



## **The potential of pyrolysis technology in climate change mitigation – influence of process design and –parameters, simulated in SuperPro Designer Software**

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# The potential of **Pyrolysis Technology** in climate change mitigation

- Influence of process design and –parameters, simulated in SuperPro Designer Software

Risø-R-Report

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Risø-R-1764 (EN)  
January 2011

Risø DTU  
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– influence of process design and –parameters, simulated in  
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Biosystems Division

**Abstract:**

This report investigates whether or not it would be possible to produce carbon-negative energy from pyrolysis of wheat straw in a series of Danish agricultural scenarios. A combination of process simulation in SuperPro Designer software, correlations derived from literature studies and experimental work, and overall balance calculations has been applied in the process.

The study deviates from other studies of pyrolysis and biochar production by the inclusion of substitution energy impact on the overall carbon-balance. Substitution energy is integrated to account for the gap between the energy production from the pyrolysis and the full energy potential of the biomass, quantified by complete conversion in either combustion or gasification systems.

It was concluded that it is feasible to produce carbon-negative energy under a variation of different settings, but also that the negative carbon-balance is only robust for the slow pyrolysis scenario.

The CO<sub>2</sub> benefit of the most carbon-negative slow pyrolysis process is estimated to be around 10 % of the atmospheric carbon stored in the original biomass when natural gas is applied for energy substitution. This process avoids the emission of around 150-200 kg CO<sub>2</sub>/ton wheat straw with substitution energy with a Denmark 2007 average carbon-intensity. This result is weighted against the net emissions of the carbon-“neutral” process of conventional combustion. This emission is in this report estimated to be around 50 – 150 kg CO<sub>2</sub>/ton straw depending on scenario settings.

The final results of the study have been compared to another study with convincing results. Results concluded that the primary force of the pyrolysis technology is the recalcitrant char product and not the pyrolysis oil. Based on this, the study suggests that despite the trend in commercial pyrolysis technology that focuses on fast pyrolysis processes with maximized bio-oil production, the twin challenge of climate mitigation and sustainable energy production is most efficiently addressed with a combination of slow pyrolysis and complete biomass conversion through combustion or gasification instead.

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# 1 Preface

This report is a joined effort between the two programmes Ecosystems and Biomass Gasification under the Biosystems divisions at Risø DTU.

First author of the report is research assistant Tobias Thomsen from Biomass Gasification Group. Project concept, development, execution and presentation have been carried out in close collaboration between Ecosystems and Biomass Gasification Group with participants: Henrik Hauggaard-Nielsen (senior scientist) and Esben W. Bruun (PhD candidate) from Ecosystems and Tobias Thomsen (research assistant) and Jesper Ahrenfeldt (Senior scientist) from Biomass Gasification Group. Senior scientists Ulrik Henriksen and Helge Egsgaard from Biomass Gasification Group have participated with validation of specific parameters and text passages.

## 2 Introduction

### 2.1 Climate change

The Intergovernmental Panel on Climate Change (IPCC) has established strong correlations between modern life and a subsequent risk of climate changes. Large scale combustion of fossil fuels, deforestation, and poor agricultural management contribute to an increased concentration of green house gases (GHGs) in the atmosphere. The increase has initiated an increase in the global average temperature (IPCC-WG1, 2007). A shift in global temperatures will cause a variety of changes on both natural and human environments, and will be devastating to many species and cultures (IPCC-WG2, 2007).

To meet this challenge, it is a widely used strategy to make energy consumption more efficient, and thereby reduce the net amount of GHGs released per quantity of products produced, kilometres driven, etc (IPCC-WG3, 2007). In this manoeuvre the carbon-balance is shifted from a given positive value closer to zero – a neutral carbon level. In most energy-production processes the carbon balance is positive, but some processes – like the combustion of biomass, are considered carbon neutral (Miljø&Energi\_Ministeriet, 2001). The difference between a carbon positive and a carbon neutral energy production is exemplified in Figure 2-I. The black arrow in scenario “A” indicates a net supply of carbon to the production – rendering the production carbon positive, which is compared to the closed carbon neutral production in “B” with no net carbon change. The positive net flux of carbon into scenario “A” will result in a build-up of carbon within the cycle. In modern business-as-usual settings this build up will take place in the atmosphere. For carbon-positive processes, there are profound differences in the level of positivity (the size of the black arrow in scenario “A”) depending on the fossil fuel, process efficiency, and many other aspects. As an example, Danish energy production from coal is more carbon positive than energy from oil, which yet again is more positive than energy from natural gas (Miljø&Energi\_Ministeriet, 2001).

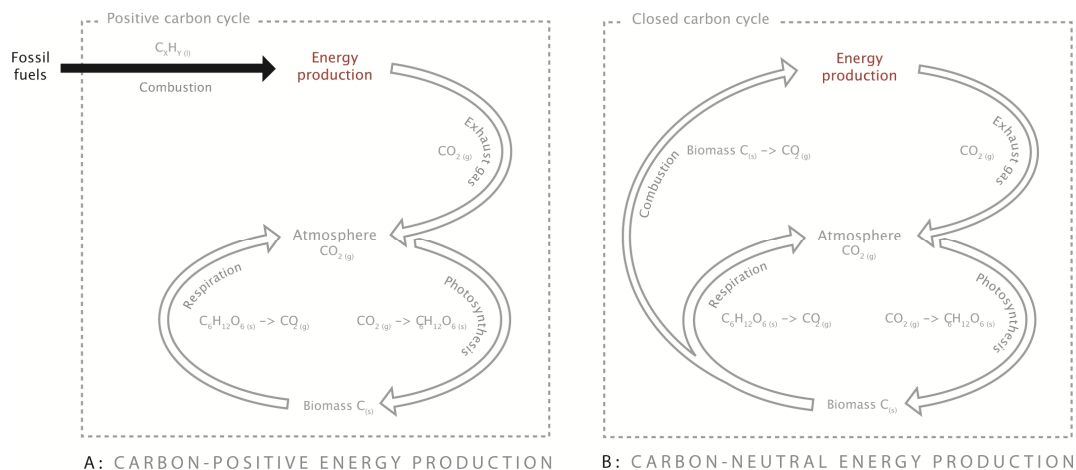


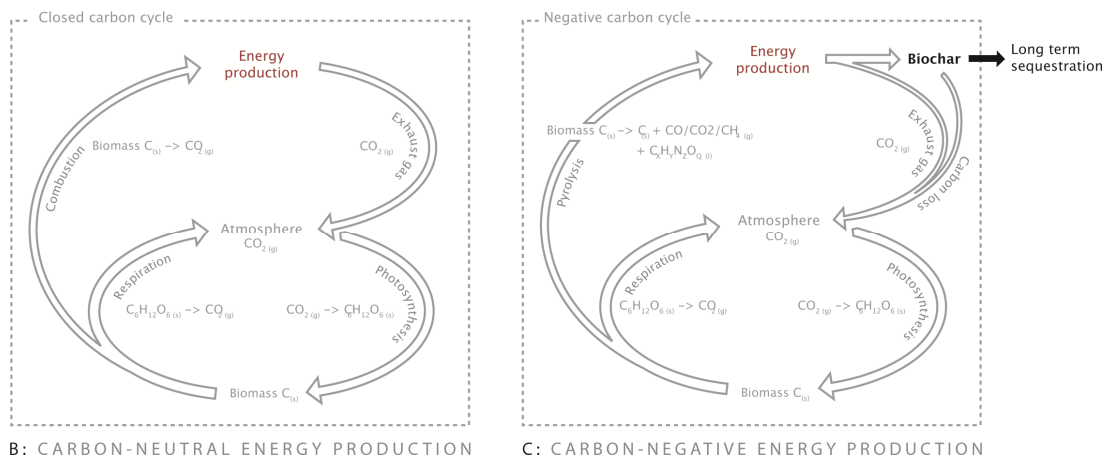
Figure 2-I: A schematic difference between a carbon positive (“A”) and a carbon neutral (“B”) process.

## 2.2 Carbon negative energy production

Increased efficiency in energy production and use can shift carbon-balances from positive towards neutral. However, efficiency alone will never shift the balance to negative, and can thus never on its own reduce the current GHG concentration in the atmosphere from the present level. This is important to be aware of when taking into account the un-ambitious approach to climate mitigation in the last decades that has already led to very high levels of GHGs in the atmosphere. The effort made to reduce the CO<sub>2</sub> level since the Kyoto treaty was signed in 1997 has proved too weak, and CO<sub>2</sub> concentrations continues to rise (IPCC-WG3, 2007). With a present CO<sub>2</sub> level around 387 parts per million (ppm) on a global yearly average (NOAA, 2009), climate changes are already happening globally, and the impact is causing increasing difficulties for people, plants, and animals day by day. More and more grass root movements and scientific organizations argue that CO<sub>2</sub> levels must be returned to around 350 ppm to avoid catastrophic consequences for areas in especially Africa and around Bangladesh (350.org, 2010). The result of the recently resolved COP15 climate summit – the Copenhagen Accord, was an agreement between world leaders to keep maximum temperature increases from GHGs on +2 °C on a global average. The CO<sub>2</sub> level agreed on in the Copenhagen Accord is thereby around twice as high as the 350 ppm, and the press coverage of the COP15 suggest that even this goal will be very difficult to meet with current levels of dedication. The Copenhagen Accord is a very light – and not legally binding, agreement. With the failure at COP15, new measures will be necessary to stabilize GHG concentrations before reaching the +2 tipping point – or ideally to reduce the concentrations to the 350 pmm level (Decision-/CP.15, 2009; Greenpeace, 2009; Holst, 2009).

These conditions lead to a requirement for the last category of energy production processes – the carbon negative process. This type of process requires that carbon is removed from the atmosphere as energy is produced. There are currently two very different approaches to meet this requirement. The first method is a validated carbon negative energy production method from pyrolysis of biomass and the concomitant production and use of biochar (Lehmann, 2006; Mathews, 2007). In this process biomass is turned into biochar – a carbon rich char similar to coke or charcoal, with bio-oil or combustible gases as energy output. Amending the char in farm soil will sequester the carbon for a very long time, as well as replenish the contents of nutrients and carbon in the soil (Swift, 2001; Zwieten, et al., 2009). Every year around  $1.05 \cdot 10^{14}$  kg of atmospheric carbon (ca 1/8 of total) is absorbed in the combined biosphere (terrestrial and oceanic), suggesting great potential for significant sequestration (Field, et al., 1998).

In Figure 2-II the impact of biochar carbon sequestration on the overall carbon cycle is illustrated. Scenario “B” is a carbon neutral energy production with a completely closed carbon cycle. This neutrality is shifted towards negative in scenario “C”, where carbon is removed from the cycle in the form of biochar and sequestered on a long term basis. Running the “C” cycle repeatedly will slowly drain carbon from the atmosphere, and thus lower the CO<sub>2</sub> concentration, as energy is produced.



*Figure 2-II: Schematics of a carbon-neutral energy production “B” and a carbon-negative energy production “C”*

An alternative proposal for carbon-negative energy production is the full combustion of biomass with CCS technology (Carbon Capture and Storage) (IPCC\_WG3, 2009). However the CCS technology is expensive and still in its infancy (Holm, 2009).

### 2.3 Main research question, scope and structure of the report

Based on the rising demands for truly carbon-negative energy production technologies, and the apparent qualities of pyrolysis of biomass and biochar sequestration in this regard, – the aim of this report is to answer the following question:

*Is pyrolysis of biomass with subsequent biochar sequestration in a Danish agricultural scenario, a truly carbon-negative bio-energy technology?*

The approach to this question will be to set up guidelines for the carbon-balance of pyrolysis concepts, and propose a process to yield a carbon-negative energy production in a given scenario or set of scenarios. Using the simplified representation of a pyrolysis bio- energy infrastructure in Figure 2-III, the present study is to develop a set of tools to solve an inequality like the following:

$$A\% + B\% + D\% + E\% + F\% + G\% + I\% < 100\%$$

In this equation, the variables are all based on the carbon-fluxes in Figure 2-III, indicated by black or red arrows. This version of the inequality might prove to be insufficient compared to the final assessment on which factors to include, but it will work as a guide in the process.



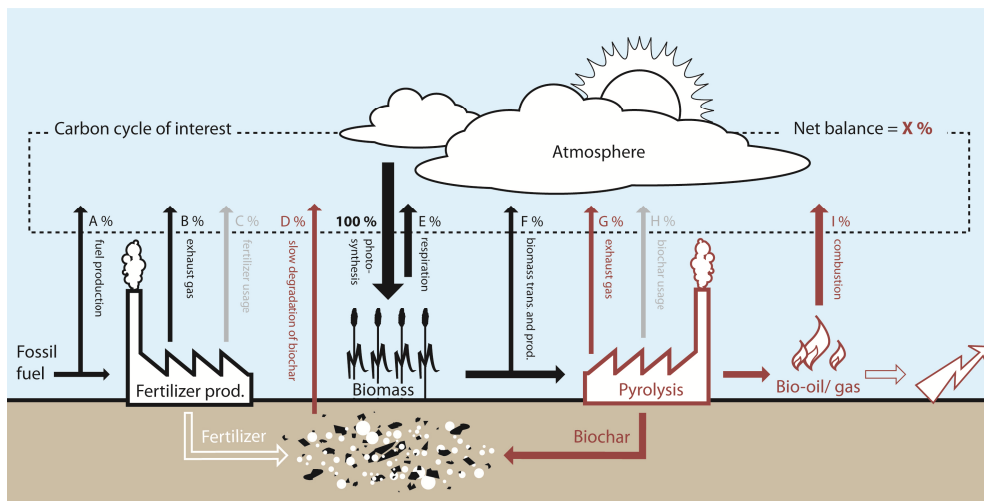


Figure 2-III: Variables included in carbon balance calculations. Red arrows are thoroughly investigated, black arrows are researched through literature survey, and grey arrows are possibly omitted from this work.

The colour indications in Figure 2-III describe the level of work subjected to the specific flux variable in this work. The variables indicated by red arrows are subjected to the most thorough investigation through either simulation- or laboratory studies. The black variables are investigated through a literature survey, and the grey variables are probably omitted in the process to limit the work. The grey variables are assumed to have only insignificant impact on the overall carbon balance. To investigate the different variables three main steps are carried out:

- The process design and parameters – red arrows around the pyrolysis plant and combustion operation (G, I). In this step the industrial process of biochar production from pyrolysis of biomass is investigated. To establish a flexible platform for later process evaluation, the pyrolysis process is modelled using the process design software SuperPro Designer 7.5 (Intelligen, 2009).
- Char stability – red arrow from biochar (D). To evaluate the model output, it is important to establish some knowledge about the stability of different kinds of biochar in the soil, and thereby the influences of the process design on the sequestration potential. This is done through a small scale incubation study experiment of biochar/soil mixtures with biochar produced under different conditions.
- Overall balance – literature review and data collection (A, B, E and F). In this final step, the different model inputs and outputs are to be collected and used in combination with knowledge about the impact of the variables as well as fertilizer utilization, etc. A set of scenarios in Danish agriculture present the limits of the analysis, and the output of the overall investigation is a suggestion to a specific bio-energy production process designed to secure a carbon-negative energy production within the given scenario.

## 3 Biochar processes - the carbon balance

### 3.1 Biochar – public and political integration and acknowledgement

Biochar is no new investigation; it is basically charcoal with a new label and purpose. Production of traditional charcoal has been known to the human race for thousands of years, and the first production may date as far back as 7000 years (Emrich, 1985). Use of charcoal as soil amendment for fertilising purposes is thought to be just as old, as evidenced by the terra preta in the Amazonas (Lehmann, 2006). In modern times, this utilization has been systematically researched for a relatively long period - more than 150 years (Trimble, 1851). However, the use of charred biomass as a mean for carbon sequestration and mitigation of climate change is new – no more than 10 years (Sombroek, et al., 2003). The word biochar is even younger and appears for the first time in the article “Bio-char Sequestration in Terrestrial Ecosystems – a Review” from 2006 (Lehmann, et al., 2006). The term Biochar was introduced as the appropriate term to use, where charred organic matter is applied to soil with the intent to improve the soil’s properties (Lehmann, et al., 2009).

Today, the number of biochar initiatives is growing at high speed. The International Biochar Initiative (IBI, 2006), TERRA – The Earth Renewal and Restoration Alliance (TERRA, 2009), the CarbonZero Project (CarbonZero, 2009), Biochar Carbon Sequestration (BCS, 2006) and The Biochar Fund (BiocharFund, 2008) are just a few of the many organizations, who use their time and effort to support and promote the use of biochar. Commercial initiatives are also growing in numbers, and “old” companies like Dynamotive (Dynamotive, 1991), EPRIDA (EPRIDA, 2002) and BEST Energies, Inc (BEST, 2006) are no longer alone on the market (Miles, 2007).

Biochar production is also gaining acknowledgement on the political scene as a tool for climate mitigation and soil enhancement on a global scale. Pyrolysis processes for the production of biochar is on the list of technologies being scoped for the 5<sup>th</sup> assessment report of the IPCC in the investigation of the limited possibilities for low GHG level stabilization scenarios (IPCC\_WG3, 2009), and biochar has been mentioned repeatedly in the UN as a tool to combat desertification and climate change. In the preparation for the COP15 in Copenhagen in December 2009 (AWG-LCA\_4, 2008; UNCCD, 2009), many individual countries have submitted reports to the UNFCCC containing references to the use and benefits of biochar (IBI, 2009). Biochar - and pyrolysis of biomass in general, is growing in both awareness and acknowledgement, as new research is conducted and new technology progresses. There are, however, still many unanswered questions, giving fuel to critics and self-proclaimed prophets, who taint the discussions and debates with exaggerations, extreme scenarios (both pro and con), and silver-bullet fixes. Doubts about the benefits of the technology are present on all levels, and critics target the overall concept, as well as specific characterizations or scientific results. See for example the critical debate from the Guardian on a pop article on biochar by James Lovelock (Lovelock, 2009), a commentary doubting the negativity of the carbon-balance (Bruun, et al., 2008), the highly critical briefing “Biochar for climate change Mitigation: Fact or Fiction?” from the organisation Biofuel Watch (Ernsting, et al., 2009) or an article about acceleration of humus carbon mineralization by biochar (Wardle, et al., 2008).

### 3.2 Biochar and carbon-negativity

In regard to climate change mitigation, the main effect from application of biochar is the carbon-negativity of the production process. In this process, the energy output reduces GHG emissions by fossil fuel displacement, and is in itself an example of carbon-neutral energy production. The long term sequestration of carbon in soil renders the overall-process carbon-negative. Any additional effects of biochar amendment – e.g. reduction of soil emissions of CH<sub>4</sub> and N<sub>2</sub>O or increased crop production and thereby carbon capture through photosynthesis, will not be addressed quantitatively in this report, but is regarded as a significant plus in the struggle for reducing GHG emissions (Renner, 2007; Zwieter, et al., 2009).

The overall carbon-balance of an energy production based on biomass depends on many parameters. These parameters can push the process towards, or away from, carbon-negativity. Box 3-I illustrates an example of two bio-energy production processes, which have the primary difference of biochar sequestration in the second. In both scenarios, the energy production is based on conversion of biomass grown with fertilizer, which requires the use of fossil fuels to produce. The values represent carbon fluxes in relation to the main value: the flux of carbon from the atmosphere to the biomass through photosynthesis. The values are generally feasible values used for illustrative purposes, and based on a simplified model by (Lehmann, 2007).

Box 3-I: Shift in the carbon-balance in the production of bio-energy

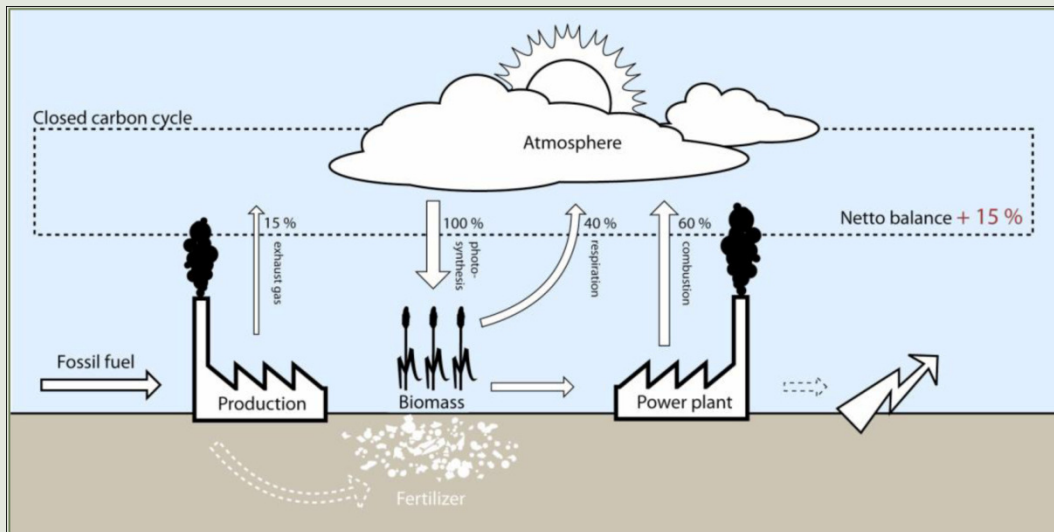


Figure 3-I: Illustration of a “carbon-neutral” bio-energy production process

**Carbon-“neutral” bio-energy:** In Figure 3-I biomass is produced through the photosynthetic capture of atmospheric carbon (CO<sub>2</sub>) fuelled by soil, water, and fertilizers made from fossil fuels. The biomass is burned or gasified completely to produce electricity, (heat), and ash. This process is labelled carbon-neutral despite the fact that fertilizer comes from a carbon-intensive production process. Fertilizer nitrogen (N), for instance, is the largest single crop nutrition input, with an estimated energetic efficiency of about 50 MJ kg<sup>-1</sup> N for urea production in the most efficient plants operating, equivalent to about 1.4 kg CO<sub>2</sub> kg<sup>-k</sup> urea N manufactured (Boddey, et al., 2009). In Denmark the average fertilizer N application was 83

kg N ha<sup>-1</sup> in the 2007-2008 season distributed on a cultivated area of about 2.6 million hectares (Statistikbanken, 2010\_A; Statistikbanken, 2010\_B). This sums up to more than 3·10<sup>5</sup> tonnes CO<sub>2</sub> for N application alone, and shifts the balance to carbon-positive. Only with organic production of the biomass, no wear and tear on process equipment and no use of external utilities (for unit operations, transport etc.) would the process be truly carbon-neutral. This would, however, pose the long term problem of nutrient depletion (Cassman, 1999).

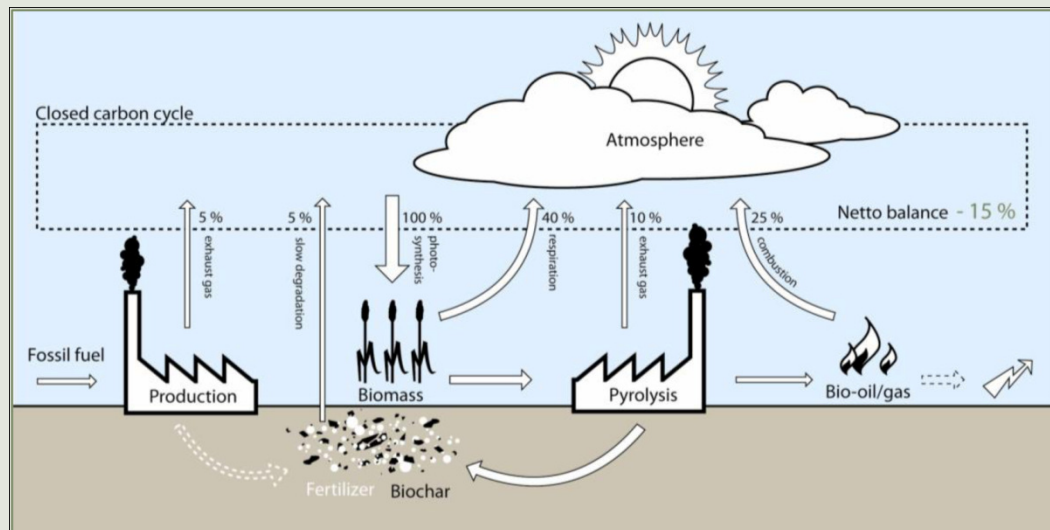


Figure 3-II: Illustration of a carbon-negative bio-energy production process

**Carbon-negative bio-energy:** In this scenario biomass is produced in almost the same manner as in the previous, but with less fertilizer and with the addition of biochar instead. Studies have shown that biochar can enhance soil quality both chemically and physically. It does so for instance by sorbing nutrients from fertilizer and thus securing them from being washed away (Lehmann, et al., 2006; Sohi, et al., 2009). These studies have been done mainly on sandy tropical soils, but for the purpose of this example, they are assumed valid for temperate soils also. The biochar is made during the energy production process via pyrolysis of biomass. When returning the char to the soil, nutrients are somewhat recycled, carbon-pools in the soil are replenished (by a small, labile fraction of the amendment), and carbon from the atmosphere is sequestered on the long term. This has the potential to render the overall energy-production carbon-negative.

As indicated by the shifting electricity symbol in Box 3-I, the pyrolysis process produces less electricity and heat than the full combustion process, but maintains or even rebuilds soil fertility and structure. It also mitigates climate change in the energy producing process by sequestering atmospheric carbon, where combustion of biomass is normally slightly carbon-positive (conventional farming) or soil degrading (organic farming). This draws up an important difference: full combustion of biomass yield the highest amount of immediate energy, but has increased costs on the long term (reducing soil quality and depleting the carbon storage), where energy production

including biochar use gives a smaller immediate energy yield, but addresses the problems of soil fertility and long term crop productivity in the same process.

Whether the carbon-balance of the processes in Box 3-I example should tip to one side or the other is controlled by the overall mass- and energy-balances of the specific process, which is again heavily influenced by such parameters as transportation, utility consumption, process-efficiency, etc. Specific process design features and -parameters have high impact on process yields of bio-oil, char, gas, heat, electricity etc (Brown, 2009; Hornung, 2008; Sohi, et al., 2009). However, changing parameters from one value to another will not always shift the carbon balance sufficiently. The first process in Box 3-I could never become carbon-negative from slight adjustments, but could shift from carbon-positive to almost neutral, as efficiency of the process increases, and less and less carbon is injected into the cycle. However, the second process can shift all the way from negative to positive; this could happen if a process variation reduced the char yield increasing energy output, and a technological deficiency added an increase in the consumption of utilities and transportation.

### **3.3 Biochar energy system calculations**

#### **System boundary considerations – in space and time**

Energy system boundaries are important to specify in both space and time. Fluctuations in the need for heat and power with geography and seasonal changes play an immense part in the assessments of energy systems on many levels. Also, stability of biochar – or biomass, is very dependent on the time-span in which it is assessed.

One could claim that coal-power is carbon neutral as long as the time-span is wide enough, or that nothing is carbon-neutral if the time-span is short enough. The influences of space-oriented system boundaries can play similar grotesque roles on carbon- and energy-balances. In a very small system containing only a family and a cooking fire – the heat and light from the fire could be carbon negative if some char remains after cooking, and it remains there beyond the time-oriented system boundaries - or even if all wood is burned, but it was collected beyond the system boundaries. In another system a coal-fired plant within the boundaries can influence the entire system, rendering the overall energy production carbon-positive despite any biochar-initiative.

It is decided to address only some of the influence of space-oriented system boundaries in this report. The system confines of Denmark and the nation's energy consumption, and influence from beyond these boundaries is integrated only to the extent of the GHG-cost of procuring energy carriers like coal, oil or natural gas, and transporting it into the system.

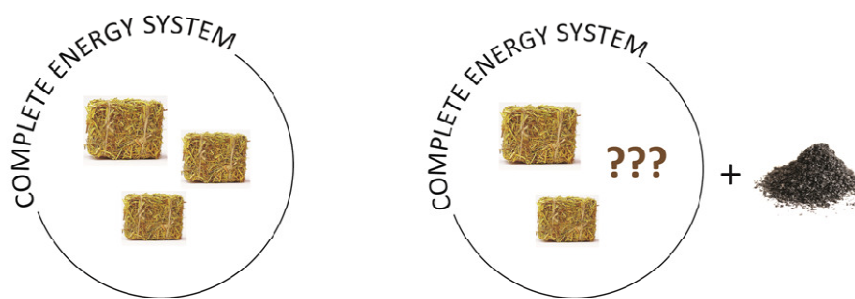
The complexity of integrating the effect of time-spans on the carbon- and energy-balances of biochar energy systems in Denmark is too big a task for this report, and it is decided to skip seasonal fluctuations in electricity and heat requirements. This is done roughly with the following assumptions:

- Heat is always equally needed, and electricity is therefore always produced with simultaneous heat production for district heating. In this way the report gives an evaluation as under stable winter conditions, without addressing the differences in summer >< winter consumption. This assumption is briefly regarded in the final chapters, conclusion and recommendations on further work.

### Methodical influential factors on carbon-negativity calculations

Biochar-focused energy production has a drawback, which is important to address before examining the impact of other variations on the process carbon balance. The char that is removed represents energy, as the char could have been fully gasified instead of incorporated in soil. This is illustrated in Figure 3-III. Calculations on energy balances that do not acknowledge this prerequisite will yield much better results than calculation systems that do. Calculation systems that operate with unlimited biomass resources will add new biomass to existing energy systems and the suppressing of fossil fuels from the energy production itself as well as the carbon benefit from burying biochar will then both add to the overall benefit. Operating with unlimited biomass resources undermines the scalability of the calculations.

In this report it is the origin of the calculations that biochar energy systems are introduced in an energy system that already utilizes the optimal biomass energy potential. In this case the introduction of biochar energy systems will always lead to an energy deficit compared to the reference. Therefore substitution energy systems are needed to balance the energy production of the biochar system to the reference system.



*Figure 3-III: A special calculation prerequisite to acknowledge in biochar energy systems is the removal of energy potential from the reference in the shape of biochar.*

Simply put, one could imagine an existing energy system – like an isolated country. In many biochar assessments the investigation method would introduce new biomass – e.g. bales of straw, in the isolated system along with the biochar technology. This will give both energy and negative carbon balances, but it is only useful as long as new biomass resources can be added. In this report the biochar technology is introduced without adding new biomass to the system, but instead converting some of the already existing bales of straw in pyrolysis instead of the conventional way – incineration. This will sequester carbon, but yield less energy from conversion of biomass within the system. Therefore substitution energy is required.

The energy production method used to replace the biochar energy potential is essential for the carbon balance. Key characteristics and assumptions regarding various possibilities within the Danish energy sector are given in Table 3-I. Carbon costs calculations are based on Danish infrastructure and can be investigated further in a report from 2001 by the Danish Ministry of the Environment and Energy department (Miljø&Energi\_Ministeriet, 2001). The table shows the carbon-cost of combined energy production (electricity and district heating) from various energy sources. Electricity is the main parameter in the energy-balance assessments, but in the present calculations heat is also included as useful energy, as district heating grids in Denmark are widespread.

Table 3-I: Carbon cost of various energy production methods in Denmark (Miljø&Energi\_Ministeriet, 2001).

Source	Kg CO <sub>2</sub> GJ <sup>-1</sup>	Comments
Coal	106	Retrieving, transporting and processing coal for energy production requires large end-emissions of GHGs. Adding this to the combustion emissions, and emissions from the biochar production would render the total process very carbon-positive. The use of biochar will still have other advantages, but in relation to the carbon-balance the process would be pointless.
Oil	81	Energy production from oil combustion is still less carbon intensive than energy production from coal combustion. This may, however, change as oil reservoirs are depleting faster than coal reservoirs.
Natural gas	60	In Denmark natural gas is a good alternative to coal for energy production, and replacing the energy stored as biochar with natural gas combustion may yield a favourable carbon balance in some situations.
Wind power	0	Assumed carbon-neutral. Accounts for ca 20% of Danish electricity production, and is assumed to increase further (DKvind, 2008)
DK 2007 - average	70	A combination of all the used energy-sources and the associated emissions of GHG's similar to the situation in Denmark in 2007. Calculated from (IEA, 2009; IEA, 2007)

### Specific influential factors on carbon-negativity calculations

In addition to the large-scale influence of the replacement energy source, another parameter –, namely the stability of the char in the soil is also very important when addressing the carbon-balance. The char is expected to be substantially more recalcitrant than the feedstock. However, it is a fact that the char will not last forever, and that it will degrade eventually. How fast this degradation happens is very important to the carbon-balance, and therefore degradation patterns of different kinds of biochar are investigated later on in experimental setups.

Process design and parameters are already mentioned earlier as highly important to the overall balances. Among the most important parameters are whether the process is fast, slow or intermediate, the feedstock- and gas retention times, the heating rate and the maximum temperature (Brown, 2009; Hornung, 2008; Sohi, et al., 2009). However, also the overall efficiency of the plant, the integration of heat exchangers, the use of process utilities, the production of the biomass and finally any transportation and storage-requirements are influential on the total carbon-balance. These factors are taken into consideration throughout the report.

## 4 Biochar processes – chemistry and technology

### 4.1 Short on biochar – characteristics, production, and use

To be able to understand how the production and use of biochar could aid in the struggle for climate change mitigation, it is essential to establish some fundamentals about biochar characteristics, use, effects, and production methods.

#### Biochar - characteristics

Biochar is a carbon-rich solid material similar to charcoal. However, where charcoal is produced (or collected) for use in e.g. cooking, heating, colouring, or filtration operations, biochar is produced with the purpose of amending it to the soil for soil quality-enhancement, soil-layer replenishing or long-term carbon sequestration (Lehmann, et al., 2009).

Biochar contains a very large organic fraction, consisting primarily of carbon in aromatic compounds where six C-atoms are sharing electrons in a ring-shape, and several rings are linked and/or stacked. If this fraction is perfectly ordered and the ring-layers stacked systematically on top of each other, the substance is called graphite. However, the organic fractions of biochar are polymorph (not ordered as graphite) and contain H- and O-molecules in addition to the carbon, as well as different minerals depending on the feedstock (Lehmann, et al., 2009). Average carbon-content from 14 different feedstocks has been found to be 543 g C · kg biochar<sup>-1</sup> (Chan, et al., 2009).

One of the most important physical characteristics for biochar is the surface area of the particles. Biochar surface areas vary a lot with production process and parameters as well as feedstock, and can range from 1 m<sup>2</sup>/g to at least 750 m<sup>2</sup>/g (Downie, et al., 2009). Other characteristics of biochar, which influence its use and effects on soil quality include porosity (nano- and macro-), density, particle size, stability, mineral content, residual oils and tars, and surface chemistry and sorption properties (Amonette, et al., 2009; Downie, et al., 2009).

#### Biochar – use and effects

Biochar is produced from biomass, and is therefore build largely from atmospheric CO<sub>2</sub> with the aid of photosynthesis and solar energy. When biochar is returned to the soil, it sequesters carbon from the atmosphere on a long term basis, and thus creates a carbon sink. The stability of the char when incorporated in soil depends on many factors such as production process, feedstock, soil, amendment process, climatic conditions, etc. The turnover time of biochar in soil is generally suggested to be in the scale of hundreds or even thousands of years - compared to a turnover time of ordinary added organic matter (AOM) – like untreated straw or other agricultural residues, of typically 6-20 years (Masiello, et al., 1998; Swift, 2001; Torn, et al., 2005). Stability is a key feature of biochar in relation to the process carbon-balance, and to the scope of this report, and it will be investigated in chapter 6 in a series of incubation studies.

