Torrefaction to improve biomass fuel properties

Probleemstelling
Torrefactie is een methode om biomassa thermisch voor te behandelen zodanig dat:
1. De calorische waarde per massa eenheid grotendeels in het materiaal behouden blijft;
2. Het materiaal een maalbaarheid krijgt vergelijkbaar met die van kolen;
3. Het materiaal hydrofoe eigenschappen krijgt;
4. Het is een methode om inhomogene stromen meer homogene eigenschappen te geven;
5. Doordat het een thermische voorbehandeling is bij een temperatuur van 200 tot 300°C is het een extra stap in het totale conversie proces.

Vragen
1. Wegen de kosten van een extra stap op tegen het voordeel dat men behaalt?
2. In welke sectoren kan men het toepassen?
3. Is het interessant om stromen met grote diversiteit tot een beperkter aantal stromen te reduceren?
4. is het een optie die import van biomassa vergemakkelijkt?
5. Welke samenwerkingsverbanden zijn mogelijk?

1. Introduction
Many (conventional) thermal conversion technologies require rather narrow feedstock specifications, which are difficult to meet by a wide range of biomass and biomass residue streams. For example, direct (co-) firing in pulverised-fuel boilers and entrained-flow gasifiers requires (sub-)millimetre-size feedstock particles. Size reduction down to this size is known to be difficult and expensive for many types of biomass, especially for (fresh) woody biomass due to its fibrous structure and tenacity. Furthermore, many biomass residues and biomass/waste mixtures do not meet the stringent chemical requirements set by conversion processes, e.g. with respect to alkali metals, chlorine or heavy metals.

In addition to the conversion process itself, also transport, handling and storage set certain requirements to biomass feedstock. In this respect, many types of biomass (residues) have inferior properties, such as low energy density, hydrophilic nature (high water uptake when stored in open air), poor flowability, susceptible to rotting and heating.

ECN has identified torrefaction as being a biomass pre-treatment technique with a high potential for converting various biomass (residue) streams into biomass fuels, which meet the narrow specifications of different thermal conversion technologies. This concerns either torrefaction as such or torrefaction as one of the unit operations in so-called Multiple-Input-Specific-Output (MISO) concepts, by which a wide range of biomass (residue) streams is processes into a limited number of high and uniform quality biomass fuels. As a first step, it was decided to study the principles of torrefaction in more detail.

2. Torrefaction principles
Torrefaction is a thermal treatment at a temperature of 200 to 300 °C at near atmospheric pressure, in the absence of oxygen and at relatively long residence times (typically 1 hour). During the process the biomass partly decomposes giving off various types of volatiles. The final product is the remaining solid, which is referred to as torrefied biomass. The name torrefaction is adopted from the roasting of coffee beans (torrefier in French), which is however done at lower temperature while using air (oxygen). In the 1930’s the principles of torrefaction were first reported in relation to woody biomass and in France research was done on its application to produce a gasifier fuel. Since then the process

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received only attention again when it was discovered that torrefied wood is a good reducing agent in metallurgic applications. This led to a demonstration plant, which was built in the mid eighties but was dismantled again in the beginning of the nineties.

Torrefaction

250-280 °C
1 hr

Biomass

Torrefaction gases

0.3M 0.1E

Torrefied Biomass

0.7M 0.9E

Figure 1. A typical mass- and energy balance of the torrefaction process. E = energy unit, M = mass unit.

Figure 1 provides a typical mass- and energy balance of torrefaction. Typically, 70% of the mass is retained as a solid product, containing 90% of the initial energy content. The other 30% mass is converted into torrefaction gases, containing only 10% of the energy content of the biomass. Therefore, a considerable energy densification can be achieved, typically by a factor of 1.3 on mass basis. The energy yield in the solid product is considerably higher than for charcoal production or pyrolysis. The latter has a typical energy yield in the solid product of 55-65% in advanced concepts down to 20% in traditional ones.

Woody and herbaceous biomass consists of three main polymeric structures: cellulose, hemicellulose and lignin. Together these polymers are called lignocellulose. Hence the thermal decomposition of biomass is generally explained on the basis of these constituents. During torrefaction numerous reactions occur and different reaction pathways can be identified. However, all these reaction pathways can be grouped to a few main reaction regimes, as is shown in Figure 2.
For each polymer similar decomposition regimes can be defined. In temperature regime A biomass physical drying occurs. When the temperature is increased to regime C, depolymerisation occurs and the shortened polymers condense within the solid structure. A further increase of temperature to regime D leads to limited devolatilisation and carbonisation of the polymers and of the solid structures that were formed in the lower temperature regimes (viz. regime C). Again a further increase of temperature to regime E leads to extensive devolatilisation and carbonisation of the polymers and of the solid products that were formed in regime D. For lignin also a temperature regime is defined in which softening of this biomass constituent occurs, a phenomenon very beneficial in the densification of biomass, as softened lignin is a good binder agent.

