Ulla Lassi, Henna Lempiäinen,
and Bodil Wikman (eds.)

BIOMASS TO ENERGY AND CHEMICALS

HighBio2 Project Publication

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Edited by Ulla Lassi, Henna Lempiäinen and Bodil Wikman

HIGHBIO2 2011-2013
Biomass to Energy and Chemicals

UNIVERSITY OF JYVÄSKYLÄ
KOKKOLA UNIVERSITY CONSORTIUM
CHYDENIUS

OULUN YLIOPISTO
UNIVERSITY of OULU

Centria
TUTKIMUS JA KEHITYS

LULEÅ
UNIVERSITY
OF TECHNOLOGY

Dedication to the memory of

Eero Kangasoja

HighBio2 publication has been dedicated to the memory of Eero Kangasoja, who suddenly passed away in October 2013. Eero was the (invisible) great man and the innovator of the down-draft gasifier of our project. During the past years, he did excellent experimental work and gave us basic knowledge and guides to innovative research projects. He was also the founder member of EK Kaasu and later Gasek company. As with the other great innovations, only the next coming generations will see the value of Eero´s innovations.

PROJECT FINANCERS

PREFACE

A major share of the world's energy production is currently based on fossil fuels. As pressure increases to shift to renewable sources instead of depleting fossil fuel sources, the importance of biomass in the production of energy, fuels, and chemicals grows. The National and European Union energy and climate policies aim to reduce greenhouse gas emissions, to increase the use of energy from renewable sources, and to improve energy and material efficiency. In Finland and Sweden, the national targets for 2020 regarding the share of renewable energy sources in final energy consumption have been set even higher than the ones laid out by European Union. And of the ways to increase the share of renewable energy, wood-based bioenergy is a significant and cost-efficient option.

In small-scale combined heat and power plants (CHP), heat and power can be produced from local ingredients, such as wood chips and waste fractions. As the use of renewable energy forms in distributed energy production increases, so does local self-sufficiency in energy production. Such an increase also promotes the aims of sustainable development and has the potential to create new jobs. By combining a CHP plant with a biomass gasifier and a biorefinery, it is possible to produce, along with heat and power, biofuels and other chemicals. This approach follows for example European Union's energy and climate targets for 2020, which includes a target for increasing the share of biofuel in transport fuels. However, more effective use of these renewable sources requires further research and development of renewable energy technologies.

To address these issues, the HighBio2 project focused on the utilization of forest biomass in energy production by gasification and on the manufacture of chemicals and transport fuels from syngas and gasification by-products. The project researched among others the development and optimization of the gasification process. In addition, purification and further treatment of syngas have also a significant potential to increase process efficiency.

Other means of increasing process effectiveness were also examined, including the utilization and recovery of gasification process by-products such as ash and carbon dioxide. Syngas produced from wood chips contains impurities (e.g., tars) that can harm the plant, so technologies for purifying syngas were also evaluated. A further project target was the development of the catalytic process for converting syngas into biofuels.

HighBio2 was implemented by the research organizations that successfully cooperated on the HighBio project (2008–2011). The University of Jyväskylä / Kokkola University Consortium Chydenius (Finland) was the project's lead partner. The other partners were Centria University of Applied Science (Ylivieska, Finland) and the University of Oulu (Finland). In addition to the Finnish partners, Luleå University of Technology in Sweden also participated.

During the HighBio2 project researchers gathered several times to make measurements at different gasification plants. In the figure Jaakko Pulkkinen and Pekka Tynjälä prepared solutions used for tar analysis at a pilot gasification plant in Sievi in November 2012.

We are grateful to all the parties that have contributed to HighBio2. Every researcher, employee, financier, company, and project event participant has been important for the project's success. With our combined effort we have achieved significant results and established exciting cooperation relationships for the future.

Kokkola, 1st of October, 2013

Ulla Lassi
Professor, Applied Chemistry
Leader of the HighBio2 project

Henna Lempiäinen
Project Coordinator

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BIOENERGY PROCESSING

The HighBio2 project in short

Bodil Wikman[1], Tero Tuuttila[1], Ulla Lassi[1,2]

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Applied Chemistry, Finland
[2] *University of Oulu, Department of Chemistry, Finland*

The HighBio2 project "Biomass to Energy and Chemicals" was developed to continue the research started during the HighBio project which was carried out during the period 2008-2011 between universities and research institutions in the Central and Northern part of Finland and Northern part of Sweden. The aims of both projects were from the beginning to promote the utilization of renewable energy, in particular the use of forest biomass and residues which are abundant in the project region. The project has focused on the development of an environmentally sustainable technology, i.e. gasification technology for the production of heat, energy and chemicals. In practice the idea has also been to promote a distributed energy model, instead of a centralized one.
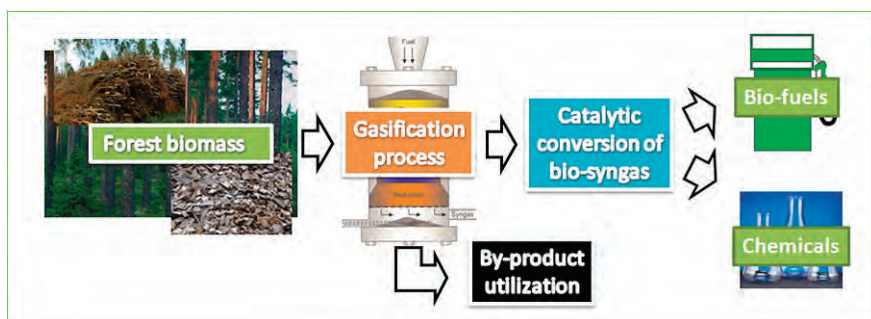

FIGURE 1. *A schematic presentation of the route to produce biofuels and chemicals from biomass-based syngas.*

Gasified forest biomass can thus further be used for combined heat and power production, as well as for the production of chemicals, such as

transportation fuels. If the gas is not only burned but further processed it needs to be cleaned. In the project a specific process to synthetize biodiesel has been studied, that is the Fischer-Tropsch synthesis. There are also other ways to produce value-added products from bio-syngas, such as fermentation and mixed alcohol synthesis. Please see figure 2 for a short summary of the processes.
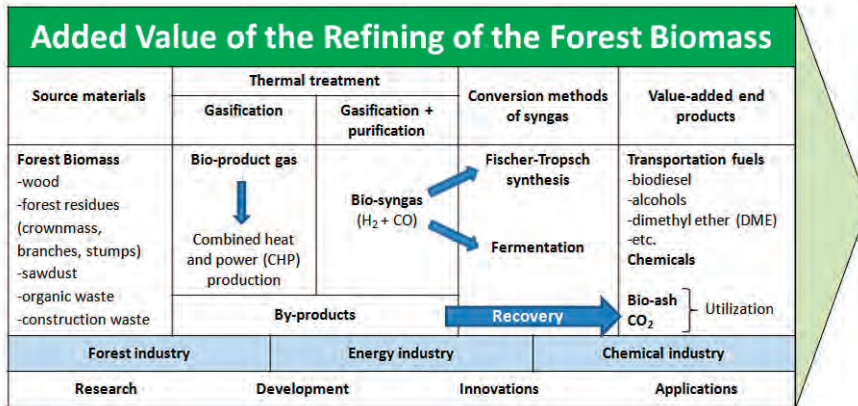

FIGURE 2. *A value chain describing the potential of the forest biomass as a source material for value-added end products.*

The HighBio2 project has been divided into four different main work packages (WPs): The work packages have further been divided into sub-work packages, and the responsibility for the implementation of these has been divided according to the expertise of the participating organisations. The work packages are the following:

WP1 – Optimization of the gasification process
  WP1.1 Improved control of the gasification process
  WP1.2 Analysis of syngas quality
  WP1.3 Evaluation of material and energy balance, and carbon conversion

WP2 – Purification of syngas
  WP2.1 Improved purification process
  WP2.2 Recovery of CO_2
  WP2.3 Tar sampling and analysis

WP3 – Utilization of purified syngas and gasification by-products
  WP3.1 Development and optimization of Fischer-Tropsch synthesis
  WP3.2 Study of other catalytic routes
  WP3.3 Utilization of by-products

WP4 – Information distribution

WP4.1   National and international information distribution
WP4.2   Project administration and reporting

In Finland Centria University of Applied Sciences has focused on the research on small scale gasification and combined heat and power production (work packages 1.1, 1.2, and 2.1). Centria has a gasification pilot plant in Sievi, where researchers have tested and developed the down-draft gasification technology and also the use of a Stirling engine in the combustion of product gas. The Department of Chemistry, Renewable Natural Resources and Chemistry of Living Environment at University of Jyväskylä has contributed with knowledge on the development of mathematic models for gasification, including calculation of mass and energy balances (work package 1.3).

The Department of Applied Chemistry at Kokkola University Consortium Chydenius, which is also a part of Jyväskylä University, has focused on the catalytic conversion of biomass-based syngas, in particular the Fischer-Tropsch synthesis, as well as on the analysis of tar compounds in the gas (work packages 3.1 and 2.3). University of Oulu, the Department of Chemistry has special expertise in the area of characterization, utilization and upgrading of by-products from the biogas, especially gasification bio-ash as well as biodegradation of cleaning waters from the gasification process (work package 3.3).

In Sweden, the Division of Energy Sciences/Energy Engineering at Luleå University of Technology has studied the development of computer models regarding the recovery of CO_2 from syngas using ionic liquids and compared them to experimental data (work package 2.2). This process thus implies the purification of syngas. At Oulu University, the Department of Chemistry has also made an overview of the different methods to separate CO_2 from a gas mixture.

Kokkola University Consortium Chydenius has been responsible for the project leading and the administration of the project (work package 4). Information about the project can be found at the project web pages http://www.chydenius.fi/en/natural-sciences/research/highbio2. Seminars, regarding project research topics, have been arranged for project researchers, other researchers and the public. The present report is also one of the results of the project. In addition the project has also produced a project video which will be published on the internet pages of the project.

Collaboration with other projects, organizations and individuals has been essential to the project, to mention for example the Processum Biorefinery Initiative AB linked to the Forest Refine project and the former HighBio project coordinator Ulf-Peter Granö, who have contributed with articles to this publication.

Bioenergy Processing: Using Local Energy Resources

Ulf-Peter Granö, Finland

Introduction

Forests contain a large amount of unused wood in the form of forest biomass. This wood biomass can be effectively used in local bioenergy processes as energy and raw materials. In the near future, new small-scale solutions will play a significant role in bioenergy processing. Harvesting, handling and further local processing, along with the use of local energy resources for local and regional consumers, all contribute to sustainable development.

Biomass can be processed into various types of fuel materials, including solid and liquid forms, or into finished products, such as electricity and heat. Coordination and management made via energy terminals can provide synergistic benefits in integrated production that utilizes local resources. Through the appropriate combination and correct application, a higher utilization level can be achieved in processing. This means less waste and fewer unused by-products, which helps to reduce the environmental impact.
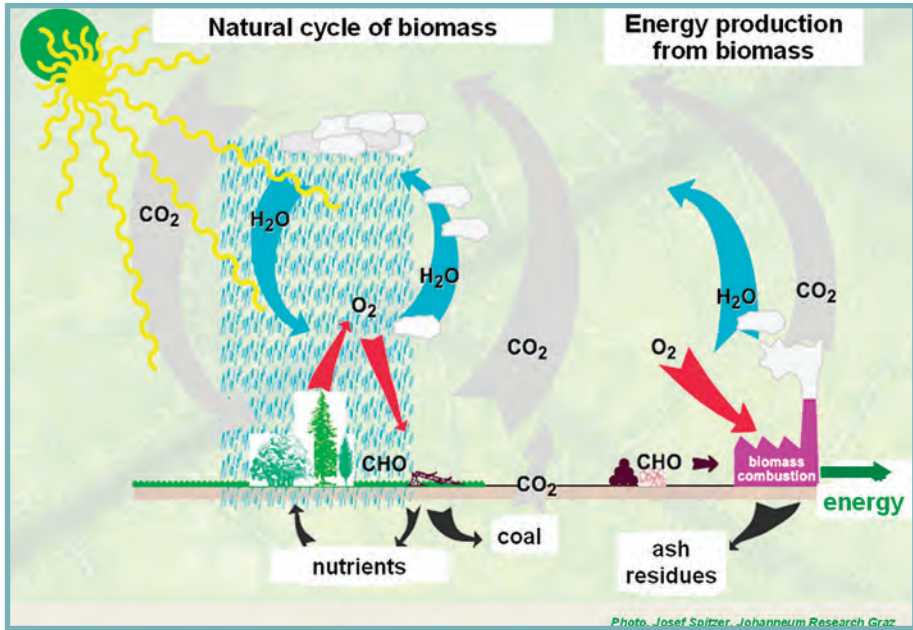
FIGURE 1. *The natural cycle of biomass and biomass energy production and their contribution to sustainable development.*

Alternative liquid fuel: Gas from biomass can partly replace and supplement fossil gas

Biosyngas is a synthetic gas derived from biomass gasification or a biogas derived from a true fermentation process. In the near future, after a purifying process these biogases may replace and supplement fossil gases such as natural gas (NG). With the right chemical process the synthetic gas can be converted to SNG (synthetic natural gas or bio-SNG). The wood gas or so-called product gas obtained through gasification of biomass is purified, cooled and filtered. This biosyngas is an important raw material in fuel feedstock for future biofuels.