Biochar is also expected to have several positive effects on soil fertility. Like active charcoal, biochar has the ability to adsorb various ions and compounds. This could prevent valuable nutrients from being washed from soil layers into the ground water, as well as it could help to reduce emissions of CH<sub>4</sub> and N<sub>2</sub>O from the soil (Zwieten, et al., 2009). Furthermore, water holding capacity and soil structure and architecture has

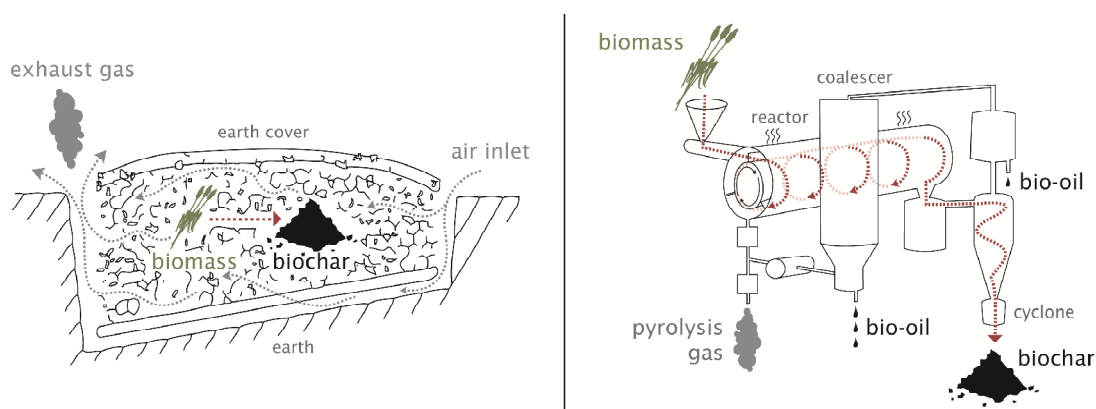


been known to be positively influenced by biochar on sandy soils (Laird, et al., 2009; Lehmann, et al., 2009; Thies, et al., 2009).

### Biochar – Production

Biochar is formed when biomass is heated under moderate temperatures (400-700 °C) with insufficient oxygen for full combustion. The technical term for this thermal decomposition of organic matter is pyrolysis, and the process can take on many shapes depending on the desired products. These products can be combustible, non-condensable gases, or bio-oil in addition to the biochar (Lehmann, et al., 2009).

Generally pyrolysis processes are divided into fast-, intermediate- and slow pyrolysis (Hornung, 2009\_A). These overall designs will be described and discussed in more detail in the next chapter. To show the span in pyrolysis techniques in use today, two extremes are presented below Figure 4-I:



*Figure 4-I: To the left: A large traditional pit kiln operated as a slow batch process (Brown, 2009). To the right a lab scale flash PCR (Pyrolysis Centrifuge Reactor) operated as a fast continuous process (Bech, 2008).*

The large pit kiln in Figure 4-I is a traditional, low tech, method for producing charcoal, which has been used for thousands of years. The pit kiln can vary from about 1 m<sup>3</sup> in volume to more than 30 m<sup>3</sup>. The kiln is dug out in the ground, filled with biomass, covered, and lit with a small fire. Controlling the air inlet is crucial, as too much air will lead to full combustion of the biomass, and insufficient air will kill the heat source prematurely. The product of the kiln pyrolysis is char, at a yield around 12.5-30 wt%, and the process can take as much as 2-3 days (Brown, 2009).

The PCR is a highly advanced pyrolysis process that produces oil-, gas-, and char-fractions. The gas is combusted in the heating process, while the bio-oil the char is collected. The pyrolysis reaction takes place at the inner surface of the heated reactor at temperatures around 480-620 °C, where small particles are twirled onto by high-speed centrifugal powers. Estimations on large scale versions of the unit predict a capacity of around 330 kg · m<sup>-1</sup> · hour<sup>-1</sup> (Bech, 2008).

## 4.2 Process design, feedstock and products

In pyrolysis processes there is a strong relation between the design of the process, the feedstock, and the process output products (Brown, 2009). This is investigated in the following sections.

### Biomass – biochar feedstock and main reactions

Pyrolysis is an extremely robust chemical operation, capable of converting a long range of different materials. It has been proposed several times as a way of addressing various waste problems – e.g. management of animal or crop wastes, sewage sludge, paper mill waste, old tyres or mixed plastic waste (Demirbas, 2002; Jung, 2009; Seung-Soo, et al., 2009; Shinogia, et al., 2003). The process is also readily applied to other feedstock sources like e.g. coal, rape seed or algae (Miao, et al., 2004; Morris, 1990; Onay, et al., 2003). For additional feedstock examples see (Yaman, 2004).

In this report, focus is on wheat straw as feedstock for bio-energy production. A lignocellulosic feedstock like straw, is mainly composed of the three polymers: cellulose, hemicelluloses, and lignin, with small fractions of water, organic extractives, and inorganic materials (ash) (Brown, 2009). Biomass of this composition includes various forms of agricultural residues, energy crops, wood residues and paper waste. Examples of the variations in composition with biomass type are shown in Table 4-I.

Table 4-I: Examples on the content of biomass (dry basis) (Brown, 2009). \* (Brown, 2003)

Feedstock	Cellulose (wt%)	Hemicelluloses (wt%)	Lignin (wt%)	Extractives (wt%)	Ash (wt%)
Willow	43	21	26	-	1
Switchgrass	32	25	18	17	6
Miscanthus	38	24	25	5	2
Maize stover	39	19	15	-	4.6
Wheat straw*	38	36	16	-	10

### Cellulose

Cellulose is normally the most abundant of the three major fractions of lignocellulosic biomass materials (Brown, et al., 2001). Cellulose is composed of repeating units of cellobiose, each unit consisting of two anhydroglucose units, and made from linear condensation of  $\beta$ -(1-4)-D-glycopyranose sugars. A cellobiose unit is shown in Figure 4-II.

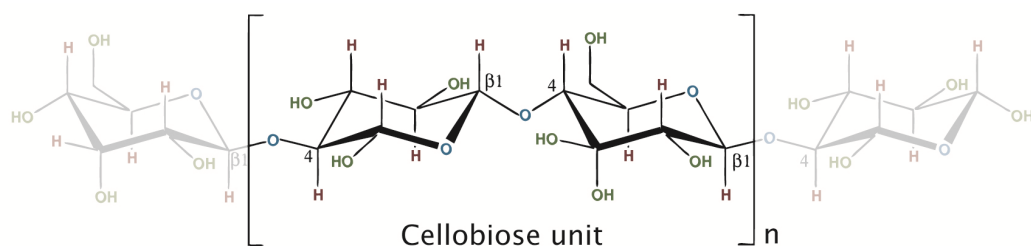


Figure 4-II: The repeating unit in cellulose – the cellobiose constituent (Mohan, et al., 2006)

Cellulose structure is crystalline, consisting of long linear chains coupled by hydrogen bonds and van der Waal's forces. The number of glucose units in each cellulose chain is known as the Degree of Polymerization (the DP). The DP of cellulose is around 10,000 on average (Brown, 2009). During pyrolysis the cellulose fraction decomposes, and the DP decrease continuously. Finally when DP reaches values less than around 8, the fractions become volatile and evaporate from the solid mass (Overend, 2004). Cellulose degradation occur around 240-350 °C to produce anhydrocelluloses and levoglucosan in two parallel reaction pathways. The complex decomposition pattern of cellulose involves both endothermic and exothermic reactions, and the final products would normally involve biochar, CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub>, other volatiles, and a range of condensable gases and/or tar (Brown, 2009).

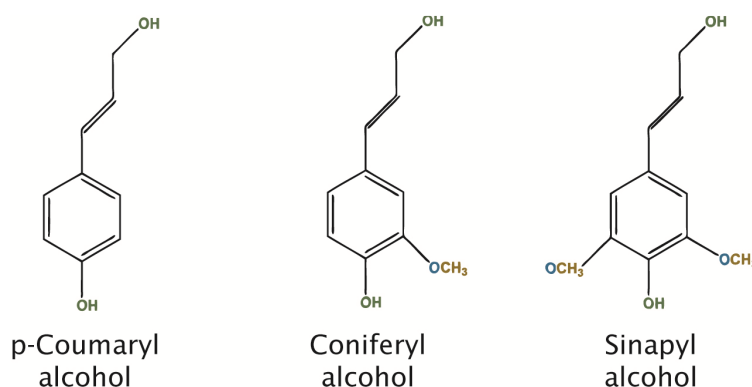
### *Hemicelluloses*

Hemicelluloses is a much less uniform polymer than cellulose. Where cellulose is build from glucose molecules alone, hemicelluloses is build from a large variety of hexoses, pentoses and deoxyhexoses. Also the structure is different, and the chains in hemicelluloses are branched with small side-chains along the main. The branching and variations in composition give a less crystalline structure in hemicelluloses than in cellulose and much smaller polymers – DP only around 150 (Mohan, et al., 2006). The consequence of the more amorphous structure is lower chemical and thermal stability, causing hemicelluloses to decompose at lower temperatures than cellulose - around 200 - 260 °C.

The decomposition of hemicelluloses yields more volatiles, less tars, and less chars than decomposition of cellulose. Pyrolysis products of hemicelluloses include a range of non-condensable gases (CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>, etc.), some low molecular weight organic compounds (e.g. aldehydes and alkanes) and water (Rutherford, et al., 2004).

### *Lignin*

The last of the three major fractions is lignin. Lignin is the largest non-carbohydrate fraction of lignocellulosic material, and differs in many ways from both cellulose and hemicelluloses. Lignin is constructed from three different alcohols, all containing an aromatic ring (Brown, 2009). The three constituents are depicted in Figure 4-III.



*Figure 4-III: The constituents of lignin (Mohan, et al., 2006).*

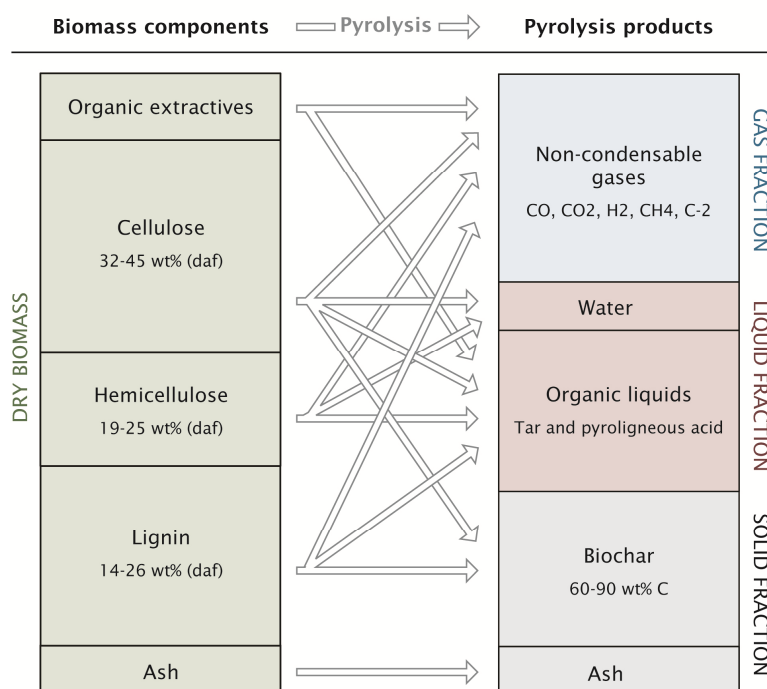
Lignin has a highly amorphous structure, and the individual units can link in many different ways. This cross-linked resin serves as a binder in the lignocellulosic material, holding fibrous cellulosic components together and at the same time

providing a shielding effect against microbes and fungus (Mohan, et al., 2006). In lignin biosynthesis, the constituent units undergo radical dimerization and oligomerization, before they polymerize and cross-link. Ether bonds dominate in lignin material, but also carbon-carbon linkages exist. Unlike cellulose and hemicelluloses, lignin cannot be depolymerized back to its original monomers (Brown, 2009; Mohan, et al., 2006).

The differences in lignin compositions and structure from one biomass to another, and changes in the material occurring from the applied extraction manoeuvres, make it difficult to describe the thermal decomposition of lignin in biomass from studies of extracted lignin (Mohan, et al., 2006). However, investigations suggest that decomposition occurs around 280-500 °C (Rutherford, et al., 2004). The pyrolysis of lignin is more exothermal than pyrolysis of cellulose and hemicelluloses, and yield more char than the other fractions, together with around 10 % (weight of original material) non-condensable gases – CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>4</sub>, a liquid fraction consisting of insoluble tar (~15%) and pyroligneous acid (~20%). The pyroligneous acid typically consists of methanol, acetic acid, acetone, and water, while the tar fraction is mostly homologous phenolic compounds (Brown, 2009; Mohan, et al., 2006). The methoxy substituents on the majority of the phenylpropane monomer units in lignin lead to a relatively large production of methanol. For a long time, wood pyrolysis has been a major source of acetic acid, acetone, and methanol. For the same reason, methanol is still known as wood alcohol (Overend, 2004).

#### *Biomass components and degradation patterns for modelling purposes*

Figure 4-IV shows a schematic pattern of biomass decomposition via pyrolysis. The qualitative pattern forms the basis for modelling the thermal degradation of wheat straw in chapter 5.



*Figure 4-IV: Generalized decomposition pattern of biomass from thermal decomposition in pyrolysis. Model adapted from Brownsort (2009) with additional reference to Brown (2009).*

To limit the complexity of the model work in the next section of the report, the fraction of wheat straw known as Organic Extractives are neglected (wheat straw values ~0 – see Table 4-I) and the inorganic content of the biomass has been grouped and labelled ash. To further simplify the model, variations in hemi-cellulose and lignin are neglected, and only the overall content of the main constituents are assumed to influence the quality and quantity of the pyrolysis products.

### Pyrolysis process design

Depending on design and operating conditions, pyrolysis processes can be divided into several sub categories from slow pyrolysis over intermediate- and fast pyrolysis to a full gasification Table 4-II. The general bio-oil, bio-char, and process gas product distribution estimation from Table 4-II is useful when trying to establish an initial understanding of the size of the different product fractions in relations to overall process design. Descriptions of the different process categories are given below, together with more thorough investigations on products quantities.

*Table 4-II: Distribution of mass percentage on products of various pyrolysis processes (Bridgwater, 2007\_A)*

	Liquid (bio-oil)	Solid (biochar)	Gas (process gas)
<b>FAST PYROLYSIS</b> Moderate temperature (> 500 °C) Short vapour residence time (<2s)	75% (25% water)	12%	13%
<b>INTERMEDIATE PYROLYSIS</b> Low-moderate temperature (< 500 °C) Moderate hot vapour residence time	50% (50% water)	25%	25%
<b>SLOW PYROLYSIS (&lt; 500 °C)</b> Low-moderate temperature, Long residence time	30% (70% water)	35%	35%
<b>GASIFICATION</b> high temperature (>800 °C) Long vapour residence time	5% (5% water)	10%	85%

### Main parameters

The most influential design-specific parameters on the pyrolysis process are peak temperature and residence time (Sohi, et al., 2009). However, process parameters like heating rate, gas retention/sweep gas scenarios, feeding rate and pressure, as well as feedstock/pre-treatment parameters (e.g. particle size and water content) can also have significant additional influence on the process (Antal, et al., 2003; Overend, 2004).

### Slow pyrolysis

Traditional slow pyrolysis by batch in kilns of various sorts is an example of the pyrolysis wave phenomena in massive biomass. The process progresses through solid biomass like a wave from a central initiation point. The starting point is normally the burning of a small amount of the wood charge which then provides the initial heat to start the wave reaction. In these kilns, good isolation is a key parameter for minimizing the amount of air needed to support the ongoing reaction. The global average charcoal yield from this kind of operation is around 30 wt%, ranging from less than 25 wt% in primitive African pit and Mound kilns to more than 45 wt% in South American industrial kilns (Overend, 2004). Traditionally gas and oil are lost through exhaust pipes or holes in this kind of process, but in modern kilns it is possible to use part of the gases in external heating of the process and collect some of the tar and oils from the process outlets (Brown, 2009).

Modern slow pyrolysis often takes place in continuous reactors – e.g. drum pyrolysers, screw pyrolysers, or rotary kilns (Brown, 2009). These plants are highly energy efficient compared to traditional kilns, and are capable of producing biochar, bio-oil, and gas. The general principle in all these processes is comparable to the simplified drum pyrolyser in Figure 4-V.

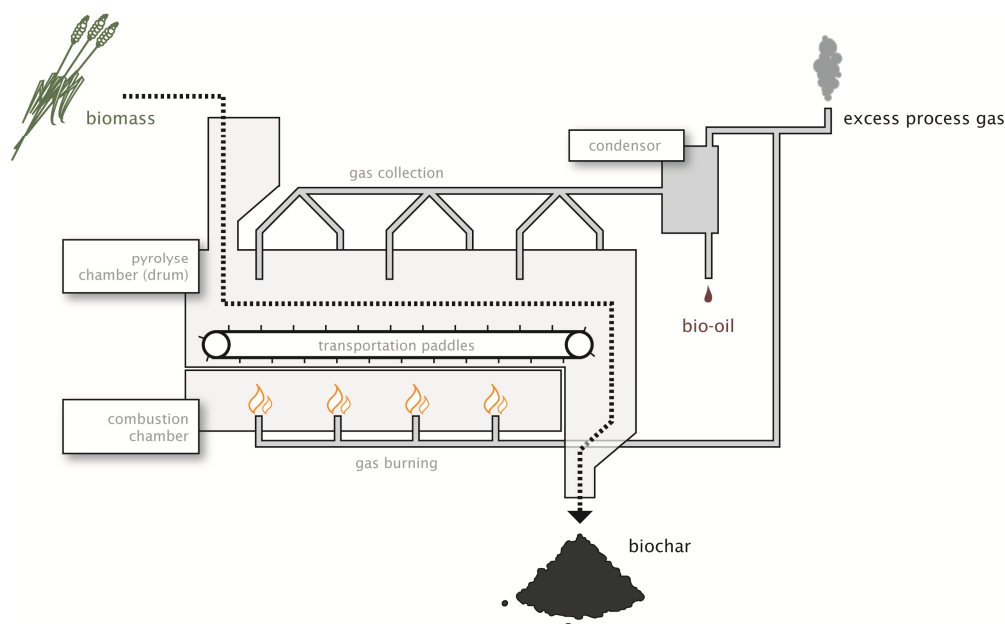


Figure 4-V: Schematic of drum pyrolysers, a modern slow pyrolysis process with external heating. Own work with reference to Brown (2009)

The illustrated process in Figure 4-V has an external heating-source, where pyrolysis gases from the process are burned to keep the reaction going. This kind of heating is often used for modern slow pyrolysis, because it is technically fairly simple and good for the long retention times. However, it is also possible to use one of the following alternative heating techniques (Maschio, et al., 1992):

- Direct heating: Heating of the biomass through contact with an inert heating medium, such as an inert gas, solid steel balls or hot sand.
- Partial oxidation: The original pyrolysis heating process where a little oxygen is introduced into the reactor and heat is provided by the partial combustion of the pyrolysis products.

A study by Peacocke of the characteristics of modern and traditional slow pyrolysis processes, has led to the following characteristics (Peacocke, et al., 2009):

- Long residence times of 5 s + for volatiles and minutes to days for solids
- Relatively low reactor temperatures < 450 °C
- Atmospheric pressure
- Very low heating rates ranging from 0.01 °C/s to up to 10 °C/s
- Low rate of thermal quenching of the products - minutes to hours

The Biomass Gasification Group at the Technical University of Denmark conducted a series of studies of the slow pyrolysis of wood chips in 2005 to characterize the release of tar as a function of pyrolysis temperature. The results showed that almost all the tar produced in a process with a heating rate of 6 °C/min was released in the temperature interval between 300 °C and 400 °C, and that no additional tar was released after reaching 600 °C (Ahrenfeldt, et al., 2005). When setting up the pyrolysis process model later in the report, the temperature range to simulate is based on these results. Therefore, focus will be on building model which yields valid results in the temperature span from 400 °C to 600 °C.

### *Fast pyrolysis*

Fast pyrolysis or rapid pyrolysis plants are a category of high-tech continuous processes, converting biomass to pyrolysis products in a few seconds. To secure this instant conversion of the feedstock particles, preparations must be made to avoid significant diffusion barriers and temperature gradients in the particles during the heating process. These preparations include thorough shredding/pulverizing and drying to a water content < 10 wt% (Emrich, 1985).

In general, the methods of heating a fast pyrolysis plant are categorized similar to the heating of the conventional pyrolysis plant above. However, the technology is a lot more advanced than the technology in most slow pyrolysis plants, and the specific approach varies a lot from one plant to another. Examples of the different kinds of fast pyrolysis reactors and heat carriers are given in Table 4-III. For additional examples see e.g. Bridgwater et al. (1999).

*Table 4-III: Examples of fast pyrolysis reactors and heat carriers (Bech, 2008; Hornung, 2008).*

Fast pyrolysis reactor	Description of heating source
Fluidised bed or fluid bed	The feedstock is blown into a bed of heated sand, and mixed instantly. Close packing of sand and biomass secure rapid heat transfer and conversion.
Ablative reactor	The feedstock is pressured against a heated metal disc. The disc is rotating at high speed, melting the biomass.
Twin screw reactor	Two parallel screws, rotating at high speed transport and mix heated sand and biomass.
Pyrolysis Centrifuge Reactor by (Bech, 2008) characterized as Flash pyrolysis	The feedstock is blown into a heated centrifuge at high speed. Biomass is transported and converted along the inner surface of the heated shell.

Fast pyrolysis technical equipment does not exist in a primitive version like the original slow pyrolysis kilns, and therefore this category have smaller process parameter intervals. A general overview of these parameters could be as follows (Maschio, et al., 1992; Peacocke, et al., 2009):

- High heating rates  $> 200 \text{ }^\circ\text{C/s}$
- Reactor temperatures greater than  $450 \text{ }^\circ\text{C}$
- Short residence times – volatiles  $< 2 \text{ s}$ , solids  $< 5 \text{ s}$
- Small particle size  $< 1 \text{ mm}$

For a given feedstock, there is an optimal operating temperature for the maximization of liquid product yield in fast pyrolysis processes. For wheat straw this optimum temperature is around  $525 \text{ }^\circ\text{C}$  in a Pyrolysis Centrifuge Reactor, independent of the feedstock moisture content (Ibrahim, et al., 2008). Fast pyrolysis of wood shows approximately the same behaviour – see Figure 4-VI.

Yield, wt% on dry feed

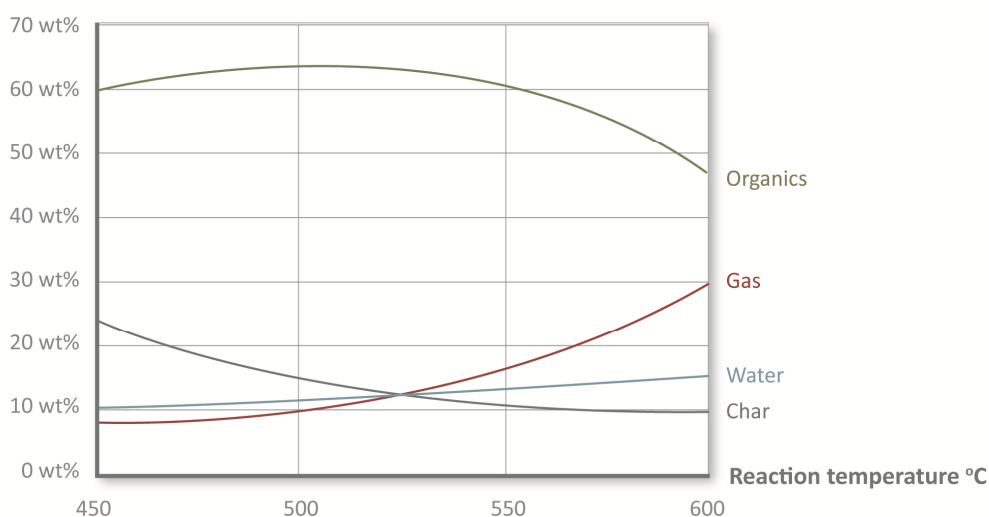


Figure 4-VI: Typical yields from fast pyrolysis of wood, wt% on dry feed basis. Adapted from Bridgwater et al. (1999)

Also the residence time is essential in fast pyrolysis plants, when aiming at bio-oil production. Especially the vapour residence time has to be short to minimise secondary reactions. Best practice is typically around 1 s, although good yields are still possible with vapour residence times of up to 5 s if the vapour temperature is kept below  $400 \text{ }^\circ\text{C}$  (Bridgwater, et al., 1999).

### Flash pyrolysis

Flash pyrolysis is the extreme end of the fast pyrolysis category. The distinction was originally of some importance, but has by now largely disappeared. Today, the term “flash” is gradually being replaced by a more generalised definition for fast pyrolysis (Peacocke, et al., 2009).



### Intermediate pyrolysis

The intermediate pyrolysis process is a combination of the low temperatures (350 °C – 500 °C) and long solid residence time of the slow pyrolysis, with the short gas residence time of the fast pyrolysis process. The result is a robust, continuous process capable of handling many different kinds of feedstock while yielding large amounts of liquids (Hornung, 2009\_B; Robert, et al., 2009).

The technical approach to the intermediate pyrolysis differs from one plant to another. The design is often based on slow pyrolysis technology with additional focus on gas flow management. Examples of intermediate pyrolysis reactors in use are:

- Electrically heated rotary kiln with gas-heated steel balls for heat transfer, and rotation of the cone for mixing (Robert, et al., 2009).
- Fixed kiln with two coaxial conveyor screws to mix biomass and gas-heated steel balls for heat transfer (Apfelbacher, 2009).

### Gasification

Gasification technology aims to convert the feedstock to a maximum amount of gas (mostly CO, CO<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub>), with a small ash fraction and a water fraction as additional outlets (Brown, 2009).

Gasifiers can take on many different shapes and sizes, and it is out of the scope of this report to characterize them all. However, for discussion purposes later on gasification may prove to be an important alternative to pyrolysis in some given scenarios. It is therefore important to have at least one type of gasifier to relate to. A suitable alternative to the isolated pyrolysis process is the Danish 75 kW, two-stage gasifier Viking (Henriksen, et al., 2006). This gasifier produces a combustible gas with very small amounts of tar. This is important as tar damages internal combustion engines, gas turbines, and other machinery - see Figure 4-VII for simplified process schematics.

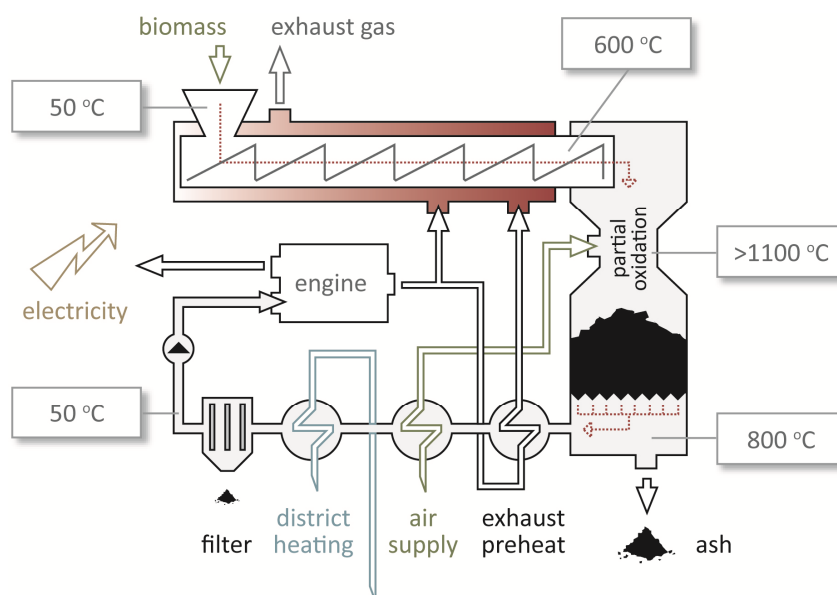


Figure 4-VII: Example of gasification – the Viking gasifier (simplified).  
Adapted from Henriksen et al. (2006)

The first stage in Viking is feeding, drying, and pyrolysis of the biomass (wood chips). The heat supply to this process comes from external heating by two streams – one is a direct exhaust stream from the plant gas engine, running on either natural gas or the produced gas, and the other is a similar stream that is heated additionally by heat exchanging with a gas stream from the gasification unit (Henriksen, et al., 2006). The first section of the pyrolysis unit is a drying zone, evaporating of the water vapour, and then follows the pyrolysis process. This stage is in many ways directly comparable to the similar procedure in a pure pyrolysis plant.

In the second stage of the gasification unit, air is supplied to partially oxidize the pyrolysis products and raise the temperature of the stream to as much as 1270 °C. This oxidation removes a significant amount of tar by cracking, and produce energy for the following endothermic char gasification. During the gasification water and CO<sub>2</sub> from the drying and the pyrolysis reacts with the char fraction due to the high temperatures (~ 800 °C) and a conversion from char and tar to gas takes place. After removing the ash fraction, the stream is used for heat exchanging with the pyrolysis heat stream, the air inlet for the oxidation process as well as district heating. Finally, the gas is combusted in the gas engine, producing electricity and heat for the pyrolysis (Henriksen, et al., 2006).

The gasification technology is an interesting alternative to the pyrolysis in scenarios where no biochar is needed or wanted. The plant produces electricity with high efficiency, it needs only little maintenance and the waste streams are small. For additional information on the Viking gasifier see e.g. Gassner et al. (2009), Henriksen et al. (2006) or Chen et al. (2003).

Based on the previous sections, some outlines for process designs and parameters to include in the pyrolysis process model in chapter 5 are suggested. These outlines are presented in Table 4-IV. Within these boundaries, the models should yield feasible results when compared to experimental values. Designs and parameters outside these boundaries are only considered qualitatively.

*Table 4-IV: Outlines for pyrolysis processes and design parameters to be included in the pyrolysis process modelling*

	Solid residence time	Temperature increase	Max temperature
Slow pyrolysis	10 – 60 minutes	5 – 20 °C min <sup>-1</sup>	350 – 550 °C
Fast pyrolysis	0.5 – 5 seconds	100 – 1000 °C sec <sup>-1</sup>	450 – 650 °C
Gasification	Not modelled. Qualitative considerations only.		

### **Present state technology**

The scenario build up in the modelling part of this report will strive to resemble reality on many aspects – including size, capacity and availability of the pyrolysis technology assumed to be used. As mentioned in chapter 3.1, there is already a substantial industry centred on the production of biochar, pyrolysis systems or related products. Pyrolysis plants of various designs and size are operated all over the world for

research purposes, energy production, or a production of oil, gas, char, or specific high value chemicals. The number and variations among the plant are huge, and it is out of the scope of this report to do a thorough investigation. To get some idea of the span of processes being presently operated, a few examples are given in Table 4-V. Lab scale pyrolysers processing only small amounts of biomass (a few grams or kilos per hour) are omitted from the table, as it is not feasible to engage in the use of such small capacities for energy production purposes. For additional information on different pyrolysis plants and gasifiers, see e.g. Bridgwater et al (2000) or Beenackers (1999).

Table 4-V: Examples of commercially available pyrolysis technology

	Product /reference	Capacity	Characteristics
EPRIDA/ EGenesis industries (Turn-key)	1-ton Pyrolysis System (eGen, 2008)	1 t/hr	Utilizes steam and nitrogen. Produce ~ 26 kg char and 126 kg gas on 100 kg biomass, 7 kg N and 88 kg steam.
UOP/ENSYN (Envergent) (Turn-key)	Rapid Thermal Processing (RTP) Plants (UOP_LL, 2008)	10 - 100 t/d	Fast pyrolysis plant. 500 °C. 65 – 75 wt% bio-oil from woody biomass. Char and gas used for heating.
Dynamotive (Turn-key)	Fast Pyrolysis Pilot Plant (Dynamotive, 2009)	15 t/d	Fast pyrolysis plant. 450–500 °C. 60-75 wt% bio-oil, 15-20 wt% char. 10-20 wt% gas. Gas and some char used for heating.
BTG (Turn-key)	BTG-BTL pyrolysis Plant (BTG, 2009)	1 - 5 t/hr	Fast pyrolysis plant. 50-70 wt% bio-oil. Char used for heating.
Castle Capital, In Nova Scotia (Turn-key)	Continuous Ablative Regenerator (C.A.R.) (Brown, 1995)	50 t/d (dry basis)	Indirect hot plate heating. Operated under pressure. Operation temperature 500- 700 °C. Produces gas for gas turbines.
BEST energies (Turn-key)	BEST energies Pyrolysis Process (Downie, et al., 2007)	2 t/hr	Slow pyrolysis plant. Drum kiln with solids residence time ~ 30 min. 550 °C. High gas yield, no liquids and moderate char yield.
University of Tübingen (Research facility)	The Stenau process (Bridgwater, et al., 2000)	1 t/d	Slow pyrolysis plant. Rotary kiln at low temperatures. 1 t feed yields 300 kg bio-oil, 71 m <sup>3</sup> gas and 560 kg solid residue.
Aston University /EBRI (Research facility)	BtVB process and Pyroformer reactor (Apfelbacher, 2009)	~ 10 t/d	Intermediate pyrolysis 350-500 °C. Variable feedstock. Wheat straw at 450 °C yields ~ 30 wt% char, 50 wt% oil and 20 wt% gas.

For local small scale scenarios in the modelling section of the report, it is feasible that turn-key technology could be applied, and therefore this type of plant is heavily represented in Table 4-V.

## Process outputs – the pyrolysis products

Quality and quantity of all three product fractions from modern pyrolysis processes – biochar, process gas and bio-oil, are very dependent on feedstock characteristics and process design. All three fractions have a role in the overall carbon-balance estimations of the pyrolysis process, and correlations between feedstock, process design, and product features and quantities are essential to understand for drawing usable overall conclusions on the carbon balance of a given scenario.

### Biochar

The biochar fraction of the pyrolysis process and the potential for carbon sequestration through soil amendment of this recalcitrant substance is the one parameter of biomass pyrolysis that has the potential to render the entire process carbon-negative (see section 2.2). In the assessment of the process carbon balance, the main characteristic of biochar to focus on is the recalcitrance and the stability of the char in soil. How process parameters influence these characteristics is examined and discussed in chapter 6,

The other main aspect of the biochar correlation with process design and the carbon balance is the quantitative output of biochar from a given process. In this respect, maximum temperature and gas phase residence time are very important variables. In a simplified way, an increase in temperature will lead to more volatile material being forced out of the solid residue – reducing char yield, but increasing C-fraction in the char (Antal, et al., 2003). It is assumed that the recalcitrance of the remaining solid fraction increases with peak temperature, as more volatiles leave the compounds, the labile fraction of the solid residuals decreases and the ration of fixed-carbon increases (Antal, et al., 2003). This is illustrated for three different feedstocks in Figure 4-VIII (Demirbas, 2006).

C content in char, wt% dry ashfree basis

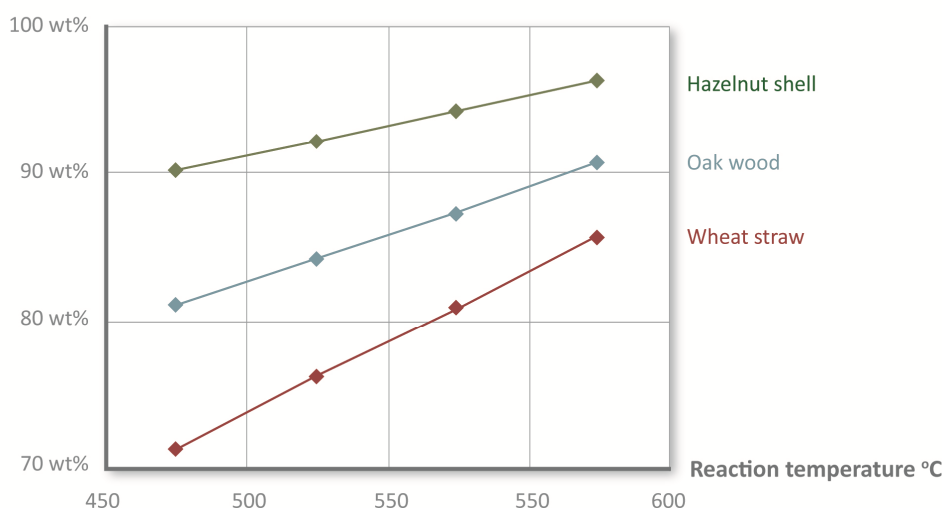


Figure 4-VIII: C-content in char as function of pyrolysis temperature.