Figure 2 also includes the torrefaction temperature regime and the blue line splits it into a low (<250 °C) and high temperature regime (>250 °C). In general hemicellulose is the most reactive polymer followed by lignin and cellulose is most thermostable. In the lower torrefaction temperature regime the main biomass decomposition comes from the limited devolatilisation and carbonisation of hemicellulose. Minor decomposition is to be expected from lignin and cellulose except for changes, which do not lead to a significant mass loss. At higher torrefaction temperatures, decomposition becomes more vigorous as hemicellulose extensively decomposes into volatiles and a char-like solid product and also lignin and cellulose show limited devolatilisation and carbonisation.

During torrefaction numerous reaction products are formed. Their yield strongly depends on the torrefaction conditions (temperature, residence time) and on the biomass properties. Figure 3 gives an overview of the torrefaction products, classified based on their state at room temperature, which can be solid, liquid or gas. The solid phase consists of a chaotic structure of the original sugar structures and reaction products. The reaction products that remain solid are large modified sugar structures, newly formed polymeric structures with possibly a certain degree of aromatic rings, typical carbon-rich char structures and the ash fraction. The gas phase includes the gases that can be considered permanent gases. In general, these are compounds with a boiling point below –33 °C, but also light aromatic components such as benzene and toluene.

The condensables or liquids can be divided into three product groups. One group is reaction water as a product from the thermal decomposition (in addition to the freely bound water that has been released
from the biomass by evaporation). The organics sub-group consists of organics that are mainly produced during devolatilisation and carbonisation (see Figure 2). The lipids are a group of compounds that are present in the original biomass and are therefore not really reaction products. This sub-group contains compounds such as waxes and fatty acids. Although these components are mainly liquids, some can be solid at room temperature.

One way to compare the characteristics of torrefied biomass with biomass and other conventional fuels is by using the Van Krevelen diagram, as shown in Figure 4. It can be seen that the highest H/C and O/C ratios belong to wood and the lowest belong to coal. Torrefied wood lies in between and the higher the torrefaction temperature (and/or the residence time), the more the composition moves from wood to coal. The elemental composition of torrefied wood produced in the higher temperature region is close to that of peat.

![Van Krevelen diagram for torrefied wood (TW) produced under various conditions (torrefaction temperature indicated between brackets), untreated wood, coal, charcoal and peat.](image)

From Figure 4 it can be seen that, upon torrefaction, biomass loses relatively more oxygen and hydrogen than carbon. The main consequence of this is an increase of the calorific value. Depending on the torrefaction conditions, the net calorific value (LHV) is in the range from 18 to 23 MJ/kg (dry basis). For comparison, the LHV\textsubscript{dry} of untreated wood, coal and charcoal is typically 17-19 MJ/kg, 25-30 MJ/kg and 30 MJ/kg respectively.

Another favourable feature of torrefaction is that the solid product becomes hydrophobic. Biomass is completely dried during torrefaction and after torrefaction the uptake of moisture is very limited (typically 1-6% wt). The main explanation for this is that, by the destruction of many OH groups in the biomass through dehydration reactions, torrefied biomass has lost the capability to form hydrogen bonding with water. In addition, more unsaturated structures are formed which are non-polar. The low water content and the hydrophobic nature largely prevent the torrefied product from rotting.

3. ECN R&D programme

Although the principles of torrefaction are known, torrefaction of biomass for energy purposes has been applied only on demonstration scale and only for specific applications. Most attention was paid to its application in the metallurgic industry (mid. eighties) and to its application as a smokeless fuel in domestic uses (barbecue, cooking). Although this has led to a reasonable knowledge base and to the development of ‘demonstration’ technology, many aspects relevant to the application of torrefaction for upgrading biomass into biomass fuel for thermal conversion processes, such as co-firing in pf boilers, were not addressed. This includes:
− The scale of operation in relation to reactor technology and process layout. Given the required large throughputs (typically 50-100 ktoN/year), minimisation of the reactor residence time is an important objective. From literature, torrefaction is known to be a time demanding process (45-90 min), which inherently leads to high reactor costs and a limited scale of operation.

− The characterisation and quantification of product quality and how this relates to torrefaction process conditions. Especially the quantification of the grindability is an important, un-addressed topic, but also the combustion and gasification properties of torrefied biomass are not well known.

− The nature and quantity of possible emissions to air and water as a function of process conditions.

− The prospects of heat integration of process streams including the utilisation of the energy containing torrefaction gases.

− The economic viability of torrefaction as a biomass pre-treatment technique for bulk applications.

Therefore, it was decided at ECN to initiate an extensive R&D programme with the following main objectives:

− To determine the relation between product distribution, product quality and quantity, and important process parameters (e.g., temperature and residence time) through bench-scale parametric testing.

− To develop tools to characterise the solid and gaseous products.

− To characterise the combustion/gasification properties of torrefied biomass through lab-/bench-scale testing.

− To develop (optimised) reactor and process concepts and to perform detailed evaluations of the economic viability of torrefaction for various biomass (residue) streams and thermal conversion processes.

