amount of energy is available for breakage, but with the advantage that there's less to break. The stress will now propagate throughout the feed particle causing breakage of more weaker hemicellulose connections. Therefore, more lines of fracture are formed following the orientation of the macrofibrils. Merely this mechanism would lead to even thinner particles, but because cellulose depolymerisation has broken up the macrofibrils (or resulted in formation of weak spots which easily can burst), the resulting particles also have decreased length.

As the impression of Figure 4.7 reflects, not only smaller needle shaped particles may be the result of these mechanisms. Also particles with increased spherical shape may be resulting depending on the weakest lines of breakage in both hemicellulose and cellulose. It also reflects the impression that hemicellulose decomposition and cellulose depolymerisation are both randomly occurring processes throughout the biomass. This would clarify the shift from a power distribution for untreated biomass towards a uniform distribution for torrefied biomass. As depolymerisation at higher temperature is more fiercely, this would explain the dependence of particle size distribution on temperature as can be observed in Figure 4.3.

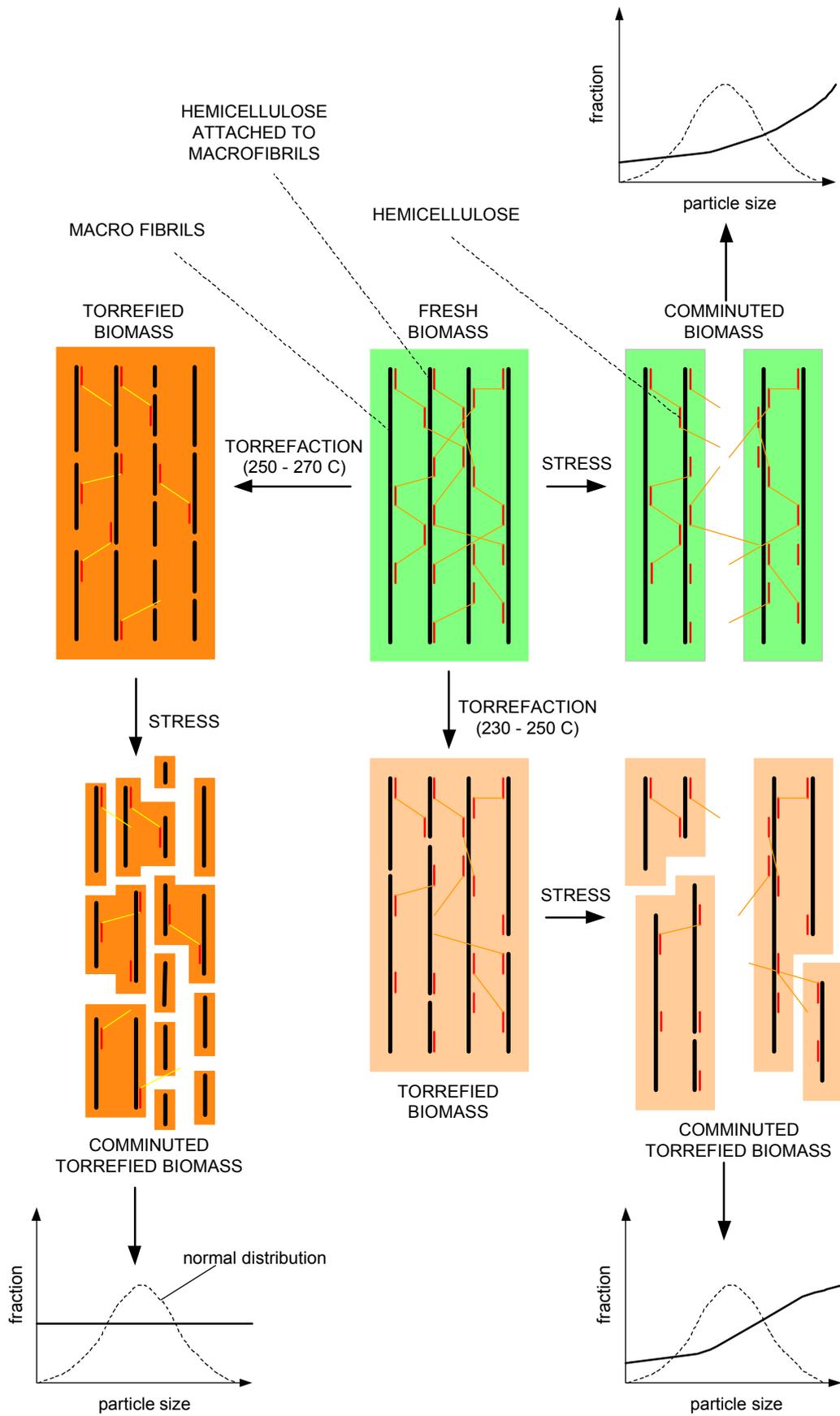


Figure 4.7 Artist impression of particle breakdown of fresh biomass and torrefied biomass