Adapted from Demirbas (2006)

The correlation based on the work by Demirbas is implemented for later modelling of slow pyrolysis of wheat straw. To also model the fast pyrolysis of wheat straw, a similar correlation is done based on the fast pyrolysis data in Table 4-VI. The two correlations are:

- Fast pyrolysis of wheat straw: Biochar C-content wt% =  $0.08 \cdot T + 15.9$
- Slow pyrolysis of wheat straw: Biochar C-content wt% =  $0.11 \cdot T + 20.8$

In general, biochar yields are considerably less in real life than the theoretically possible (from chemical equilibrium calculations). In traditional kilns the yield can be as low as 8 %. This is, among other things, because the traditional kilns admit O<sub>2</sub> into the pyrolysis chamber, partially oxidizing the char to CO and CO<sub>2</sub> (Brown, 2009). However, even a completely oxygen deprived pyrolysis process might yield lower than expected. This happens especially if vapours and gases are removed from the reaction zone before thermodynamic equilibrium is attained. Biochar is formed in two general reaction pathways – one where de-volatilized biomass leaves behind a carbonaceous residue (primary biochar), and one where organic vapours (tars) decompose on the residue surface to form coke (secondary biochar) (Brown, 2009). Variations in the venting of pyrolysis of cellulose have been verified to cause a shift from a few % biochar yields to almost 20 % yield (Suuberg, et al., 1996). The mentioned aspects of char formation are important when understanding the difference in slow-, intermediate-, and fast pyrolysis processes.

Another important char characteristic is the energy content. This is expressed by the heating value, and examples of such are given in Table 4-VI. The higher heating value (HHV) is an energy measurement which includes the heat that can be obtained by condensing the water vapour produced by combustion of the char. HHV is used for the remainder of this work, as the energy production facilities assessed often integrate energy extraction from vapour condensation.

Table 4-VI: Examples of the dependence between char heating value and pyrolysis process parameters

Process description	Higher heating value	Elemental composition <sup>a</sup>	Reference
Fast pyrolysis 550 °C. Danish wheat straw	20 MJ/kg	<b>C: 53 H: 3.6 N: 1</b> <b>O: 17 S: 0.4 Ash: 25</b>	(Bech, 2008)
Fast pyrolysis 577 °C. Wheat straw	23 MJ/kg	<b>C: 64.3 H: 2.4 N: 0.5</b> <b>O: 14.3 S: 0.3 Ash: 18.2</b>	(Di Blasi, et al., 1999)
Fast pyrolysis 800 °C. Swedish straw	26 MJ/kg	<b>C: 77.3 H: 1.9</b> <b>N: 0.7 O: 19.7 S: 0.4<sup>b</sup></b>	(Zanzi, et al., 2002)
Slow pyrolysis 10 °C·min <sup>-1</sup> -> 800 °C. Danish straw	27 MJ/kg	-	(Henriksen, et al., 1991)

<sup>a</sup> Oxygen to balance wt%      <sup>b</sup> Ash free composition

There are several other important characteristics of biochar which are influenced by feedstock and process design. These characteristics include porosity (Brown, 2009; Rutherford, et al., 2004), elemental composition, surface charge, application properties (density, dust fraction) (Blackwell, et al., 2009; Hammes, et al., 2009), etc. but as they have to do mainly with soil improvement and not the process carbon balance, they will not be thoroughly investigated in this report.

### Non-condensable gases

As indicated in Figure 4-VI, gas production in pyrolysis processes is favoured at high process temperatures where it happens mainly on expense of the bio-oil fraction. This is in good agreement with the description of thermal decomposition of the feedstock components in section “Biomass – biochar feedstock and main reactions”. The large condensable compounds which form the liquid phase cracks under additional thermal treatment to lighter gases, refractory tars and steam following a complicated pattern with increasing temperature from 500-1000 °C (Fjellerup, et al., 2005). Tar particles in gas are difficult to control and a potential source of damage to many types of unit operations. For this reason, it is important to diminish the amount of tar by cracking if the heavy compounds are not removed early in the downstream process. There are several ways to crack tar, and this has been practiced intensely in gasification processes. In the Danish Viking gasifier, the process is done in two steps – first a partial oxidation with thermal cracking at temperatures beyond 1100 °C, which reduces the tar content in the gaseous phase with a factor of ~ 100, and then through a char bed in a char gasification reactor, reducing the tar content with an additional factor of 100 (Henriksen, et al., 2006).

Examples of the gas phase compositions and higher heating values from various setups to be used in the model work are given in Table 4-VII.

Table 4-VII: Gas-phase values for modelling

Process description	HHV	Gas composition (vol%, dry)	Reference
Slow pyrolysis 600 °C. Wheat straw	10.0 MJ/kg <sup>a</sup>	CO <sub>2</sub> : 35.7 CO: 30 H <sub>2</sub> : 20.9 CH <sub>4</sub> : 11.8 C <sub>2</sub> H <sub>6</sub> /C <sub>2</sub> H <sub>4</sub> : 1.6	Calculated from (Di Blasi, et al., 2000)
Fast pyrolysis 550 °C. Wheat straw	11.2 MJ/kg	CO <sub>2</sub> : 50 CO: 37 H <sub>2</sub> : 1.1 CH <sub>4</sub> : 2.2 CH <sub>3</sub> CHO: 1.6 Additional C <sub>2-4</sub> : 8.1	(Bech, 2008)
Fast pyrolysis 800 °C. Straw	14.9 MJ/kg <sup>a</sup>	CO <sub>2</sub> : 23.7 CO: 28, H <sub>2</sub> : 35 CH <sub>4</sub> : 9.5 C <sub>2</sub> H <sub>6</sub> : 0.1 C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> : 3.1 Benzene: 0.6	(Zanzi, et al., 2002)
Slow pyrolysis -> 800 °C. Straw	13.0 MJ/kg	CO <sub>2</sub> : 36 CO: 26.1 H <sub>2</sub> : 22.9 CH <sub>4</sub> : 12.7 C <sub>2</sub> H <sub>6</sub> : 1.6 C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> : 0.6	(Henriksen, et al., 1991)
Two-step gasifier 800 °C / 900 °C. Straw	16.5 MJ/kg	CO <sub>2</sub> : 21.7 CO: 30.5 H <sub>2</sub> : 29.3 CH <sub>4</sub> : 17.4 C <sub>2</sub> H <sub>6</sub> : 0.0 C <sub>2</sub> H <sub>2</sub> /C <sub>2</sub> H <sub>4</sub> : 1.1	(Henriksen, et al., 1991)

<sup>a</sup> Calculated from composition

Divided into slow and fast pyrolysis processes for use in the modelling section, elemental compositions of pyrolysis gases calculated from Table 4-VII:

- Fast pyrolysis of wheat straw: ~39 wt% C, 58 wt% O and 3 wt% H
- Slow pyrolysis of wheat straw: ~36 wt% C, 60 wt% O and 4 wt% H

### Bio-oil

Bio-oil from pyrolysis of biomass has been known to contain more than 300 different compounds in various amounts, and the variations in quality and quantity of the oil with feedstock and process design and parameters are enormous. A thorough investigation of bio-oil characteristics and properties from a long range of different feedstocks and pyrolysis processes is given by Mohan et al. from 2006, together with a review of possible ways to alter the composition of the oils, and use them as a raw material for the production of specific chemicals (Mohan, et al., 2006). The production of specific chemicals from bio-oil, and the whole bio-refinery concept is out of the scope of this report, and focus will be on bio-oil from pyrolysis as fuel for energy purposes only.

As a general rule, fast pyrolysis processes yield higher liquid fractions than slow pyrolysis. Development of modern fast pyrolysis processes have succeeded in yielding as much as 80 wt% liquids on dry feed basis in extraordinary cases (Bridgwater, et al., 1990).

The pyrolysis oil itself consists of water and a long range of organic compounds that are collected by quenching a hot, char- and ash free, vapour stream. The speed of the quenching is important as it “freezes in” the intermediate products of the fast degradation of the biomass in a somewhat stable form (Mohan, et al., 2006). The liquid has a large water fraction bound by the polarity of the oxygenated organics (Bridgwater, et al., 1990). Some ash and char particles will normally remain in the oil, but hot-gas filtration techniques can bring the level beneath 0.01 wt%, thus meeting the requirements of the best quality diesel fuel (Bridgwater, et al., 1990).

Pyrolysis liquids are often dark brown free flowing substances with a strong distinctive smoky smell. It has a very high density (~ 1.2 kg/litre) compared to light fossil fuel oil (~ 0.85 kg/litre) and a viscosity that varies significantly with the water content and aging of the oil (Bridgwater, et al., 1990). Pyrolysis oils vary significantly, but some characteristic values are given in Table 4-VIII.

Table 4-VIII: Examples of typical pyrolysis oil characteristics (Bridgwater, et al., 1990)

Physical property	Typical value
Moisture content	15 - 30 wt%
pH	2.5
Elemental analysis (dry basis)	C: 56.4 wt%    H: 6.2 wt% O: 37.3 wt% (by difference)    N: 0.1 wt%
HHV as produced (depends on moisture)	16-19 MJ/kg
Viscosity (at 40 °C and 25 wt% water)	40-100 cp
Solids	Char < 0.5 wt%, Ash ~ 0.1 wt%
Distillation possible	Max 50 wt% due to instability

As a fuel oil, bio-oil has some advantages and disadvantages compared to conventional fossil diesel fuel. Besides the obvious advantages on the carbon-balance, there are also other environmental benefits worth mentioning. Burning bio-oil emits

essentially no SO<sub>x</sub> compounds, as the level of sulphur in plant biomass is insignificant, and less than 50% of the NO<sub>x</sub>'s from diesel oil depending on plant N-levels and specific diesel oil type (Mohan, et al., 2006). Helge Egsgaard, senior scientist at Risø DTU suggests that one of the reasons for the diminished NO<sub>x</sub> emissions could be an in-situ de-NO<sub>x</sub> effect in the bio-oil by relatively high ammonia content.

A large disadvantage of bio-oil is the low energy content. With a HHV normally around 16-19 MJ/kg, the energy density in bio-oil from pyrolysis is less than half of that in hydrocarbon fuels with energy content around 40-44 MJ/kg. Volumetric heating value in bio-oil with 20 wt% water is approximately the same as in 95 % ethanol (Bridgwater, et al., 1990). This obviously makes some aspects of the logistics in energy production with bio-oil a lot more demanding than in fossil energy production, but as fossil fuels becomes more energy-demanding to acquire this balance may shift. One commonly used method to remove water from various liquids is distillation. This would increase the energy density in the bio-oil, and thus reduce transportation costs and improve the energy balance of transportation. Unfortunately, the possible distillation of bio-oil is only ~ 50 wt% (Table 4-VIII), because heating of pyrolysis oil initiates a fast reaction that transforms ~ 50 wt% of the liquid into a char-like residue that cannot be re-liquefied. The instable nature of the pyrolysis oil increases with temperature, and therefore it is preferable to store pyrolysis oils at room temperature or lower (Bridgwater, et al., 1990).

The use of bio-oil for energy purposes presents a series of other challenges. Using bio-oil in a normal diesel engine, for instance, will rapidly corrode or erode it due to the acidity of the bio-oil in combination with char fines (Bridgwater, et al., 1990). Table 4-IX present some examples of the troublesome aspects of bio-oil, and some methods to solve these problems.

Table 4-IX: Bio-oil characteristics, and methods to alter them. From Mohan et al (2006)

Characteristic	Effect	Solution
Contains suspended char	Leads to erosion, equipment blockage, combustion problems due to slower rates of combustion; 'sparklers' can occur in combustion leading to potential deposits and high CO emissions.	Hot vapour filtration; liquid filtration; modification of the char for example by size reduction so that its effect is reduced; modification of the application.
Contains alkali metals	Causes deposition of solids in combustion applications including boilers, engine and turbines; in turbines the damage potential is considerable, particularly in high performance.	Hot vapour filtration; processing or upgrading of oil; modification of application; pre-treat feedstock to remove ash.
Low pH	Corrosion of vessels and pipe work.	Careful materials selection - stainless steel and some olefin polymers.
Incompatibility with some polymers	Swelling of destruction of sealing rings and gaskets.	Careful materials selection.



Characteristic	Effect	Solution
High-temperature sensitivity	Liquid decomposition and polymerization on hot surfaces leading to decomposition and blockage; adhesion of droplets on surfaces below 400 °C.	Recognition of problem and appropriate cooling facilities; avoidance of contact with hot surfaces > 500 °C.
High viscosity	High-pressure drops in pipelines leading to higher cost equipment and/or possibilities of leakage or even pipe rupture. Higher pumping costs.	Careful low temperature heating, and/or addition of water, and/or addition of co-solvents, such as methanol or ethanol.
Water content	Complex effect on viscosity, lowers heating value, density, stability, pH, homogeneity, etc. Can lead to phase separation.	Recognition of problem; optimization with respect to application.
In-homogeneity	Layering or partial separation of phases; filtration problems.	Blending with methanol or ethanol.

Today it is possible to adapt equipment for energy production to run successfully on bio-oil, and tests have been carried out for many years with various tares of success. A test in 1995 of a low speed, 1.4 MW diesel engine with a special self-cleaning filter, and a ceramic coated special stainless steel fuel injector gave a thermal efficiency of 45% in a four hour run, with no signs of corrosion or other problems (Jay, et al., 1995). In another test, a 2.8 MW gas turbine designed for the alkaline environment of salt water spray was run on bio-oil produced with hot-gas filtering and gave a thermal efficiency of 28% (Andrews, et al., 1996). Other successful tests include a 1.4 MWe modified dual fuel diesel engine with at least 500 hours of operation on bio-oil over a few years, and a 2.5 MWe gas turbine modified for bio-oil utilization (Bridgwater, et al., 1990). Modern large scale testing of bio-oil as energy source is also well under way. The Biomass Technology Group (BTG) in the Netherlands has co-fired a 350 MWe natural gas fired power station with 15 tons of bio-oil producing 25 MWh of electricity. The combustion campaign revealed that natural gas-fired power plants can use the bio-oil with minimal retrofitting and high system reliability. The bio-oil must be completely ash-free, as there is no dust-collection unit at the natural gas power station and the price of this oil will be ~ 6 €/GJ, which compares to the cost of natural gas in the Netherlands (Wagenaar, et al., 2008). For a more thorough review of bio-oil applications see e.g. Czernik et al. (2004).

It is assumed for the remainder of this report that it is feasible to produce electricity and heat from bio-oil in a Danish energy scenario. The main parameter to investigate for use in the modelling section is the energy content in the oil. The energy content depends on many parameters involving feedstock composition and process design. However, (Bridgwater, et al., 1990) points out that the main variation comes from water content. This could be very useful in the modelling section, and a correlation between bio-oil water content and HHV is suggested in Figure 4-IX.

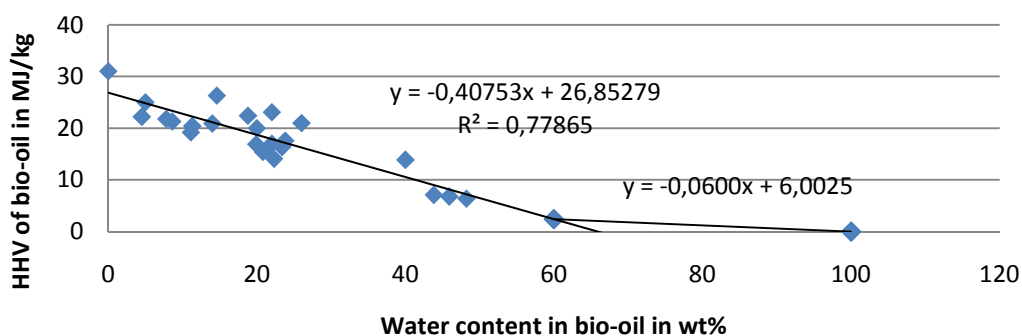


Figure 4-IX: Correlation between bio-oil water content and energy content (HHV = Higher heating value)

The correlation in Figure 4-IX is substantially simplified but assumed valid for the purpose of this report. The linearity could be suspected as if the correlation was regarded as a simple dilution. To avoid negative values in the modelling, an assisting function is created to take over the correlation when the water content exceeds 60 wt%. This function is linear from 60 wt% and HHV 2.4 MJ/kg until 100 wt% water and HHV 0 MJ/kg.

Another useful correlation for bio-oil characteristics is between the oils elemental composition and energy content. This matter has been thoroughly investigated – see e.g. Channiwala et al. (2002). However, for the scope of this report, a simpler approach is necessary. A suggestion to such a simplified correlation is given in Figure 4-X.

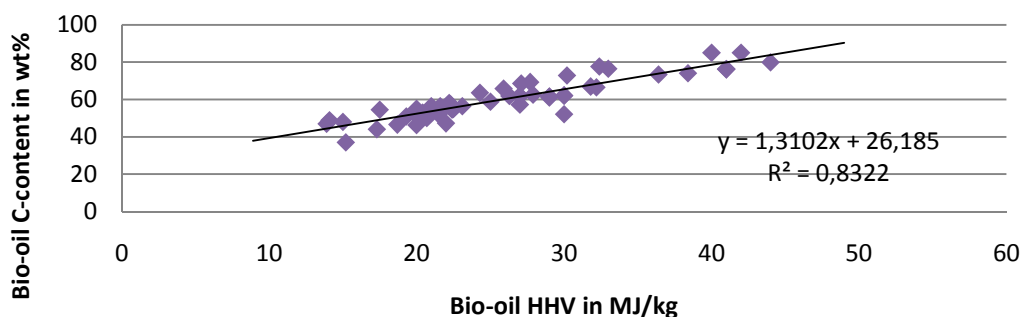


Figure 4-X: Simplified correlation between bio-oil C-content and HHV

Data behind the above correlations includes experimental results from both slow and fast pyrolysis processes with different designs and process parameters, and many different feedstocks (Bech, 2008; Bridgwater, et al., 2007\_B; Demirbas, 2004; Maggi, et al., 1994; Miao, et al., 2004; Onay, et al., 2003; Özcimen, et al., 2004; Sipilä, et al., 1998; Mohan, et al., 2006). The data used in the correlations is given in more detail in Appendix 1 and Appendix 2.

## 5 Pyrolysis process simulation

In the final chapters of the report the goal is to combine the information and correlations from the previous chapters with the use of Intelligen's SuperPro Designer software to examine the overall carbon-balance of pyrolysis processes. The first step in this process is to build a model of the pyrolysis process. The viability and usability of this model is essential in the carbon balance examination, and it is expected to function within the following boundaries:

- Fast – and slow pyrolysis processes with standard operation parameters are investigated
- Only general unit operations within the different processes are included
- Peripheral units are investigated mainly to the extent of utility consumption.

The model build up is done in two steps. First, the main reactor in a fast and a slow pyrolysis process has to be set up and validated. Afterwards, additional standard unit operations are added to the model until it resembles a complete pyrolysis process. The work is based on a literature survey, and discussions with gasification expert, senior scientist Jesper Ahrenfeldt from Risø DTU.

### 5.1 About the software – SuperPro Designer

SuperPro Designer is a modelling tool used for evaluation and optimization of integrated processes in a wide range of industries (Pharmaceutical, Biotech, Specialty Chemical, Food, Consumer Goods, Mineral Processing, Microelectronics, Water Purification, Wastewater Treatment, Air Pollution Control, etc.). SuperPro Designer was originally developed for through-put optimization, project economic assessment, waste/pollution reduction and control as well as utility and work force management (Intelligen, 2010\_a; Intelligen, 2010\_b).

In the work with the pyrolysis process model, the main model focus will be on carbon- and energy balances, including some considerations of utility consumption. This will make use of SuperPro Designers material- and energy balances, built-in unit operations for up- and downstream processing and default values for utility consumptions. Building the pyrolysis process model in SuperPro Designer, would open a wide spectrum of possibilities for future work using the program strengths on throughput- and economic optimization, environmental management and impacts as well as scheduling and work force assessments. These investigations could prove very useful in situations where a concrete pyrolysis process was considered, or in helping define an optimal process in a given socio-economic setting. It is thus possible that many of SuperPro Designers unused features could become useful in future work beyond the scope of this report.

The SuperPro Designer software package is chosen for the pyrolysis process model because it integrates all unit operations in the process, and therefore yields a total energy- and carbon balance of the process. The software is not chosen because it is assumed to provide the best and most accurate model of the pyrolysis reactor. This task has been met with other more specific software like the DNA simulation tool or the EES Gasifier (Elmegaard, et al., 2005; Fock, et al., 2000).

## 5.2 Modelling the pyrolysis process in SuperPro Designer

### The main reactor build-up

The build of the main pyrolysis reactor in SuperPro Designer is the most crucial step in the modelling process, as it is unprecedented and not within the software's core competences. SuperPro Designer includes 140 different pre-designed unit operations, but not one of them is suited for use as a detailed pyrolysis reactor. It would be possible to implement kinetic one-step pyrolysis reactions in standard continuous reactors (Plug flow reactors or Continuously Stirred Tank Reactors), based on kinetic parameters from academic literature e.g. Shafizadeh et al. (1977), Lanzetta et al. (1998) or Van de Velden et al. (2010), but the result would be a model that is only capable of simulating very accurate results in a very narrow spectre of process variations (Miller, et al., 1996). To build a robust model, it is assumed necessary to level out the uncertainties, so that the model will work reasonably well in many scenarios, instead of very well in only a few.

On this background, it is decided not to use a single unit operation for the thermal reactions, but instead try to model the process in a parallel sequence combining three standard reactors processing cellulose, hemicelluloses, and lignin separately. Each reactor should apply build-in kinetic reaction calculations with kinetic parameters from suitable experiments. This approach for modelling of general biomass pyrolysis is using a superposition principle with individual reactions of cellulose, hemicelluloses, and lignin kinetics. This makes the model capable of transforming various feedstocks from knowledge about feedstock composition, instead of only wheat straw, and it increases the model robustness due to the interaction of several reaction pathways instead of only one. The concept is illustrated in Figure 5-I based on the work by Miller et al. (1996).

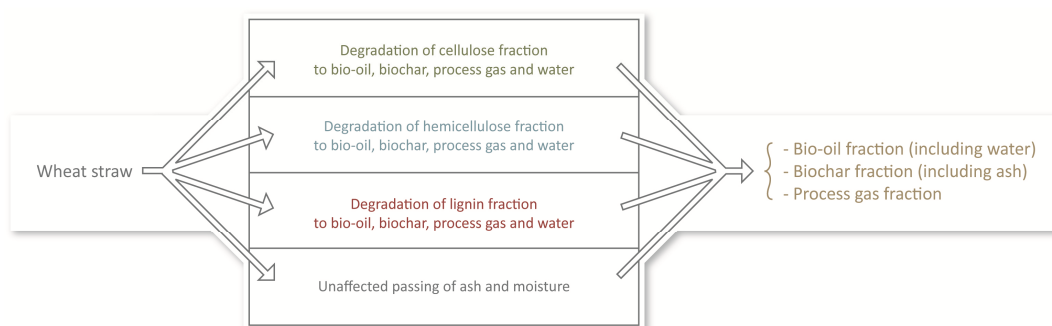


Figure 5-I: The superposition principle for degradation of biomass via individual constituent reactions. Own work with reference to Miller et al. (1996)

### Main differences in slow- and fast pyrolysis reactors

The fast- and slow pyrolysis processes differ mainly in heating rates and solid retention times (see section 0). Detailed control of heating rates in SuperPro Designer standard reactors is very difficult as it is not possible to program detailed temperature variations over time. Based on this it is found necessary to find an unorthodox method for controlling reactor heating rates.

The fast pyrolysis has extremely high heating rates, and short residence times (see section 0), and may very well be considered isotherm without any significant impact

on reaction rates and pathways. This assumption reduces the problem with heating control and enthalpy integration to the slow pyrolysis process. These processes have long solid residence times and slow heating rates, and therefore it is not viable to assume all slow pyrolysis processes isotherm.

After thorough consideration it is decided to split the slow pyrolysis process into sections linked in series. Each of these sections will in itself be isotherm, but increasing temperature from section to section will resemble the effect of controlled heating rates in one reactor. The SuperPro Designer depiction of this setup with 4 sections is shown in Figure 5-II.

Heating occurs by heat exchanging the feed with a hot gas stream. For each pass through the heat exchangers, temperature increases in the next section of the reactor, and the hot gas stream lose an equivalent amount of energy. To complete the integration between reactors and heating stream, the enthalpy of the reactions need to be applied. Applying enthalpy calculations to the reactors is a possibility in SuperPro Designer, but it leads to many software errors, which the program cannot solve. This problem is addressed in section 0.

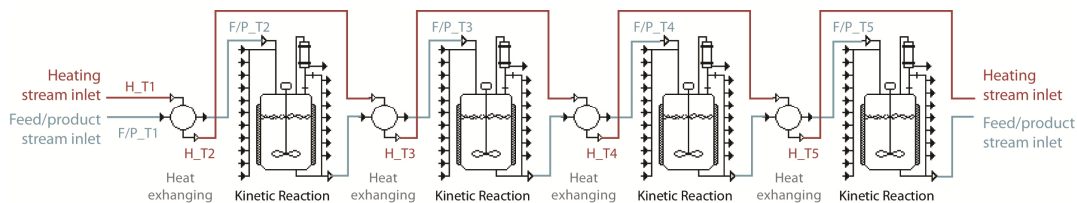


Figure 5-II: SuperPro Designer slow pyrolysis reactor setup.

The sectional approach gives good possibilities for temperature variations throughout the reactor. As an alternative to a uniform heating rate along the pyrolysis reactor, it is common to have a drying section at one temperature and a pyrolysis section at another. The sectional build-up of the reactor can also provide valuable information about the reaction progress in the reactor. It is now possible to follow the development of products and degradation of feedstock components from one section to the next, by monitoring the connecting streams.

The final build of the main pyrolysis reactors for the fast- and slow pyrolysis processes is illustrated in Figure 5-III. The illustration is of the fast pyrolysis process, but exchanging section 2 with 3 parallel versions of Figure 5-II would give the setup for the slow pyrolysis plant. In this build-up, the feed stream is first divided into main fractions of cellulose, hemicelluloses, and lignin (including ash and water). Then each stream is kinetically transformed in one isotherm reactor (fast pyrolysis) or several sections with the same or increasing temperature (slow pyrolysis). Finally, the streams are cosmetically altered – labelling e.g. carbon+ash+celluloses residue as biochar, before they are mixed into one stream, adding similar product fractions together and giving a final output of biochar, bio-oil, water, and process gas.

Heating is omitted from the diagram in Figure 5-III for better overview. In the fast process the feed would be heated by heat exchanging with a warm gas stream to reaction temperature just before section 1. After the heating the reaction would occur under isotherm conditions in section 2, and then reaction enthalpy influence is integrated in section 3. This would lead to a change in stream temperature, and to shift this temperature change to the heating stream, a final heat exchanging would occur

after section 4. For the slow pyrolysis process heat exchanging would also occur between each section of the combined reactor as indicated in Figure 5-II.

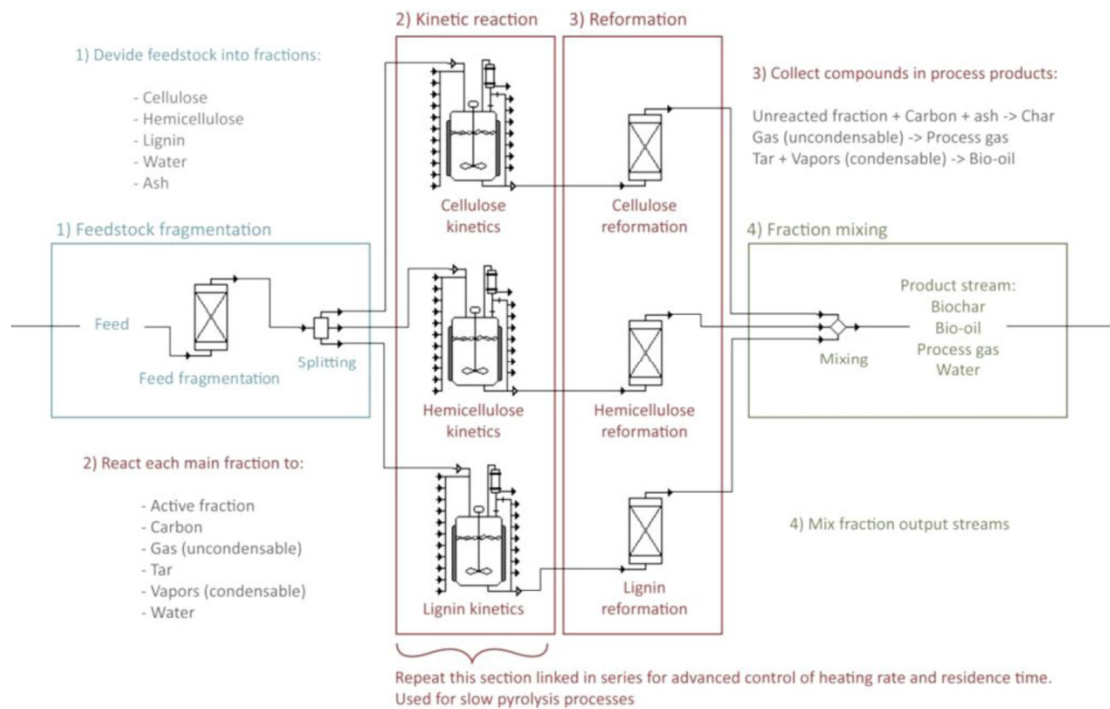


Figure 5-III: SuperPro Designer modelling - structure of slow- and fast pyrolysis main reactors

### SuperPro Designer kinetics for main reactor

To build a temperature- and time dependent pyrolysis model, the main reactors is based on biomass degradation kinetics. In SuperPro Designer, all reactions for these kinds of operations are assumed to follow Arrhenius kinetics. This mean that reaction-rate constants are temperature dependent following  $k(T) = A \cdot e^{-E_a/RT}$ . Here  $k(T)$  is the reaction-rate constant,  $A$  is the pre-exponential factor,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $E_a$  is the activation energy. For simplicity purposes all reactions are assumed to be 1<sup>st</sup> order, irreversible reactions in this work. This is important as most kinetics studies of pyrolysis of biomass are based on this assumption. This leads to a reaction-rate expression  $-r_B = k_B(T) \cdot C_B$  for a given reaction  $F \rightarrow P$  where  $C_B$  is the concentration of compound B. In a first-order reaction following Arrhenius kinetics,  $k(T)$  is in  $s^{-1}$ ,  $A$  (the frequency factor) is also in  $s^{-1}$ ,  $T$  is normally in K, and  $E_a$  is dependent on  $R$  and could be in  $kJ \cdot mol^{-1}$  if  $R$  is in  $kJ \cdot K^{-1} \cdot mol^{-1}$  (Fogler, 2006).

### Degradation pathways and kinetic parameters

#### Cellulose degradation and kinetics

The approach chosen for modelling the cellulose degradation is illustrated in Figure 5-IV.

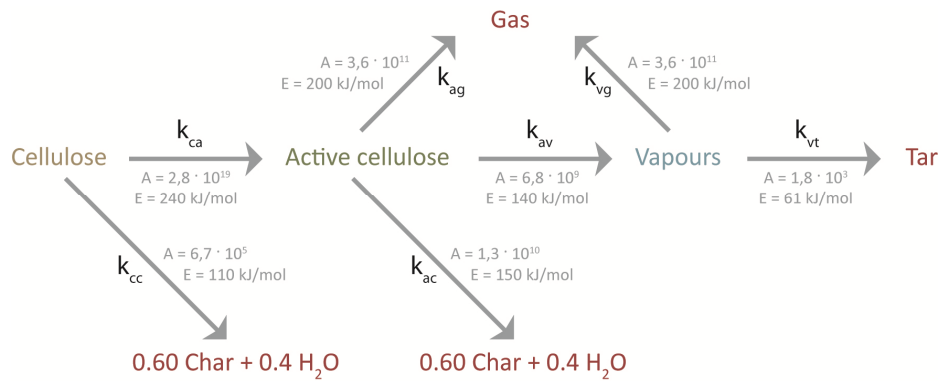


Figure 5-IV: Degradation pathways and kinetic parameters for pyrolysis of cellulose (Diebold, 1994)

In the first step in Figure 5-IV, two reactions compete for converting the celluloses: Transformation to “active celluloses” – a product with lower DP, by chain cleavage, or formation of char and water (including small amounts of by-product gases) from a dehydration reaction. After transformation to “active cellulose”, three reaction pathways compete for further conversion: Direct cracking to secondary gases, volatilization to primary vapours or dehydration into biochar and water (including small amounts of by-product gases). The primary vapours can crack again to form secondary gases, or form secondary tars (including small amounts of by-product gases and water) (Diebold, 1994). Unreacted celluloses fractions (active and inactive) will end up in the biochar yield.

#### Hemicelluloses and lignin degradation and kinetics

Main reaction scheme and kinetic parameters for both hemicelluloses and lignin are primarily based on the work by Miller et al. (1996), and illustrated in Figure 5-V and Figure 5-VI.

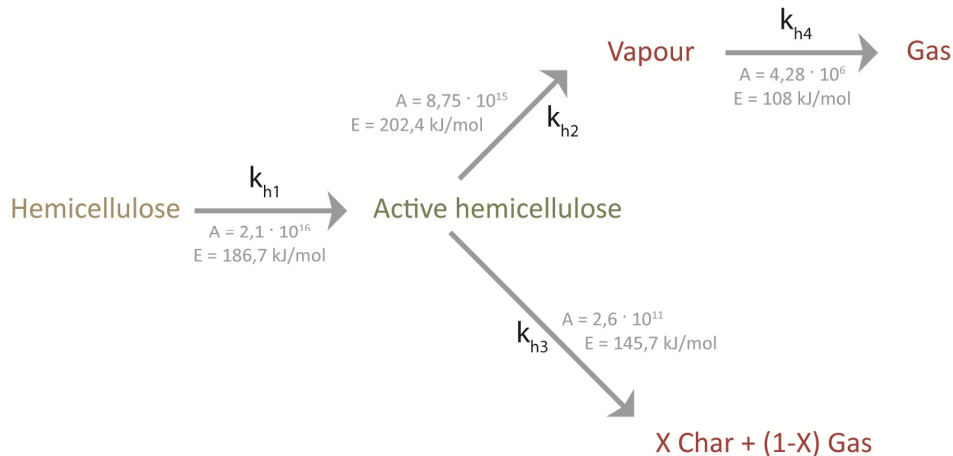


Figure 5-V: Degradation pathways and kinetic parameters for pyrolysis of hemicelluloses (Miller, et al., 1996)

The modelling by Miller et al. (1996) is comparable to that of the cellulose degradation, but simplified from 7 global pathways to 4. There is also a degradation proposition for cellulose in the work by Miller, but a more advanced approach by Diebold (1994) was chosen here.

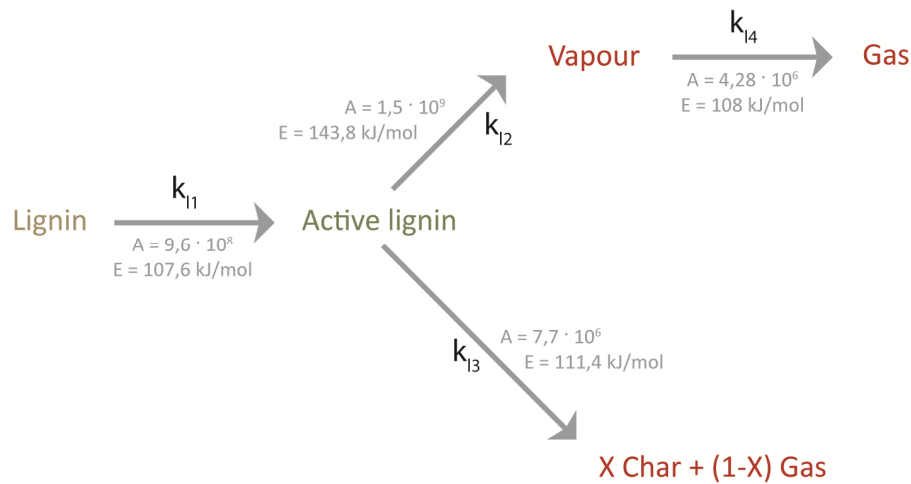


Figure 5-VI: Degradation pathways and kinetic parameters for pyrolysis of lignin (Miller, et al., 1996)

Vapour phases from hemicelluloses are divided into 60 % condensables and 40 % gases while it is 42 % condensables and 58 % gases from lignin vapours. X-values for reaction of active hemicelluloses and lignin to char and gas are 0.6 and 0.75 respectively (Miller, et al., 1996).