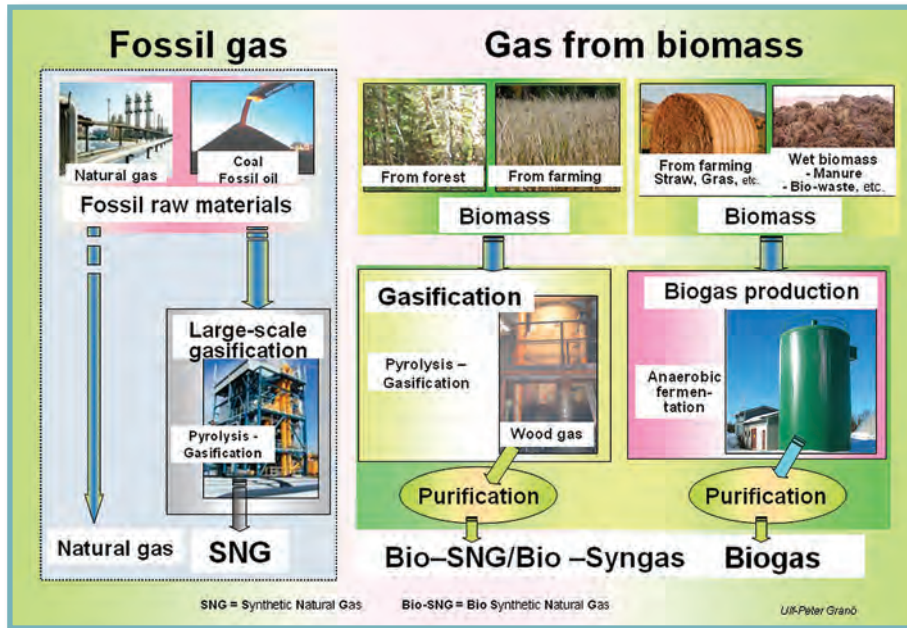## The difference between fossil gas and gas from biomass

FIGURE 2. *A comparison of fossil gases and biomass gas.*

Figure 2 presents a simplified overview of various types of gases that can be used as fuel or fuel feedstock for further processing. The diagrams show the differences between the various types of gases.

Fossil gas

Besides natural gas, synthetic natural gas (SNG) can be produced from coal and oil. For the gasification of coal, the crushed coal is often suspended, prepared and injected into a so-called entrained flow gasifier.

Gas from biomass

Gas produced from biomass is a renewable energy carrier. As opposed to fossil gas, the term green gas can be used. The easiest way to use the gas from biomass is combustion. When the gas is used as fuel in, for example, a gas turbine engine at a CHP plant, there must be a good purification process. In particular, gases that contain tars can cause significant problems if they are not treated.

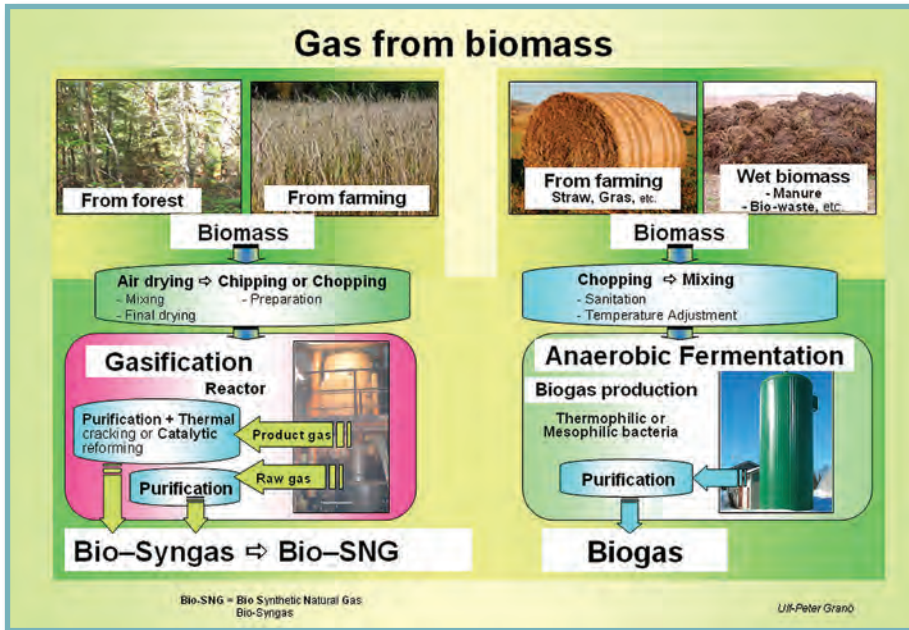## The difference between gasification and fermentation

FIGURE 3. *The two main routes for gas from biomass gasification and anaerobic fermentation.*

The production of gas from biomass can be made according to two main principles: gasification and anaerobic fermentation. The general guideline is that woody biomass is mainly used for gasification.

Gasification

Gasification is the thermo-chemical conversion of biomass by heating it with a limited oxygen supply. The biomass is heated to a temperature at which it is converted into gaseous form. Gasification is usually divided into three ranges: low, medium, and high.

– Low-temperature gasification: 800ºC–1000ºC
– Medium-temperature gasification: 1000ºC–1200ºC
– High-temperature gasification: 1200ºC–1400ºC

In English-language literature on the subject, the gas that is produced is typically called product gas when the gasification is below 1000ºC. The gas from the reactors with temperatures above 1200ºC is called biosyngas, because the gas at these higher temperatures consists almost entirely of H_2 (hydrogen) and CO (carbon monoxide), apart from CO_2 (carbon dioxide) and H_2O (water).

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Anaerobic fermentation

By allowing bacteria to digest biomass in an oxygen-free environment, biogas is produced (figure 4). The type of bacteria used depends on the temperature level in the reactor. Bacteria are sensitive to temperature variations and can only operate well within a limited range. Typically, a normal mesophilic environment and a higher thermophilic bacterial environment of the reactor can be separated.

Temperature ranges in the biogas reactor:

– Psycophilic, 15ºC–30ºC (not used)
– Mesophilic, 35ºC–40ºC
– Thermophilic, 55ºC–65ºC

Along with the production of biogas, sanitation (e.g., 70°C for one hour) must be used. Sanitation sterilizes the raw material and prevents the spread of infection, especially if the raw material (manure and biomass) comes from several farms.
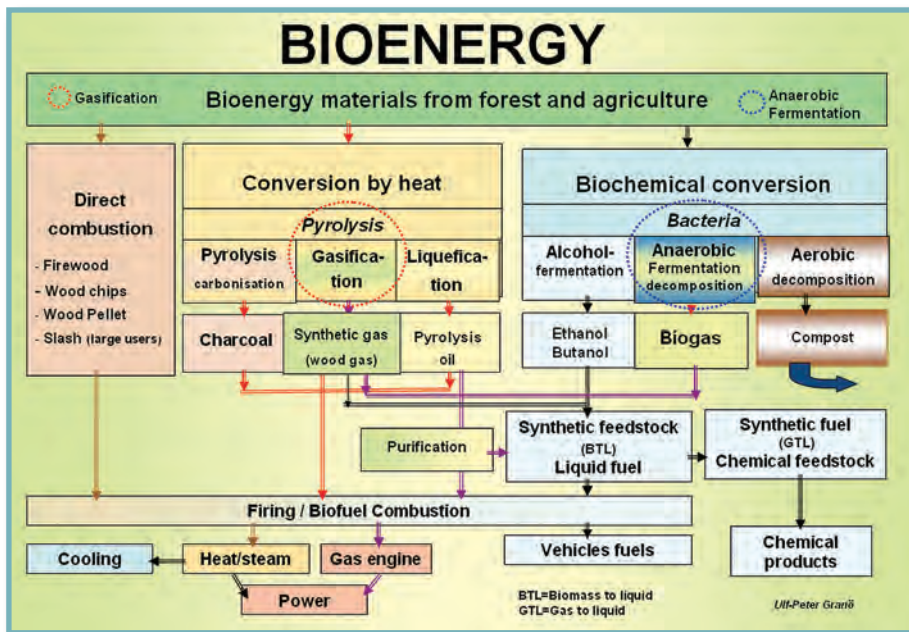
FIGURE 4. *Overview of options for using and processing the gas from biomass: 1) Conversion of heat as gasification. 2) Biochemical conversion using anaerobic fermentation.*

Renewable energy – green energy

Solid and gaseous biofuels

Biofuels derived from the first stage of biomass processing can be divided into three groups:
- – Solid fuels
- – Liquid fuels
- – Gaseous fuels

Solid, liquid and gaseous fuels

Solid biofuels obtained from forests consist mainly of firewood, wood chips, wood pellets, *crushed* slash (i.e., *forest residues),* and stumps
- – Production methods for gaseous biofuels:
- – Gasification through heating
- – Anaerobic bacteria process
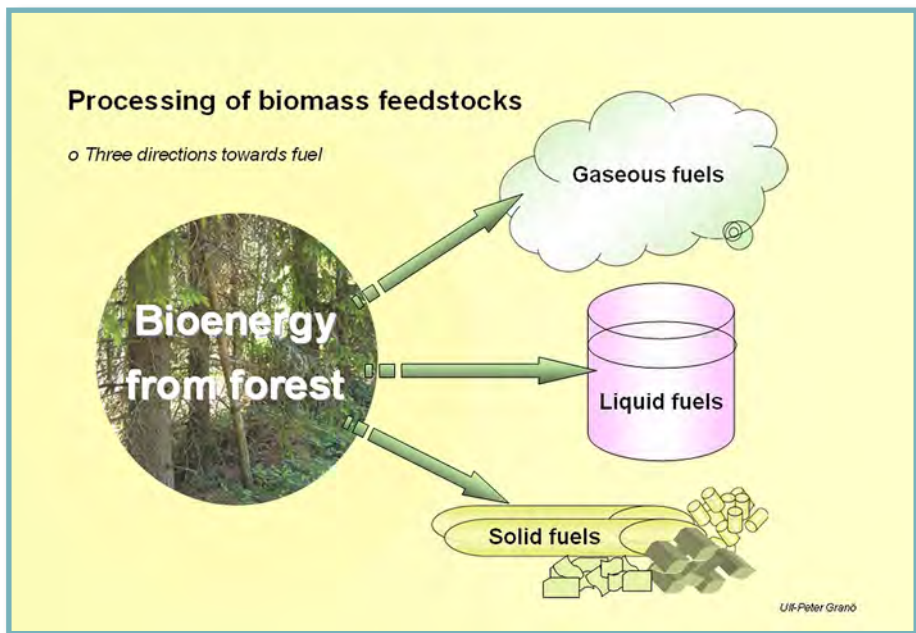
FIGURE 5. *Bioenergy materials from the forest can be processed into various solid, gaseous, or liquid biofuels.*
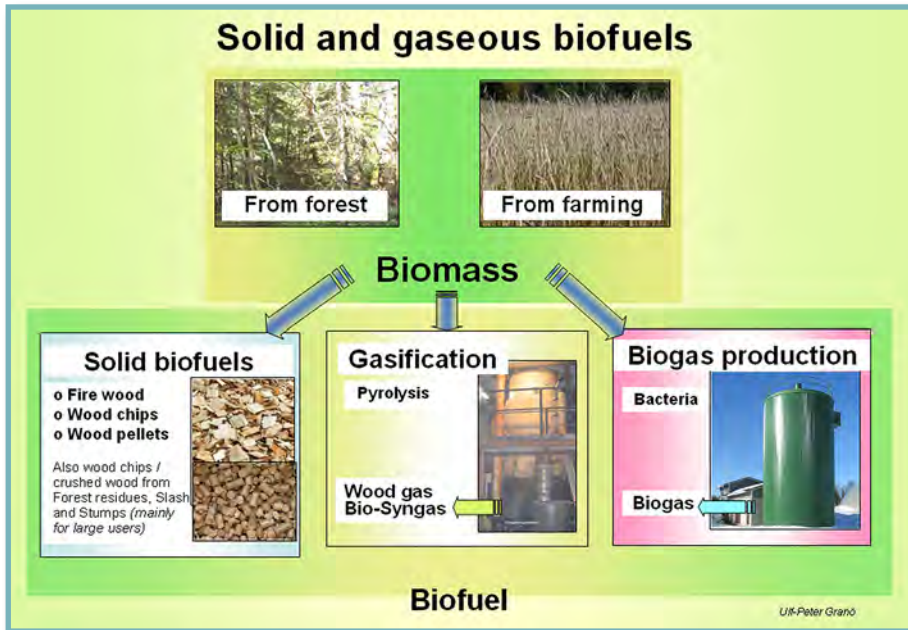
FIGURE 6. *The classification of solid and gaseous biomass for burning or further processing.*

Liquid biofuels are advanced products and can be obtained by various means, such as further refinement, using the following techniques:

– Wood gasification
– Alcohol fermentation
– Anaerobic degradation
– Liquefaction (pyrolysis oil)

Processing biomass by heat

The goals of the heat conversion process (pyrolysis) have varied over the years. Often it has been linked to the availability of fossil fuels. There are three routes of pyrolysis:

– Gasification (wood gasification was first developed during the war for producer gas operation)
– Liquefaction produces pyrolysis oil
– Pyrolysis - Carbonization (used for charcoal production)
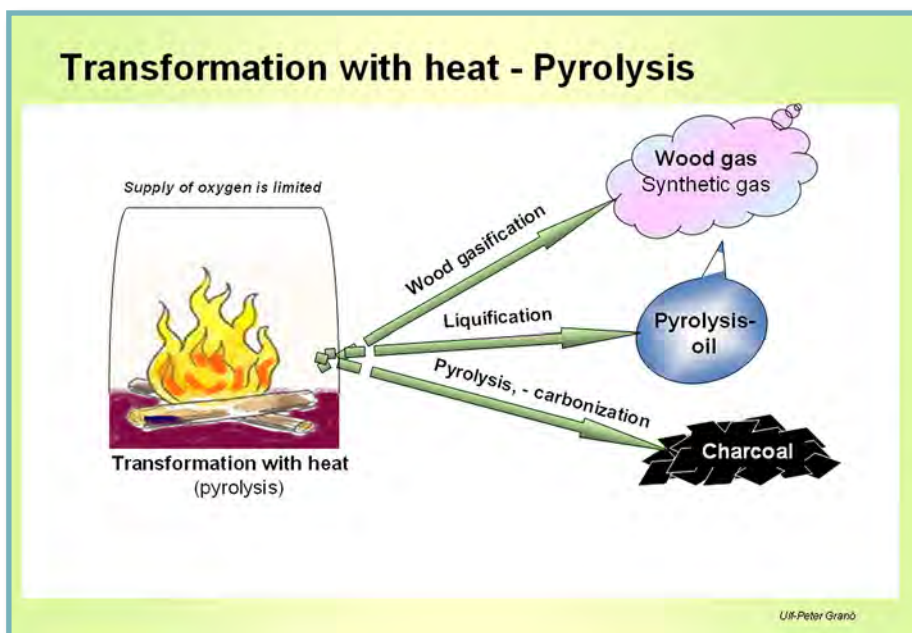
FIGURE 7. *Processing biomass by heat, wood gasification, liquefaction, and carbonization.*

Green chemistry

Through the chemical processing of syngas or producer gas, a variety of commodities (feedstocks) and different kinds of products can be produced. The main expectation is related to vehicle fuel as a substitute for fossil fuels. When forest biomass is the main feedstock it does not compete with crops that are suitable for food production. By developing green chemistry, the dependence on fossil oil products can be reduced. Local bioenergy resources can be better utilized, which can increase employment and self-sufficiency in the region.