5. Conclusions and recommendations

5.1 Conclusions

Torrefaction

In general, the conducted experiments reveal that torrefaction can be applied with a high biomass to solid energy yield ranging from 95-100% within the lower temperature region (<250 °C) to 83-95% within the higher temperature region (250-270 °C). At a temperature exceeding 270 °C, the energy yield drops further, but can still be limited when the reaction time is kept short. The corresponding mass yields are consistently lower and range from 90-100% within the lower temperature region and 80% to 90% in the higher temperature range (up to 270 °C). From the analysis of the volatiles, it is concluded that the increased production of water and CO₂ with increased temperature mainly explains the interrelation between both yields. The production of these non-combustibles leave the energy yield unaffected while the mass yield is decreased.

The observed order of reactivity of the examined biomass types is larch << willow/beech < straw. This order is mainly determined by their mutual differences in the hemicellulose content and composition, which is the most reactive polymer constituent in biomass. This leads in general to higher mass and energy yield, but smaller increase of heating value in the case of coniferous wood (larch) compared to deciduous wood (willow, beech). Small differences can be expected within a population of these two main wood classes.

Within the examined operating window, reaction time has a smaller influence on the mass and energy yields than temperature. The effect of particle size [0-10 mm, 10-30 mm, 30-50 mm willow size bins] was found to be insignificant, indicating kinetically controlled reactions and the absence of heat and mass transfer limitations for the examined size ranges.

Size reduction

Torrefaction has a substantial effect on the operation of particle size reduction of biomass. When comparing to untreated biomass, a reduction up to 85% of the energy requirements and a mill capacity increase of 6.5 times are possible when the biomass is first torrefied. These utmost improvements are achievable at temperatures above 250 °C while the reaction time can be as low as 8 min. Below 250 °C, the conditions are believed to be insufficiently fierce to achieve these improvements. At 230 °C, the reduction in power consumption is comparable to bone-dried biomass (willow). Insufficient hemicellulose decomposition is concluded to be the main reason for this. The observed size reduction characteristics are found to be very similar for all the examined biomass types (larch, willow, beech) and were not affected by particle size. After torrefaction smaller particles are more easily produced with a decreased length-to-diameter ratio and particle size distribution shifts from a power distribution (untreated wood) to a rectangular distribution.

The power consumption characteristics can be coupled to the hemicellulose decomposition, which can be described by a two-step decomposition mechanism. It is argued that in the first step wherein hemicellulose decomposes into other chaotic polymer structures with a reduced degree of polymerisation. This results in loss of tenacity and mechanical strength and the production of thinner particles. Cellulose depolymerisation (especially at higher temperature) is believed to reduce the length of the particles after milling and increases the milling capacity.

Fluidisation behaviour

In contrast to untreated biomass, torrefied biomass can be fluidised in the regime of smooth fluidisation. The most important reason for this is the decreased length-to-diameter ratio. The best result was found for 100 µm particles torrefied at 270 °C and 30 min reaction time (willow). The smooth fluidisation quality was not as good as observed for coal, but further optimisation of torrefaction conditions (mainly temperature) may positively change this.

Torrefaction and entrained-flow gasification

It is concluded that torrefied biomass provides a solution to the feeding problem that will be encountered in feeding untreated biomass to an entrained-flow gasifier. Therefore, by the implementation of torrefaction into the overall biomass to syngas production chain, this main technical obstacle in this route is eliminated. It is demonstrated that the energy yield of torrefaction can be as high as 90-95%, indicating that a torrefaction process can be high in overall efficiency. Consequently, the overall efficiency of such a production chain is not extremely affected by torrefaction. Besides, size reduction of torrefied biomass is proven to be an energy-friendly operation by which the overall energy efficiency is improved. Not only operational costs will be reduced thereby, but also the possible capacity increase reduces the investment costs considerably.