The applied kinetics has been fitted originally to match experimental results from thermal degradation of many different feedstocks at once (Diebold, 1994; Miller, et al., 1996). Based on this knowledge, it is assumed a good idea to validate - and potentially re-fit, the pyrolysis model parameters for wheat straw in a SuperPro Designer reactor before using it for process predictions. This will integrate feedstock, the superposition principle, reactor build-up, and kinetics, and clarify process simulation deviations and uncertainties.

### Validation of the main pyrolysis reactors

First step in the validation of the pyrolysis process model is to find suitable experimental results to validate against. The experiments should use wheat straw as feedstock, and the description in literature should have a level of details suitable for imitation. The experiments used for this exercise are described in Table 5-I.

Table 5-I: Experiments for use in validation of the main pyrolysis reactor model

Experiment	Process description	Main product yields
<b>Slow pyrolysis 1</b> (Raveendran, et al., 1996)	<b>Feedstock:</b> Cellulose, hemicelluloses (xylan) and lignin extracted from wood. <b>Temp. profile:</b> Isotherm at 500 °C <b>Retention:</b> ca 10 min (solids)	20.4 % biochar, 39.0 % liquids and 40.6 % gas. Calculated from straw with 42.2 % cellulose, 40 % hemicelluloses and 17.8 % lignin.



<b>Slow pyrolysis 2</b> (Di Blasi, et al., 2000)	<b>Feedstock:</b> Undefined wheat straw with 5.25 % ash and 7 % moisture.  <b>Temp. profile:</b> 20 °C·min <sup>-1</sup> from 25 °C to 500 °C.  <b>Retention:</b> ca 24 min (solids)	28.5 % biochar, 48 % liquids and 23.5 % gas (dry basis).
<b>Slow pyrolysis 3</b> (Hornung, 2009_B)	<b>Feedstock:</b> Undefined wheat straw.  <b>Temp. profile:</b> Isotherm at 450 °C.  <b>Retention:</b> ca 10 min (solids)	28 % biochar, 50 % liquids and 22 % gas (dry basis).
<b>Slow pyrolysis 4</b> (Raveendran, et al., 1995)	<b>Feedstock:</b> Well defined wheat straw  <b>Temp. profile:</b> 50 °C·min <sup>-1</sup> from 25 °C to 500 °C.  <b>Retention:</b> ca 10 min (solids)	24.9 % biochar and 75.1 % volatiles.
<b>Fast pyrolysis 1</b> (Ibrahim, et al., 2008)	<b>Feedstock:</b> Defined wheat straw. 6.2 % water.  <b>Temp. profile:</b> Isotherm at 525 °C.  <b>Retention:</b> 2 seconds.	25.9 % biochar, 56.2 % liquids and 19.4 % gas.
<b>Fast pyrolysis 2</b> (Scott, et al., 1999)	<b>Feedstock:</b> Wheat straw with 1.3 wt% water and 4.6 wt% ash content  <b>Temp. profile:</b> Isotherm at 550 °C.  <b>Retention:</b> 1.5 seconds.	24.5 wt% biochar, 52.8 wt% liquids and 17.8 wt% gas.
<b>Fast pyrolysis 3</b> (Zanzi, et al., 2002)	<b>Feedstock:</b> Wheat straw  <b>Temp. profile:</b> Isotherm at 800 °C.  <b>Retention:</b> 1.5 seconds.	13.2 wt% biochar, 11.0 wt% liquids and 75.8 wt% gas (dry ash free basis).

To validate the pyrolysis model reactors capabilities on predicting product fraction yields, simulations are conducted with settings that resemble the experimental setups as closely as possible. Where no information about a given parameter has been available, common values have been used. Comparison of experimental results and model product values are given in Figure 5-VII. Deviations on experimental data are estimated to be around  $\pm 5$  % uncertainty on measurements of product yields when no uncertainty information is available (Brownsort, 2009).

Comparing the two models in Figure 5-VII, it is obvious that the fit of the fast pyrolysis model is noticeably better than the fit of the slow pyrolysis model. This is no surprise as the original kinetic parameters from Diebold (1994) and Miller et al. (1996) are fitted to be used in one-step models. The original parameters were not

intended for use in a sectional approach like the one in the slow pyrolysis model. However, results from a one-step slow pyrolysis model showed very poor results when comparing to non-isothermal experiments, and therefore it was important to make the sectional approach work. It was decided to re-fit the sectional slow pyrolysis model to new wheat straw data despite the possible expense of fit to results from other feedstock. The re-fitting was very modest – changing 14 of 30 parameters up to 8 % with an average of ~ 2%. For two parameters in the lignin degradation scheme the re-fitting was done by exchanging the parameters from Miller et al. (1996) with parameters from a more detailed study by Caballero et al. (1996). All original and improved parameters are enclosed in Appendix 3.

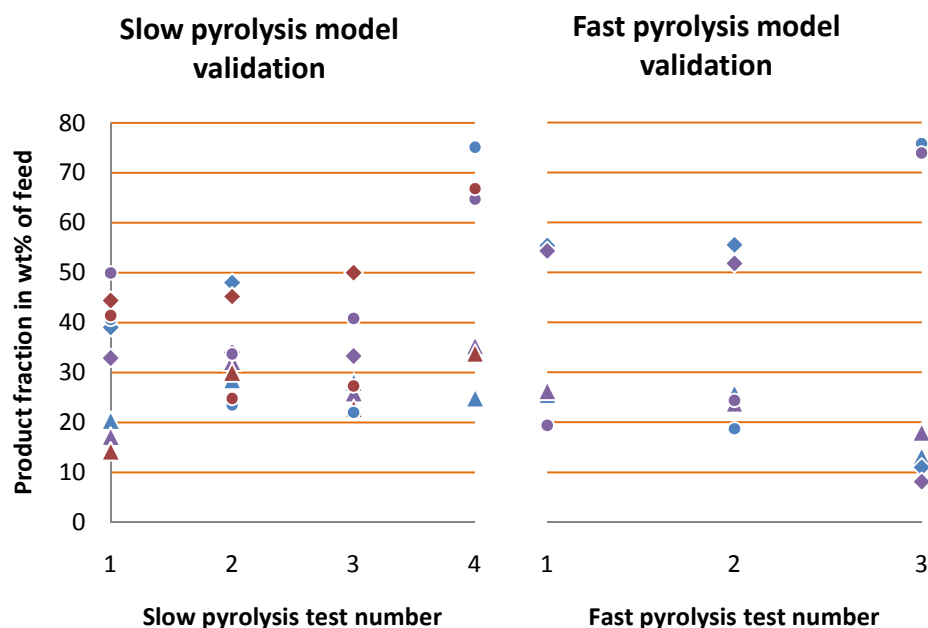


Figure 5-VII: Validation of product yields from pyrolysis process model. Blue values are experimental results, Purple values are model results with original kinetic parameters, and Red values are model results with fitted kinetic parameters. Triangles are biochar yield, diamonds are liquid fraction yields and circles are process gas yield.

Even though the re-fitting has been limited, it has improved the accuracy of the slow pyrolysis model to a usable level. To validate and compare the quality of the different models, deviations are collected in Table 5-II.

Table 5-II: Deviations between experimental results and modelled values

Experiment	Deviations from experimental results
<b>Slow pyrolysis</b> Original kinetic parameters	<b>Span of deviations: 2.1 – 18.8 wt%</b>
	Average deviation of 4 biochar fractions: 4.9 wt%
	Average deviation of 3 liquids fractions: 12.3 wt%
	Average deviation of 4 process gas fractions: 12.2 wt%
	<b>Average deviation of all 11 fractions: 9.6 wt%</b>

<p><b>Slow pyrolysis</b></p> <p>Improved kinetic parameters</p>	<p><b>Span of deviations: 0.0 – 8.9 wt%</b></p> <p>Average deviation of 4 biochar fractions: 5.5 wt%</p> <p>Average deviation of 3 liquid fractions: 2.7 wt%</p> <p>Average deviation of 4 process gas fractions: 3.9 wt%</p> <p><b>Average deviation of all 11 fractions: 4.5 wt%</b></p>
<p><b>Fast pyrolysis</b></p> <p>Original kinetic parameters</p>	<p><b>Span of deviations: 0.3 – 5.7 wt%</b></p> <p>Average deviation of 3 biochar fractions: 2.5 wt%</p> <p>Average deviation of 3 liquid fractions: 2.6 wt%</p> <p>Average deviation of 3 process gas fractions: 2.6 wt%</p> <p><b>Average deviation of all 9 fractions: 2.6 wt%</b></p>

The results in Figure 5-VII and Table 5-II show that the main reactors of both the fast pyrolysis process and the slow pyrolysis process are now of usable accuracy. The slow pyrolysis reactor are assumed valid in the temperature span from 25 °C and up to at least 500 °C with heating rates from 0 °C·min<sup>-1</sup> (isotherm) to 50 °C·min<sup>-1</sup>, and retention times of 10 to more than 25 min. The fast pyrolysis model is assumed to give usable results for reaction temperatures from 525 to 800 °C. Retention times in the fast pyrolysis model should be maintained in the 1-2 seconds region.

### Integration of reaction enthalpy

To complete the energy balance of a full pyrolysis model where process gas is used for heating of the reactor, it is important to regard the overall reaction enthalpy of the pyrolysis process. The energy produced or consumed in the process influence the overall balance significantly.

Enthalpy of pyrolysis reactions has been variously suggested to range from endothermic to exothermic, and it has been shown that many factors influence the heat of pyrolysis. Mok et al. (1983) found an endothermic process and an exothermic process, and attributed the main endotherm to the devolatilization of levoglucosan (reaction 5 in Figure 5-VIII) and the main exotherm to the in-situ carbonization of levoglucosan (reaction 6 in Figure 5-VIII) (Brown, 2009; Mok, et al., 1983). There are many reactions partitioning in the degradation of cellulose, and their qualitative contribution to the overall heat of pyrolysis is depicted in Figure 5-VIII. The studies of pyrolysis enthalpy reveal complex correlations between process parameters, product yields, and overall reaction enthalpy and suggest that further investigation of pyrolysis control could improve not only product yields, but also the energy balance of the reaction (Brown, 2009).

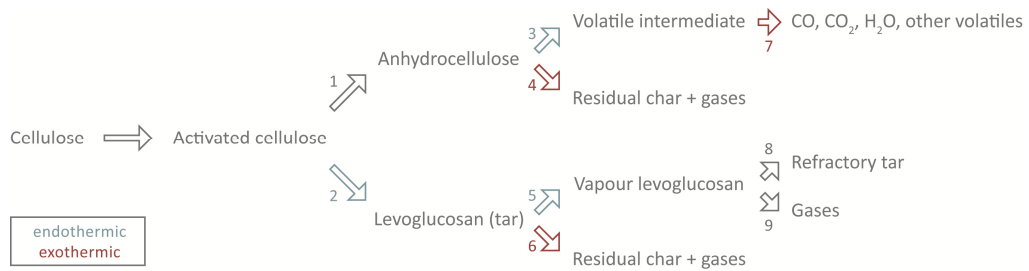


Figure 5-VIII: Detailed reaction pathways for the decomposition of cellulose (Mok, et al., 1983).

Enthalpy integration in kinetic reactors in SuperPro Designer has caused several problems and errors in the model build-up. To limit the work, it has been decided to introduce the impact of process enthalpy as simple as possible. This is done by postponing the enthalpy calculations until after the kinetic reaction, and introducing it in the stoichiometric and cosmetic reactors in section 3 of Figure 5-III. Doing it this way includes enthalpy impact on the energy balance while avoiding many software errors. The way the enthalpy is integrated on the different reactions, and the specific values used in the integration are shown in Table 5-III.

Table 5-III: Enthalpy integration in the SuperPro Designer pyrolysis process model

Main reaction pathway	Partial reaction enthalpy introduction
<b>Cellulose degradation</b>	The reactions in this pathway use enthalpy values from cellulose experiments from the work by (Milosavljevic, et al., 1996) that proposes endothermicity for all reactions <b>evolving volatiles (538 J/g)</b> and exothermicity for reactions leading to <b>char formation (2000 J/g)</b> .
<b>Hemicelluloses degradation</b>	No usable reaction enthalpy values have been found for the pyrolysis of hemicelluloses. Therefore the product specific parameters from the cellulose degradation have been applied. This approach should exclude some of the errors from the use of enthalpy values from cellulose pyrolysis.
<b>Lignin degradation</b>	All reactions in this pathway use the endothermic enthalpy <b>116 J/g</b> . This value is the result of modelling work in fine agreement with experimental results from pyrolysis of Kraft lignin done by Caballero et al. (1996).

Tests of these enthalpy settings in the pyrolysis process model led to satisfying results. The test was done using an average specific heat capacity for the combined product fractions of  $1.6 \text{ J}\cdot\text{g}^{-1}\cdot\text{C}^{-1}$  which is proposed in both (Miller, et al., 1996) and (Kofoed, et al., 1991). Results from a run in the slow pyrolysis model at  $450 \text{ }^\circ\text{C}$  gave a total heat of reaction of  $520 \text{ kJ/kg}$  wheat straw while a test in the fast pyrolysis model at  $525 \text{ }^\circ\text{C}$  gave a total heat of reaction of  $360 \text{ kJ/kg}$  wheat straw. Comparable results

from literature deviate almost as much – from 375 kJ/kg to 500 kJ/kg (Van de Velden, et al., 2010), and therefore the enthalpy settings are assumed viable for further use.

### **Peripheral unit operations, energy circuit and consumption of utilities**

It is now time to set up the rest of the pyrolysis plant in the SuperPro Designer simulation, and integrate use of the process gas for reactor heating. The completion of this step will reveal:

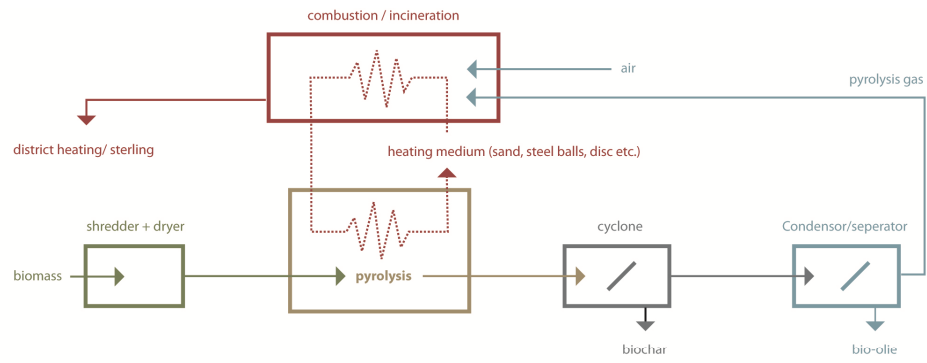
- Which unit operations are necessary, and what utilities are consumed in the process?
- Does a specific process produce enough gas for continuous heating of the reactor?
- What will be the total impact on the overall plant energy balance?

### *Integration of up- and downstream unit operations*

To make as general a model as possible, only the most basic unit operations are included in the model. A preliminary literature review, and discussions with senior scientist Jesper Ahrenfeldt from Risø DTU, has led to the following list of essential unit operations to include (Antal, et al., 2003; Bech, 2008; Bridgwater, et al., 1999; Brown, 2009; Dynamotive, 2009; Hornung, 2009\_B; Henriksen, et al., 2006; Scott, et al., 1999):

- Feedstock dryer (only for fast pyrolysis)
- Feedstock fine shredder (only for fast pyrolysis)
- Screw conveyer or other mechanical transport in main reactor
- Cyclone for ~90 % solids separation
- Filter for final solids (~10 %) removal
- Condenser/quencher for separation of condensable fractions (bio-oil)
- Robust pump with heating to transport gas after separation of condensable fractions
- Incinerator used to burn process gases, and build a hot gas stream for reactor heating
- Pump for air feed to incinerator
- Various heat-exchangers.

Integration of the above mentioned unit operations in a SuperPro Designer process is a lengthy task. In this study it was done in separated phases using the validated pyrolysis reactor as starting points. One section at a time was then added, following the simplified schematics of the two processes in Figure 5-IX. After integration of each new unit operation, the unit parameters as well as stream characteristics and mass balances were evaluated and potentially corrected.



Simplified fast pyrolysis process schematics

Simplified slow pyrolysis process schematics

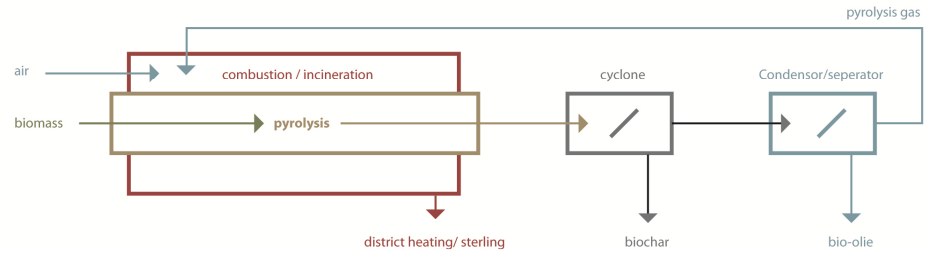


Figure 5-IX: Simplified schematics of a slow- and a fast pyrolysis process

The software has difficulties with integrating a heating stream directly in reactors, and therefore the assumed use of a heat carrier (and thus heat exchanging) has been applied to both processes.

SuperPro Designer depictions of the final fast- and slow pyrolysis process are shown in Figure 5-X and Figure 5-XI:

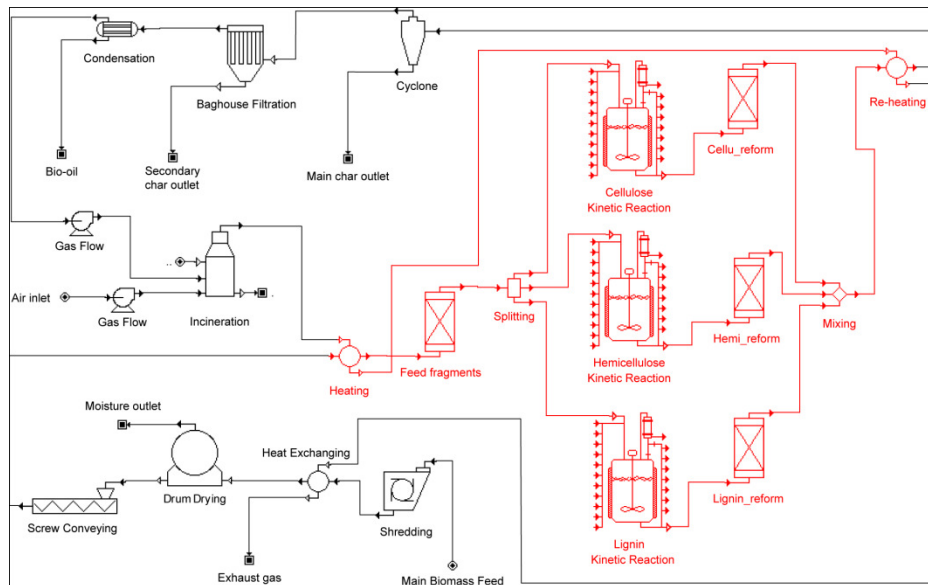


Figure 5-X: SuperPro Designer Fast Pyrolysis Model. The red part of the process is the main pyrolysis reactor.

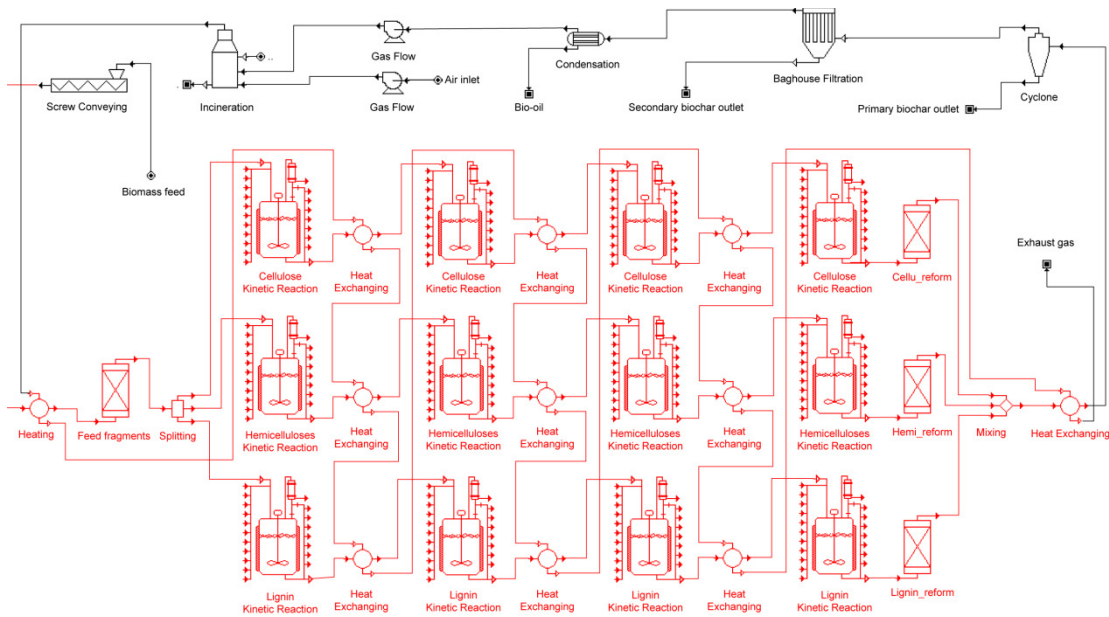


Figure 5-XI: SuperPro Designer Slow Pyrolysis Model. The red part of the process is the main pyrolysis reactor.

#### Integration of process gas for reactor heating

As seen in Figure 5-X and Figure 5-XI, the heat for the pyrolysis reactor is supplied by a gas stream from the incinerator where the complete process gas fraction is combusted. In the fast pyrolysis process, the excess energy in the gas stream is used for drying in a separate unit before it is sent out of the system. In the slow process, the gas is sent out of the system after heating the reactor.

From test runs in SuperPro Designer of the integrated model it seems that most processes (but not all) within the investigated parameter spans yield sufficient gas for integrated heating.

To get an understanding of the system, here is an example with a fast pyrolysis process running with 110 kg moist wheat straw pr hour at 550 °C with 2 seconds retention time. This process yields 27.9 kg process gas pr hour, with an average elemental compositions of these gases of ~39 wt% carbon, 3 wt% hydrogen, and 58 wt% oxygen (see Table 4-VII). Using SuperPro Designer build-in incineration modelling of a gas with this composition and default excess oxygen supply of 35 % ( $\lambda = 1.35$ ) the hot gas stream can heat the pyrolysis reactor, heat exchange with the wet biomass for drying and still have a temperature of more than 400 °C. Same process with a lower peak temperature of 525 °C produces 20.7 kg gas pr hour, influencing the temperature of the exit stream which is now only ~200 °C. Running the process at only 500 °C will yield only 14.7 kg gas pr hour, which is not sufficient for heating the reactor, and will thus require the additional combustion of some biochar or bio-oil or electrical heating to run a continuous process.

#### System boundaries and parameters

To complete energy- and carbon balances, the system in- and outlets are important as they form the system boundaries. The combined list of in- and out streams of the systems is:

- Biomass feed: Inlet stream feeding the process with biomass (wheat straw)
- Air inlet: Inlet stream with air for oxygen supply in incineration operation
- Moisture outlet (fast process only): Removal of water from drying operation
- Primary biochar/ash outlet from cyclone
- Secondary biochar/ash outlet from filter operation
- Bio-oil outlet from condensation/quenching operation
- Exhaust gas stream.

Default SuperPro Designer parameter values have been applied to most of the unit operations. However, some have been altered in agreement with senior scientist Jesper Ahrenfeldt, Risø DTU.

Main changes in the parameters have been made to the power consumption of the conveyer screw in the fast pyrolysis plant. This screw represents the mechanical part of the pyrolysis reactors. For the slow pyrolysis plant, the default value of 0.02 kWh/kg is assumed viable as the mechanical part of the slow pyrolysis plant is a slow turning snail with almost no friction in the bearings. However, for the fast pyrolysis plant there are often substantially more energy used in the reactor mechanics. For the PCR reactor the energy consumption is ~ 0.155 kWh/kg due to the extremely high rotation speeds of the reactor (Bech, 2008). This is thought to be in the high end of fast process energy consumptions, and the value is adjusted to 0.12 kWh/kg.

Changes have also been made in the default value for oxygen supply to the incineration process. It is recommended to use an excess oxygen level of 60 - 100 % ( $\lambda = 1.6 - 2$ ) to avoid  $\text{NO}_x$  creation.

The default heat transfer coefficient of 1500 W/(m<sup>2</sup>·K) of the applied heat exchangers may prove reasonable for the heat exchanging between the hot reactor tube and the fast moving biomass particles in a fast pyrolysis plant like the PCR, but this should probably be adjusted to ~ 50 W/(m<sup>2</sup>·K) in the slow pyrolysis conveyer screw reactor. Regarding the other heat exchangers, something in between could be assumed feasible. However, variations in heat transfer coefficients in SuperPro Designer are compensated by automatic changes in heat exchanger size. As size primarily affects prize, and economics is not a part of this study, no more effort will be put into finding better parameters for the heat exchangers. For a complete list of process parameters from the SuperPro Designer slow- and fast pyrolysis models, see Appendix 5 which also includes more detailed process illustrations.

### **Model result patterns**

It has been shown that the two pyrolysis models yield feasible results for point-data comparison. Based on these tests it is assumed that the two models can be used in an overall evaluation of pyrolysis of wheat straw. However, before initiating this evaluation it would benefit to validate that the models yield feasible result patterns instead of just feasible point data. This validation is attempted by running the two models for a series of process parameters and comparing the diagrams to process patterns known from literature. Modelling of a fast pyrolysis process is shown in Figure 5-XII.



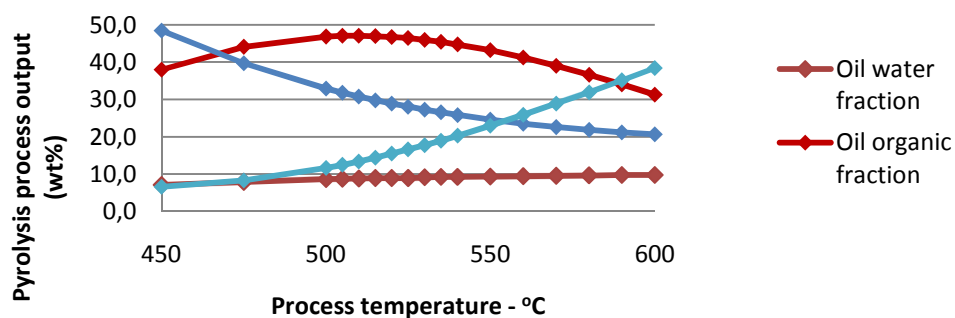


Figure 5-XII: Process pattern for fast pyrolysis of wheat straw with 1.5 seconds retention time and various peak process temperatures

The product yield pattern in Figure 5-XII is qualitatively comparable to the fast pyrolysis product yield diagram in Figure 4-VI. There are obvious quantitative differences between the two, which are due to differences in feedstock. The diagram (Bridgwater, et al., 1999) is based on fast pyrolysis of wood, and the differences in composition between wheat straw and wood pose significant impact on specific product quantities (Mohan, et al., 2006). A similar diagram for modelling of a slow pyrolysis of wheat straw is given in Figure 5-XIII. The process is run with same solids retention of 30 min consisting of 10 min drying at 110 °C and 20 min heating at heating rates from  $\sim 12^{\circ}\text{C}\cdot\text{min}^{-1}$  to  $19.5^{\circ}\text{C}\cdot\text{min}^{-1}$  with correlated changes in peak temperatures. This approach which varies the process in both heating rates and the correlated peak temperature is used to investigate the largest possible span of processes with the same retention time and reactor size.

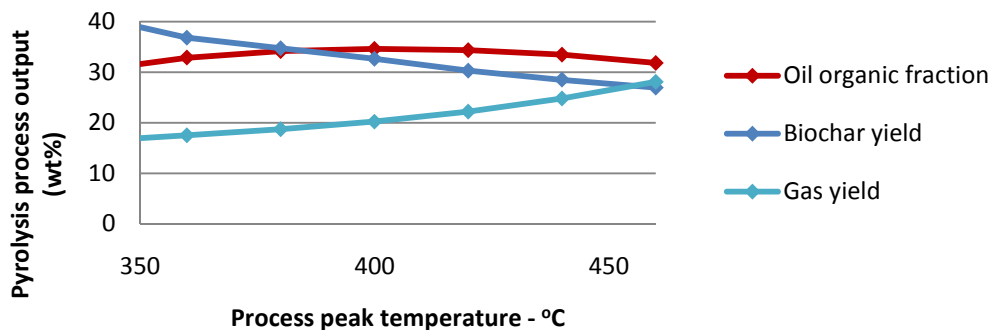


Figure 5-XIII: Process pattern for slow pyrolysis of wheat straw with 30 min retention (10 min drying and 20 min heating) and various heating rates to give various peak temperatures

The best empirical data found for validating the reaction pattern of the slow pyrolysis model, was from an intermediate pyrolysis process by Hornung (2008) shown in Figure 5-XIV. The comparison is somewhat difficult as the intermediate process ran on special dry wheat straw pellets with a solid retention time of 2 minutes and unknown heating rates. However, the qualitative behaviour of the two processes is definitely comparable and follows the same pattern.

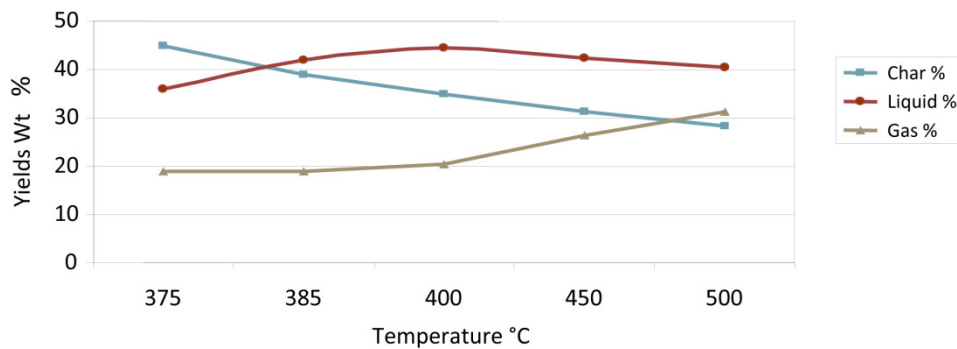


Figure 5-XIV: Intermediate pyrolysis of dry wheat straw pellets with various process temperatures (Hornung, 2008)

To see how much influence retention time has on product yields in the slow pyrolysis process model a few tests have been done. Both isotherm processes with varying retention times as well as processes with variations in both heating rates and retention times have been tested. The results are enclosed in Appendix 4 and show that the slow pyrolysis model give very small changes in product yields for retention times from 10 min and above. Changes in heating rate give similar small changes for variations above  $5\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$  and imply that care should be taken in using these features of the slow pyrolysis model. Due to the limitations of the slow pyrolysis model, focus will be on temperature variations instead of retention time variations for the remainder of the work.

### Model simplifications

The build of the models have included a long list of assumptions and simplifications. To guide future work on improvements, and to understand the origin of some of the model deviations and uncertainties, it is important to recognize the nature of some of the essential simplifications. For the build of the pyrolysis model, these simplifications have included among others:

- No particle size calculations. Particle size is not included in the model, even though this is very important for real life processes. In fast pyrolysis, particles have to be very small to get a uniform and complete reaction during the short residence in the reactor. In slow pyrolysis processes larger particles are usable, as there is longer time for complete reaction. In a detailed slow pyrolysis, model temperature gradients across large particles and diffusion barriers should be assessed (Miller, et al., 1996).
- No sweep gas inclusion. In many pyrolysis processes, sweep gas (e.g. nitrogen) is used to remove volatiles from the reactor before equilibrium and secondary reactions occur. This is especially important in fast- and intermediate pyrolysis processes where focus is on enhancement of the liquid fraction (Hornung, 2008; Brown, 2009). In SuperPro Designer it has no influence on the reactor kinetics or the product yields whether sweep gas is applied or not. To simplify the simulations it has therefore been omitted, but to enhance the possibilities of controlling the pyrolysis process it could be included in future work.
- Reactor variations. Specific design of the pyrolysis reactors (PCR, Fluid bed, Abrasive reactors, etc.) has not been integrated in the model. The

large differences between reactor types (see section 0) will influence the energy balance in real life.

- Equipment limitations. The correct use of modelled unit operations requires great knowledge about the specific operation. Unknowns such as the efficiency of a heat exchanger depending on type, stream characteristics and fouling, or the decreased efficiency and endurance of a filter bag due to high temperature, etc. are factors that influence the overall energy and carbon balances. In this work much equipment is assumed ideal, or applied with default values, and this will often produce favourable results compared to real experience.

## 6 Incubation study

The overall purpose of the incubation study is to investigate the influence of pyrolysis process parameters on the degradation of biochar in soil, using a Danish wheat straw feedstock, Danish soil samples, and Danish climatic conditions. With these data, it will be possible to make a simplified quantification of the sequestration potential of a given char from knowledge about the process design and parameters in a Danish wheat straw scenario. The experiments, data collection and calculations are done in collaboration with PhD student Esben W. Bruun.

The experiments are done by mixing different biochars with soil, and measuring the CO<sub>2</sub>-flux (respiration + abiotic degradation) from the samples under controlled conditions to get a measure of the degradability of the char. The degradation rate of the biochar is obtained by subtracting the CO<sub>2</sub> flux from a reference (soil without biochar) from incubations with biochar.

### 6.1 Materials and methods

#### Experimental setup

The incubation experiment was conducted in two parallel sessions – one comparing an untreated straw sample to a slow and fast pyrolysis char produced at the same process temperature, and one comparing chars produced with variations in pyrolysis temperature in the same process.

#### *Pyrolysis*

The feedstock for the biochar samples was conventional Danish wheat straw (*Triticum sp.*) with a moisture content of 6.2 wt% and an ash content of 6.02 wt%. The straw samples were dried and grinded to ~2 mm before pyrolysis. The fast pyrolysis was carried out at the Department of Chemical and Biochemical Engineering, DTU, Lyngby in a pilot scale PCR (Pyrolysis Centrifugal Reactor) like the one illustrated in Figure 4-I. For additional information about the PCR used for the pyrolysis see Bech (2008). The fast pyrolysis was done at 475 °C, 500 °C, 525 °C, 550 °C, and 575 °C. The slow pyrolysis biochar was prepared by the Biomass Gasification group under the Biosystems Division at Risø DTU. A sample of the same wheat straw was pyrolysed in an electrically heated oven in a process similar to the following: Heating rate of 6 °C·min<sup>-1</sup>, a total solids residence time ~2 hours, constant nitrogen gas sweep, and a max temperature of 525 °C (Ahrenfeldt, et al., 2005).

#### *Incubation experiment*

The biochar was amended to soil collected in the top 25 cm in a Danish agricultural field near Risø characterized as a sandy loam (Typic Hapludalf) with 11% clay, 14% silt, 49% fine sand and 25% coarse sand (Hauggaard-Nielsen, et al., 2001). The soil was sieved to a max grain size of 2 mm and the soil moisture was measured. 40 g soil (38 g dry weight) was then mixed with either 2 g biochar from the five fast pyrolysis samples, 2 g biochar from the slow pyrolysis, or 2 g wheat straw in 100 ml containers with perforated rubber lids (ID = 48mm). Finally, the water content was adjusted to 30 % of water holding capacity (WHC). 4 pure soil reference samples with water content at 30 % of WHC were also prepared. All CO<sub>2</sub> flux measurements were done in 4 replicates.

Soil samples mixed with varying types of biochar are incubated at constant room temperature for 70-100 days with a water content kept constant at ~30 % of WHC. Water content is adjusted by weighing the samples regularly and compensating for evaporated water.

### **Biochar analysis**

The microbial carbon dioxide (CO<sub>2</sub>) respiration from the incubated samples was measured using infra-red gas analysis (LICOR 8100). Measurements were conducted manually once per day, five days per week in the first period, and then on weekly basis.