Bio-refinery

As fossil fuels prices have increased, the interest in the enhanced processing of renewable resources such as biomass has increased as well. The tars in the wood gas (product gas) are one of the biggest problems for most companies, because purifying the gas of these tars is complicated and difficult. However, tar-free reactors for tar cracking and product gas cleaning are currently under development.
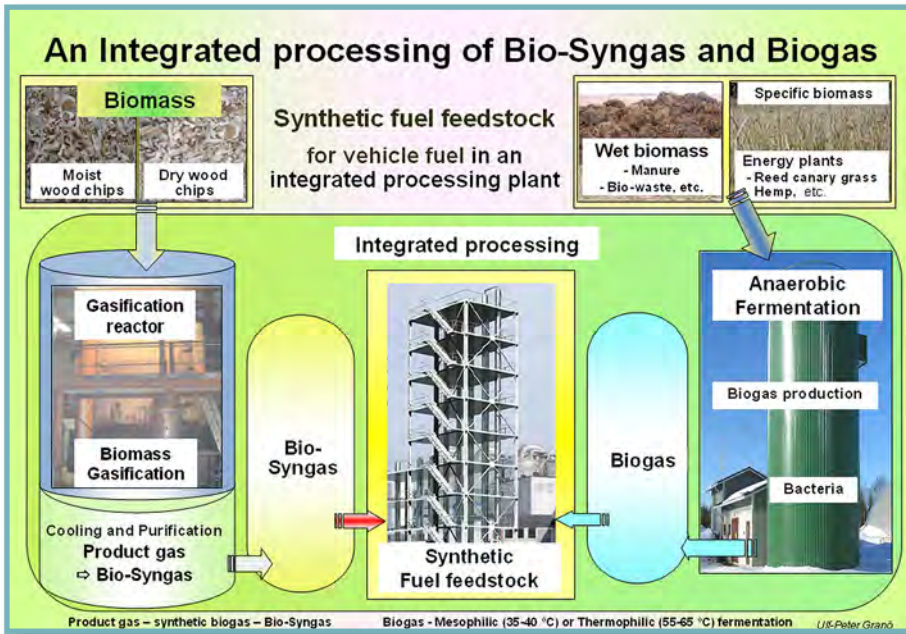
FIGURE 8. *Future processing plants for synthetic fuels may use both biosyngas and biogas commodities.*

From wood gas to liquid fuel

The product gas from wood materials can today serve as raw material for the production of liquid fuel after it has undergone a couple of processes. The most known is the Fischer-Tropsch (FT) process. The FT process was developed in Germany. Today, the technology has been refined and the process consists of second and third generation FT processes.

Smaller units for refining

When gasification and refining is arranged next to a CHP plant, a good chance for synergy exists. The heat from the gasification process can be effectively utilized and the product gas can be upgraded. This way it is possible to ensure that low-grade gas and heat produced in the plant can be used in the CHP plant for the district heating network.

Small gasification plants that utilize biomass and which are connected to the local CHP plants are mainly suitable for the production of electricity and heat. Especially if there is access to one of the future gasification reactors that can use damp or dry wood chips, and also can produce a product gas without tar particles. For CHP units with biomass gasification that require drying of wood chips and efficient cleaning of tars, the unit must be large enough to be profitable for the production of biosyngas.

Local heating and CHP

Small-scale solutions for processing biomass from the local area for consumers in nearby regions have not received the desired and adequate development resources. Governments and policy makers have had neither the interest nor the ability to see the significant potential of small-scale solutions such as cogeneration (CHP).

Local heating produced by biomass

Heat delivered from a common heating unit to several buildings (either residential or business) can be distributed with what is known as a local heating network or small district heating system. In municipalities and urban centers, there can also be major consumers (e.g., schools, health clinics, retirement homes, and churches) that are connected to the local district heating network.
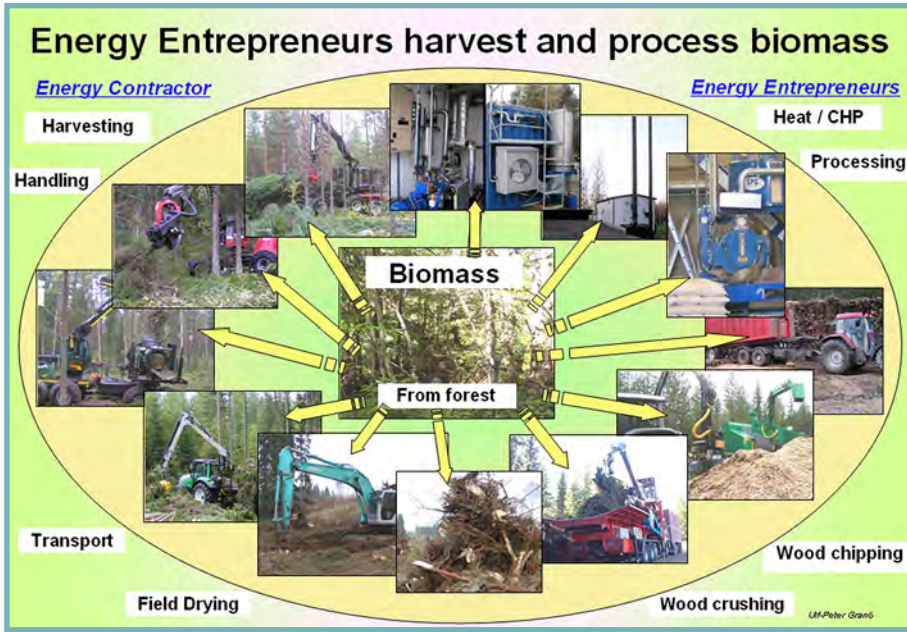
FIGURE 9. *Local energy contractors and energy entrepreneurs collaborate with energy co-operatives to create the conditions to manage the local biomass processing and heating or combined heat and power production. In Finland there are many good examples of energy co-operatives, energy entrepreneurs, machinery contractors, and small businesses who harvest and process biomass locally.*
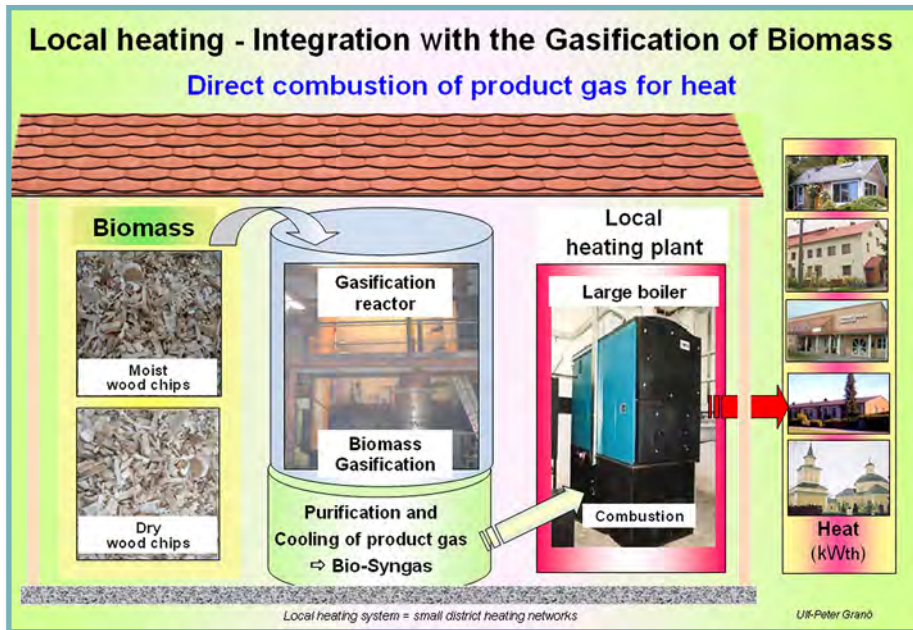
FIGURE 10. *Through the coordination or integration of gasification and combustion in a local heating plant, the emissions of flue gas particles from the unit can be reduced.*

In many municipalities in Finland, energy cooperatives have taken responsibility for the production of the heat in the pipes, serving the local district heating network.

Reduced dust emissions in flue gas

Many smaller heating units lack the demand and resources to have effective systems for flue gas cleaning. A new option for small heating units that use wood chips as fuel is to first gasify biomass and then burn the product gas (i.e., wood gas) in the boiler. The right gasification technology removes dust residue from the producer gas during the primary wood gas cleaning. When burning this product gas, there is no dust in the flue gas.

Combined heat and power units (CHP)

Small cogeneration units or CHP units produce heat and electricity. There are many different options and principles for how small-scale power generation in conjunction with a local heating unit can be arranged. The two most common groups are as follows:
- Wood burning boilers and the conversion from thermal energy into power and heat.
- Gasification units and the conversion of biosyngas into power and heat.
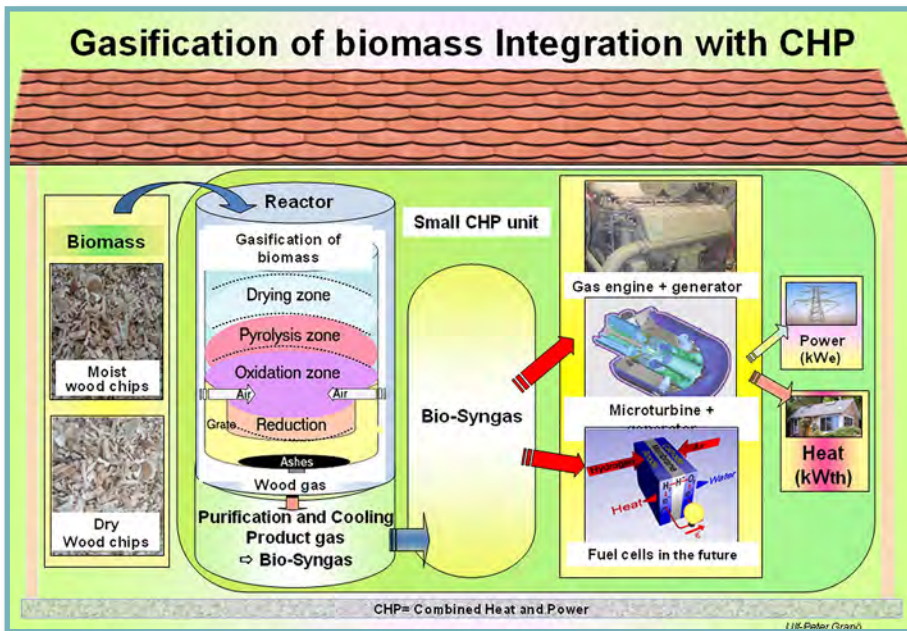
FIGURE 11. *With proper purification and cooling, the product gas can be used as fuel gas in a piston or turbine engine in a CHP unit.*

Integrated energy units

In order to use the product gas as engine fuel, the gas should be completely free of tars and tar particles. In small wood gasifiers it is easier to control and maintain a stable temperature during the gasification process. At temperatures above 1000°C, there is some cracking of the tars. The raw wood gas (i.e., the product gas) from the gasifier needs to be purified and cooled. Purification can be done with water or oil-cleaning devices, known as scrubbers, and by dry-filtering. The purified gas is known as biosyngas, a synthetic gas from biomass.