The economical feasibility of the torrefaction process is likely to depend on the costs of the reactor technology, which is to a large extent determined by the required biomass residence time. From open literature, this is typically 1 hour. This work has revealed that the desired product quality may very well be achievable within 15 min. This could substantially reduce the investment costs of torrefaction.

5.2 Recommendations

It is recommended to further study the technical and economic feasibility of a biomass-to-syngas production chain including torrefaction as a biomass pre-treatment step. The outcomes of this work can very well contribute to this in considering the design of the torrefaction process and size reduction. Torrefaction will add production costs, but decreases the production costs of size reduction and, depending on the overall chain efficiency, feedstock costs may be reduced as well. Additionally it is recommended to study the gasification characteristics (e.g., carbon-conversion, cold-gas efficiency) of torrefied biomass experimentally.

Further optimisation of the torrefaction conditions is recommended to further increase the powder quality for optimal feeding. The torrefaction temperature is considered the most important parameter in this respect. The higher this temperature, the more thinner and shorter and hence more spherical particles can be obtained after size reduction. In this work, 270 °C was the highest temperature explored and further optimisation should be focussed on the temperature range of 270-300 °C. In this work, the length-to-diameter was qualitatively evaluated by visual observations. It is also recommended to apply a quantitative method (e.g., optical microscope) in future research.

In further improving the knowledge base on torrefaction, it is recommended to focus on the polymeric composition of the feed biomass. Available analysis methods known from biology-oriented research fields to determine this composition could be used. Knowledge about the relationship between the exact polymeric composition and torrefaction characteristics such as mass and energy yield and production of volatiles would be very important for the development of predictive tools to optimise the process.

Distinct differences have been identified between coniferous and deciduous wood. Most effort in this work has focused on deciduous wood, but as coniferous wood will be a main source in biomass to energy production chains, improvement of the knowledge base on this biomass is recommended. For instance, it would also be interesting to see whether coniferous wood, which shows relatively little reactivity in the range of 230-270°C, becomes much more reactive at higher temperatures.

The analysis method to determine the heating value of feed and product (adiabatic bomb calorimeter) has an inaccuracy of $\pm 1.5\%$. Since the difference in heating value between feed and product is not very high, such an inaccuracy complicates the interpretation and understanding of experimental data. Statistically justified conclusions seem only to be possible on the basis of a high number of experiments. It is recommended to investigate whether this measurement can be improved.

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7. Used symbols and abbreviations

Symbol or Abbreviation	Unit	Explanation
SR		Size Reduction
SRP		Size Reduction Process
W		Willow
L		Larch
B		Beech or intermediate reaction product in willow decomposition model
TU/e		Technical University of Eindhoven
ECN		Energy research Centre of the Netherlands
HC		Hemicellulose
t_h	min	Heating time to drying
t_{tor}	min	Reaction time at desired torrefaction temperature
$t_{tor,h}$	min	Heating time torrefaction from 200°C to desired torrefaction temperature
$t_{tor,c}$	min	Cooling time from the desired T_{tor} to 200 °C
T_{tor}	°C	Desired torrefaction temperature
$t_{h,int}$	min	Intermediate heating time from drying to torrefaction
t_{dry}	min	Drying time
t_c	min	Cooling time to ambient temperature
EF		Entrained-flow
LDR	-	Length over Diameter Ratio
A	wt%	Reactive part in willow during torrefaction
C	wt%	Char produced from intermediate products during willow decomposition
k_1		Reaction constant of first decomposition step in willow decomposition
k_2		Reaction constant of second decomposition step in willow decomposition
B_t	wt%	Concentration of intermediate product B at time t in willow decomposition
C_t	wt%	Concentration of char produced from intermediate products during willow decomposition at time t
$A_{t=0}$	Wt%	Initial reactive part of biomass
k_0	1/s	Pre-exponential factor in Arrhenius equation
E_{act}	kJ/mol	Activation energy in Arrhenius equation
DP	Pa	Pressure Drop
u_{mf}	m/s	Minimum fluidisation gas velocity
u_{mb}	m/s	Minimum fluidisation gas velocity at which gas bubbles start to form