The bulk composition of the biochar was determined using classical wet chemical methods. The biochar was subjected to a strong acid hydrolysis after which the hydrolysates were filtrated, and the lignin plus char content is determined as the weight of the filter cake subtracted its ash content. The composition of released carbohydrates in the filtrate is determined by a combination of HPLC-analysis and conversion into acetates with subsequent GCMS analysis (Bruun, et al., 2009). Results of the analysis are given in Table 6-I.

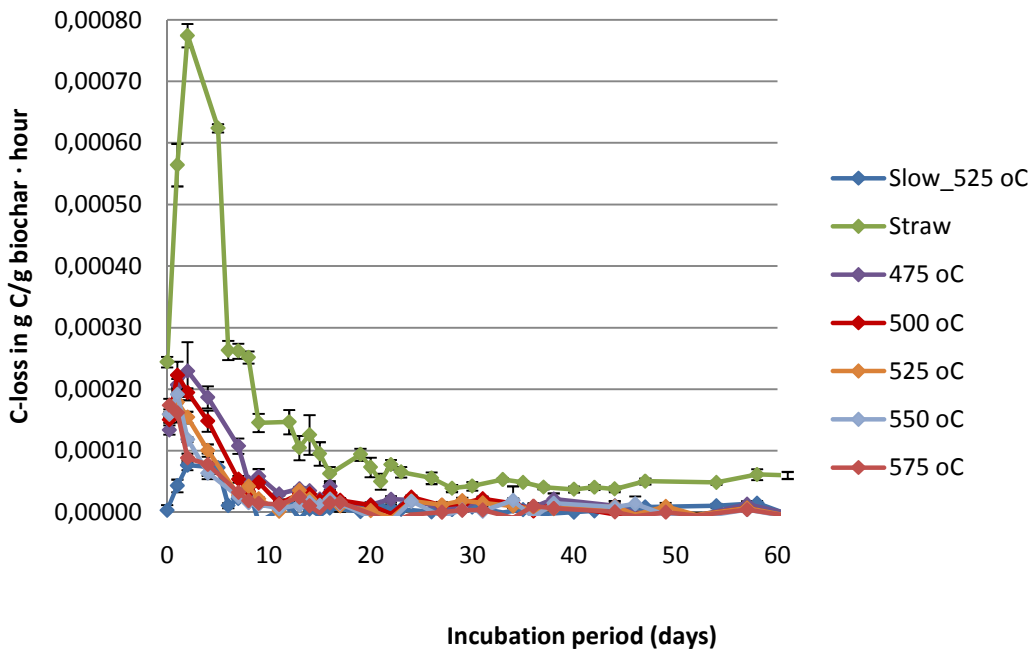
## **6.2 Results and discussion**

This short term study may give key knowledge about the influence of possible labile biochar fractions, and thereby indications about the relations between char characteristics and the long term stability.

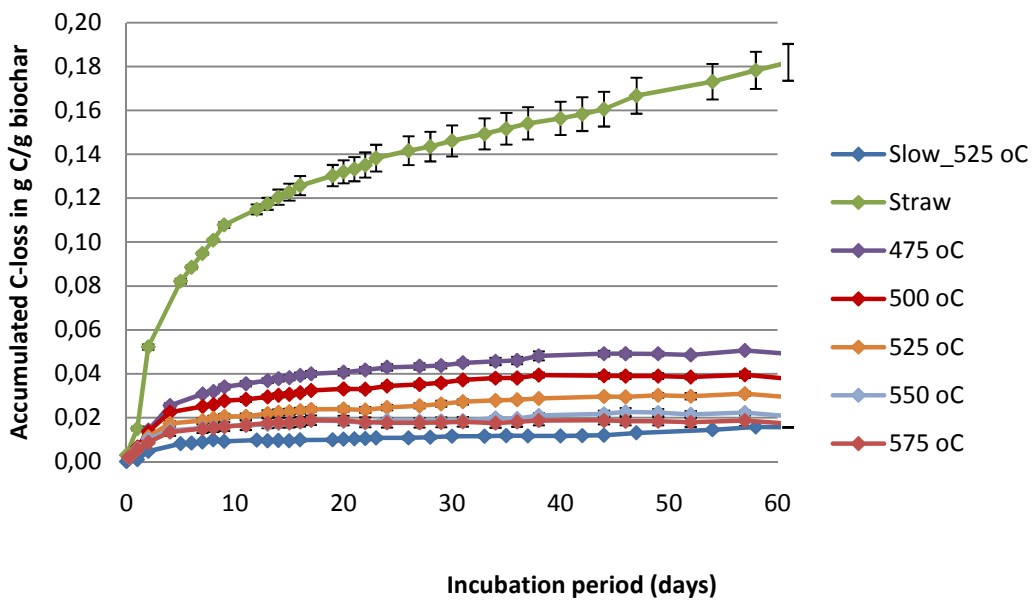
Incubation data from both experiments is presented in Figure 6-I - a and b. Fluxes are calculated with initial subtraction of the reference soil flux to focus on char degradation. Averages of 4 replicates are used in the calculations. The calculations are shown in example in Appendix 6.

The results of both experiments show distinctive degradation patterns. There are more detailed versions of both graphs in Appendix 7.

All the incubation studies show a rapid loss of carbon in the first 5-10 days succeeded by a decline in the C-loss rates until they reach almost zero additional C-loss after 50-70 days. It is suggested by a number of studies that this pattern is due to a fast degradation of a labile fraction of the char, while another is recalcitrant and stable on the long term (Hamer, et al., 2004; Steiner, et al., 2008).



A: Changes in C-loss rate (g carbon / g biochar) from soil samples as a function of time



B: Accumulated C-loss as g carbon /g biochar as function of time

Figure 6-I: Investigation of biochar stability through incubation studies

From Figure 6-I it is evident that all char types are much more recalcitrant than the straw sample, and that the stability increases with temperature of the pyrolysis process. It also looks as if biochar from a slow pyrolysis process is more stable than biochar from fast pyrolysis made under same or higher process temperatures. To examine what fractions of the char that are related to the shift in stability char bulk analysis was conducted as described earlier. The results of the analysis are given in Table 6-I, and they show a clear increase in remaining cellulose and hemicelluloses

with lower pyrolysis temperatures. These fractions seem to be the char fraction degraded in the first days after mixing the char with soil. Increasing the temperature of the fast pyrolysis converts more of these fractions, and yields a more recalcitrant biochar. Unfortunately, the slow pyrolysis biochar has not been analysed in this way, but according to literature the long solid residence times in the slow pyrolysis process are an even better way to fully convert the biomass constituents to recalcitrant biochar (Lehmann, 2007). This is important to assess in the evaluation of the pyrolysis process model later on in the report.

The column to the right in Table 3-I shows the accumulated level of carbon lost from the different samples at the end of the incubation period. The values are based on the data in Figure 6-I b.

Table 6-I: Biochar analysis. Adapted from Bruun et al. (2009)

	Cellulose (wt %)	Hemicelluloses (wt %)	Lignin and char (wt %)	Ash (%)	Biochar C-loss (g C/g biochar)
Biochar (475 °C)	30.0	5.5	46.3	15.8	0.049
Biochar (500 °C)	16.0	3.0	59.9	20.1	0.038
Biochar (525 °C)	7.4	1.4	69.0	21.6	0.029
Biochar (550 °C)	4.2	1.5	66.0	26.4	0.021
Biochar (575 °C)	2.7	0.8	66.4	27.9	0.017
Biochar, slow (525 °C)	-	-	-	-	0.015

For modelling purposes, it is optimal to correlate the biochar content of cellulose and hemicellulose to the stability of the char. To do this, it is essential first to evaluate how well the pyrolysis process model predicts cellulose and hemicelluloses fractions in the char. This is done by running simulations with process parameters identical with the parameters used to produce the char analysed in Table 6-I. Simulations were done with cellulose and hemicelluloses combined in one labile fraction and a model retention time for solids of 1 second. Based on the comparison between modelled and experimental values in Figure 6-II, it is assumed that the pyrolysis process model is suited for predicting labile fractions in biochar. The average deviation for the 5 value comparisons was 2.9 wt%, the largest was 5.7 wt% and the smallest 1.1 wt%. Validation was only possible for fast pyrolysis processes due to a lack of data from slow pyrolysis biochar, but it is assumed to apply for slow pyrolysis processes as well, as char from this process often contains little or no labile fractions at all (Lehmann, 2007).

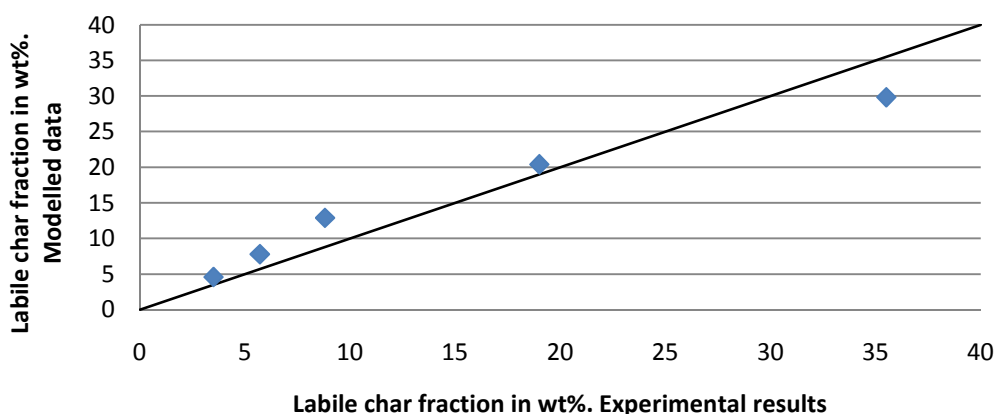


Figure 6-II: Validation of pyrolysis process model quality for prediction of residual fractions of cellulose and hemicelluloses in produced biochar.

Having validated the models ability to predict labile fractions in biochar, the next step is to correlate this to char stability values. This is done in Figure 6-III. The use of this correlation in the scenario section of the report is based on the assumption that the stable levels indicated by Figure 6-I b will hold for a period of time significant enough to qualify as a carbon sink. Whether this period is decades, centuries or more is out of the scope of this report to investigate.

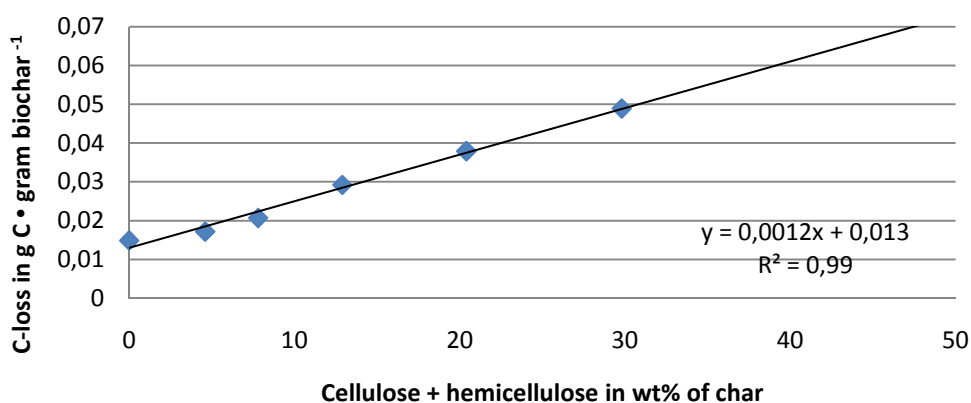


Figure 6-III: Correlation between biochar labile fraction and stability

The linearity in Figure 6-III includes all 5 biochar samples from the experiment on different production temperatures, as well as the char produced with slow pyrolysis (labile fraction ~0 wt% according to model and literature). The fit of the correlation to the data is very strong.

With the stability correlation from Figure 6-III the study of biochar stability for modelling purposes is concluded. The next section of the report will utilize all the collected information and the proposed correlations together with the pyrolysis process model to estimate carbon balances in Danish wheat straw pyrolysis scenarios.



## 7 Process evaluation: mass- and energy balances

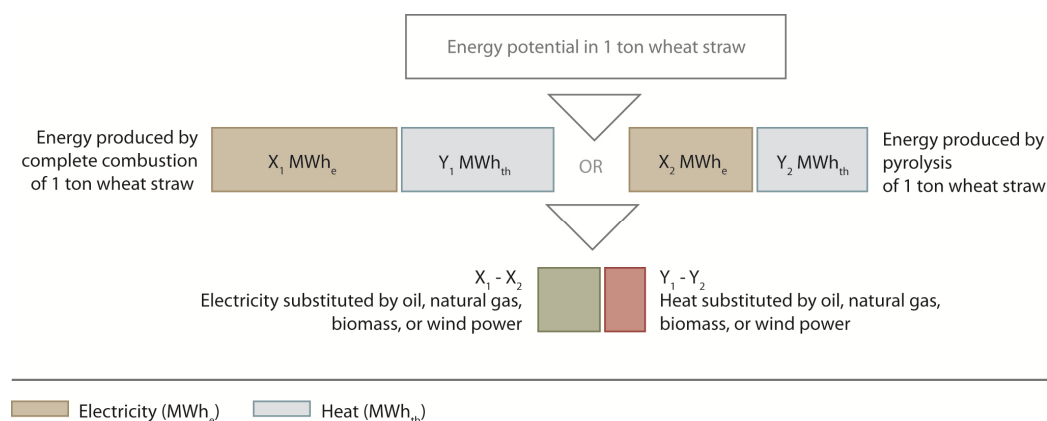
The goal of this section is to give viable estimations of the overall energy production and coherent carbon-balance in a few exemplified wheat straw pyrolysis processes.

### 7.1 Preliminary assumptions and considerations

Environmental aspects and pollution potential of different technologies is not discussed beyond CO<sub>2</sub>-emissions. This would require a much higher complexity level, and is out of the scope of this report. Additional simplifications and assumptions are listed in the following:

#### *Quantifying amount of substitution energy*

When burying biochar, a part of the biomass energy potential is not fulfilled in relation to end user consumption. In Denmark today, a significant amount of straw is used for co-firing in coal-plants or fired directly into special straw-fired plants. This is a difficult process, but it is well tested and will therefore act as the “full biomass energy potential” for the remaining work. Thus, the overall energy calculations are done following the pattern in Figure 7-I. This approach determinates the amount of substitution energy necessary to account for the unreleased energy potential from 1 ton of wheat straw pyrolysed in a specific process. The values X1, Y1 are dependent on the efficiency of a given straw fired plant, where values X2 and Y2 are dependent on the product distributions and energy requirements of the pyrolysis process as well as the efficiency of the plant burning the pyrolysis oil for electricity and heat.



*Figure 7-I: Overall calculation pattern for determination of substitution energy quantity for a given pyrolysis process*

The combined amount of X1 and Y1 will always be larger than X2 and Y2 as long as the pyrolysis process produces biochar, and use the pyrolysis gases in the process. Therefore it can be assumed that some amount of energy substitution will always be necessary. The energy source chosen for a specific substitution will be dependent on the scenario in which the demand arises (see below).

### *Carbon balances and system boundaries*

Even though there is still burned a lot of coal in the Danish energy sector, the process is under pressure due to the extremely high carbon costs of coal energy (see Table 3-I), and the production of energy based on coal is declining (1994: 120 PJ, 2007: 72 PJ, 2008: 60 PJ) (Energistyrelsen, 2009). For the remainder of the report it is assumed that the system boundaries are set on a national level, but that the presence of coal is being diminished. The possible energy sources to replace lost energy from biochar sequestration are instead: oil, natural gas, biomass, wind power and an average based on the Danish energy sector in 2007 (see Table 3-I).

### *Limitations on the included biochar benefits*

Biochar is used in these calculations exclusively for building a carbon sink in the soil. The possible effects of biochar amendment on emissions of N<sub>2</sub>O and CH<sub>4</sub> from soil are not integrated in the assessment. To read more on this topic see section 0 or Zwieter et al. (2009). Amendment of biochar in farm soil is by many expected to reduce the amount of fertilizer needed in the biomass production. This could also affect the overall carbon balance effect, but the potential impact is ignored in the carbon-balance calculations to limit the extent of this report. See also (Laird, et al., 2009; Lehmann, et al., 2009; Thies, et al., 2009). The effect of the above mentioned biochar characteristics on the carbon balance are qualitatively mentioned in the end of this chapter. For an example on quantification see Gaunt et al. (2008).

## **7.2 Energy production in Denmark: Three scenarios**

It is decided to build three simple scenarios within the Danish energy sector, to test the carbon balance in energy production from pyrolysis of wheat straw. This is done to make sure that the results obtained from the calculations are relatively robust, and also to render the selection of a given set of parameters probable to imitate a realistic situation. Descriptions of the scenarios are given in Table 7-I. The choice of scenario includes the following considerations:

- What types of facilities are available for combustion of baled wheat straw and bio-oil respectively? Choices in this category are based mainly on an official Danish report that describes all available energy production technologies in the Danish energy sector (Energistyrelsen, 1995). Where data from this report was insufficient, additional references was included.

**Straw:** For a large centralized straw fired facility it is decided to use a Low Temperature Circulating Fluidised Bed (LT\_CFB). This is a gasification technology that is capable of large scale conversion of many different biomasses – including straw, with very high efficiency and good conditions for reuse of the ash fraction (Stoholm et. al., 2010).

Information about small scale sterling engines and correlated energy production setups is available online (StirlingDK, 2009). It is assumed possible to convert the wheat straw in an updraft gasifier + Stirling engine with no penalty to wood. This is a severe assumption as the high ash content of wheat straw can melt to cinder under high temperatures, and thus foul the equipment.

**Bio-oil:** For combustion of pyrolysis oil, 2 scenarios assume co-firing with natural gas as described from large scale testing in section 0. This method is assumed valid for a 350 MWe plant producing energy from bio-oil and natural gas. The electric efficiency of the plant is assumed to be ~41% of the bio-oil energy content calculated by estimate from work by Wagenaar et al. (2008). This value is comparable to efficiencies for gas fired Heat and Power plants in Denmark with total efficiencies around 91% and electrical efficiencies around 41% (Rambøll, 2008). The last scenario combusts bio-oil in a boiler connected to a sterling engine. In this process energy efficiencies are assumed to be the same as for combustion of wood in the same boiler (StirlingDK, 2009). The last process could be driven with gas combustion instead of the intermediate step of oil production, but that possibility is not included in this work.

- What are the regional settings? How far is the wheat straw production/pyrolysis plant from the combustion facility? Values in this category are strictly imaginative, and used primarily to integrate transport distance in the carbon-balance assessment.
- Losses of electricity and heat in local grid systems? The basis values used are 21 % heat loss in district heating grids which is used in a report by Rambøll Denmark A/S called Varmeplan Denmark (Heat plan Denmark) and 5 % electricity loss (senior scientist Ulrik Henriksen, Risø DTU).
- What kinds of energy sources are available for substitution of lost energy potential? For all scenarios, energy from more than one source is assessed, and to consider the relationship between the different substitution energies, all four are assessed in Scenario 1.
- What are the scenario impacts on the pyrolysis process and the production of the wheat straw? This may have only minor influence on the overall balance, but it is assumed important enough to incorporate.

*Table 7-I: Descriptions of scenario settings for assessment of carbon-balances in energy production with pyrolysis*

	<b>Scenario 1:</b> Centralized combustion	<b>Scenario 2:</b> De-centralized combustion	<b>Scenario 3:</b> Local combustion
Straw combustion facility	Large, straw-fired LT- CFB Size: 5-100 MW 45% electric efficiency 50% heat efficiency	Small straw-fired steam turbine plant. Size: 5-50 MW 26% electric efficiency 59% heat efficiency	Updraft gasifier with Stirling engine. Size: 200kW+ 17% electric efficiency 68% heat efficiency

Pyrolysis oil combustion facility	Co-firing of pyrolysis oil with natural gas in Combined Cycle Plant. Size: 75-400 MW 41% electric efficiency 50% heat efficiency	Co-firing of pyrolysis oil with natural gas in small gas turbines. Size: 5-15 MW 30% electric efficiency 55% heat efficiency	Oil boiler connected with sterling engine. Size: 200kW+ 12% electric efficiency 74% heat efficiency
Distance to combustion facility	100 km	20 km	0 km
Loss of electricity and heat in user grids	5 % electricity 21 % heat	5 % electricity 21 % heat	5 % electricity 21 % heat
Substitution energy available	Oil/Natural gas/biomass/wind power	Oil/Natural gas/biomass/wind power	Oil/Natural gas/biomass/wind power
Impact on pyrolysis process	90% of excess heat from pyrolysis used for district heating. Back-up energy for pyrolysis deducted from electricity production with 5% penalty to grid losses.	Same as for centralized scenario.	90% of excess heat from pyrolysis contributes to Stirling engine. Back-up energy for pyrolysis is taken from oil combustion with a 10% penalty.
Impact on wheat straw production and handling	Normal growth and handling of wheat straw for combustion. For pyrolysis, wrapping of the bales are omitted, but biochar distribution is included.	Same as for centralized scenario.	Straw bales are not wrapped for either process. Biochar is distributed after pyrolysis.

In addition to the three scenarios above there is also a special case of Scenario 3. This scenario is based on the work of (Bech, 2008), and it involves an in-situ fast pyrolysis process where the pyrolysis plant is combined with the harvester. The biochar is thus amended directly into the soil and bio-oil is collected during harvesting and taken home to the farm for combustion. Transporting the oil is estimated as half the cost of transporting the straw and this approach will therefore save pressing, transportation, and storing of straw bales as well as subsequent distribution of the char. The concept is highly hypothetical. A brief description of the scenario is given in Table 7-II. All considerations omitted from the table are similar to Scenario 3.

Table 7-II: Descriptions of In-situ scenario for assessment of carbon-balances in energy production with pyrolysis

**Scenario 3-II: Local combustion, In-situ pyrolysis**

Impact on pyrolysis process	No use of excess energy in exhaust gas, and no back-up energy available for pyrolysis with insufficient gas production – this results in a process temperature requirement of 525 °C or more. Max power consumption from pyrolysis process 100 kW. Only fast pyrolysis available.
Impact on wheat straw production and handling	No pressing, wrapping or transportation of straw, or biochar distribution on the fields. Oil is transported home at half the cost of transporting the straw.

The reason for the limitations in the In-situ pyrolysis scenario is based on the assumption that a mobile unit can only be expected to supply a certain amount of energy for the processes it takes part in. If the In-situ process was of the fluid bed type with a capacity of 10t·h<sup>-1</sup>, then the power input required for the process would be approximately 440 kW. This is in addition to the requirements from harvesting. Only the largest agricultural tractors are rated above 150 kW and all together this will put some critical restrains on the process design and capacity (Bech, 2008).

Many additional parameters could be included to distinguish the scenarios further: e.g. biochar effect on fertilizer consumption, local geography, or wheat straw availability. It could also prove beneficial to consider additional or alternative scenarios, but for the purpose of this work the scenarios and parameters discussed above are assumed sufficient to make a robust assessment of the overall carbon-balance of the pyrolysis process.

**7.3 Overall carbon-balance calculation model**

The overall calculation model is based on the carbon flux arrows from Figure 2-III. However, it has been decided to set carbon balance system boundaries on a national level, and therefore an extra carbon flux, arrow J, is included to account for the carbon cost of substitution energy. Carbon flux E is subtracted from the main flux arrow into the system (atmospheric carbon), and a couple of smaller fluxes are combined leaving the final balance calculations as in illustrated in Figure 7-II.

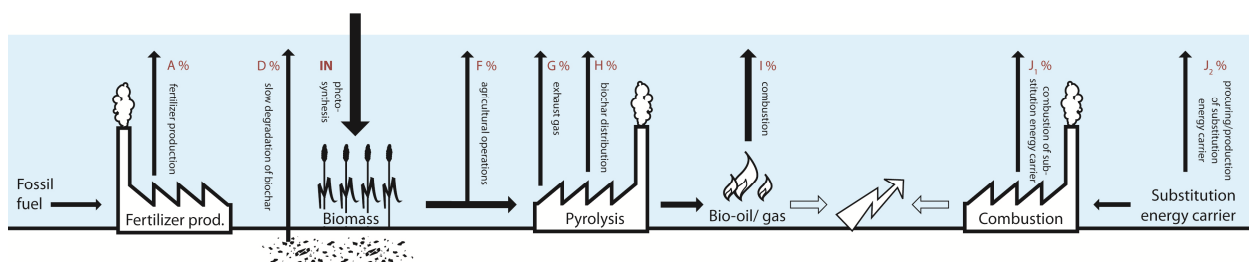


Figure 7-II: Carbon fluxes included in overall carbon balance assessment

The fluxes in Figure 7-II are combined with the scenario variables from Table 7-I/Table 7-II, the energy substitution principle from Figure 7-I, and the SuperPro Designer pyrolysis process model to form the final calculation pattern for carbon balance assessments illustrated in Figure 7-III. Now the task is to fill in parameters, model results, and correlations in the different boxes. This is explained briefly for each section below.

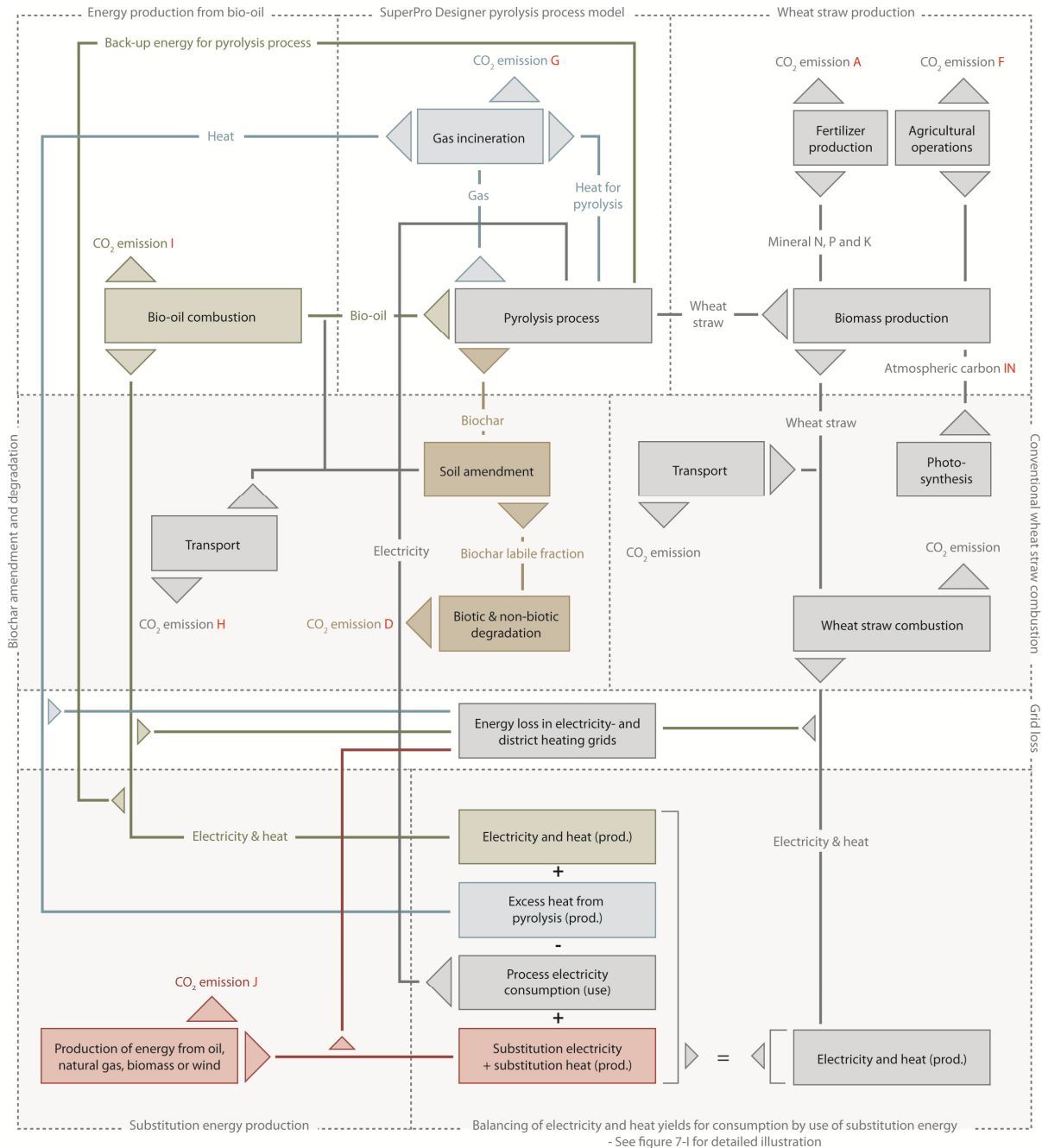


Figure 7-III: Overall calculation pattern for assessment of pyrolysis process combined energy- and carbon-balances

## Sectional description of the carbon-balance calculations

The principle of using substitution energy in the evaluation of carbon-costs founds the basis for the split calculations above with two pathways from the biomass. The sections marked by dotted lines in Figure 7-III are described below, and parameters and correlation equations that are used in the calculations are given for all three scenarios (with reference) in Appendix 8.

### *Wheat straw production*

The production of wheat straw is included with fertilizer use, a series of standard agricultural operations (ploughing, seeding, etc.), and capturing of atmospheric carbon by photosynthesis. The calculations in this section include many values based on average Danish wheat straw production (Jørgensen, et al., 2004; Miljø&Energi\_Ministeriet, 2001; Statistikbanken, 2010\_B). One of the most important parameters in the calculations in this section is the weighing of the production costs on grain versus straw. Allocation of the costs is, in this report, based simply on weight distribution. For every 1 ton of collectable straw produced on average in Danish agriculture, 1.5 ton of grain is produced. Therefore 40% of the total resources spent in the combined production of grain and straw is allocated to the straw (Miljø&Energi\_Ministeriet, 2001). The calculations in this section are to a large extent unaffected by scenario changes.

### *Conventional wheat straw combustion*

Calculations in this section are based mainly on power plant efficiencies reported in Table 7-I, and are therefore highly sensitive to scenario changes. Combining the energy yields from the combustion of the straw and the results from the previous section yields the carbon balance for the carbon-neutral energy scenario. Carbon-balances for the three scenarios are given in Table 7-III.

*Table 7-III: Carbon-balances for “carbon-neutral” energy from combustion of wheat straw*

	Energy yield	Carbon balance
<b>Scenario 1: Centralized</b>	3.9 MWh per ton straw (2.0 MWh <sub>e</sub> and 1.9 MWh <sub>th</sub> )	37 kg CO <sub>2</sub> /MWh
<b>Scenario 2: Decentralized</b>	3.4 MWh per ton straw (1.2 MWh <sub>e</sub> and 2.2 MWh <sub>th</sub> )	25 kg CO <sub>2</sub> /MWh
<b>Scenario 3: Local</b>	3.3 MWh per ton straw (0.8 MWh <sub>e</sub> and 2.5 MWh <sub>th</sub> )	20 kg CO <sub>2</sub> /MWh

It is clear from the results in Table 7-III that energy production from combustion of wheat straw within the settings of this report move closer to a carbon-neutral level as the process is decentralized, but that the largest energy production is at the largest scale. If the calculation method was based on introduction of new biomass, repression of fossil fuels might give the centralized plant the best carbon-balance as well as the highest energy production.

### SuperPro Designer pyrolysis process model

Concept, development, and use of this model have been described in detail in chapter 5. The model calculates the following from process parameters (temperature, retention, heating rate, and biomass composition): Biochar yield (with labile fraction), Bio-oil yield (with water content), Process gas yield (used for heating of the pyrolysis reactor), Plant electricity consumption, and Energy balance in process (excess energy >< insufficient energy).

Using only process peak temperature as variable makes it simple to draw diagrams for the five outputs with varying process setups. These diagrams are shown in Figure 7-IV. All product yield curves follow the primary axis with unit *kg product per ton straw* and the Plant heat balance- and electricity consumption curves follow the secondary axis with unit *kWh*.

The curves in the diagrams have subsequently been divided into sections and trend lines were fitted as 3<sup>rd</sup> to 6<sup>th</sup> degree polynomials with R<sup>2</sup> goodness-of-fit values from 0.97 to 0.99 (1 is optimal). The equations for the curve segments were finally incorporated in the overall calculations. This provided quick and direct calculation of all five process outputs from changes in a single variable, process peak temperature, and the high flexibility in the calculation sequence made it simple to shift between the different scenarios. The polynomial equations are given in Appendix 8 with a few decimals, along with the rest of the parameters and correlations used in the calculations.

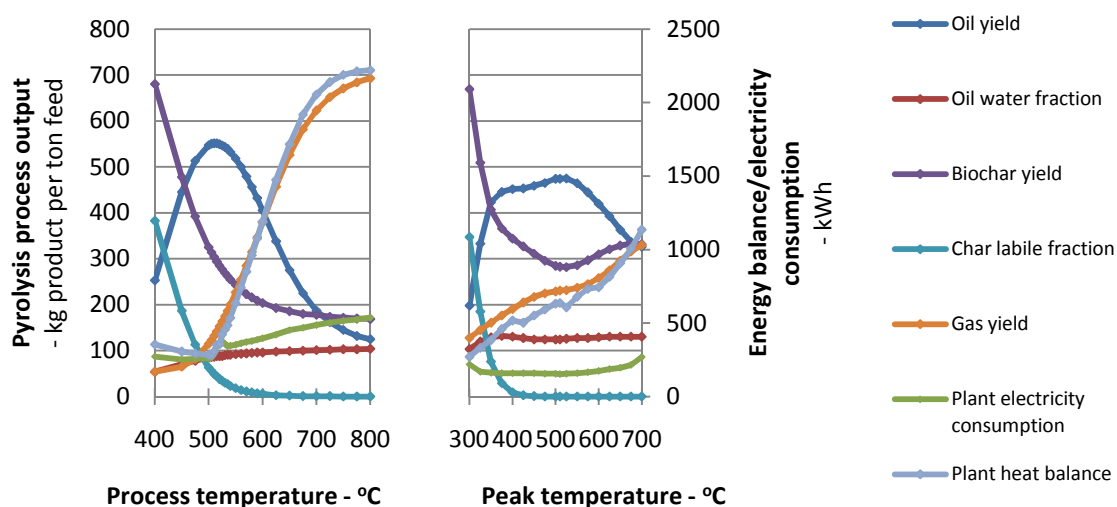


Figure 7-IV: SuperPro Designer process output diagrams. On the left is a fast pyrolysis process with 1.5 seconds retention time and varying process temperatures. On the right is a slow pyrolysis process with 30 minutes total retention (incl. drying) and varying peak process temperatures (and correlated heating rates)

### Energy production from bio-oil

This section functions as a parallel to the “Conventional wheat straw combustion” calculations. The output from this section is based on the bio-oil yield and water content from the pyrolysis model, as well as the scenario specific bio-oil combustion facility.



### *Biochar amendment and degradation*

This section uses the correlation founded in chapter 6 that relates the amount of labile material in the biochar to a carbon-loss from degradation of the char over time. This correlation has only been validated for ~100 days, but the pattern of the degradation data curve renders it feasible that the long term degradation will be somewhat similar. The other main variable in this part of the calculations are amount of biochar amended to the soil, and the labile phase in wt% of the biochar. These data are extracted from the SuperPro Designer simulation result curves.

### *Grid loss*

It was decided to incorporate grid losses in the calculations. The effect of grid losses is based on standard values that could be expected in Danish electricity- and district heating grids. The suggested values were 5% loss in electric grid suggested by Ulrik Henriksen, senior scientist at Risø DTU and 21% loss in district heating grid (Rambøll, 2008). These values are used for energy transport from the various production facilities including the application of substitution energy.

### *Substitution energy production*

The carbon-cost of substitution energy is based on average values for procuring and consuming oil, natural gas, and biomass (and wind energy, assumed zero) in the Danish energy sector based on values from 2001 (Miljø&Energi\_Ministeriet, 2001). The costs are influenced by the kind of substitution energy chosen, the amount of electricity and thermal energy required, and the losses in electricity- and district heating grids. It is assumed that electricity and heat can be substituted independently of each other.