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Combining biogas and wood gas

In early planning it may be necessary see the possibility of combining a wood gasifying unit with a biogas plant in rural areas. This is especially true when the product gas is used for heat and power, and the unit is connected to a local district heating network. In the future, in some areas outsourced CHP units will benefit from a coordinated feedstock pool, which can consist of raw materials for biogas and forest biomass for gasification of product gas (wood gas). Both gases can be used for a piston or turbine engine in a CHP unit.
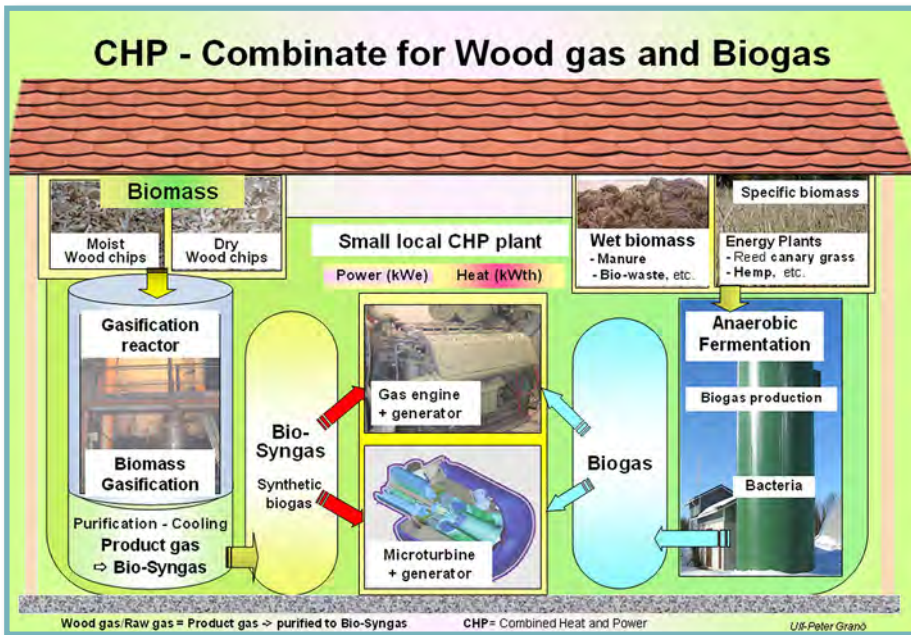
FIGURE 12. *Future outsourced CHP units in some areas will benefit from a coordinated commodity pool, which can consist of raw materials for biogas and forest biomass for gasification of product gas (wood gas).*

Green feed-in tariffs for CHP

To create better economic conditions for small-scale CHP units, politicians and government officials have to recognize the need for electricity tariffs on green energy. It mainly involves small-scale CHP units using renewable energy resources from forests and agriculture that need feed-in tariffs. Smaller units that produce power from biomass through gasification, direct combustion or through biogas have a huge potential for the local

processing of bioenergy materials. Local CHP are also important for employment, environmental considerations, and local self-sufficiency in power and heat.
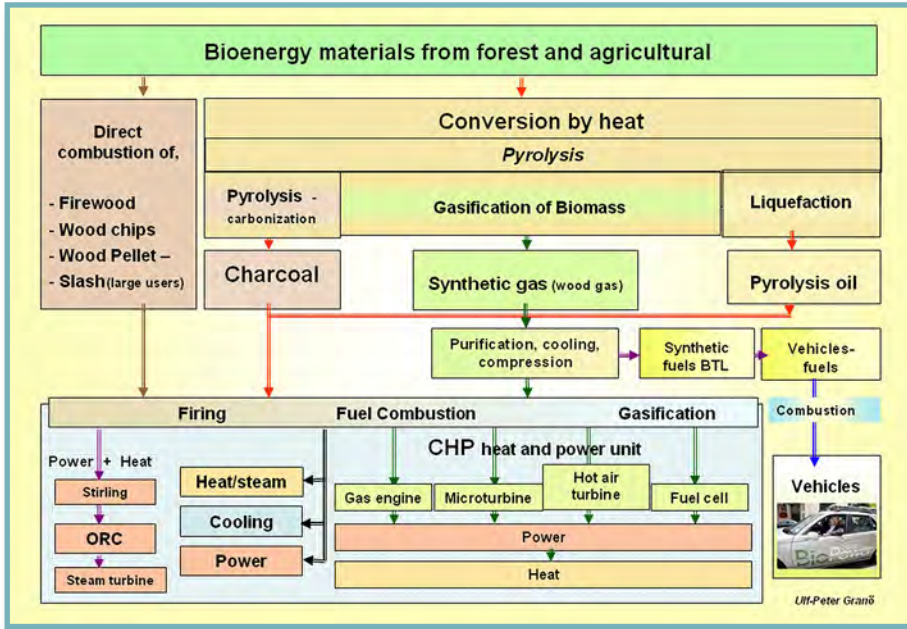
FIGURE 13. *Examples of pathways for processing biomass raw materials into electricity and heat through direct combustion and conversion by heat.*

Solar panels can be combined with a heating unit

An interesting solution is to combine the local heating system with solar panels in order to utilize additional heat from the Sun. Especially from spring to fall, the heat from solar panels can be a very effective addition to the heating system.
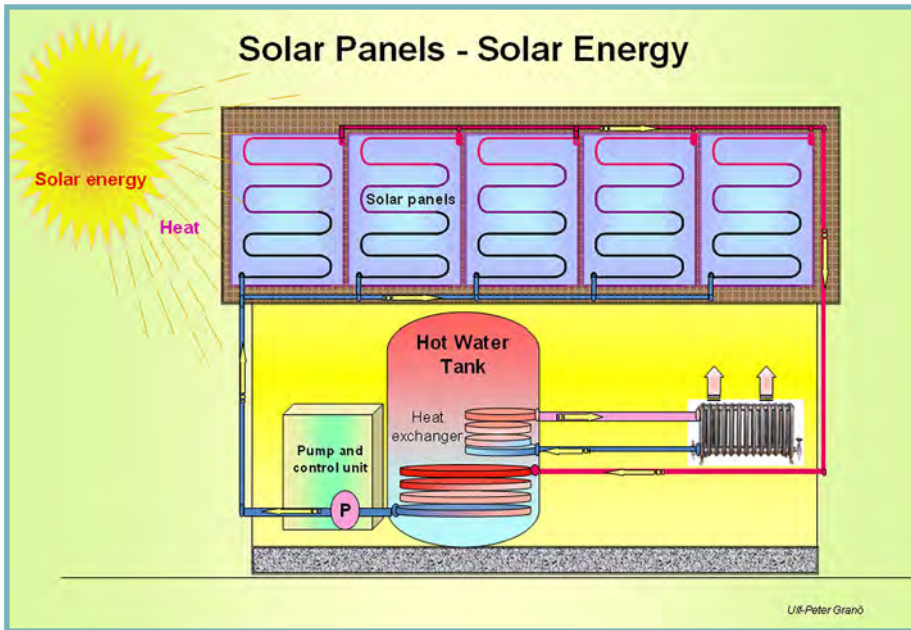
FIGURE 14. *Synergies can be achieved by combining the solar panels with a heating plant for local district heating. Especially during the summer months when the heating need is low, solar panels can often be responsible for part of the heat production.*

Integration with Geothermal energy

Heat energy from the ground and bedrock is an excellent addition to some local heating systems and units. Depending on the amount of heat wanted from the bedrock, boreholes should be drilled between 100 and 200 meters deep. Successful planning requires that the company or advisory organizations with sufficient expertise are hired at an early stage. Geothermal energy comes mainly from geothermal bedrock heat (vertical), sea/lake or pond heat, and from horizontal ground heat. The geothermal system can alternatively be used for heating or also combined for cooling.

Many opportunities for integration

There are many opportunities and routes for integrating cooperation. Individual energy co-operatives or contractors have a chance to select the way that is the most beneficial for them. Developing a so-called terminal and processing plant requires local management and cooperation regarding the use of the available local biomass feedstock.
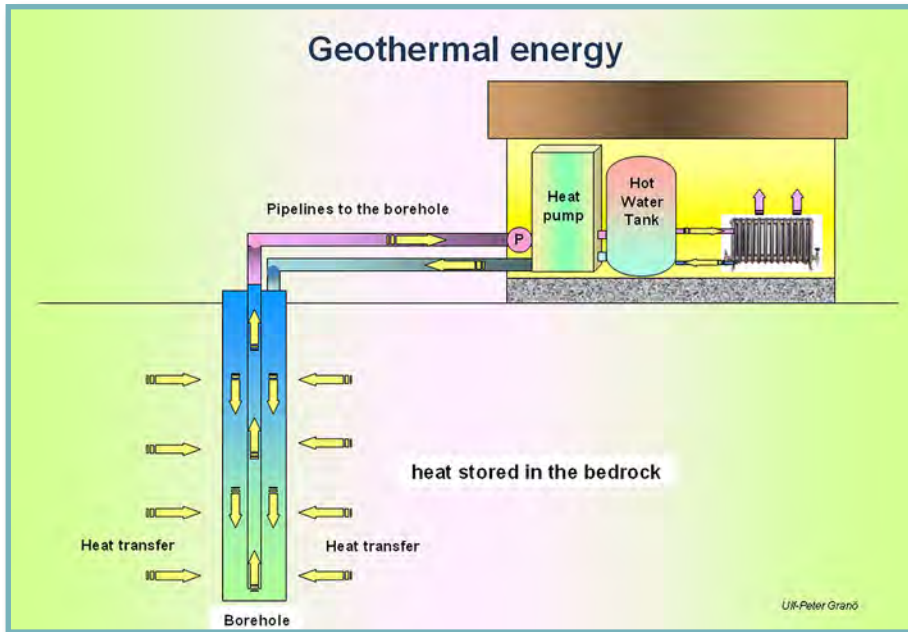
FIGURE 15. *Heat is transferred from the drill holes in the rock to the water in the pipes that lead to the heat pump. The heat pump raises the temperature and transmits the heat to a heat exchanger, which then heats the water in a local district heating system or the boiler house.*

Gasification of biomass to fuel

Biomass gasification presents many interesting possibilities for further processing of wood gas. The product gas is produced after an initial purifying and cooling of the wood gas or raw gas. Biosyngas is produced after better filtering and cleaning to remove particles and tars.

Gaseous or liquid fuels

In the gasification of biomass, there are different objectives for the use of the product gas or biosyngas. The simplest step is to use the product gas for direct combustion in a boiler.

For further processing into gaseous or liquid fuel feedstocks, the following rough classification can be used. The classification is based on the target and processing concerns.

- Gaseous fuel
  - For direct combustion of the product gas: biosyngas *(heating alt. heating and power)*
  - As fuel for gas engines or micro turbines *(CHP, heat and power)*
  - For conversion into bio-SNG *(synthetic natural gas)*
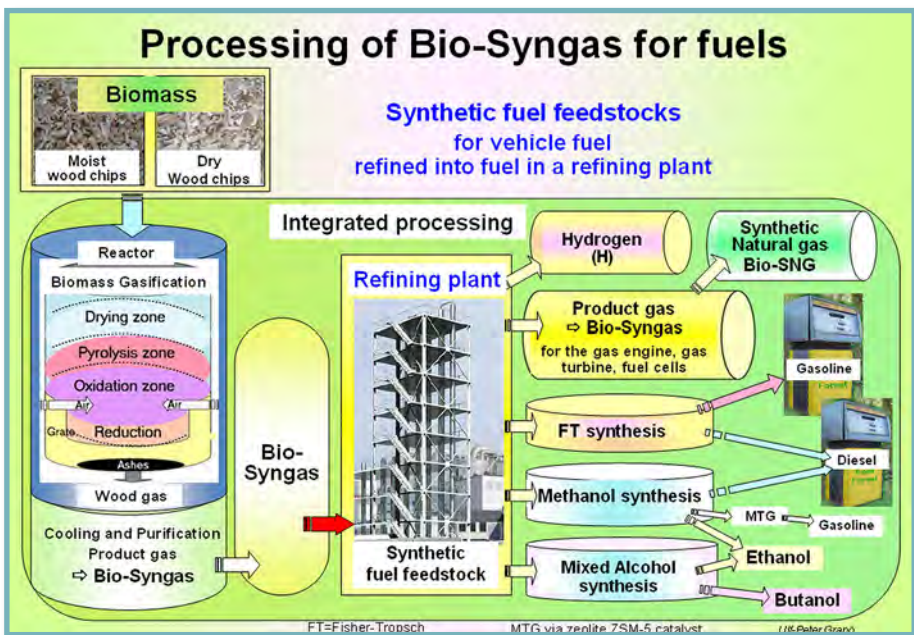
FIGURE 16. *An overview of the gasification process and further processing of vehicle fuels.*

- Liquid fuel
  - Using Fischer-Tropsch synthesis to produce gasoline or diesel
  - Through methanol synthesis processing to produce diesel or gasoline additives
  - In a mixed alcohol synthesis, produces ethanol or butanol
- Special fuel products
  - For example, the separation of hydrogen (H) from biosyngas *(hydrogen H_2)*

Various catalytic routes

It is customary to divide the catalytic processes into three alternative routes or types of synthesis:
  - Fischer-Tropsch synthesis
  - Methanol synthesis
  - Mixed Alcohol synthesis

In the conversion of biosyngas to liquid fuel products, the catalysts used in the various syntheses are keys to the efficient functioning of the process. A catalyst can be composed of several active elements attached to a carrier. The catalyst may have one or more active components, such as Fe (iron), Co (cobalt), Ru (ruthenium), and Cu (copper).