The parametric testing has been, and is being, performed in both a continuous, externally heated screw reactor and a bench-scale fixed-bed reactor, which is heated by a combination of trace heating and pre-heated nitrogen. The testing has resulted in a large data base on the torrefaction behaviour of a wide variety of biomass streams, including different types of fresh wood, demolition wood and straw, as a function of process conditions. Results of a typical torrefaction experiment are given in Figure 5, while an example of the liquid product yield is given in Figure 6. An important general finding is that the torrefaction residence time can be reduced substantially (down to 10 min.), while still achieving a good quality solid product. Furthermore, experiments with selected waste streams revealed the potential of torrefaction to improve the uniformity of the solid product and to reduce contaminant levels (e.g. chlorine and high-volatile heavy metals).

![Torrefaction Diagram](image)

Figure 5. Results of a typical torrefaction experiment.

To characterise the grindability of the solid product, a dedicated milling facility was set up, which allows the determination of the power consumption. In general, it appears for woody biomass, that the
overall milling characteristics are largely improved by the application of torrefaction. Milling experiments showed that the power consumption can be reduced by 50-85%, depending on the applied torrefaction conditions (see Figure 7). Basically, in terms of required power consumption torrefied biomass becomes similar to coal. Simultaneously, the capacity of the mill increases by a factor of 2 to 6.5. Furthermore, these improvements are observed independent of the type of woody biomass (willow, larch, or beech). The improvements were related to the destruction of the hemicellulose by which the cellulose fibres in biomass become much more easily detachable. Moreover, the depolymerisation of cellulose shortens the length of the fibres. The largest improvements were obtained within the higher torrefaction regime (see Figure 2).

Figure 6. Liquid (condensables) product yield in torrefaction of willow at different conditions.

Figure 7. Specific power consumption when milling biomass, dried biomass, torrefied biomass and coal. For torrefied biomass, the torrefaction temperature (230-270 °C) and the torrefaction time (32 min) are indicated between brackets.

4. Reactor and process design
In parallel with the experimental work aimed at building up a quantitative knowledge base on torrefaction and new quantitative methods to characterise product quality, ECN focused as well on
both reactor and process design. In general, given the bulk quantities that have to be processed, the torrefaction reactor should be rather simple and robust, and it should have a high throughput. Furthermore, particular attention should be paid to the heat input, with torrefaction being a slightly endothermic process. In the process design, proper treatment of the torrefaction off-gases and heat integration are main points of attention. However, actually a whole range of technical aspects has to be considered, as is shown schematically in Figure 8.

Taking into account this whole range of technical aspects has resulted in new reactor and process concepts, which are now ready for further evaluation and optimisation through pilot-scale testing. The reactor and process concepts are based on direct heating for the torrefaction step as being most energy efficient and leading to a more uniform product quality as opposed to indirect heating concepts. A basic process concept based on direct heating through a (hot) gas recycle is shown in Figure 9. The economic evaluation of torrefaction for different specific applications, based on these new reactor and process designs, has confirmed the large (economic) potential of this new pre-treatment technique.

Figure 8. Technical aspects to be considered for the proper design of a torrefaction production plant.
Finally, also work on the combination of torrefaction and densification (pelletisation) was started. Initial experimental work revealed that high quality pellets can be produced at similar cost than for conventional pellet production (although additional production costs are introduced by the torrefaction operations, considerable savings in the processing costs of size reduction, pelletisation and product storage are the result). The resulting pellets are of a higher quality in terms of calorific value, bulk density, energy density and hygroscopic nature (no water uptake, no swelling).

5. Conclusions and further development (pilot-scale testing)
In conclusion, torrefaction has a high potential as a biomass pre-treatment technique in the production of biomass fuels for bulk applications (e.g. power production and the production of syngas as a feedstock for the production of transportation fuels and chemicals). Important advantages of torrefaction are:

- The grindability of biomass is largely improved (becomes similar to coal), allowing direct (co-) firing in pulverised-fuel boilers and entrained-flow gasifiers up to high percentages.
- The energy density on a mass basis, and in combination with a densification process also on a volume basis, is largely improved, which reduces transport, handling and storage cost.
- The product has low moisture content and has become hydrophobic, which allows open air storage and largely prevents it from rotting.
- The product is more uniform and contaminant levels can be reduced (e.g., chlorine and high-volatile heavy metals).
- Torrefaction in combination with pelletisation leads to high-quality pellets at no or hardly any additional costs, which can be used for domestic and small-scale applications.
- In comparison with other densification techniques, such as charcoal production and pyrolysis, the energy yield is considerably higher. This is of particular importance in case of biomass import from areas, where an energy surplus cannot be readily applied.

Finally, torrefaction also has a potential as a unit operation in biorefinery concepts.

Economic evaluation of torrefaction for different specific applications has revealed a large economic potential of this new pre-treatment technique.

Pilot-scale testing is now foreseen as the next step in the RD&D trajectory.