It is important to notice that yields in the production of electricity and thermal energy also vary with the scenarios. Electricity production is strongly favoured at centralized facilities, and could be even higher than suggested in this report. Modern power plants (coal, gas, biomass etc.) have the option to operate in a condensing mode where extra electricity is produced from the energy extracted by condensing water vapour. However, this cancels the possibility to produce district heating, and is in this report omitted as a special case. In future work it could be interesting to include a seasonal approach to the different scenarios comparing them summer, winter, spring, autumn and a yearly average of heat- and electricity consumption.

### *Balancing the yields of electricity and district heating for consumption*

In this central calculation section, the amount of substitution energy required for balancing the pyrolysis process to the complete combustion is calculated. The following parameters influence the balance:

- The amount of electricity and heat produced by complete combustion of the wheat straw in a non-condensing mode
- The amount of heat and electricity produced by combustion of the bio-oil in a non-condensing mode
- The heat used or generated by the pyrolysis process from either excess energy in the exhaust stream or insufficient energy for completing the pyrolysis process
- The electricity used in the pyrolysis process
- The loss in electric- and district heating grids.

After having adjusted the amount of substitution energy necessary to balance the two processes, the complete carbon balance can be calculated. It is done simply by adding

the CO<sub>2</sub>-emissions in flux A, D, F, G, H, I, and J to see if the sum is more or less than the CO<sub>2</sub> captured by photosynthesis in stream IN. Dividing this carbon-price with the amount of energy produced in the process, the result is the overall carbon-balance per unit of energy.

### Carbon-balance results in three Danish scenarios

A calculator has been build from the pattern described in the first part of section 7.3. The calculator has been used to test the overall carbon-balances a slow- and a fast pyrolysis of wheat straw for energy production in three different scenarios within the Danish energy sector. The pyrolysis processes are tested on all three scenarios with the parameters described in Table 7-IV.

Table 7-IV: Pyrolysis process settings for carbon-balance calculations

	Slow pyrolysis process	Fast pyrolysis process
<b>Solid retention time</b>	30 min	1,5 sec
<b>Feedstock composition</b>	39.4 wt% cellulose (dry), 37.2 wt% hemicelluloses (dry) 16.6 wt% lignin (dry), 6.8 wt% ash (dry) and 6.2 wt% water	
<b>Process capacity</b>	1 ton/hour	
<b>Process peak temperature</b>	Complete: 300 - 700 °C Feasible: 350 - 550 °C	Complete: 400 - 800 °C Feasible: 450 - 650 °C
<b>Heating rate</b>	Complete: 9.5 - 29.5 °C·min <sup>-1</sup> Feasible: 12 - 22 °C·min <sup>-1</sup>	Isotherm

Results from the carbon-balance calculations build on Table 7-IV, and Table 7-I are given in Figure 7-V to Figure 7-XI. There are four small diagrams connected to each of the three scenarios, comparing slow and fast pyrolysis two by two. The first two diagrams illustrate the impact of process design (slow >< fast pyrolysis) on the overall carbon-cost in kg CO<sub>2</sub> per MWh consumable energy (no distinction between electricity- and district heat joules), depending on process temperature and the substitution energy used. The second two diagrams illustrate the impact of process design (slow >< fast pyrolysis) on how much of the total consumable energy that is produced in the pyrolysis process (gap filled by substitution energy). The diagrams also show the influence of process temperature (fast pyrolysis) or peak process temperature (slow pyrolysis) on carbon-balance or energy production.

Based on these diagrams, the ideal pyrolysis process would yield a very low carbon-cost (or high carbon-benefit), give close to 100% of the maximum energy potential (with focus on electricity), and be robust for large intervals in process temperature.

The error bars in the bottom of the diagrams give an indication of the overall uncertainty of the data in the specific point, and they are described in the next section on “Estimating model uncertainties”.

Errorbars use the 2<sup>nd</sup> axis units and all curves use the 1<sup>st</sup> axis units. Diagrams share axis two by two.

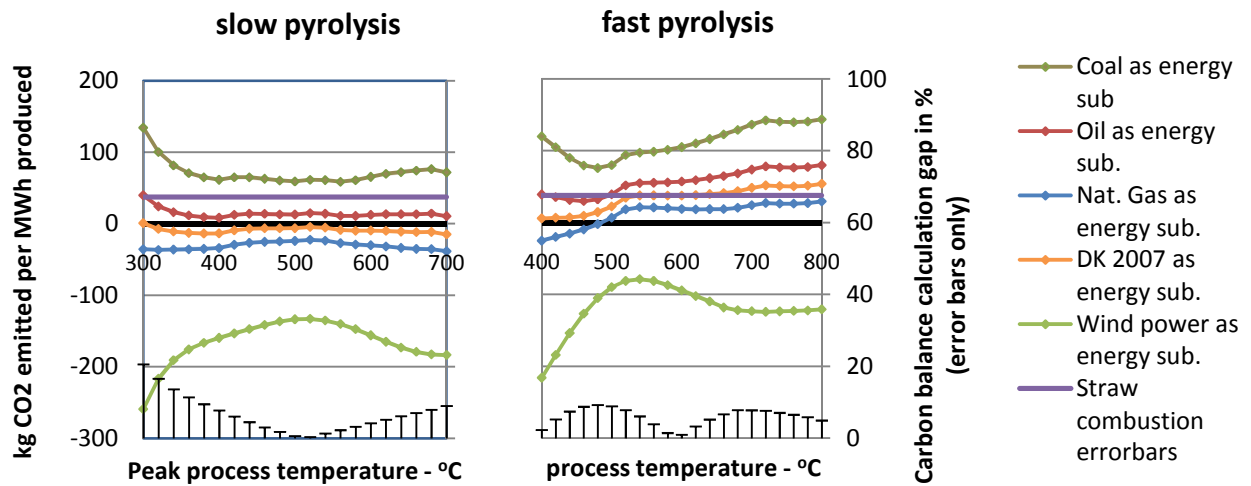


Figure 7-V: Carbon-balance for slow and fast pyrolysis in scenario 1

From the diagrams in Figure 7-V: Carbon-balance for slow and fast pyrolysis in scenario 1 (Figure 7-V), it is evident how much the characteristics of the substitution energy influence the carbon-balance. The purple line indicates the carbon-cost of “carbon-neutral” energy from complete conversion of straw (in this case incineration). Above the purple line is the highly carbon-positive curve that represents a pyrolysis process with coal combustion as substitution energy carrier. This would be a pointless operation from an energy- and carbon-based perspective. However, if any other substitution energy source was used (and even the DK 2007 average, incl. coal) the slow pyrolysis process will give a better carbon balance than the conventional combustion for almost all process temperatures. Substituting the lost energy with the DK 2007 average, natural gas or wind power will give carbon-balances below the neutrality level (black line), yielding carbon-negative energy production from slow pyrolysis of wheat straw in this scenario!

In the fast pyrolysis process only pure wind power substitution can give a carbon-negative energy production, and only with pure wind power or natural gas will the process give a better carbon balance than the conventional combustion (purple line).

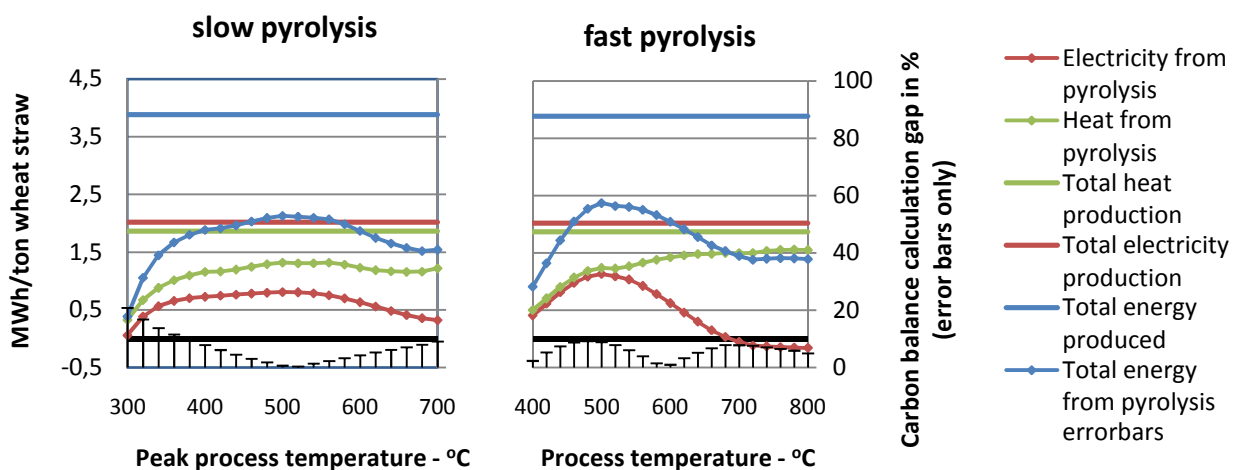


Figure 7-VI: Energy production from slow and fast pyrolysis in scenario 1

In Figure 7-VI, the curves are joined by colour. The straight blue line represents the total energy (electricity and district heating) available for consumption by combusting the straw (full energy potential), and the curved blue line represents the total energy available for consumption from the pyrolysis process. The green lines are the available district heating and the red lines are the available electricity. It appears that the fast pyrolysis produces more electricity and total energy than the slow process, but that they produce almost the same amount of district heating. The slow process is more robust, as the fast process has a clear production peak. It is important to notice that the conventional combustion produces a lot more electricity than both pyrolysis systems

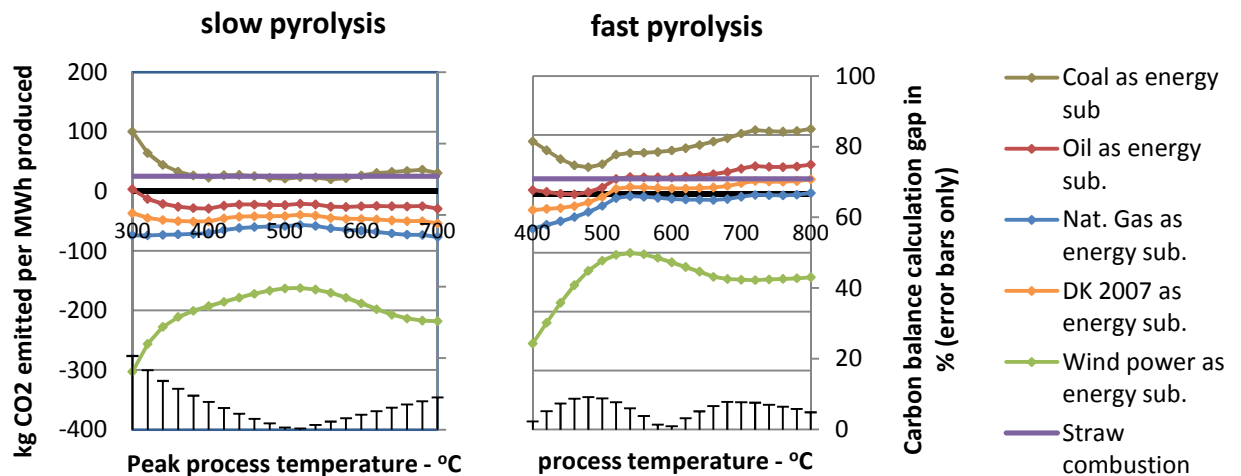


Figure 7-VII: Carbon-balance for slow and fast pyrolysis in scenario 2

Curves are similar in shape to scenario 1, but in this scenario, slow pyrolysis with coal substitution will give more or less the same carbon-balance as conventional straw combustion. If these results hold, it could open up to the use of biochar's many additional benefits on a larger scale, and in a more recent future. The influences of some of these benefits are described in the end of this chapter in the section "Additional biochar characteristics' influence on the carbon balance".

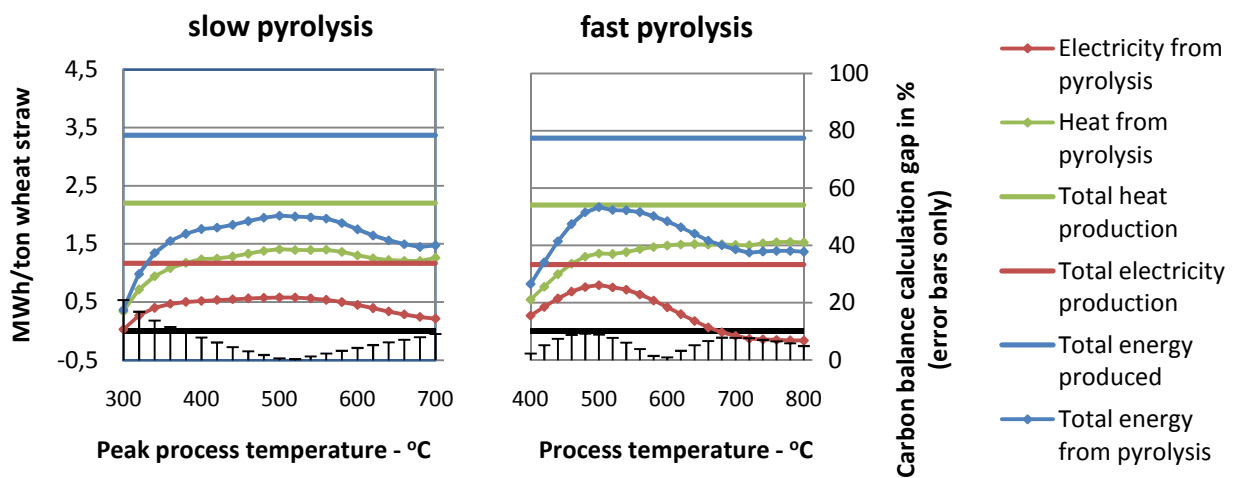


Figure 7-VIII: Energy production from slow and fast pyrolysis in scenario 2

From scenario 1 to scenario 2, there is observed a general shift in the carbon balance, rendering the average carbon cost more negative in the decentralized scenario. The slow pyrolysis process is now carbon negative for all feasible peak process temperatures with substitution from all available sources, except coal. The fast pyrolysis process is carbon negative for substitution with wind energy, and for low temperature processes also with natural gas or DK 2007 average as substitute. The fast pyrolysis process still produces more electricity and overall energy than the slow pyrolysis process. Both pyrolysis processes produce closer to the full energy potential and give better carbon-balances in the decentralized scenario than in the centralized.

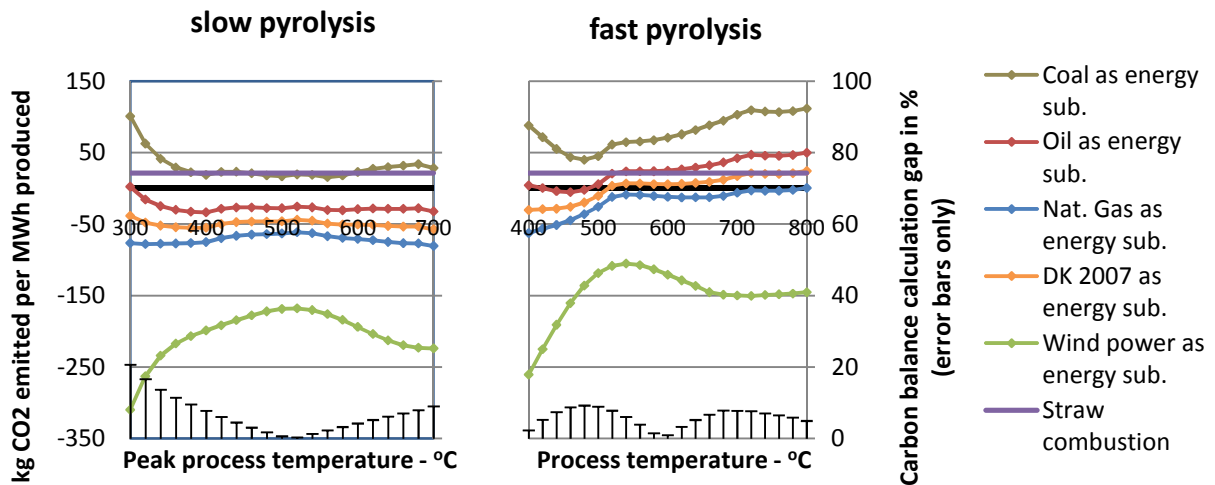


Figure 7-IX: Carbon-balance for slow and fast pyrolysis in scenario 3

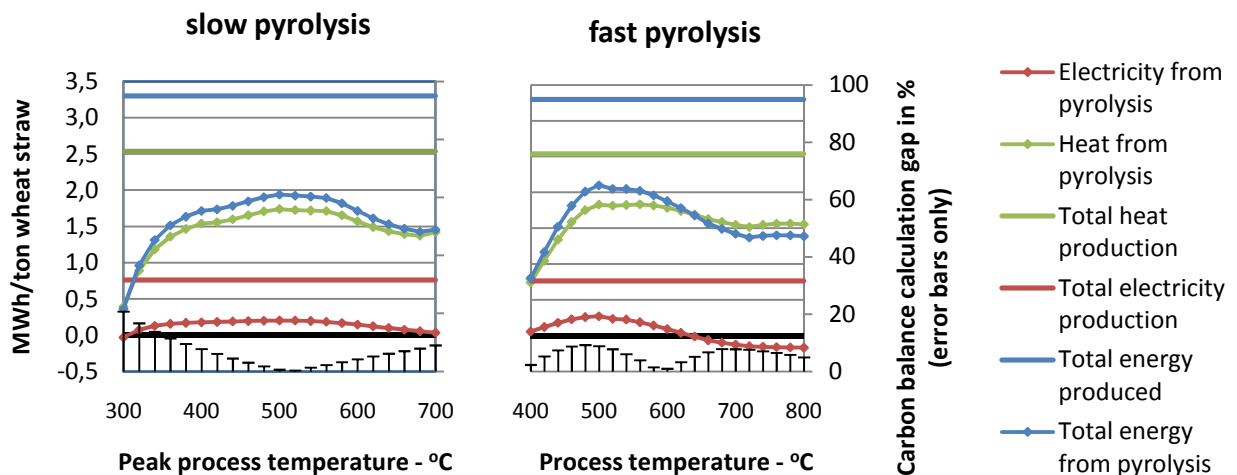


Figure 7-X: Energy production from slow and fast pyrolysis in scenario 3

The variation in the carbon-cost of energy from pyrolysis of wheat straw in the decentralized and the local scenario is insignificant, and questionable due to uncertainties. However, the variation in energy-production is obvious. The pyrolysis plants in the local scenario produce mainly heat, and not much electricity. This is important as electricity is energy of much higher quality than heat. The influence of seasonal changes in energy requirements is omitted from this report, but it is

nevertheless essential to keep in mind that heat is not required all year in equal amounts, and only large, modern facilities has the ability to increase electricity production on behalf of district heating production by running in a condensing mode (Energistyrelsen, 1995).

In addition to the slow pyrolysis plant and the conventional fast pyrolysis plant, the hypothetical in-situ fast pyrolysis plant is also assessed. The diagrams are the same as the previous. However, the temperature span is smaller as the in-situ process cannot use backup energy (it is isolated in the field) and it must therefore run above ca 525 °C in order to produce sufficient gas to sustain the process.

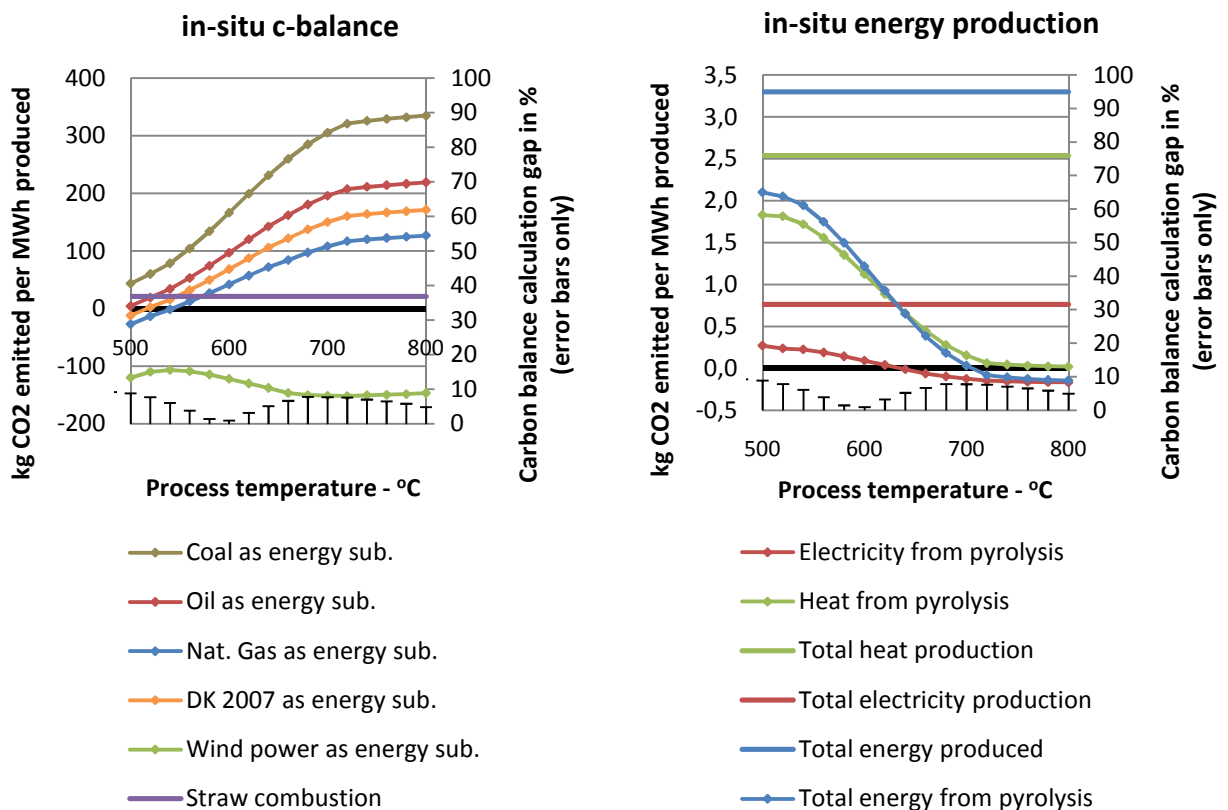


Figure 7-XI: Carbon-balance and energy production from In-situ fast pyrolysis in scenario 3-II

Apparently, the restrictions of the in-situ fast pyrolysis in scenario 3-II make it almost impossible to produce carbon-negative energy with this technology when substituting the energy gap with oil or even natural gas. The limitations on process temperature also influence the energy-yields (especially district heat production), and the process does not seem favourable in this respect compared to either fast- or slow pyrolysis.

The slow process shows the most stabile behaviour with changing parameters and from scenario to scenario. This could have practical importance, as it would require more highly skilled personnel to maximise the outputs from the fast pyrolysis processes. As the slow processes seem to be more robust with fewer variations from both process temperature changes and scenario changes, it is less important to run the process under optimal conditions at all times. In addition, the carbon-cost of the slow pyrolysis energy is better in all scenarios than the cost of the fast pyrolysis energy. The carbon-balance of the slow plants reach negative levels with several different substitution energies, and the same level as conventional combustion for substitution

with coal in 2 of 3 scenarios. This is possible due to the high energy-content of coal compared to bio-char (charcoal) and the result is that other aspects of biochar energy systems can be investigated – starting today, without increasing the overall carbon-emissions in the Danish energy-sector.

Fast pyrolysis gives a better energy yield in all scenarios. It has a clear production peak around 525 °C, which makes it difficult to adapt but easy to guide. The carbon-cost of fast pyrolysis energy shifts significantly with process temperature, but they never reach the same low levels as is the case for slow processes.

### *Estimating modelling uncertainties*

For every process simulation, a simple estimation of the overall interaction of correlations is done simultaneously. This check is done as a carbon-balance of the pyrolysis reactor weighing the amount of carbon going into the reactor against the amount going out. This will give some indication about which settings will make the many correlations used in the reactor calculations work well - or not so well, together. The misfit is presented as a % C-gap. The gap value is illustrated as error bars on the percentage scale on the curves in Figure 7-V to Figure 7-XI. This indication is useful when trying to assess with which parameters the model works the best. On the error bars in Figure 7-V to Figure 7-XI, it is clear that the correlation interaction test shows the smallest errors in the high end of the feasible temperature intervals of slow pyrolysis (see Table 7-IV) and in centre values of the fast pyrolysis process. In general, the errors in the calculations of the fast pyrolysis process are significantly smaller than the errors in calculations of the slow pyrolysis process. This indicates some general misfit in the correlation pattern of the slow pyrolysis carbon-balance calculation, and therefore care should therefore be taken when making conclusions based on the results from the low process temperatures in the slow pyrolysis process.

The sensitivity of 31 of the used variables has been investigated by changing each variable by +10% one at a time, and track the changes in output parameters. The test is enclosed as Appendix 9, and show that the parameters are *straw C-content*, *Straw HHV*, *thermal efficiency of straw combustion facility* and the correlation between *bio-oil carbon and HHV* gave large deviations in the overall carbon balance (90%, 55%, 40% and 35% respectively) from the 10 % variation. The average deviation in carbon-balances and energy yields from a 10% change in the 31 parameters was 5% in 124 outputs, and only 16 outputs showed more than 10 % deviation. The carbon-balances are much more sensitive to parameter variations than the energy yields. No further uncertainty assessment is done in this study, and with the note of caution on the four parameters mentioned above, the outputs are assumed as rough estimates.

### **Highlights and discussion of results**

It is decided to focus on slow pyrolysis from 400 - 550 °C and fast pyrolysis from 500 - 650 °C and to assess only the Denmark 2007 average energy production and wind power as energy substitutes. This is to simplify the data for conclusions, and to establish a business-as-usual scenario in one end, and an optimal scenario in the other. It is more likely to regard 2007 average carbon-costs as a worst case substitution than a realistic one. The use of oil for energy production in Denmark has been declining over the last 10 years, while the use of natural gas has increased slightly (Energistyrelsen, 2009). Furthermore coal is a politically very sticky topic, and it seems almost impossible to expand – or even maintain the current level of coal consumption. On the other hand, wind power in Denmark is abundant, and the wind sector has begun expanding again (Østergaard, 2010). Bio-oil could serve as back-up energy source when wind is absent. In addition, there is a strong political focus on

enhanced biogas-from-manure and other 2<sup>nd</sup> generation bio-energy systems (Klima&Energiministeriet, 2010). These trends would all help to shift the 2007 DK average towards a lower carbon-cost. With these limitations, the results from Figure 7-V to Figure 7-XI are:

Table 7-V: Highlight results from overall carbon-balance calculations

	<b>Carbon-cost w. DK 2007<sub>ave</sub></b> (kg CO <sub>2</sub> /MWh)	<b>Carbon-cost w. Wind power</b> (kg CO <sub>2</sub> /MWh)	<b>Electricity production</b> (pyrolysis in % of total)	<b>District heat production</b> (pyrolysis in % of total)
<b>Scenario 1:</b> Slow pyrolysis	Average: <b>-7</b> Max: -5 / Min: -14	Average: <b>-142</b> Max: -133 / Min: -160	Average: <b>39</b> Max: 40 / Min: 36	Average: <b>67</b> Max: 71 / Min: 52
<b>Scenario 1:</b> Fast pyrolysis	Average: <b>35</b> Max: 39 / Min: 22	Average: <b>-91</b> Max: -79 / Min: -110	Average: <b>39</b> Max: 56 / Min: 15	Average: <b>72</b> Max: 79 / Min: 66
<b>Scenario 2:</b> Slow pyrolysis	Average: <b>-43</b> Max: -39 / Min: -50	Average: <b>-173</b> Max: -162 / Min: -193	Average: <b>48</b> Max: 50 / Min: 44	Average: <b>60</b> Max: 64 / Min: 56
<b>Scenario 2:</b> Fast pyrolysis	Average: <b>8</b> Max: 10 / Min: -6	Average: <b>-113</b> Max: -101 / Min: -132	Average: <b>47</b> Max: 69 / Min: 16	Average: <b>65</b> Max: 69 / Min: 61
<b>Scenario 3:</b> Slow pyrolysis	Average: <b>-48</b> Max: -44 / Min: -55	Average: <b>-179</b> Max: -168 / Min: -199	Average: <b>25</b> Max: 26 / Min: 23	Average: <b>65</b> Max: 68 / Min: 61
<b>Scenario 3:</b> Fast pyrolysis	Average: <b>4</b> Max: 8 / Min: -11	Average: <b>-117</b> Max: -105 / Min: -136	Average: <b>20</b> Max: 36 / Min: -2	Average: <b>71</b> Max: 72 / Min: 67
<b>Scenario 3-II:</b> In-situ	Average: <b>44</b> Max: 106 / Min: -12	Average: <b>-119</b> Max: -107 / Min: -138	Average: <b>20</b> Max: 36 / Min: -2	Average: <b>54</b> Max: 72 / Min: 26

Comparing the results across process type and scenario shows:

- All slow pyrolysis processes are carbon-negative in the feasible intervals, with carbon costs of -7 to -48 kg CO<sub>2</sub>/MWh when substitution energy comes with a carbon-cost of the 2007 average (worst case), and -142 to -179 kg CO<sub>2</sub>/MWh when substituted with wind power (best case).
- Fast pyrolysis processes are not significantly carbon-negative in any scenario, but have better carbon-balances than conventional combustion.
- The only process more carbon-positive than conventional combustion of wheat straw is the In-situ fast pyrolysis running at above 550 °C.
- Electricity output from fast pyrolysis is -2 to 69 % of the total output depending on process temperature. For slow pyrolysis the span is 23 - 50 % for the tested process temperatures.
- Total energy output (electricity + district heating) available for consumption from the fast pyrolysis process is 46 – 64 % of the full consumption potential. For slow pyrolysis the span is 49 – 59 %.



### Answering the main report work question with an example

Based on the previous, it is assumed possible to produce carbon-negative energy by pyrolysis of Danish wheat straw with a CO<sub>2</sub> benefit of around 150-200 kg CO<sub>2</sub>/MWh with substitution energy from the Denmark 2007 average and an energy output of ~ 50 % of the full potential. The process has to run as a slow pyrolysis to ensure the negative carbon-balance, and it has to be assumed that the ~50% energy gap is not substituted with burning coal.

The original work question of this report is answered by filling in the blanks of the modified version of Figure 2-III with a calculated example. The settings for the calculations is a decentralized Danish scenario with a slow pyrolysis process running on a wheat straw feed stock. The process runs with 10 minutes of drying and subsequently 20 minutes of slow heating to a max temperature of 500 °C. For substitution energy, natural gas is applied:

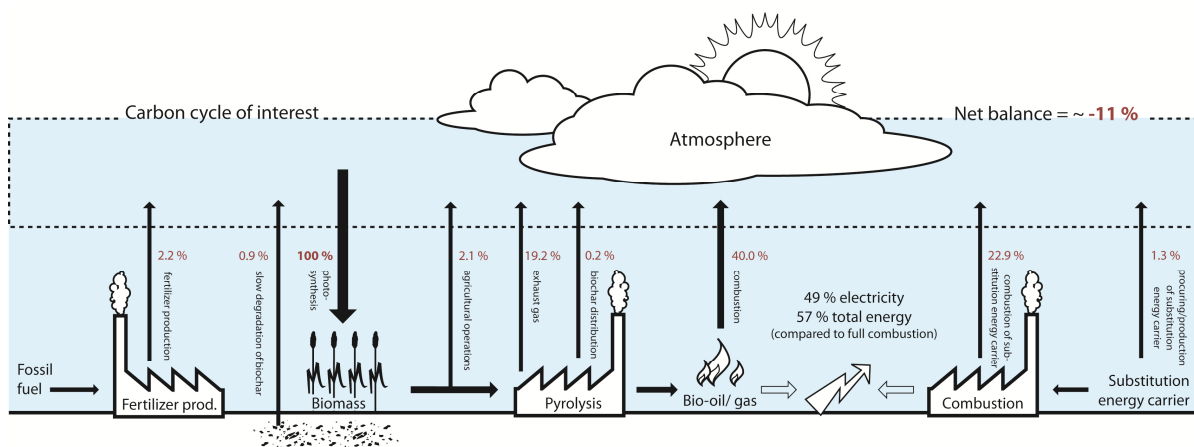


Figure 7-XII: Example of carbon-balance calculations in decentralized energy production with pyrolysis of wheat straw. Answer to main report work question.

### Validation of results

Due to the integration of many simple correlations, and the earlier assessment of uncertainties and errors, it is necessary to test the overall carbon-balance calculations against other similar investigations. It is no easy task to find usable material for this comparison, but the work by Brownsort demonstrates some useful data and results (Brownsort, 2009). Brownsort does not substitute the energy difference between pyrolysis yield and full potential. This gives a much more beneficial carbon-balance than the results in this report. Nevertheless, it is easy to remove the substitution energy from the calculations of this report and compare the results by converting the energy outputs to fossil fuel displacement values. This is done in Table 7-VI, for three processes: One slow pyrolysis process with unknown plant biomass, one intermediate pyrolysis with wheat straw, and one fast pyrolysis process with undefined wood. For all three recalculations of the results from this report, the Carbon Emission Factor (CEF) of 0.43 kg CO<sub>2</sub>-equivalent /kWh are applied as recommended by (Brownsort, 2009) for calculations in the UK energy sector.

Table 7-VI: Comparing results to the work of (Brownsort, 2009)

	Net CO <sub>2</sub> benefit kg CO <sub>2</sub> /kg dry feed (Brownsort, 2009)	Net CO <sub>2</sub> benefit kg CO <sub>2</sub> /kg dry feed (Own work)	Electricity production kWh <sub>e</sub> /kg dry feed (Brownsort, 2009)	Electricity production kWh <sub>e</sub> /kg dry feed (Own work)
<b>Test 1:</b> Slow pyrolysis	-1.2	-0.9	0.4	0.5
<b>Test 2:</b> Intermediate pyrolysis	-1.1	-0.9	0.5	0.6
<b>Scenario 3:</b> Fast pyrolysis	-0.9	-0.8	1.3	1.2

There are many small differences in the two models, but the results are very much in keeping with each other, especially in the case of the wheat straw process. There is a tendency for the net CO<sub>2</sub> benefit of the present study to be slightly lower than Brownsort's results. The difference on the net carbon benefit is 10-30% and the difference on the electricity output is 10-20%. The smaller net CO<sub>2</sub> benefit in the present study could very well originate from emission factors like fertilizer usage, agricultural operations, oil transport, etc., which are integrated in the present study, but not in the work by (Brownsort, 2009). Differences in energy output could most likely be plant efficiency.

The data from the two studies is too different to compare well, but they show a reasonable correlation and the trend in the results is similar. On this background there is assumed to be a usable agreement, and validation of the calculation model. The level of detail is questionable, but the patterns and quantitative results seem highly usefull.

#### **Additional biochar characteristics' influence on the carbon balance**

As mentioned in section 0, the use of biochar as carbon sink is believed to have several beneficial effects on the overall carbon-balance besides the ones included quantitatively in this study. One of the main possible side-effects is that N<sub>2</sub>O and CH<sub>4</sub> emissions from soil may be significantly reduced by biochar application. Studies have shown 50 – 100 % repression of CH<sub>4</sub> emission and up to 50 % repression of N<sub>2</sub>O emission from soil amended with biochar. Especially in systems with fertilizer use, is the N<sub>2</sub>O repression assumed significant (Rondon, et al., 2005). Another effect is the ability of the biochar to prevent leaching of valuable nutrients, and thus minimizing the fertilizer need of the biomass production. Greenhouse experiments by Lehmann et al. from 2003 showed a 60 % reduction in ammonium leaching from biochar amended soil after 45 days (Lehmann, et al., 2003). As indicated in Figure 7-XII, fertilizer may have measureable impact on the carbon balance, with emissions costs of more than 2 % of the carbon originally captured. Finally it has also been observed that biochar improves crop performance (Lehmann, et al., 2003; Steiner, et al., 2007). This could on one hand increase the amount of atmospheric carbon captured by plant growth, and on the other hand it could reduce the need for fertilizer. This effect has been observed primarily on old or sandy soils.

To quantify the effects above Gaunt et al (2008) estimates that N<sub>2</sub>O emissions from farm soil is reduced by 50 % and fertilizer needs are reduced by 10 % by biochar usage (Gaunt, et al., 2008). The authors calculate a CO<sub>2</sub> emission reduction of ~ 3700

kg CO<sub>2</sub> · ha<sup>-1</sup> · y<sup>-1</sup> in a slow pyrolysis scenario with winter wheat based on the reduction in N<sub>2</sub>O emissions and fertilizer requirements.