How a catalyst is prepared and the active parts involved in it are critical to its function. As a rule, it should have a maximum surface area of the active parts in right proportion. The catalyst's active design is dependent on the desired result. Furthermore, both the temperature and gas pressure must be kept within certain limits in order to get a certain type of end product.
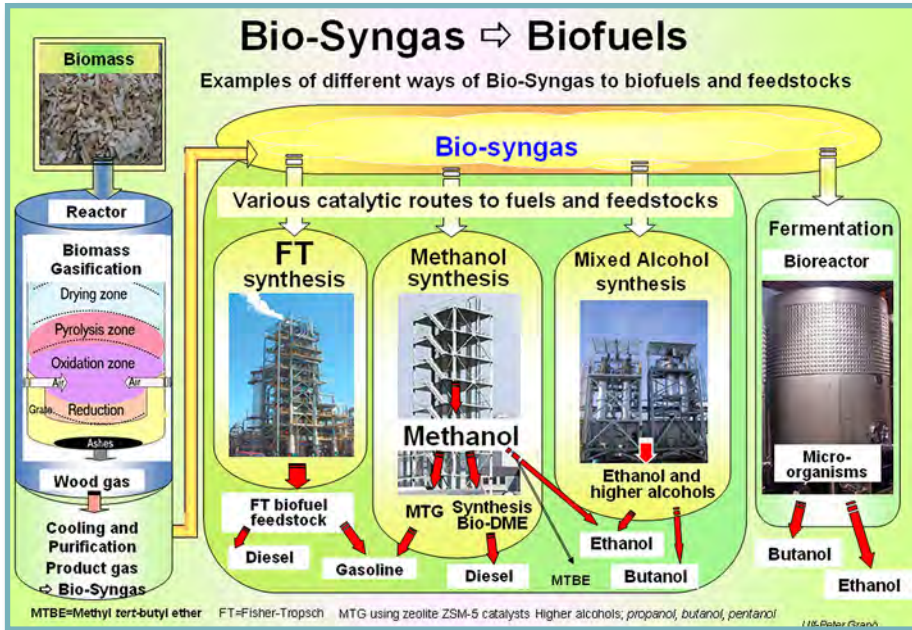
FIGURE 17. *A comprehensive and simplified overview of the three catalytic pathways and the optional fermentation process for the biosyngas used in biofuel products.*

Fermentation of biosyngas for biofuel feedstocks

A new option developed in recent years is that the product gas or biosyngas receive further processing of microorganisms in a fermentation process. Depending upon the types of microorganisms used in the process, ethanol or butanol feedstocks can be produced.

Fermentation of biosyngas requires customized and effective microorganisms.

Local small processing units

In the near future, local small processing plants in rural areas will grow and develop. After the gasification of biomass, these plants will carry out the first refinement of biosyngas for synthetic fuel feedstock and further transportation to the final refining plant. At the concentration and refinery plant, the synthetic fuel feedstock can be processed and the final fuel produced.

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OPTIMIZATION OF THE GASIFICATION PROCESS

Biomass Gasification: Material and Energy Balances

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Material and energy efficiency is an important issue in biomass gasification because biomass is a more expensive fuel than other forms, such as coal. Material and energy balances are useful because they can be used to determine a range of information about processes, including efficiency evaluation. The boundaries of the process to be examined can be established according to the type of information needed about the process. If the purpose is to acquire knowledge about the process' environmental or climate impacts, production, collection and transportation effects should also be examined. If the goal is to improve the energy efficiency of the whole production chain, a similar set of information is required. Some material or energy flows are so small that they can be ignored. If the goal is to improve the functioning of a gasifier, the examination should be limited to those issues that directly affect the device. These issues include input and output material flows of the process. Other issues (e.g., production, collection and transportation of the fuel and treatment of waste) should be excluded. This article discusses only those balances that aid process improvement (van der Meijden *et al.*, 2010).
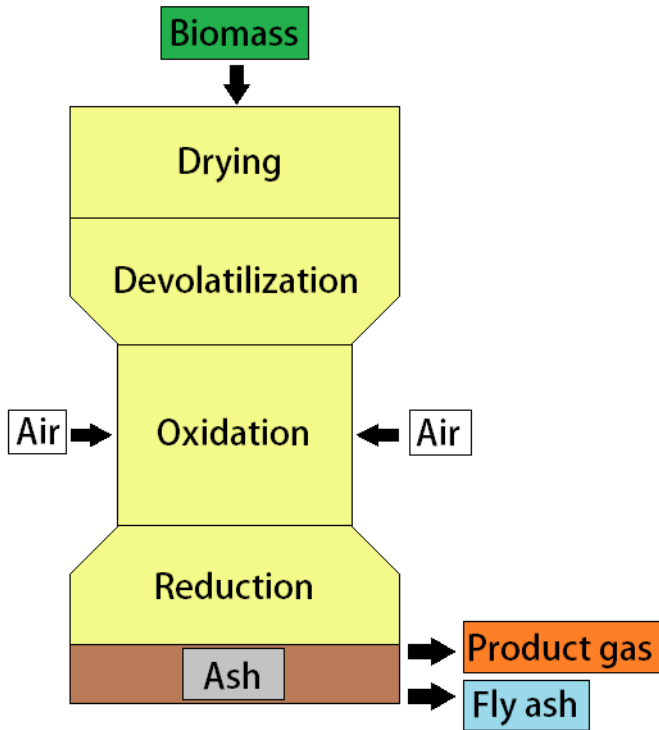
FIGURE 1. *The material flows that should be considered in material balances and gasification phases.*

Material balances are based on the material conservation law, so total material flows entering the process must be the same as the total amount of material flows coming out of the process. In other words, the material flow of air and fuel is as great as the material flow of product gas, ash, and fly ash. Similarly, all elements, such as carbon and nitrogen, can be balanced out. In material balances percentages are generally expressed in percentages of mass. In a continuous process, flows entering the process and flows exiting the process are equal when the process is considered in a given time interval and it is in a steady state during the measurements.
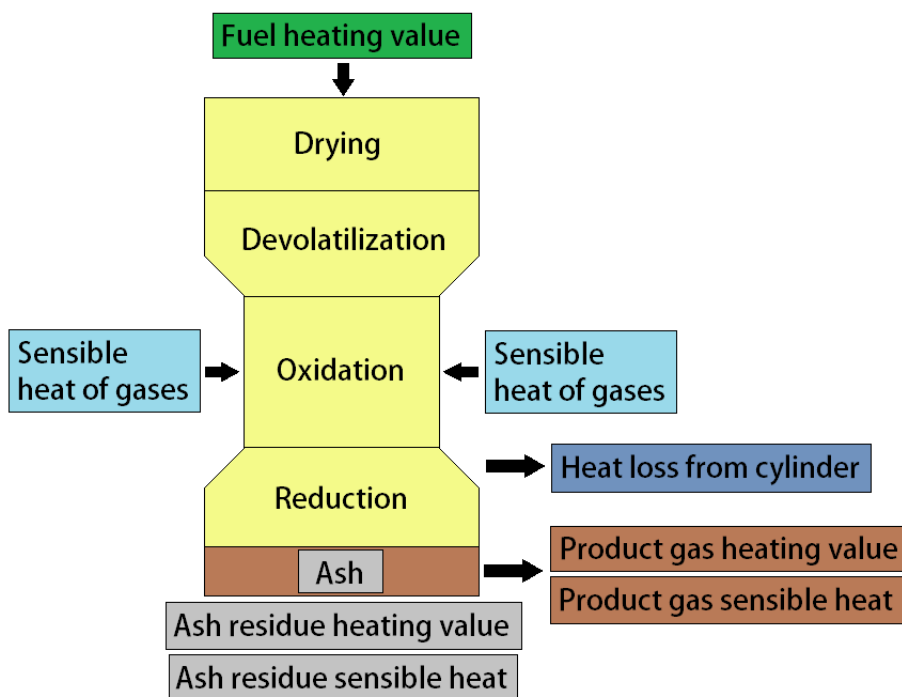
FIGURE 2. *Energy flows taken into account in drawing up energy balances.*

Energy balances are based on the law of energy conservation. Energy can be converted from one form to another, such as from chemical energy to thermal energy. The energy flow entering a process is equal to the energy flow exiting the process. Most of the energy input in gasification is derived from the fuel, but some energy results from the sensible energy of the gasifying medium. The majority of the products' energy comes from the chemical energy of the product gas and from the sensible heat of the product gas. The energy is transported from the process as heat loss from the gasifier, and in smaller quantities as ashes, heat from combustion, and sensible heat.

BENEFITS OF MATERIAL AND ENERGY BALANCES

When energy balances are drawn up, they reveal what stage of the production chain consumes a large part of the energy and allow energy use improvement to be targeted at that stage. In addition, energy balances also show how much energy and at what phases of the process that energy

is converted into a format that cannot be utilized. For example, the high temperature of the product gas takes a significant amount of energy from the process, but the gas cannot be cooled much, in order to prevent tar from accumulating in the equipment. Energy and material balances also reveal factors that have little affect on the balances. These insignificant factors may even be left out of the balance evaluation. For example, a small amount of tar is formed in downdraft gasification and it contains a small amount of energy. In this case, the energy content of the tar can be left out of the energy balance evaluation. Material and energy balances measurements are necessary to determine a variety of gasification efficiency values, such as cold gas efficiency (Simone *et al.*, 2012).

Better production conditions can be found when material and energy balances are calculated and different production conditions are compared. For example, it has been found that the heat of combustion and the hydrogen concentration of product gas can be increased to a certain extent by using steam as a gasification agent instead of air. The use of oxygen as a gasifying medium instead of air also increases the caloric value of the product gas, because the nitrogen gas that comes with air doesn't dilute the product gas. However, using air in gasification has other benefits, including inexpensiveness and ease of use.

If some material flow value is missing from measurements, the material balance can be used to evaluate it. For example, if the nitrogen content of the product gas, the fuel, and the ash are known, the flow rate of air can be estimated, because the nitrogen content of the atmosphere is always 78%. On the basis of the input air flow rate and fuel consumption rate, it is possible to evaluate the equivalence ratio, which tells which proportion of the air amount required for complete combustion is used in gasification.

Material and energy balances are useful in modeling, because many models use material and energy conservation laws as assumptions. Gasification is modeled in order to understand and explain the complex process in which greenhouse-gas neutral energy can be produced. With modeling, optimal gasification circumstances can be evaluated, including the influence of the gasifying medium, the fuel, the moisture content of the feedstock and equivalence ratio. For example, in gasification the energy efficiency of sludge and manure are considerably lower than many other biomasses (Ptasinski *et al.*, 2007). Models can also be used in the design and improvement of the gasification process. When the process is better understood, different factors can be optimized and energy can be produced more economically and better commercial gasification equipment can be developed. A functioning model allows different methods to be compared more easily and cost efficiently than with experimental work. However,

due to the large number of simplifications in the models, they will never fully replace information obtained from experimental work.

One useful factor in downdraft gasification modeling is that flows can be assumed to occur in the vertical direction, because there are no turbulent flows typical for fluidized beds. Phenomena occurring inside the gasifier can be modeled one-dimensionally, which is easier than three-dimensional modeling. Models are often divided into kinetic and thermodynamic models. Kinetic models are computationally intensive but they predict the process and the product composition better. Thermodynamic equilibrium models are not as exact as kinetic models, but they are useful tools for preliminary comparisons of gasifiers because these models are independent of the dimensions of gasifier reactors. (Pruig-Arnavat *et al.*, 2010)

MEASUREMENTS FOR MATERIAL AND ENERGY BALANCES

When elemental material balances are being drawn up, fuel, air, and product gas composition, as well as moisture content, need to be known. When those are known, and the consumed fuel mass, air and product gas flows are measured, how much material has entered and exited the process in a certain period of time can be calculated. In addition, composition, moisture content and flows of ash, tar, and fly ash are relevant, but not as much as the fuel, air, and product gas quantities from which the largest material flows are composed. Those flows also play the most significant role in the energy balance calculation. Measurement results can be compared to literature values in order evaluate their accuracy. Table 1 shows the elemental concentrations of selected small-diameter trees.

TABLE 1.   **Elemental concentrations of tree trunks in dry matter by weight percentage (Nurmi, 1993).**

	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Pine	52.34	6.09	0.08
Spruce	52.43	5.86	0.01
Downy birch	50.97	5.86	0.12
Silver birch	47.43	5.22	0.07
Aspen	46.21	4.98	0.15

The nitrogen content of the atmosphere is about 78%, its oxygen content is about 21% and the rest consists of other gases such as argon (Lide D. R., 2002). Table 2 shows a typical gas composition in commercial downdraft gasifiers operated on low- to medium-moisture content fuels.

TABLE 2. Typical gas composition in downdraft gasification (Stassen et al., 1993).

Component	Composition
H_2	12–20%
CO_2	9–15%
CH_4	2–3%
CO	17–22%
N_2	50–54%
Heating value	5–5.9 MJ/m³

When energy balances are drawn up, energy flows entering and exiting the gasifier are measured. When the model is drawn up, fuel, ash, and product gas moisture content, as well as masses and heating values, have to be known. Those are determined by laboratory analyses or, if gas composition and heat of composition of gas components are known, the product gas heat of combustion can also be calculated. Air and product gas temperatures are also measured in energy balance measurements.

Gasification phases

In order to understand how material behaves in the gasification process, it is beneficial to understand the phases of gasification. Broadly speaking, gasification is divided into four stages: drying, devolatilization, oxidation, and reduction (Figures 1 and 2). Drying occurs between 100°C and 200°C when moisture content drops below five percent. In the pyrolysis phase, biomass is thermally decomposed and small gaseous particles are released. In the oxidation phase, material reacts with oxygen and the reaction produces a significant amount of energy, a large part of which is consumed in the subsequent reduction phase reactions. The main reactions in the reduction phase are listed in Table 3. (Pruig-Arnavat *et al.*, 2010; Basu, 2010)

TABLE 3. The main reduction reactions in gasification.

Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$
Water–gas reaction	$C + H_2O \leftrightarrow CO + H_2$
Methane formation	$C + 2H_2 \leftrightarrow CH_4$
Shift reaction	$CO_2 + H_2 \leftrightarrow CO + H_2O$

Summary

In material and energy balances, the energy and material flows entering a process must be the same as the energy and material flows exiting the process. When the goal is to optimize the gasifier conditions, issues that directly affect a device are examined. Material and energy balances can be used to evaluate the size of the process flows and the efficiency of the gasification process as well as to optimize the entire process. Better production conditions can be found by calculating these balances. Material and energy balances are useful in modeling, because many models use the material and energy conservation laws as assumptions. When material balances are drawn up, the composition and flow of masses entering and exiting the process have to be measured. For energy balances, the energy flows into and out of the process are measured.

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Energy Production via the Stirling Engine

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Introduction

Combustion and steam turbine technologies are the most extensively used, particularly for large and medium-scale biomass-fuelled CHP systems (CHP, combined heat and power). Gasification based CHP systems can potentially have a higher electricity efficiency than a direct combustion CHP. The gas obtained by gasification can be utilized in diesel, gas, Stirling or dual fuel engines, or in a gas turbine. (Verigan, 2009)

Biomass, and biomass derived syngas in particular, has many advantages over conventional energy sources, as well as over some other renewable energies, in particular: relatively low costs, less dependence on short-term weather changes, promotion of regional economic structures and provision of an alternative source of income for farmers. Centria University has in Ylivieska a gasifier for research and testing operations. It is a downdraft gasifier, which consists of a feeding system for wood chips, air pre-heater and supply, gasifier with ash removal and gas cleaning system. More detailed description of the Centria downdraft gasifier and its operational conditions is given elsewhere (Muilu *et al.*, 2010).

Micro-cogeneration with Stirling engine

Biomass continues to attract much interest as a renewable, low-CO_2, and increasingly cost competitive alternative to traditional fossil fuels for heat and electric power generation. There is a strong driving force for the development of innovative small-scale CHP plants based on biofuels. The Stirling engine can easily make possible micro-scale cogeneration from

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clean fuels e.g. natural gas, landfill gas or biosyngas for both stand-alone and on-grid applications. On the other hand, fouling problems arising from deposition of unburned species, soot and ash over the surface of the heat exchanger are likely to occur, in particular when low grade fuels are burnt to produce heat for a Stirling engine. (Kuosa *et al.,* 2007)

Although there is already a high share of CHP plants in Finland and many large-scale power plants have been converted to CHP plants, it is still possible to increase the amount of CHP via small-scale and micro-scale units in distributed, local CHP production. There are many regional small-scale district heating plants that could be converted to combined power and heat production. The potential to increase CHP production in Finland has been estimated to be around 5–8 TWh per year. (Salomón *et al*., 2011)

Micro-cogeneration, which is the local generation of electrical and thermal power simultaneously to satisfy the power demands of lighting purposes, building services and the thermal demands of space heating and production of hot water in residential buildings, is an alternative to conventional oil, gas, and biomass boilers, and, to some extent, heat pumps, solar thermal, and photovoltaic systems. The most cited technologies in small-scale micro-cogeneration (less than 5 kWe) are fuel cells, internal combustion engines, and Stirling engines. According to Alanne (Alanne *et al,* 2010), micro-cogeneration with a natural gas-burning Stirling engine works best in standard houses in cold climates with the present electricity mixes, but, as expected, applies poorly to passive houses, where the electrical power demand is high when compared to that for thermal power.

Organic Rankine cycles (ORCs) and Stirling engines (SEs) are two promising and innovative technologies which are of great interest for biomass CHP plants up to 2 MWe especially in combined cooling, heating, and power (CCHP) small-scale plants. In the power range from approximately 200 kWe to 2 MWe the ORC process has demonstrated its technological maturity. There is an increasing interest in the use of Stirling engine based cogeneration systems for smaller power applications because of their prospect for high efficiency, good performance at partial load, fuel flexibility, low emission level and low vibration and noise level. SEs have also large potential in small-scale CCHP systems. A summary of the average performance characteristics and costs of both technologies is shown in table 1 (Maraver *et al.*, 2013).

TABLE 1. Summary of average performance characteristics of Stirling engines and organic rankine systems in commercial CCHP applications. (Maraver *et al.*, 2013)

	SE	ORC
Heat source	Direct fired (gas, biomass), solar radiation	Direct fired, thermal oil, overheated water (biomass, solar thermal, geothermal, waste heat)
Power range (kWe)	1–150	3–2 000
Electrical efficiency (%)	15–35	8–23
Global efficiency (%)	65–85	60–80
Heat source temperature (°C)	650–1 100	90–400
Cooling temperature (°C)[a]		20–80
Working fluids	Helium, hydrogen, nitrogen	R-245fa, R-134a, R-152a, n-pentane, toluene, siloxanes
Performance characteristics	Fast response, quiet operation, good performance at partial loads	Reliability, availability, low grade heat operation
Specific investment cost (€/kWe)	5 000–14 000	1 000–6 000
Operation & Maintenance costs (€/kWh)	n/a	0.003–0.009

[a] Cooling temperatures vary widely depending on the use mode: CHP or electricity generation only.

Stirling engine

The Stirling engine is an external combustion reciprocating engine developed by Robert Stirling in 1816 (Stirling, 1816). The main advantages are the smoothness, the flexibility toward the external heat source and the high thermodynamic efficiency. As it involves continuous burning of the fuel rather than intermittent burning presented by internal combustion engines, it burns the fuel more completely, producing lower unwanted emissions.

Stirling engines are classified according to their arrangement; alpha, beta, and gamma arrangement. The alpha configurations have two pistons in separate cylinders connected in series by a regenerator, a heater, and a cooler. One of the cylinders is heated up and the other is cooled down.

The Stirling cycle based on two opposing pistons in motion is shown in figure 1. It consists of two isothermal and two isochoric processes. During the isothermal compression (1-2), the cold piston moves towards the regenerator and heat is rejected to an external sink. In the following step (2-3), both pistons move similarly so that the volume remains constant and the working fluid is transferred through the regenerator and at the same time internal heat transfer from the working fluid to the regenerator is taking place. This step is followed by the isothermal expansion process (3-4) with only the hot piston moving and heat is added to the working fluid from an external source. In the step (4-1) both pistons move keeping the volume constant and transferring the working fluid through the regenerator and at the same time internal heat transfer from the regenerator to the working fluid is taking place. (Puech *et al.*, 2011)
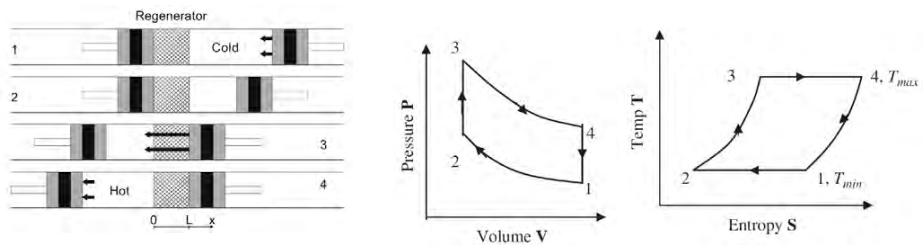
FIGURE 1. *Stirling cycle with piston position (left) (Puech et al., 2011) and PV and TS diagrams for Stirling engine with ideal isothermal and isochoric processes (right). (Thombare et al., 2008)*

Heat can be supplied to a Stirling engine hot cylinder by e.g. burning diesel oil, gasoline, liquefied propane gas (LPG), liquefied natural gas (LNG), biogas, syngas, biomass, liquid biofuels, or by directing concentrated solar irradiance.

The current applications of Stirling engine under development are heating and cooling, combined heat and power, solar power generation, Stirling cryocoolers, heat pump, marine engines, nuclear power generation, automotive engines, electric vehicles, aircraft engines, and low temperature difference engines. (Puech *et al.*, 2011)

SOLO 161 Stirling engine

The Stirling engine used in this study was a SOLO Stirling 161 micro CPH module, which is an alpha type two cylinder Stirling engine with helium as the working gas. The heater temperature in SOLO Stirling 161 micro CHP should be as high as possible although materials restrict it to be approximately 700°C. Likewise the temperature of the cooler for the Stirling process should be as low as possible. Detail technical data of the SOLO Stirling 161 engine is given in table 2. (Cleanenergy, 2011)

TABLE 2. SOLO Stirling 161 engine data. (Cleanenergy, 2011)

Solo Stirling 161 Technical Data	
Type:	V2 Stirling (alpha type) engine
Cylinder capacity:	160 ccm
Operating gas:	helium
Max. medium operating pressure:	150 bar
Nominal engine speed:	1500 rpm
Fuel consumption:	1.2-3.8 Nm^3/h (net calorific value)
Electrical output capacity:	2-9.5 kW
Thermal output capacity:	8-26 kW
Electrical efficiency:	22-24.5 %
Thermal efficiency:	65-75 %
Total efficiency:	92- 96 %

Centria micro CHP unit

Thermal and electrical power output of the SOLO Stirling 161 micro CHP unit installed at Centria renewable energy research laboratory in Ylivieska (figure 2) is 25 kWth and 9 kWe respectively. The burner used in combination with the Stirling engine was a normal natural gas burner (Bentone BG 300) modified to be used with the SOLO 161 Stirling engine (figure 3).

FIGURE 2. *SOLO Stirling 161 micro CHP-module (9 kWe and 26 kWth) installed at the Centria renewable energy research laboratory (above) and Centria downdraft gasifier (left).*
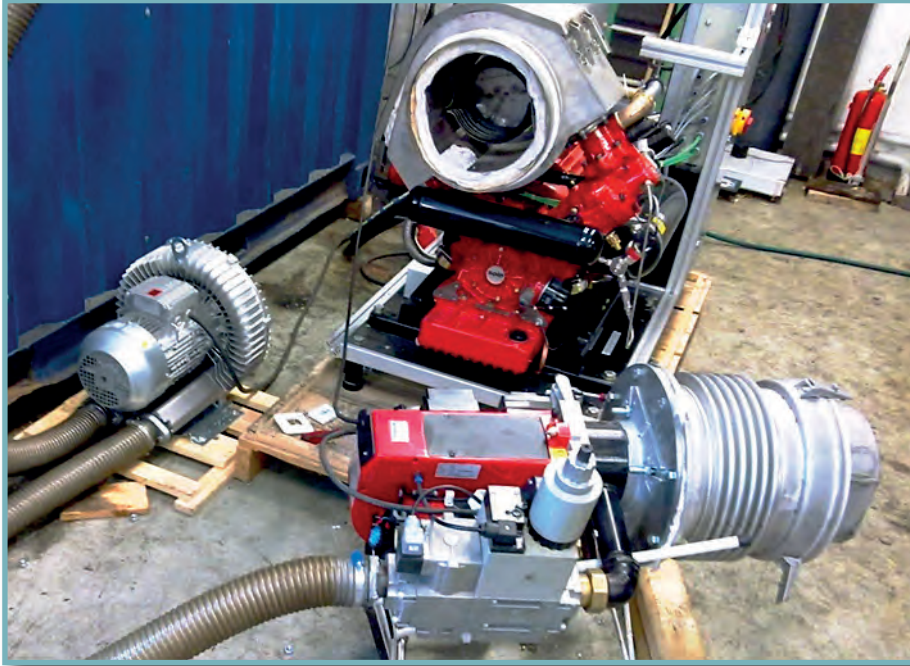
FIGURE 3. *SOLO Stirling 161 micro CPH-Module and Bentone BG 300 natural gas burner at the Centria research laboratory.*

Experimental results: Emissions of the Stirling engine CHP unit

Emissions of the Stirling engine at Centria research unit were continuously monitored by using a FTIR (Fourier Transformed InfraRed spectroscopy) gas analyzer (Gasmet Dx4000N). FTIR spectroscopy is a spectroscopic method that compares the absorbed energy from an infrared source of light. Gasmet FTIR gas analyser is commonly used for continuous emission monitoring (CEMS) in large combustion plants (LCP) and waste incinerators. The certification ranges and measurement uncertainties of Gasmet FTIR analyser as a CEMS in power production in large combustion plants are shown in table 3.

TABLE 3. Measurement uncertainties of Gasmet FTIR multicomponent gas analyser (Gasmet Ltd).

Component	Certification range	Total expanded uncertainty[*]	Unit
CO	0 - 75	3.0	mg/m^3
NO	0 - 200	8.6	mg/m^3
NO$_2$	0 - 200	11.5	mg/m^3
N$_2$O	0 - 100	4.4	mg/m^3
SO$_2$	0 - 75	4.7	mg/m^3
HCl	0 - 15	1.2	mg/m^3
HF	0 - 3	0.18	mg/m^3
NH$_3$	0 - 15	0.96	mg/m^3
CO$_2$	0 - 25	1.25	vol-%
H$_2$O	0 - 30	1.86	vol-%
O$_2$	0 - 25	0.60	vol-%

[*] Total expanded uncertainty (U_c) is calculated according to EN ISO14956 as the combined uncertainty u_c multiplied by a coverage factor of 1.96

Results of the continuous emission measurements from the Stirling engine (Pieniniemi *et al.*, 2013) are compared to the emissions of the internal combustion (IC) engine measured earlier (Muilu *et al.*, 2010) in table 4. As can be seen from table 4 nitrogen oxide (NOx), carbon monoxide (CO) and sulphur dioxide (SO$_2$) emissions from the Stirling engine CHP are significantly lower than that of the IC engine CHP using the same Centria gasifier.

TABLE 4. Composition and concentration of the flue gas main gaseous components along with the estimated combined uncertainty for the Centria gasifier using an internal combustion engine and a Stirling engine respectively. Measured with FTIR Gasmet gas analyser.

Measured flue gas component	IC engine (dry, STP (0°C, 1 atm) mg/Nm^3 (Muilu *et al.*, 2010)	Stirling engine (dry, STP (0°C, 1 atm) mg/Nm^3 6% O$_2$ (k=2) (Pieniniemi *et al.*, 2013)
O$_2$	0.4 ±0.04 vol%	4.1 ± 1.0 vol%
CO$_2$	17±2 vol%	16.6 ± 0.8 vol%
CO	170 ±19	10 ± 4
SO$_2$	25 ±4	0.4 ± 2
NOx	332 ±37	41 ± 7

Graphical presentations of the results of the continuous emission measurement of the Stirling engine CHP are given in figure 4. Measured and normalized (dry gas, 6 % O_2). Stirling engine CO, NOx and hydrocarbon (TOC, total organic carbon) emissions as 10 minutes average values along with the calculated standard deviation from figure 4 are shown in tables 5 and 6 respectively.
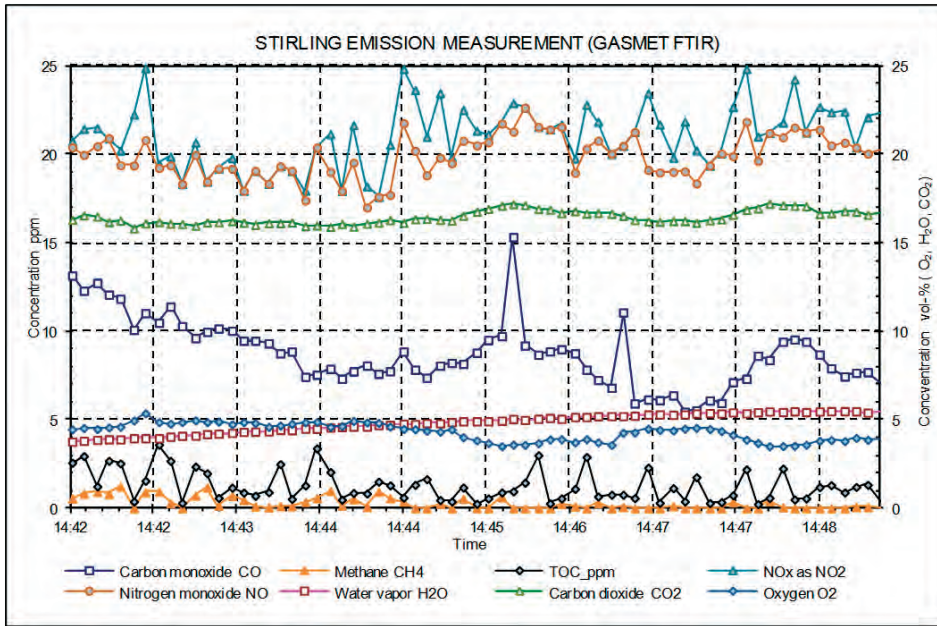

FIGURE 4. *Continuous emission measurements of the Stirling engine CHP using Gasmet analyser.*

TABLE 5. Measured CO, NOx, TOC, O_2 and H_2O concentrations as 10 min average from figure 4 with corresponding standard deviations.

CO	NOx as NO_2	TOC	O_2	H_2O
ppm	ppm	ppm	vol %	vol %
8.7± 1.7	21.3±1.7	1.1±0.8	4.1±0.5	5.0±0.6

TABLE 6. Normalised (dry, 6 % O_2) CO, NOx as NO_2 and TOC as CH_4 emission from figure 4 in STP (0°C, 1 atm) with corresponding standard deviations.

CO	NOx as NO2	TOC as CH4
mg/Nm3 (dry 6 % O2)	mg/Nm3 (dry 6 % O2)	mg/Nm3 (dry, 6%O2)
10 ± 1.9	41 ± 3.3	17 ± 13

CONCLUSION

Baumuller *et al*. (Baumuller A., 2001) has published a detailed Solo engine emission report, according to which the Stirling engine CHP unit tested showed 33% reduction in NOx emissions, and 15% and 90% reduction in CO and HC (hydro carbon) emissions respectively.

According to our measurements, the Stirling engine based CHP NOx and CO emissions were reduced more than 90% compared to the emissions of an IC engine CHP. Because of the more efficient product gas burning properties compared to traditional IC engine based technology, the CO and NOx emissions of the Stirling engine CHP are significantly lower, i.e. 94% and 88% respectively.

Cleaning problems of the producer gas in Stirling CHP applications can be avoided and the high temperature of the producer gas is an advantage compared to IC engine based CHP units. Fouling of the hot heat exchange, which is a major problem in direct wood chip burning applications, can be totally avoided when burning wood gasification producer gas instead of direct combustion of the wood chips in a Stirling engine. Accordingly very low emissions of all the wood gas burning applications can be expected because of the better mixing properties of the combustion air and the gaseous fuel.

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PURIFICATION OF SYNGAS

CO$_2$ Separation Techniques

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Introduction

The removal of CO_2 from a gas mixture represents a great challenge to power plants and other members of the CO_2 emitting industries. CO_2 capture techniques can be used, for example, in natural gas cleaning and in the production of hydrogen, ammonia, and other industrial chemicals. The captured CO_2 is sequestered underground or deep in the ocean. Recently, the possibility to use the captured CO_2 as a raw material for the production of useful chemicals in different industries has been investigated (Metz *et al.*, 2005). The decisive parameter in the selection of a carbon dioxide removal technique from a product gas is the partial pressure of CO_2 in the gas stream.

The overall need for gas purification is, however, dependent on the downstream requirements for the utilization of the important gas components. Furthermore, the existing regulations on greenhouse gases emissions have prompted a search for a capture and separation technology that could limit the release of CO_2 to a bearable level and maintain the production costs at a relatively low level in the power plants and other related industries. There are four basic options for the capture of CO_2 in industries. These options are CO_2 capture from an industrial process stream, pre-combustion capture, post-combustion capture, and oxy-fuel capture (Metz *et al.*, 2005).

CO_2 can be captured from an industrial process stream with multiple techniques. These techniques are outlined in the following sections. Generally, CO_2 is stored only if there are clear incentives or provisions for its storage. In pre-combustion capture, the fuel reacts with the air or steam to yield syngas via partial oxidation, gasification, or reforming

reactions. The CO in the syngas undergoes a further reaction with steam in a catalytic reactor to yield more hydrogen, in addition to CO_2, where H_2 is combusted in gas engines and the CO_2 is separated (Metz *et al.*, 2005). The post-combustion capture is performed with a downstream process where the separation of CO_2 is carried out after the combustion of the product gases. In this option, the flue gases are passed through equipment capable of separating most of the CO_2 for storage and venting the remaining flue gas into the atmosphere (Metz *et al.*, 2005). Although the post-combustion capture has a higher thermal efficiency with respect to the conversion to electricity compared to pre-combustion, it has some challenges in the separation of CO_2. These challenges include the design challenges presented by the higher temperature of the flue gases, the need for a powerful chemical solvent in the separation of low concentration CO_2, and the higher energy penalty in the regeneration of the solvent (Mondal *et al.*, 2012). Oxy-fuel, on the other hand, is a modified version of the post-combustion capture, which yields a flue gas comprised mainly of CO_2 and H_2O via combustion with pure oxygen instead of with air (Mondal *et al.*, 2012; Metz *et al.*, 2005). In this situation, the CO_2 can be purified at low cost, and the water vapor (H_2O) in the flue gas is removed by condensation (Mondal *et al.*, 2012).

In principal, in any of the options mentioned above, there are a number of techniques used in the removal of CO_2 from the gas stream. Some of the techniques mentioned below have already reached the development stage, but others require further improvements in technical capabilities and cost reduction.

Absorption

Absorption is based on the solubility differences of different gas components in a liquid solvent. Absorption processes can be further divided based on the solvent type into physical and chemical. The usage of a physical solvent is more advantageous when the concentration of CO_2 in the feed gas is high (Burr & Lyddon, 2008). Some of the physical solvents that could be used for the gas purification of CO_2 are selexol, rectisol, purisol, and flour processes (Korens *et al.*, 2002). Selexol and rectisol are the most commonly used physical solvents especially in integrated gasification combined cycle processes (Korens *et al.*, 2002). In a chemical solvent process, amine solution, aqua ammonia, and dual-alkali are typically used. However, the amine process is the most mature technology in wide use by the natural gas industry (Yang *et al.*, 2008). Furthermore, hybrid absorption such as sulfinol and amisol processes that combine the advantages of the

absorption efficiency of a chemical solvent and low energy regeneration potential of a physical solvent for gas separation are often used. In the hybrid absorption processes, the physical solvent removes most of the impurities, but the final purification is performed with the chemical solvent (Marklund & Öhrman, 2011). Ionic liquids (ILs) can also be used to absorb CO_2 from a gas stream. ILs have attracted interest due to their multiple beneficial properties. ILs are organic salts with an extremely low vapor pressure. In addition, they are non-flammable and have a low toxicity level (Zhao, 2006).

ADSORPTION

Adsorption is a gas separation technology where certain gas components adsorb preferentially on an adsorbent. The technique is currently used by, for example, the natural gas industry to remove water and other impurities (Tagliabue *et al.*, 2009), in the removal of CO_2 and other gases in a post-combustion process (Ebner & Ritter, 2009), in the purification of methane in coal mining (Tonkovich, 2004), and in biogas cleaning (Alonso-Vicario *et al.*, 2010). Adsorption has also been applied in odor control (Rezaiyan & Cheremisinoff, 2005). Similarly, as in the absorption processes, the adsorption process has a sorptive stage and a regenerative stage. Adsorption can either be physical or chemical in nature. The process phenomenon is based on the creation of a suitable surface area on a material to which the gas components can bind at a low temperature (Marklund & Öhrman, 2011; Watson *et al.*, 2009). The regeneration is based on the utilization of differences in adsorption loadings at various temperatures (thermal-swing adsorption, TSA) and at different pressures (pressure-swing adsorption, PSA) (Watson *et al.*, 2009). In PSA, the bed can be regenerated by reducing the pressure, but for TSA, regeneration is often done by raising the temperature (Yu *et al.*, 2012). Examples of adsorbents are molecular sieves, activated carbon, metal-organic frameworks (MOFs), and lithium compounds.

CRYOGENIC FRACTIONATION

CO_2 can also be removed from a gas stream by cooling and condensation where the concentration of the CO_2 in the stream is high. This process is known as cryogenic fractionation. In post-combustion capture the gas stream is cooled to a very low temperature for CO_2 to be captured in a liquid form and subsequently separated. The greatest benefit for this

capture and separation technique is the possibility to produce liquid CO_2, which can be transported by ship (Burt *et al.*, 2009). In addition to this, pollutants such as Hg, SO_x, NO_2, and HCl can be removed with a high efficiency (Burt *et al.*, 2009). However, the challenges for this technology are the high-energy consumption, high costs and the formation of frosted CO_2 (Meisen & Shuai, 1997; Tuinier *et al.*, 2010).

Membrane separation

In membrane separation, the separation is based on the relative permeation rates of each component. The component with the fastest permeation rate concentrates on the permeate side. Due to the simplicity of a membrane process, higher energy efficiency, and environmental compatibility (Xiao *et al.*, 2009; Zhang *et al.*, 2013), membrane separation is considered to be one of the future techniques in CO_2 separation. Gas separation by membranes offers high selectivity by differentiating gases according to their sizes, shape, and chemical properties (Metz *et al.*, 2005). In general, for a membrane to be competitive in CO_2 separation it should have high CO_2 permeability and selectivity, it should be thermally and chemically robust, resistant to plasticization and aging, and it should be cost effective as well as be able to be manufactured cheaply into different membrane modules (Powell & Qiao, 2006). Membranes for gas separation are broadly classified into polymeric and inorganic membranes. The polymeric membranes provide low cost, high performance separation, easier synthesis, and mechanical stability more than inorganic membranes (Scholes *et al.*, 2009). Inorganic membranes, on the other hand, are highly stable at high temperatures and can withstand harsh conditions compared to polymeric membranes (Caro *et al.*, 2000). Inorganic membranes can be made from alumina, carbon, glass silicon carbide, titania, zeolite, or zirconia.

Generally, membranes are supported on different substrates, such as α-alumina, γ-alumina, zirconia, zeolite, or porous stainless steel (Yang *et al.*, 2008). However, the molecular weight of alumina limits its application for gas separation, but due to the mesoporous structure of α-alumina and γ-alumina and their chemical as well as hydrothermal stabilities beyond 1000°C, those substrates have found application mainly as support materials (National Energy Technology Laboratory, 2003). Carbon membranes, on the other hand, are classified into supported and unsupported carbon membranes. Generally, the support is made of a porous material. Unsupported carbon membranes are brittle and mechanically unstable. Thus, problems may arise in the handling of unsupported carbon membranes (National Energy Technology Laboratory, 2003). In general,

carbon tends to exhibit substantial changes in pore size in an oxidizing environment (Centeno & Fuertes, 2000). Silica is foreseen as an interesting material for gas separation due to its exceptional thermal, chemical, and structural stability in both oxidative and reductive atmospheres. In addition, silica is a very versatile material for gas separation membranes because its structure can be tailored by changing the preparation method and conditions (National Energy Technology Laboratory, 2003). However, diffusion in amorphous silica with very small pores is relatively slow.