### Closing perspective on Energy, climate mitigation and technology

Examining the pyrolysis processes has pointed towards a robust, carbon-negative energy production when applying the slow pyrolysis in Danish wheat straw scenarios. The fast pyrolysis process produces more energy than the slow pyrolysis, but the overall carbon-balance of the fast process is not significantly negative in any of the tested scenarios. It is assumed that incorporation of the omitted effects of biochar mentioned above would have some impact on the fast pyrolysis carbon-balance, but even more effect on the carbon-balance of the slow process. There could be several reasons why the slow pyrolysis process achieves a better carbon-balance than the fast process:

- The mechanics of the fast pyrolysis reactor and peripheral units are highly energy consuming compared to the slow process.
- The focus on oil production pushes the total heat of the pyrolysis reaction towards the endotherm, where the slow pyrolysis favours a more exotherm char-producing process.
- The recalcitrance of the rapidly produced biochar is lower in biochar from the fast processes than for slow pyrolysis biochar.

All in all it seems that the fast pyrolysis process yields the extra amount of oil at a very high price. In addition, senior scientist at Risø DTU, Jesper Ahrenfeldt has experience with wheat straw pellets that can obtain the same energy density as lignite (~10 to 20 MJ/kg) and becomes hydrophobic over time. With this processing the straw product could potentially match the bio-oil in both energy density, transportability and storage aspects, and still yield higher total energy outputs.

Based on the findings in the report, a brief assessment of the examined energy technologies is given in Table 7-VII. The assessment includes the possibility of recycling the process ash to the field, as this is a subject of much interest. This is not done normally in processes with high temperatures (+800 °C) due to a concomitant production of polyaromatic hydrocarbons (PAHs) that might be harmful.

Table 7-VII: Qualitative comparison of energy technologies included in the present study

	Slow pyrolysis	Fast pyrolysis	Complete combustion
<b>Electricity yield</b>	20 - 50 %	0 - 70 %	100 %
<b>Transportable /storable energy</b>	As semi stable bio-oil or upgraded gas	As semi stable bio-oil or upgraded gas	As baled straw or straw pellets
<b>Recycling of ash</b>	yes	yes	no
<b>Carbon-balance</b> (with oil or natural gas used for substitution)	Negative to neutral	Neutral to positive	Neutral to positive

<b>Effect on soil layer</b> quality and quantity	The organic carbon in biochar rebuilds old and sandy soils	Less char production than in slow pyrolysis. Higher energy cost/unit char	Removal of biomass slowly depletes soil layer nutrients and organic carbon
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Based on the characteristics in Table 7-VII, it is proposed that a combination of slow pyrolysis and complete combustion/gasification might give the best overall result in many scenarios. A 50/50 combination would render the total process carbon-negative, return some ash and carbon to the soil, and produce 65 - 75 % of the electricity possible. The fast pyrolysis process is in between the two other technologies, but it uses more energy to produce biochar than the slow process, and it is less efficient in energy production than the complete conversion.

This perspective is in some opposition to the trend in commercial pyrolysis technology where focus is strongly on bio-oil production. The reasons for this could be many, but it is not unthinkable that the following aspects could play a role in the popularity of fast pyrolysis:

- Most investigations of pyrolysis processes with production of both bio-oil and bio-char does not include assessments of substitution energy for the energy lost in the char. Therefore, the overall carbon-balance of the fast pyrolysis process will appear carbon-negative. As the fast pyrolysis process produce more oil, which is sellable, the choice of a fast process would give a better economy in the project. To a politician or researcher concerned with the amount of collectable biomass, and the actual carbon-balance on a broad perspective including substitution energy, this approach would be incorrect.
- Slow pyrolysis processes are specialized for biochar production, but there is no fast money in biochar. There is no quick commercial success in maintaining the soil layer fertile for the future, and it is still not possible to cash in carbon credits by building a farm soil carbon sink. Commercial interests need a cash flow to sustain their existence, and therefore the fast pyrolysis with the large production of (apparently) carbon-negative bio-oil acquires the most attention.
- The thought of swapping the fossil fuel in the old car, tractor or truck with green clean-conscience bio-fuel is broadly appealing. Therefore, it sells products regardless of how farfetched the process might be.

## 8 Conclusion

In this report the main concern has been to disclose whether or not it would be possible to produce genuine carbon-negative energy from pyrolysis of wheat straw in a series of Danish agricultural scenarios. A combination of process simulation, correlations derived from literature studies and experimental work and overall balance calculations has been applied to fill the blanks in the main inequity:

$$\text{Carbon in process } CO_2 \text{ emissions} < \text{Atmospheric carbon stored in wheat straw}$$

The modelling work showed good correlation with point data reference and qualitative behaviour of reference experimental results. Two complete pyrolysis processes have been constructed in the SuperPro Designer software, and they are assumed capable of predicting process yields from various lignocellulosic feedstocks, varying fast pyrolysis temperatures, and slow pyrolysis peak temperatures and temperature scenarios. Using the capacities of SuperPro Designer in a next level improvement of the pyrolysis simulations could result in a valuable tool for broad process assessment on throughput optimization, scheduling, work load, environmental impact, utility consumption and economy.

The uncertainty of the overall calculations has been briefly examined, and it was concluded that the results could hold for rough estimation purposes as long as attention was given to key parameters. The final results have been compared to another study with convincing results.

The investigation of the overall carbon-balance of slow and fast pyrolysis was done in three different scenarios, explicitly centralized, decentralized and local, and different substitution energy supplies were considered for filling the gap between the energy yielded by the pyrolysis and the full bio-energy potential of the wheat straw, quantified as complete combustion or gasification. It was concluded that it is feasible to produce carbon-negative energy under the following settings:

- 2/3 slow pyrolysis scenarios with oil as energy substitute.
- 3/3 slow pyrolysis scenarios with Denmark 2007 average carbon-cost, natural gas or wind power as energy substitute.
- 0/3 fast pyrolysis scenarios with oil as energy substitute.
- 2/3 fast pyrolysis scenarios with very low temperatures and Denmark 2007 average carbon-cost or natural gas as energy substitute.
- 3/3 fast pyrolysis scenarios with wind power as energy substitute.
- The hypothetical in-situ fast pyrolysis scenario with wind power substitution but not with DK 2007 average, oil or natural gas substitution.
- 2/3 slow pyrolysis processes yielded the same carbon-balance as complete combustion when substituting with coal.

The negative carbon-balance is only robust for the slow pyrolysis scenario, which is therefore conceived as the only process capable of producing carbon-negative energy based on this report.

The CO<sub>2</sub> benefit of the most carbon-negative slow pyrolysis process is estimated to be around 10 % of the atmospheric carbon stored in the original biomass when natural gas is applied for energy substitution. This process avoids the emission of around 150-200 kg CO<sub>2</sub>/ton wheat straw with substitution energy with a Denmark 2007 average carbon-intensity. This result is weighted against the net emissions of the carbon-

“neutral” process of conventional combustion. This emission is in this report estimated to be around 50 – 150 kg CO<sub>2</sub>/ton straw depending on scenario settings. The investigation did not include effects of biochar amendment on N<sub>2</sub>O/CH<sub>4</sub> emissions from the soil, the reduction in fertilizer usage, or the enhancement of biomass production. These effects are assumed to have beneficial influence on the overall carbon-balance of the processes.

Results showed that it was difficult to find optimal usage of the fast pyrolysis process in the Danish energy scenarios, as the process produce biochar at a higher cost than the slow process, and energy at a higher cost than the conventional combustion processes. Pyrolysis for energy cannot compete with full conversion through combustion or gasification. The primary strength of the pyrolysis technology is the recalcitrant char product and not the pyrolysis oil. The present study implies that despite the trend in commercial pyrolysis technology that focuses on fast pyrolysis processes with maximized bio-oil production, the twin challenge of climate mitigation and sustainable energy production is most efficiently addressed with a combination of slow pyrolysis and conventional biomass conversion instead.

The pyrolysis process makes no sense when strictly considering the energy- and the carbon-balance of sequestering coal-like biochar and then digging up and burning coal for energy purposes. However, coal combustion is a politically smoking gun, and in most parts of the industrialized world it is very difficult to gain acceptance of new coal based initiatives. Coal has to be phased out of energy supplies to meet the demands for political ambitions of +2° or back-to-350-ppm, and when burning coal is phased out, sequestering of char could be phased in. To break the growing curve of GHG concentration carbon-negative energy production is a must! There is no way around it, and as soon as any nation is coal free it could become economically feasible for that nation to begin the production of biochar. Until coal is phased out, biochar demonstration plants and field trials should be carried out. The results of this report shows that slow pyrolysis of wheat straw with biochar production and amendment has the same carbon-balance as conventional straw combustion in de-centralized or local scenarios – even with coal as energy substitute! This implies that even large scale trials will have no unintended influence on the carbon-concentration in the atmosphere – no matter what kind of substitution energy is applied. If such results on additional positive biochar effects are good, then the carbon-balance will not be a problem as long as the pyrolysis is slow and conditions are de-centralized or local. There is no reason not to begin right away...

Another sticky point is the scarcity of biomass. As long as nations struggle to cast the shackles of fossil fuels biomass should mainly be used for energy purposes. However, the use and potential benefits of using biochar should be thoroughly investigated and considered to find the optimal use of the technology. Some of the key characteristics of the biochar process include:

- Slow pyrolysis is an extremely robust thermal conversion process that is applicable with many different feedstocks. Almost all industrial- and agricultural waste streams may be converted in the process, creating biochar that is free of polyaromatic hydrocarbons (PAHs); a class of compounds which may have undisclosed effects in farm soil.
- With every other substitution energy carrier than coal, biochar production will be capable of yielding genuine carbon-negative bio-energy as either bio-oil or gas for combustion.

- Biochar may prove to be a valuable tool in closing the nutrient cycle of bio-energy and farm crops wastes, and at the same time in the building and maintaining of fertile soils. This could prove to be the main argument for biochar production in many parts of the world. The increase in biomass productivity that could follow biochar amendment would in the long run minimize the gap between energy production from pyrolysis and complete combustion.

Biochar is a good story, but it is a difficult one to sell. There is still no easy and fast way to commercial success by maintaining the soil layer thick and fertile for future generations, and it is still not possible to cash in carbon credits by building a farm soil carbon sink. This might change.

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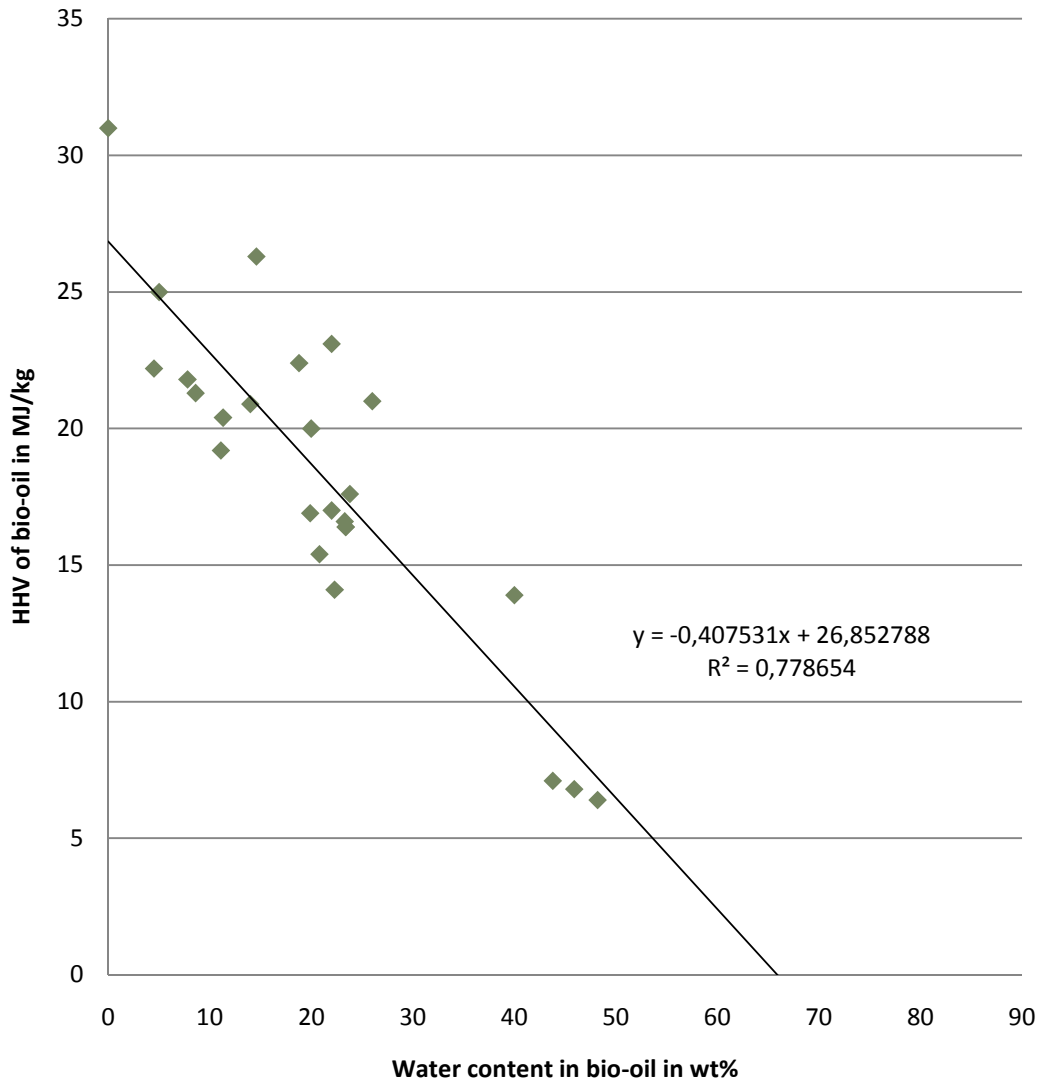
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**Appendix 1:****Data for correlation between bio-oil water content and bio-oil HHV (2 pages)**

Water content (wt %)	HHV MJ/kg	
45.9	6.8	(Bridgwater, et al., 2007_B)
8.6	21.3	
48.2	6.4	
11.3	20.4	
43.8	7.1	
7.8	21.8	
19.9	16.9	(Sipilaé, et al., 1998)
11.1	19.2	
0	31	(Demirbas, 2004)
23.4	16.4	(Bech, 2008)
20.8	15.4	
23.8	17.6	
22	17	
26	21	(Mohan, et al., 2006)
22,3	14,1	
40	13,9	
18,8	22,4	
20	20	
14,6	26,3	
4,5	22,2	
14	20,9	
22	23,1	
23,3	16,6	
23,4	16,4	
5	25	

### Simple correlation between bio-oil water content and higher heating value



## Appendix 2:

### Data for correlation between bio-oil C-content and bio-oil HHV (2 pages)

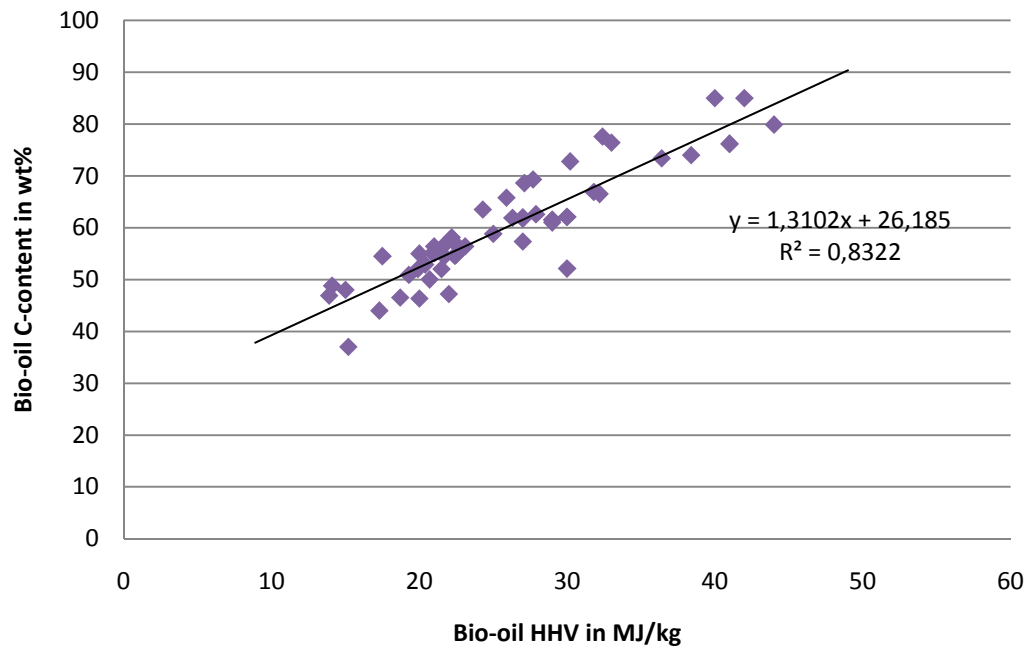
C-content (wt %)	HHV	
62,1	<b>30</b>	(Miao, et al., 2004)
61	<b>29</b>	
55,1	<b>21</b>	(Maggi, et al., 1994)
73,4	<b>36,4</b>	(Özcimen, et al., 2004)
68,6	<b>27,1</b>	(Sipiláé, et al., 1998)
55,3	<b>21,1</b>	
56,4	<b>21,6</b>	
69,3	<b>27,7</b>	
65,8	<b>25,9</b>	
50,9	<b>19,3</b>	(Demirbas, 2004)
52	<b>19,9</b>	
52,9	<b>20,4</b>	
54,5	<b>21,7</b>	
50	<b>20,7</b>	(Bech, 2008)
52	<b>21,5</b>	
37	<b>15,2</b>	
44	<b>17,3</b>	
85	40	(Mohan, et al., 2006)
57,3	<b>22,3</b>	
46,5	18,7	
54,6	<b>22,4</b>	
48	15	
63,5	<b>24,3</b>	
76,4	33	
79,9	<b>44</b>	
56,4	21	
61,5	<b>29</b>	
52,1	30	
76,2	<b>41</b>	
85	42	
62	<b>27</b>	
54,8	22,5	
72,8	<b>30,2</b>	
58,8	25	
55,1	<b>21</b>	
61,7	27	
74	<b>38,4</b>	
66,9	31,8	
62,1	<b>30</b>	
76,2	41	

C-content (wt %)	HHV MJ/kg	
61,5	<b>29</b>	(Mohan, et al., 2006)



48,8	14,1
46,9	<b>13,9</b>
54,6	22,4
72,8	<b>30,2</b>
58,8	25
55,1	<b>21</b>
61,7	27
74	<b>38,4</b>
66,9	31,8
62,1	<b>30</b>
76,2	41
61,5	<b>29</b>
48,8	14,1
46,9	<b>13,9</b>
54,6	22,4

### Simple correlation between bio-oil carbon content and higher heating value



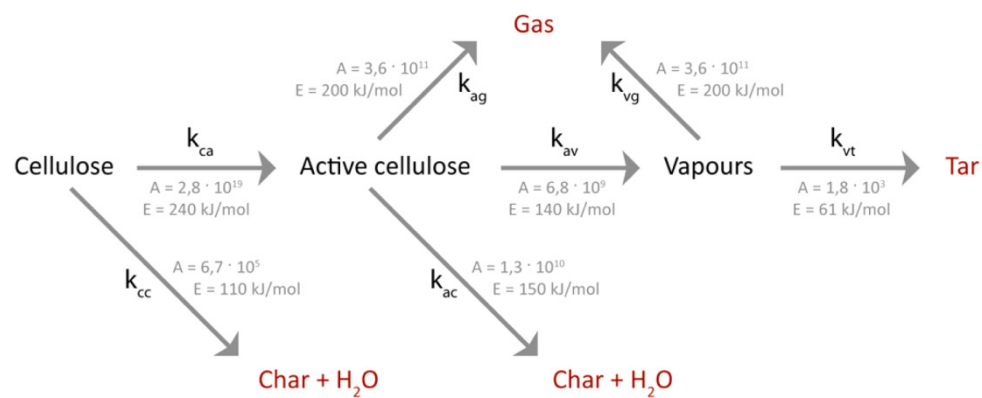
## Appendix 3:

### Kinetics parameters for degradation of biomass constituents (3 pages)

All reaction assumed to be 1<sup>st</sup> order reactions with Arrhenius kinetics and therefore  $k(T) = A \cdot e^{-E/RT}$

#### Cellulose kinetics:

Original parameters (Diebold, 1994):



Char-reactions 1 & 2 are defined with 100 % biomass reacting to 60 % char to 40 % water. Values adapted from hemicellulose kinetics (Miller, et al., 1997).

Slow pyrolysis fitting:

$E_{cc}$  changed from 110 kJ/mol to 115 kJ/mol (ca 4.5 %)

$E_{ac}$  changed from 150 kJ/mol to 155 kJ/mol (ca 3.5 %)

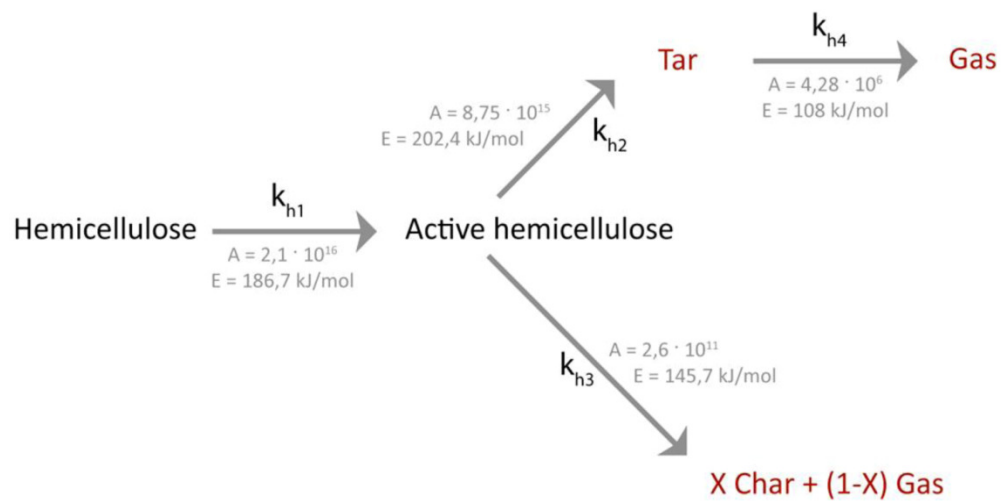
$E_{ag}$  and  $E_{vg}$  changed from 200 kJ/mol to 185 kJ/mol (ca 8 %)

$E_{av}$  changed from 140 kJ/mol to 141.8 kJ/mol (ca. 1.5 %)

$E_{vt}$  changed from 61 kJ/mol to 62 kJ/mol (ca 2 %)

## Hemicellulose kinetics:

Original parameters (Miller, et al., 1997):



X for the char reaction is 0,6 for hemicellulose degradation (Miller, et al., 1997).

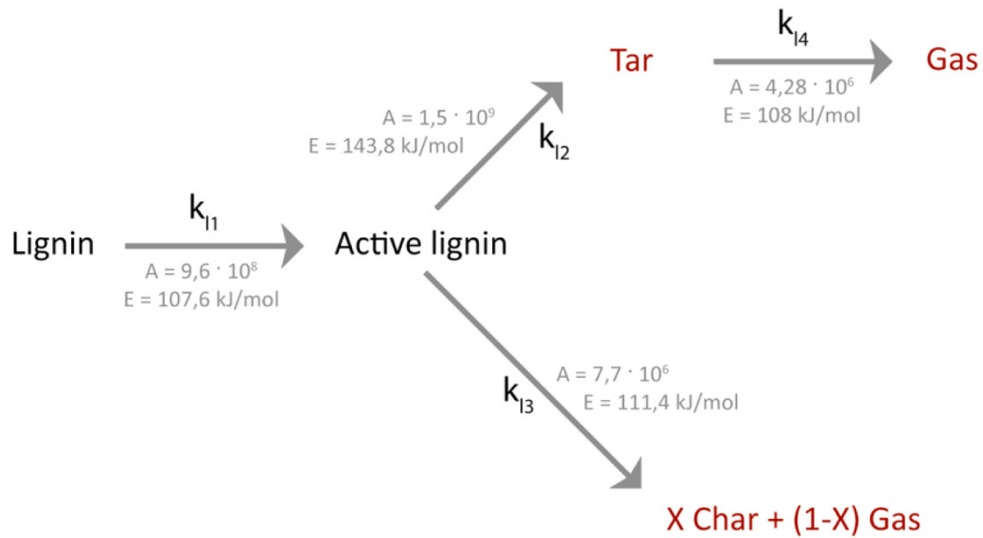
Slow pyrolysis fitting:

$E_{h2}$  changed from 202.4 kJ/mol to 200 kJ/mol (ca 1 %)

$E_{h3}$  changed from 145.7 kJ/mol to 145 kJ/mol (ca ½ %)

## Lignin kinetics:

Original parameters (Miller, et al., 1997):



X for the char reaction is 0.75 for lignin degradation (Miller, et al., 1997).

Slow pyrolysis fitting:

$E_{12}$  changed from 143.8 kJ/mol to 143 kJ/mol (ca ½ %)

$A_{12}$  changed from  $1.5 \cdot 10^9$  s<sup>-1</sup> to  $1.5 \cdot 10^{10}$  s<sup>-1</sup> (ca 0 %)

$E_{13}$  changed from 111.4 kJ/mol to 110 kJ/mol (ca 1.5 %)

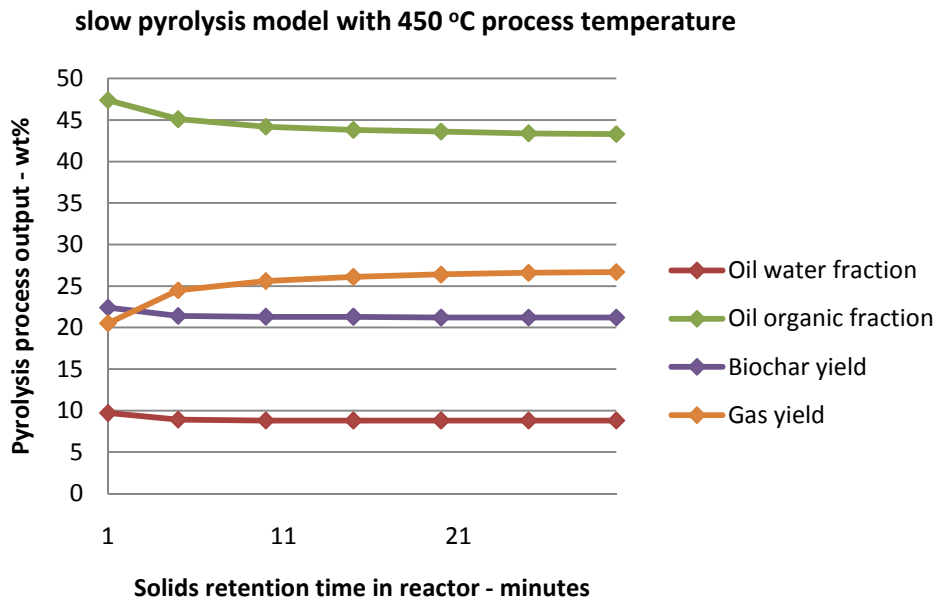
$A_{13}$  changed from  $7.7 \cdot 10^6$  s<sup>-1</sup> to  $7.7 \cdot 10^7$  s<sup>-1</sup> (ca. 0 %)

$E_{14}$  changed from 108 kJ/mol to 84.7 kJ/mol – value from (Caballero, et al., 1996)

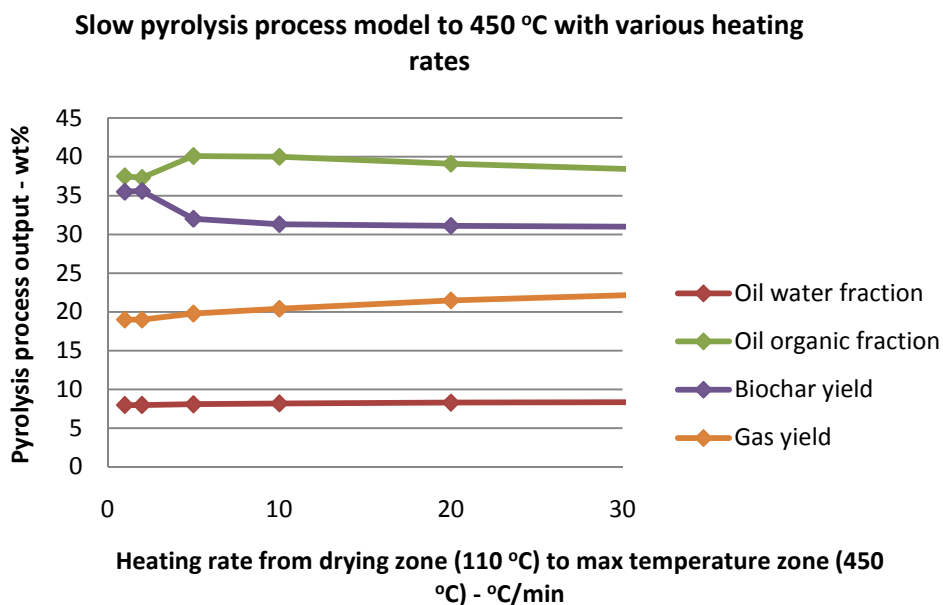
$A_{14}$  changed from  $4.28 \cdot 10^6$  to  $4.138 \cdot 10^3$  – value from (Caballero, et al., 1996)

## Appendix 4:

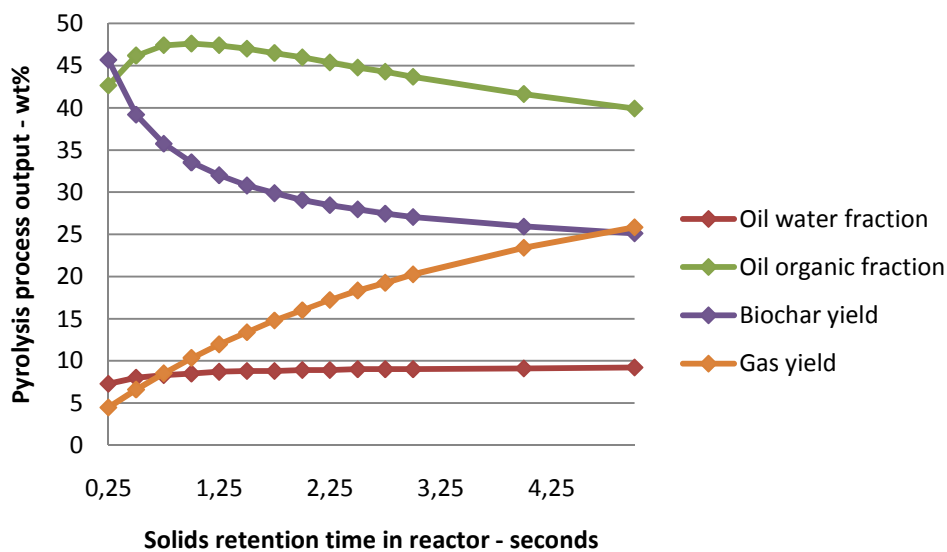
### Pyrolysis model tests of variations in retention time and heating rate (2 pages)



The above process modelling is done in a one-step pyrolysis at 450 °C and varying retentions times. The process below is modelled with 10 minutes drying at 110 °C, and then varying heating rates and correlated retention times to 450 °C, and then finished at this temperature for 10 minutes.



Fast pyrolysis process model with 510 °C process temperature

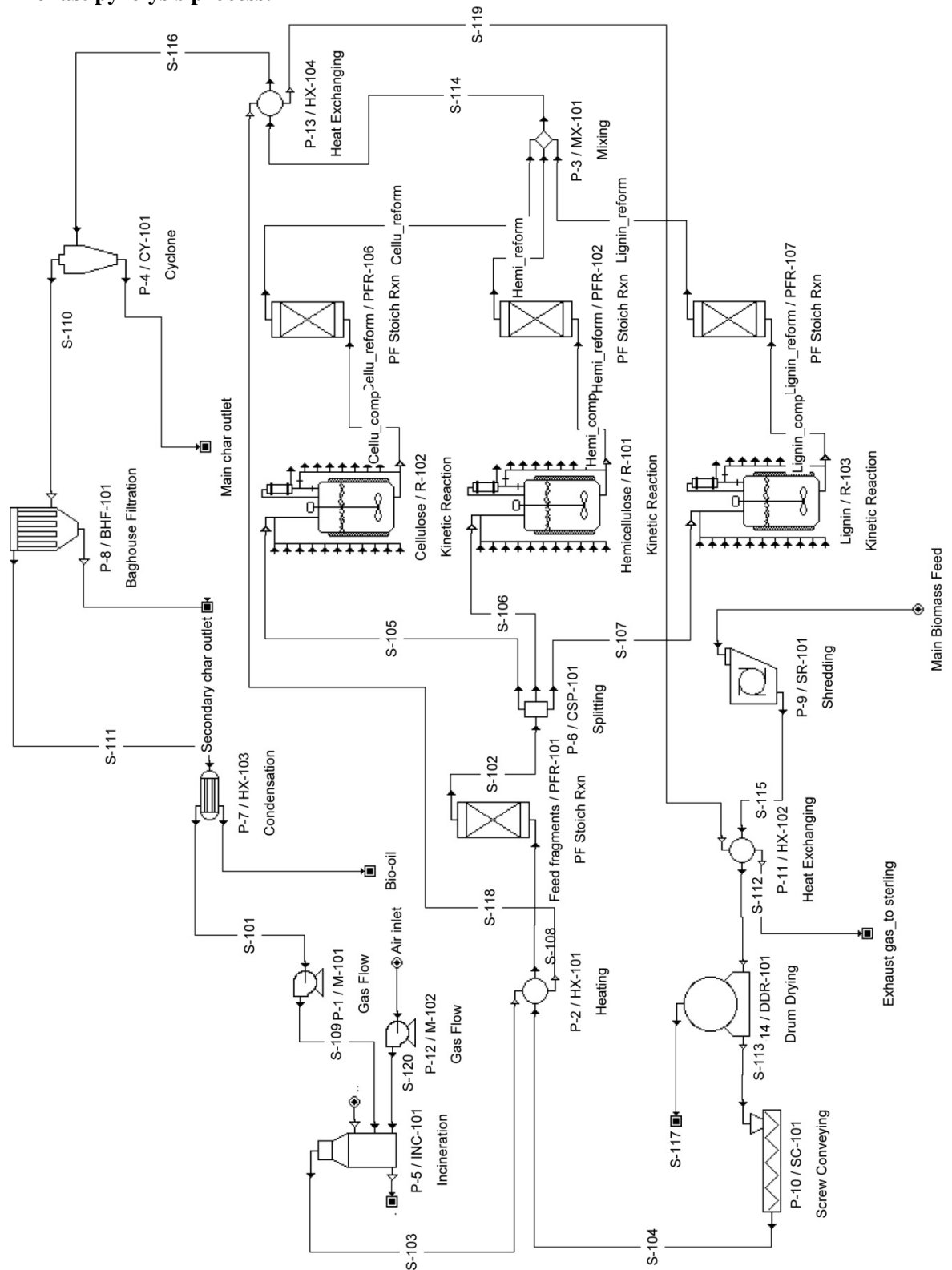


The process above is modelled with an isotherm reactor at 510 °C, and a variation in solid phase retention times.

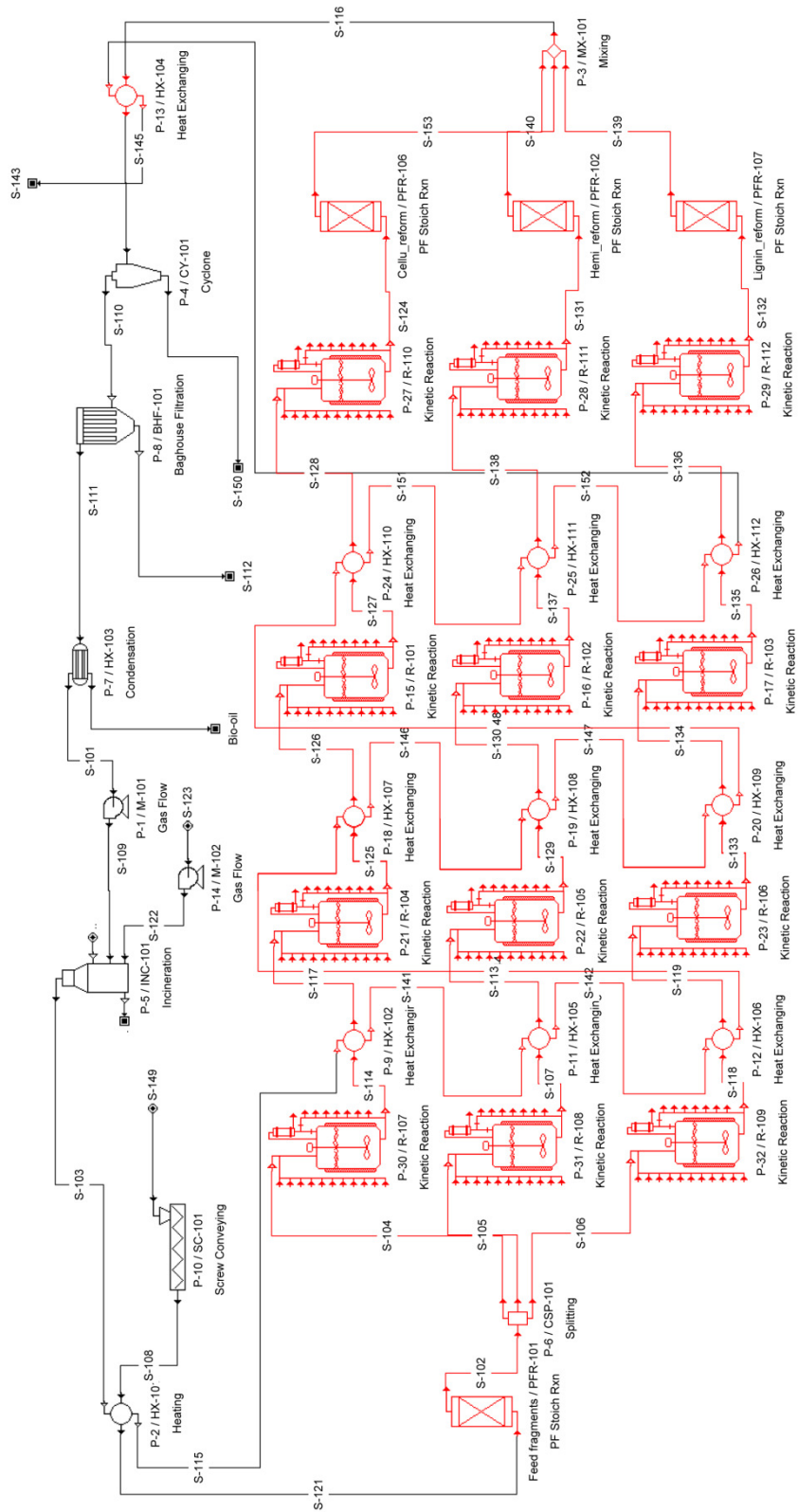
## Appendix 5:

### Overview of unit operations and parameters (4 pages)

#### The fast pyrolysis process:



# The slow pyrolysis process:





**Essential parameters:****Fast pyrolysis pre-treatment:**

## SHRED-1 (shredding):

Power consumption:	0.05	kW / (kg · h)	(default)
Power dissipation to heat:	5	%	(default)

## DRY-1 (drum drying):

Power consumption:	0.06	kW / m <sup>2</sup> drum area	(default)
Evaporation rate:	40	kg / (m <sup>2</sup> ·h)	(default)
Final LOD (loss on drying):	5	%	(default)

## CONVEY-1 (Screw conveying):

Power consumption (slow):	0.02	kW / (kg · h)	(default)
Power consumption (fast):	0.12	kW / (kg · h)	(user)

**Down-stream operations:**

## CYCLONE-1:

Velocity of inlet gas:	20	m / s	(default)
Particle removal:	90	% (of all solids)	(user)

## FILTER-1 (baghouse filtration):

Particle separation:	100	% (of all solids)	(user)
Linear velocity:	0.013	m / s	(default)
Fan efficiency:	80	%	(default)
Gas viscosity:	0.018	cP	(default)
Filter depth:	2	cm	(default)
Filter permeability x 1.0E+11:	0	m <sup>2</sup>	(default)
Particulate permeability x 1.0E+11:	0	m <sup>2</sup>	(default)
Particulate layer bulk density:	1600	g / L	(default)

## CONDENSE-1:

Condense:	100	% (all condensable)	(user)
Vapour phase model:	Ideal gas		(default)
Liquid phase:	Ideal mixture		(default)
Cooling agent:	Chilled water		(default)
Temp. Difference factor:	1		(default)
Heat transfer coefficient:	860.4	Watt / (m <sup>2</sup> · K)	(default)
Heat transfer efficiency: 90	%		(default)
Operating temperature: 40	°C		(user)
Operating pressure:	1.013	bar	(default)

## FAN-1:

Pressure change:	0.02	bar	(default)
Efficiency:	70	%	(default)
(incl. heating) Exit temperature:	50	°C	(user)
(incl. heating) Heat transfer efficiency:	100	%	(default)

## INCENERATE:

Auto-adjust air flow:	yes		(default)
Excess oxygen:	35	%	(default)
Relative humidity of air:	0	%	(default)

Ash to flue gas                      0            %                      (default)

**General equipment:**

All kinetic reactors:

Adiabatic  
Power consumption:                      0            kW / m<sup>3</sup>                      (default)

All stoichiometric reactors (cosmetic units):

Adiabatic  
Power consumption:                      0            kW / m<sup>3</sup>                      (default)

SPLIT-1 (splitter) / MIX-1 (mixer) (cosmetic units):

Power consumption:                      0            kW / m<sup>3</sup>                      (default)  
Efficiency:                                      100        %

Heat exchangers:

Correction factor:                              1                                      (default)  
Heat transfer coefficient:                      1500        Watt / (m<sup>2</sup> · K)                      (default)  
Pressure drop:                                      0            bar (on both sides)                      (default)

Heat exchangers for slow pyrolysis reactor:

Heat transfer coefficient:                      50            Watt / (m<sup>2</sup> · K)                      (user)

## Appendix 6:

### Calculations for processing of incubation study data (1 page)

In the following is given an example of the calculations done to process the data from the incubation study.

Original data from the first measurement of the first fast biochar+soil sample in the Slow><Fast study is on the form:

File Name	Date	Flux
F5.00.05	15-07-2009 15:30	1.1

The unit of the original flux measurement is in  $\mu\text{mol CO}_2/\text{m}^2\cdot\text{s}$

First the averages  $\text{CO}_2$ -flux of the soil samples are subtracted, to isolate the  $\text{CO}_2$ -flux based on the degradation of the biochar.

$$\left(1.1 \frac{\mu\text{mol CO}_2}{\text{m}^2} \cdot \text{s} \cdot 0.97 - 0.085 \frac{\mu\text{mol CO}_2}{\text{m}^2} \cdot \text{s} \cdot 0.98\right) \cdot 3600 \frac{\text{sec}}{\text{hour}} \cdot \frac{83.7 \text{ cm}^2}{10000 \text{ cm}^2/\text{m}^2} \cdot 10^{-6} \frac{\text{mol}}{\mu\text{mol}} \\ = 0.0000296 \frac{\text{mol CO}_2}{\text{hour}}$$

The factors 0.97 and 0.98 represent the relationship between the original LICOR chamber volume, and the actual volume available for  $\text{CO}_2$  gas build up. The actual volume is smaller due to the space taken by the sample. Volume of the samples varies, and this is reflected in the factor.

$83.7 \text{ cm}^2$  is the area of the LICOR chamber.

In the next step the measurement is transformed into “amount of carbon released from the biochar per amount of char per hour”.

$$0.0000296 \frac{\text{mol CO}_2}{\text{hour}} \cdot 44,01 \frac{\text{g CO}_2}{\text{mol CO}_2} \cdot 0,273 \frac{\text{g C}}{\text{g CO}_2} \cdot 2.0 \text{ g biochar}^{-1} = 0.000178 \frac{\text{g C}}{\text{g biochar} \cdot \text{hour}}$$

This value is used for Figure 6-I A.

To build Figure 6-I B measurements has to be transformed into an accumulated flux value. This is done by assuming that the measured flux is a stable value for the flux from the specific sample until the next time the sample is measured.

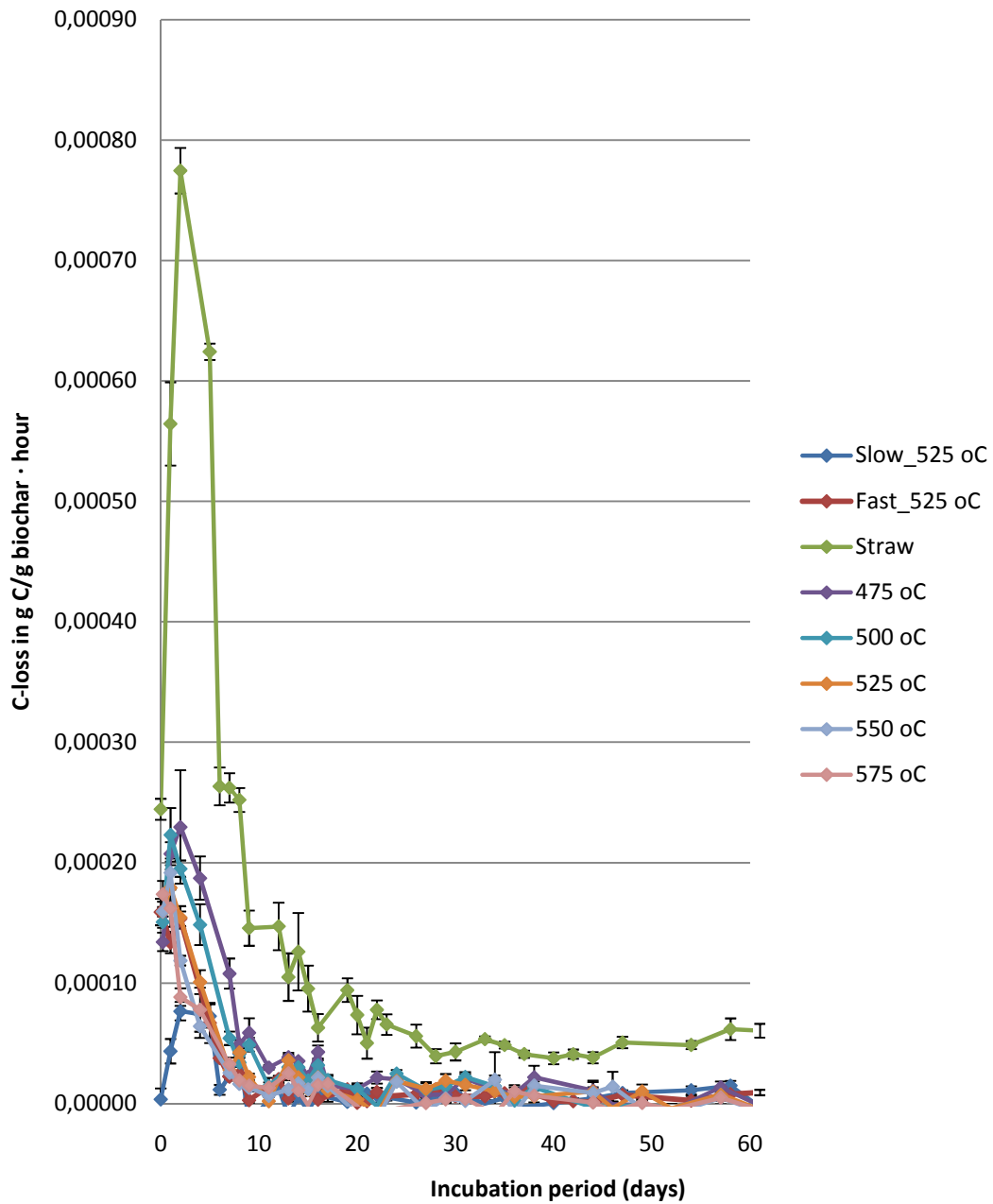
$$0.000178 \frac{\text{g C}}{\text{g biochar} \cdot \text{hour}} \cdot 12 \text{ hours} = 0.00213 \frac{\text{g C}}{\text{g biochar}}$$

The final step towards Figure 6-I B is to sum these values over time, and use the average of the 4 replicates to build the graph.

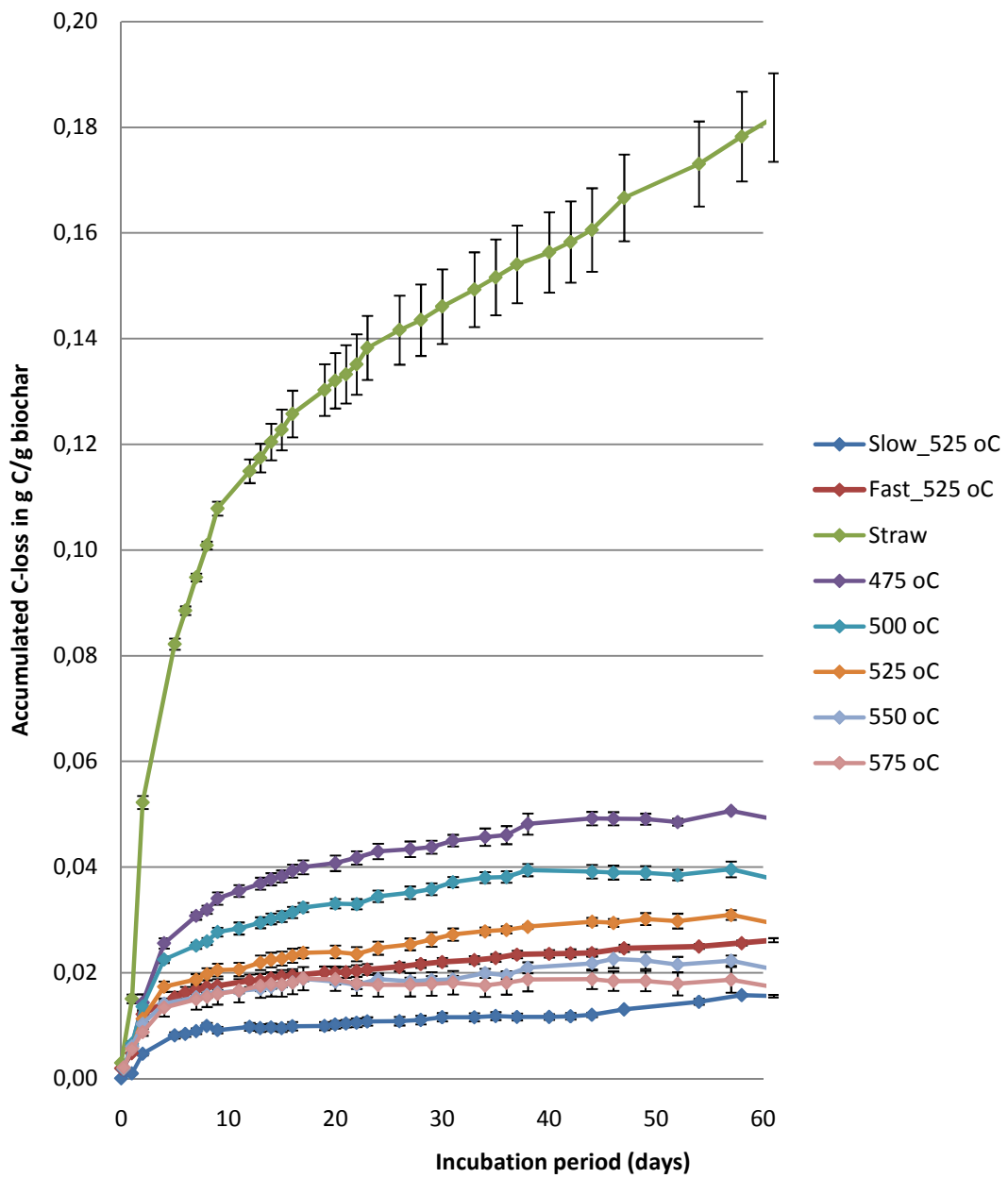
## Appendix 7:

Data from biochar stability studies through incubation experiments (2 pages)

### C-loss rate as indicator of biochar stability



## Accumulated C-loss as indicator of biochar stability



## Appendix 8:

### Parameters and equations for overall carbon-balance calculations (5 pages)

Parameter	Value/equation	Reference
<b>General parameters incl. transport</b>		
Energy content in average diesel	44 MJ/kg	Bridgwater (1990)
Density of diesel	0,87 kg/litre	Bridgwater (1990)
Energy-output from consumption of 1 L diesel	38,3 MJ/litre	Calculated
C-emissions from combustion	1,13 kg C/litre	Gaunt et al (2008)
Transport trucks capacity	8,5 ton	Miljø- og Energi-ministeriet (2001)
Truck energy consumption (fully loaded)	11,2 MJ/km	Miljø- og Energi-ministeriet (2001)
Truck energy consumption (empty)	7,9 MJ/km	Miljø- og Energi-ministeriet (2001)
Truck engine efficiency	32%	Ulrik Henriksen, Senior scientist Risø DTU
Diesel consumption pr km distance (out and back at full capacity)	0,18 l diesel/(km*ton cargo)	Calculated
Distance to combustion facility centralized scenario	100 km	Assumption
Distance to combustion facility decentralized scenario	20 km	Assumption
Distance to combustion facility local scenario	0 km	Assumption
Conversion factor	1 kWh = 3,6 MJ	www.unitconversion.org
C/CO2 weight ratio	0,27	Calculated
<b>Wheat straw production</b>		
Denmark average wheat straw production (collectable):	4,2 ton/ha	Miljø- og Energi-ministeriet (2001)
Denmark average grain production:	6,3 ton/ha	Miljø- og Energi-ministeriet (2001)
Straw weight fraction of total yield:	40 wt%	Calculated
Denmark average fertilizer usage:		
Mineral phosphor:	3 kg P/ha	Statistikbanken, seson 2008-2009
Mineral potassium:	10 kg K/ha	Statistikbanken, seson 2008-2010
Mineral nitrogen:	75 kg N/ha	Statistikbanken, seson 2008-2011
Fertilizer production cost (energy):		
Mineral phosphor:	12 MJ/kg P	Jørgensen et al (2004)
Mineral potassium:	7 MJ/kg K	Jørgensen et al (2004)
Mineral nitrogen:	50 MJ/kg N	Jørgensen et al (2004)
Total fertilizer requirements:	3856 MJ/ha	Calculated
Growth operations (Denmark average)		
Ploughing + 3xharrowing + seeding +	45 l diesel/ha	Miljø- og Energi-ministeriet (2001)

rolling		
Distribution of fertilizer	2 l diesel/ha	Miljø- og Energi-ministeriet (2001)
3 x harrowing against weeds	6 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Combine harvesting	14 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Shredding	4 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Pressing	2 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Wrapping	6 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Smaller operations	3 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Transport of straw in from field	8 l diesel/ha	Miljø- og Energi-ministeriet (2001)
Uptake of atmospheric Carbon:		
Wheat straw C-content	49 wt% (daf)	Bech (2008)
Wheat straw ash content	6,8 wt% (dry)	Brown (2003)
Wheat straw water content	6,2 wt%	Brown (2003)
CO <sub>2</sub> -input for photosynthesis	1570 kg CO <sub>2</sub> /ton wheat straw	Calculated
<b>Conventional wheat straw combustion</b>		
Straw energy content (wet):	17 MJ/kg	HHV from Bech (2008)
Combustion of straw	1570 kg CO <sub>2</sub> /ton wheat straw	Calculated
Centralized scenario		
Large LT-CFB electricity efficiency	45%	Stoholm et al (2010)
Large LT-CFB heat efficiency	50%	Stoholm et al (2010)
Large LT-CFB overall efficiency	95%	Stoholm et al (2010)
Plant utilities consumption	??? kWh	Unused parameter
Decentralized scenario		
CHP Plant electricity efficiency	26%	Energistyrelsen (1995)
CHP Plant heat efficiency	59%	Energistyrelsen (1995)
CHP Plant overall efficiency	85%	Energistyrelsen (1995)
Plant utilities consumption	??? kWh	Unused parameter
Local scenario		
Straw-fired steam turbine - electricity efficiency	17,50%	Stirling.dk (2010)
Straw-fired steam turbine - heat efficiency	67,50%	Stirling.dk (2010)
Straw-fired steam turbine - overall efficiency	85%	Stirling.dk (2010)
Plant utilities consumption	??? kWh	Unused parameter
<b>SuperPro Designer pyrolysis process model</b>		
Slow pyrolysis temperature (T)	300-700 ° C	Assumption
Fast pyrolysis temperature (T)	400-800 ° C	Assumption
Bio-oil yield		
Fast pyrolysis 400-675 °C (kg/ton)	$-1,7E-09 \cdot T^5 + 4,8 \cdot 10^{-6} \cdot T^4$	Trend line from SuperPro Designer

straw)	$0,005 \cdot T^3 + 2,9 \cdot T^2 - 757 \cdot T + 77650$	simulation
Fast pyrolysis 675-800 °C (kg/ton straw)	$0,006 \cdot T^2 - 9,3 \cdot T + 3882$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-700 °C (kg/ton straw)	$-2,1 \cdot 10^{-12} \cdot T^6 + 0,000000008 \cdot T^5 - 0,00001 \cdot T^4 + 0,008 \cdot T^3 - 3,2 \cdot T^2 + 683 \cdot T - 59412$	Trend line from SuperPro Designer simulation
Bio-oil water content		
Fast pyrolysis 400-675 °C (kg/ton straw)	$-0,00082 \cdot T^2 + 1,03 \cdot T - 228$	Trend line from SuperPro Designer simulation
Fast pyrolysis 675-800 °C (kg/ton straw)	$0,0000012 \cdot T^3 - 0,0027 \cdot T^2 + 2,1 \cdot T - 455$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-700 °C (kg/ton straw)	$1 \cdot 10^{-10} \cdot T^5 - 2,8 \cdot 10^{-7} \cdot T^4 + 0,0003 \cdot T^3 - 0,16 \cdot T^2 + 41,7 \cdot T - 4098$	Trend line from SuperPro Designer simulation
Bio-char yield		
Fast pyrolysis 400-675 °C (kg/ton straw)	$0,000000001 \cdot T^5 - 3,3 \cdot 10^{-6} \cdot T^4 + 0,0036 \cdot T^3 - 1,9 \cdot T^2 + 492,7 \cdot T - 48483$	Trend line from SuperPro Designer simulation
Fast pyrolysis 675-800 °C (kg/ton straw)	$5,3 \cdot 10^{-6} \cdot T^3 - 0,01 \cdot T^2 + 8,05 \cdot T - 1683,5$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-700 °C (kg/ton straw)	$3,4 \cdot 10^{-12} \cdot T^6 - 1,1 \cdot 10^{-8} \cdot T^5 + 0,000015 \cdot T^4 - 0,01 \cdot T^3 + 4 \cdot T^2 - 816 \cdot T + 69815$	Trend line from SuperPro Designer simulation
Fast pyrolysis C-content in biochar	Biochar C-content (wt%) = $0,0772 \cdot T + 15,918$	Correlation temperature/C-content Data from table 4-VII
Slow pyrolysis C-content in biochar	Biochar C-content (wt%) = $0,1 \cdot T + 10$	Correlation temperature/C-content Data from Demirbas (2006) (- ash content)
Biochar labile fraction		
Fast pyrolysis 400-675 °C (kg/ton straw)	$-8,6 \cdot 10^{-12} \cdot T^6 + 2,9 \cdot 10^{-8} \cdot T^5 - 0,00004 \cdot T^4 + 0,03 \cdot T^3 - 12,9 \cdot T^2 + 2700 \cdot T - 239580$	Trend line from SuperPro Designer simulation
Fast pyrolysis 675-800 °C (kg/ton straw)	$3,6 \cdot 10^{-6} \cdot T^3 - 0,0079 \cdot T^2 + 5,8 \cdot T - 1410$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-700 °C (kg/ton straw)	$8,9 \cdot 10^{-13} \cdot T^6 - 3,2 \cdot 10^{-9} \cdot T^5 + 4,8 \cdot 10^{-6} \cdot T^4 - 0,0038 \cdot T^3 + 1,7 \cdot T^2 - 384,6 \cdot T + 36697$	Trend line from SuperPro Designer simulation
Process gas yield		
Fast pyrolysis 400-675 °C (kg/ton straw)	$-4,0 \cdot 10^{-12} \cdot T^6 + 1,2 \cdot 10^{-8} \cdot T^5 - 0,000017 \cdot T^4 + 0,013 \cdot T^3 - 5,3 \cdot T^2 + 1162 \cdot T - 105833$	Trend line from SuperPro Designer simulation
Fast pyrolysis 675-800 °C (kg/ton straw)	$0,000031 \cdot T^3 - 0,075 \cdot T^2 + 60 \cdot T - 15746$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-700 °C (kg/ton straw)	$-1,0 \cdot 10^{-12} \cdot T^6 + 2,8 \cdot 10^{-9} \cdot T^5 - 3,2 \cdot 10^{-6} \cdot T^4 + 0,0019 \cdot T^3 - 0,6 \cdot T^2 + 101 \cdot T - 6974$	Trend line from SuperPro Designer simulation
Gas carbon content		
Fast pyrolysis	39 wt%	Data from Table 4-VIII
Slow pyrolysis	36 wt%	Data from Table 4-VIII
Gas heat capacity	1,8 kJ/(kg*oC)	Kofoed (1991)
<b>Energy production from bio-oil</b>		
Centralized scenario:		

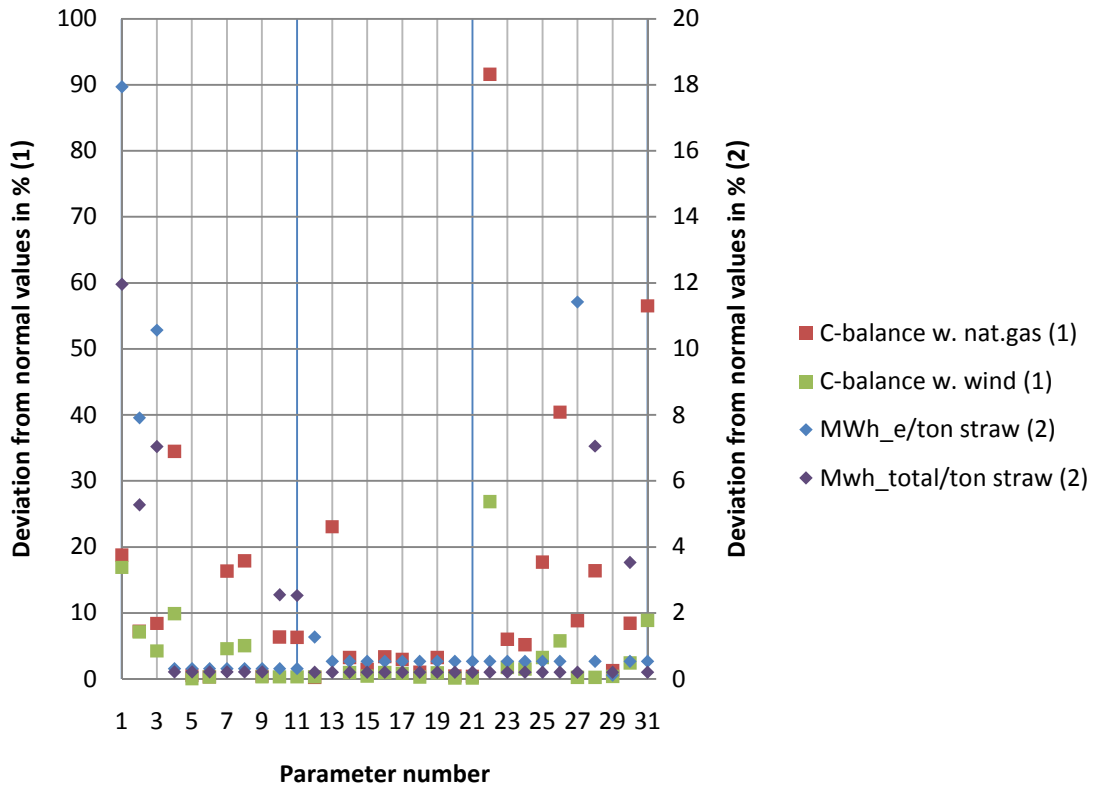


Combined-cycle natural gas plant electricity efficiency	41%	Rambøl (2008)
Combined-cycle natural gas plant heat efficiency	50%	Rambøl (2008)
Combined-cycle natural gas plant overall efficiency	91%	Rambøl (2008)
Decentralized scenario:		
Combined-cycle natural gas plant electricity efficiency	30%	Adjusted from 34% Energistyrelsen (1995)
Combined-cycle natural gas plant heat efficiency	55%	Adjusted from 57% Energistyrelsen (1995)
Combined-cycle natural gas plant overall efficiency	85%	Adjusted from 91% Energistyrelsen (1995)
Local scenario/In-situ scenario:		
Small gas turbine - electricity efficiency	12%	Calculated from Stirling.dk (2010)
Small gas turbine - heat efficiency	74%	Calculated from Stirling.dk (2010)
Small gas turbine - overall efficiency	86%	Calculated from Stirling.dk (2010)
Bio-oil HHV (MJ/kg)	$HHV (MJ/kg) = -0,408 * \text{water content (wt\%)} + 26,9$	Correlation for water content < 60 wt% (See Appendix 1)
Bio-oil HHV (MJ/kg)	$HHV (MJ/kg) = -0,06 * \text{water content (wt\%)} + 6,0025$	Correlation for water content > 60 wt% (See Appendix 1)
Bio-oil C-content (wt%)	$\text{Bio-oil C-content (wt\%)} = 1,3 * HHV + 26,2$	Correlation between HHV and C-content (See Appendix 2)
<b>Biochar amendment and degradation</b>		
Distribution of biochar	6 l diesel/ha	Set as 3 x distribution of fertilizer
Carbon loss from biochar over time (kg C/kg biochar)	$\text{Carbon-loss from biochar (kg C/kg biochar)} = 0,0012 * \text{Labile fraction (wt\%)} + 0,013$	Correlation C-loss/labile fraction Data from Bruun et al (2009)
<b>Grid loss</b>		
Grid losses for substitution energy		
All scenarios Electricity	5%	Ulrik Henriksen, Senior scientist Risø DTU
All scenarios Heat	30%	Ulrik Henriksen, Senior scientist Risø DTU
Grid losses for pyrolysis back-up energy		
All scenarios Electricity	5%	Assumption
Local scenario heat	10%	Assumption
Loss in scenario electricity grid		
Centralized scenario	30%	Ulrik Henriksen, Senior scientist Risø DTU
Decentralized scenario	25%	Assumption
Local/In-situ scenario	20%	Assumption
Loss in scenario district heating distribution		
Centralized scenario	5%	Ulrik Henriksen, Senior scientist Risø DTU

Decentralized scenario	4%	Assumption
Local/In-situ scenario	3%	Assumption
<b>Substitution energy production</b>		
Oil to close electricity gap	80,5 Kg CO2/GJ	Miljø- og Energi-ministeriet (2001)
Oil to close heat gap	80,5 Kg CO2/GJ	Miljø- og Energi-ministeriet (2001)
Natural gas to close electricity gap	60,2 Kg CO2/GJ	Miljø- og Energi-ministeriet (2001)
Natural gas to close heat gap	60,2 Kg CO2/GJ	Miljø- og Energi-ministeriet (2001)
Biomass to close electricity gap	3 Kg CO2/GJ	Miljø- og Energi-ministeriet (2001)
Biomass to close heat gap	3 Kg CO2/GJ	Miljø- og Energi-ministeriet (2001)
Wind power to close electricity gap	0 Kg CO2/GJ	Assumption
Wind power to close electricity gap	0 Kg CO2/GJ	Assumption
<b>Balancing of electricity- and heat yields for consumption</b>		
Excess heat from pyrolysis process		
Fast pyrolysis 400-510 °C (kWh heat/ ton straw)	$-0,000035*T^3+0,054*T^2-27,7*T+4659$	Trend line from SuperPro Designer simulation
Fast pyrolysis 510-675 °C (kWh heat/ ton straw)	$-0,00035*T^3+0,61*T^2-350*T+64451$	Trend line from SuperPro Designer simulation
Fast pyrolysis 675-800 °C (kWh heat/ ton straw)	$-0,031*T^2+47,8*T-16543$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-400 °C (kWh heat/ ton straw)	$-0,000059*T^3+0,064*T^2-20,3*T+2230$	Trend line from SuperPro Designer simulation
Slow pyrolysis 300-525 °C (kWh heat/ ton straw)	$-3,76E-07*T^4+0,0003*T^3+0,048*T^2-94,2*T+20078$	Trend line from SuperPro Designer simulation
Slow pyrolysis 525-700 °C (kWh heat/ ton straw)	$7,9E-10*T^6-2,9E-06*T^5+0,0044*T^4-3,6*T^3+1625*T^2-393451*T+39592319$	Trend line from SuperPro Designer simulation
Energy loss from excess energy to plant surroundings		
Centralized scenario	20%	Assumption
Decentralized scenario	20%	Assumption
Local scenario	10%	Assumption
In-situ scenario	100%	Assumption
Pyrolysis plant electricity consumption:		
Fast pyrolysis 400-510 °C (kWh heat/ ton straw)	$0,0026*T^2-2,4*T+619$	Trend line from SuperPro Designer simulation
Fast pyrolysis 510-550 °C (kWh heat/ ton straw)	$-0,000084*T^4+0,18*T^3-146,3*T^2+52496,5*T-7062018$	Trend line from SuperPro Designer simulation
Fast pyrolysis 550-675 °C (kWh heat/ ton straw)	$0,000011*T^3-0,019*T^2+11,0*T-2090$	Trend line from SuperPro Designer simulation
Fast pyrolysis 675-800 °C (kWh heat/ ton straw)	$-0,00051*T^2+0,93*T-243$	Trendline from SuperPro Designer simulation
Slow pyrolysis 300-700 °C (kWh heat/ ton straw)	$1,07*T^6-3,25E-09*T^5+4,08E-06*T^4-0,0027*T^3+0,99*T^2-190*T+15166$	Trend line from SuperPro Designer simulation

## Appendix 9:

### Sensitivity test of parameters for carbon-balance calculations (1 page)



- |    |  |    |                                      |
|----|--|----|--------------------------------------|
| 1  | oil yield  | 17 | Straw fraction of total harvest      |
| 2  | water fraction                                   | 18 | Fertilizer use in growth             |
| 3  | Bio-oil HHV >> water correlation (2 parameters)  | 19 | Growth operations diesel consumption |
| 4  | Bio-oil C-wt% >< HHV correlation (2 parameters)  | 20 | Diesel consumption per km transport  |
| 5  | Biochar yield                                    | 21 | Distance to combustion facility      |
| 6  | Biochar C-wt% >< Temp correlation (2 parameters) | 22 | Straw C-content                      |
| 7  | gas yield  | 23 | Straw ash content                    |
| 8  | Gas c-content                                    | 24 | Straw water content                  |
| 9  | gas heat capacity                                | 25 | Straw plant electrical efficiency    |
| 10 | Pyrolysis process heat balance                   | 26 | Straw plant heat efficiency          |
| 11 | Heat loss to surroundings (factor)               | 27 | Bio-oil plant electrical efficiency  |
| 12 | Plant electricity consumption                    | 28 | Bio-oil plant heat efficiency        |
| 13 | Natural gas substitution cost                    | 29 | Electrical grid loss                 |
| 14 | Energy content in 1 l diesel                     | 30 | Heat grid loss                       |
| 15 | Density of diesel                                | 31 | Straw HHV                            |

Risø DTU is the National Laboratory for Sustainable Energy. Our research focuses on development of energy technologies and systems with minimal effect on climate, and contributes to innovation, education and policy. Risø has large experimental facilities and interdisciplinary research environments, and includes the national centre for nuclear technologies.

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