One significant developing field around the world is research into using zeolite membranes for gas separation. The membranes are presumed to be attractive in gas separation due to the presence of molecular-sized cavities as well as their thermal stability, solvent resistance, and shape selectivity (Caro *et al.*, 2000). The electrical charge or polarity of the zeolites promotes the attraction or sorting of molecules. The ability of zeolite to selectively adsorb molecules by size and polarity is the key to their unusual efficiency for gas separation (National Energy Technology Laboratory, 2003).

Other applicable membrane materials include mixed matrix membranes. These are aimed at offsetting the drawbacks of selectivity and permeability of the polymeric membranes, as well as at mitigating the significantly high cost and handling as well as processing difficulty associated with inorganic membranes. A hybrid membrane, the modified version of an inorganic membrane, can also be used, as can facilitated transport membranes, which are based on the reversible reaction between a carrier agent and the penetrating species.

OTHER TECHNIQUES

Other CO_2 separation techniques are hydrate-based separation, in which the gas stream is exposed to water under high pressure to form a hydrate. Chemical-looping combustion in turn integrates two reactors (air and fuel reactors) and oxygen is circulated between the reactors for the oxidation process. In this process, a gas mixture of mainly CO_2/H_2O is formed and the formation of NO_x is offset (Morin & Corinee, 2005). In addition to these techniques, enzymes are also gaining interest as a potential technique for CO_2 separation. The benefits of enzymes include mild process conditions (e.g., energy savings, high yields, less harmful side reaction) and renewability.

Conclusions

Carbon capture offers an opportunity to reduce CO_2 emissions in the production of electricity and transportation fuels. Among the CO_2 separation techniques reviewed in this paper, absorption is the most mature. However, the process also has drawbacks, the main ones being solvent losses, corrosion, and high energy penalty in the regeneration of the solvents. These drawbacks have driven research into new techniques such as adsorption, membranes, hydrate-based CO_2 separation, chemical-looping combustion, and enzyme-based separation.

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CO_2 RECOVERY IN IONIC LIQUIDS

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INTRODUCTION

Carbon dioxide (CO_2) recovery (removal or separation) is an important step in the biomass gasification process. Specifically, it helps to obtain products and improve the efficiency of the subsequent processes. For example, in the production of synthetic hydrocarbons with Fischer-Tropsch technology, the inert CO_2 is removed to increase the efficiency and selectivity of higher hydrocarbons (C_{5+}). In methanol production, CO_2 removal is conducted to obtain a favorable ratio of the gas mixture in order to increase the production yield. In hydrogen production, CO_2 is removed to purify hydrogen. For CO_2 recovery, there is a commercial technology, amine technology, but its cost is very high and the volatility of amine causes environmental problems. A low-cost and environmentally benign technology for CO_2 recovery needs to be developed.

Ionic liquids (ILs) are molten salts that do not evaporate and are widely anticipated as potentially environmentally benign solvents. Their properties mostly depend on their chemical constitution, which makes it possible to design a particular IL to meet a specific application. ILs have shown great potential to be used as liquid absorbents for CO_2 recovery, because of their high CO_2 solubility relative to other common components, such as hydrogen H_2, nitrogen N_2, carbon monoxide CO, oxygen O_2, and methane CH_4, and lower energy requirement for regeneration. It has been estimated that IL technology could cut the costs of capturing CO_2 from coal-fired power plants to as low as US\$20 per ton (Quick, 2009).

A significant amount of research has been carried out in this area, but most of it is on the synthesis of novel ILs, and the experimental data is

mainly for CO_2 solubility in ILs. However, the application of IL-based technology for CO_2 recovery requires knowledge of CO_2 solubility, the effect of other components on CO_2 solubility, the properties, the heat and mass transport rate as well as process evaluation. Therefore, a tremendous gap exists between new technology development and implementation.

The work in our research group aims to perform a systematic research from experimental data measurement, model development to process simulation and integration in order to promote IL-based technology development and application. In this study, our group's research work on the following areas is summarized: the survey of available experimental data, the model development, and new experimental data measurements. In addition, we provide the corresponding prospects of developing and utilization IL-based technology for CO_2 separation.

AVAILABLE EXPERIMENTAL DATA

Experimental data plays an important role in model development and verification. Pure-component or binary model parameters need to be obtained from the fitting to available experimental data, and model performance needs to be verified by the experimental data. Having reliable experimental data is a prerequisite for model parameterization and verification, and model development provides more information over a wide range of conditions and gives insights into understanding interactions on a molecular level. The combination of reliable experimental data and model development is a good way in research. In this section, the gas solubility in imidazolium-based ILs is summarized.

The CO_2 solubility in ionic liquids such as $[C_nmim][BF_4]$ (1-alkyl-3-methylimidazolium tetrafluoroborate) and $[C_nmim][PF_6]$ (1-alkyl-3-methylimidazolium hexafluorophosphate), and $[C_nmim][Tf_2N]$ (1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), n = 2, 4, 6, 8 has been measured extensively and collected in the database IL Thermo (NIST, 2006; Ji *et al.*, 2012). However, most of the experimental data is for C_4mim-based ILs. For some ILs, the CO_2 solubility data is still limited. For example, there are only two sources for $[C_6mim][PF_6]$ and $[C_8mim][Tf_2N]$, and only one source for $[C_2mim][PF_6]$ and $[C_8mim][PF_6]$. New experimental data is still needed, and a predictive model is highly desirable.

The experimental data was measured at temperatures up to 450 K[1] and at pressures up to several hundred bar. Several groups of data are focused on the measurements at pressures lower than 20 bar. The data, all from different sources, shows large discrepancies. For example, the CO_2 solubility in $[C_2mim][BF_4]$ was measured in four research groups, and the discrepancies in mole fraction of CO_2 can reach 0.1. Another example was for $[C_4mim][PF_6]$, at pressures higher than 20 bar, for which six groups of experimental data were available. Five of these groups were measured at pressures lower than 150 bar, and only one of them was measured at pressures higher than 150 bar with limited data points.

The solubility of other gases, such as H_2, N_2, CO, O_2, and CH_4, in ILs has been measured with limited sources. Most of experimental data at elevated pressures was collected in Maurer's group (NIST, 2006).The solubilities of H_2, O_2, CO in $[C_4mim][PF_6]$, and that of CH_4, CO, H_2, and O_2 in $[C_6mim][Tf_2N]$ were measured at temperatures from 293 K to 413 K and at pressures up to 100 bar. In Peters' research group, the solubilities of CH_4 in $[C_4mim][Tf_2N]$ and of H_2 in $[C_6mim][Tf_2N]$ were measured at temperatures from 300 to 450 K and pressures up to 160 bar (Ji *et al.*, 2012, 2013a).

In the research of Brennecke's group, the solubilities of CH_4 and O_2 in $[C_4mim][PF_6]$ and H_2 in $[C_4mim][Tf_2N]$ were measured at temperatures from 283 K to 323 K and pressures up to 14 bar. At pressures close to atmospheric, Gomes's group measured the solubilities of CH_4, O_2, N_2, CO in $[C_4mim][BF_4]$, $[C_4mim][PF_6]$ and the solubility of H_2 in $[C_2mim][Tf_2N]$ and $[C_6mim][Tf_2N]$ at temperatures from 283 K to 343 K. Noble's group determined the solubilities of CH_4, H_2, N_2 in $[C_2mim][Tf_2N]$, $[C_2mim][BF_4]$ and $[C_6mim][Tf_2N]$ in the range of 293 K to 343 K (Ji *et al.*, 2012, 2013a).

The solubility of hydrogen sulfide H_2S in ILs has been measured extensively in literature, and the effect of temperature, pressure, cation, anion as well as alkyl length on H_2S solubility in IL has been studied. Compared to the solubility of other gases in ILs, the experimental H_2S solubility data has been measured only at pressures up to 20 bar. The high H_2S solubility in ILs and the corrosiveness of highly concentrated H_2S mixtures might be the reasons for this limitation. The detail of the available experimental data for H_2S in ILs has been described in the publication (Ji *et al.*, 2013a).

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1   Temperature expressed in Kelvin (K). The temperature in degrees Celsius (°C) can be expressed as follows: (T[°C] = T[K] − 273,15. Thus 450 K is the same as 450-273,15 = 176,85 °C.

Modeling gas solubility in imidazolium-based ILs

Experimental determination is often difficult, time-consuming, expensive and the temperature and pressure range in which the solubility is measured is limited. Therefore, it is highly desirable to develop theoretical models for estimating the gas solubility in ILs over a wide range of conditions, and then to gain a fundamental understanding of the factors that control the solubility and selectivity for the target gas CO_2.

Thermodynamic models representing gas solubilities in ILs have already been proposed, and statistical associating fluid theory (SAFT) models were recommended due to their physical background. Several SAFT-based models have been developed to represent the gas solubility in imidazolium-based ILs, including truncated perturbed-chain polar SAFT (tPC-PSAFT), PC-SAFT, soft-SAFT, heterosegmented SAFT, SAFT-γ as well as ePC-SAFT. Among the existing SAFT-based models, most need binary fitting parameters that are adjusted to gas solubility in order to represent gas solubility quantitatively.

However, the modeling of ePC-SAFT can be used to quantitatively predict CO_2 solubilities in ILs between 293 K and 450 K and up to 950 bar (Ji *et al.*, 2012). The model can qualitatively predict the solubility of H_2S in these ILs at temperatures from 303.15 K to 353.15 K and at pressures up to 20 bar, and the solubility of O_2 in ILs at temperatures from 293 K to 413 K and at pressures up to 90 bar. The model can also predict the much lower gas solubility of CH_4, CO, and H_2 in ILs compared to those for CO_2 and H_2S (Ji *et al.* 2013a). This is illustrated in Figure 1. Figure 1 (a) represents experimental and predicted solubility of H_2, CO_2 and H_2S in [C_6mim][Tf$_2$N] at 333 K, and Figure 1 (b) compares the solubility of CO, CO_2 and H_2S in [C_4mim][PF$_6$] at 313 K. The experimental observation of the very low solubilities of both H_2 and CO in ILs (10 times lower than those for CO_2 and H_2S at 100 bar) is captured correctly by applying ePC-SAFT in a predictive way. That is, without the need for binary interaction parameters, ePC-SAFT reproduces the trend of experimental gas solubilities qualitatively well (Ji *et al.*, 2013a).
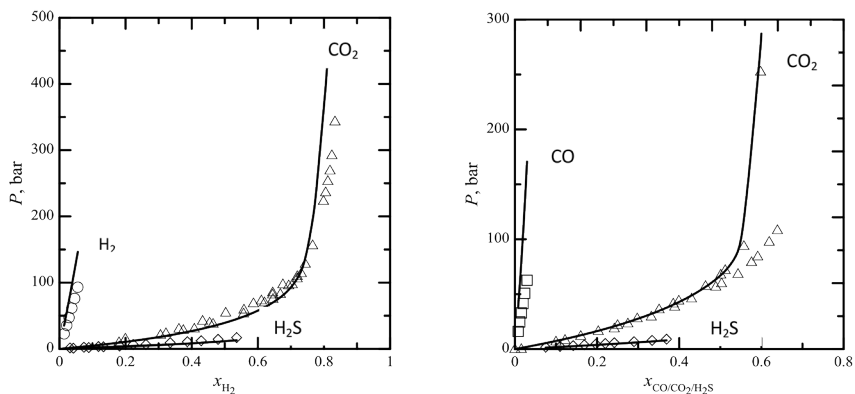
FIGURE 1. *Gas solubilities in ILs. (a) Solubility of H_2, CO_2, and H_2S in [C_6mim] [Tf_2N] at 333 K; (b) solubility of CO, CO_2, and H_2S in [C_4mim][PF_6] at 313 K. Symbols: experimental data (triangles: CO_2; diamonds: H_2S; circles: H_2; squares: CO), curves: ePC-SAFT predictions.*

EXPERIMENTAL MEASUREMENTS FOR A NOVEL IL

In general, the synthesis of ILs is a complicated process, which increases costs and hinders the progress of research and development of practical applications. In recent years, deep eutectic solvent was proposed and considered to be a new type of IL. Among this type of IL, the solvent of choline chloride/urea has shown great potential to be used as liquid absorbents for CO_2 separation due to, among other factors, its low cost, easy synthesis and bio-degradation. Several studies have been done, for example, on the CO_2 solubility in choline chloride/urea as well as on its density and heat capacity. However, the available knowledge is limited regarding its application, and both new experimental data measurement and modeling need to be studied further, including on the solubility of other gases (e.g., CO_2, N_2, CO, CH_4, and H_2), diffusivity, density, viscosity, and more. In addition, it has been observed that some properties of choline chloride-based ILs considerably depend on the water content. The water effects on density, vapor pressure, and heat capacity have been studied, but the effects of water on other properties of choline chloride-based ILs have not yet been investigated. Further research is required.

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Systematic research on experimental measurements for choline chloride/urea was carried out in the HighBio2 project (Ji, *et al.*, 2013b; Xie *et al.* 2013). The density, interfacial tension, and viscosity at atmospheric pressure were measured at temperatures from 298.2 K to 333.2 K. The solubilities of CO_2, CH_4, H_2, CO, and N_2 in choline chloride/urea were determined at temperatures of 308.2 K, 318.2 K and 328.2 K and at pressures from 0.4 to 4.6 MPa. The water effect on these properties has been studied. The results show that the solubility of CO_2 is larger than that of four gases and the sequence is $CO_2 > CH_4 > N_2 > H_2 \approx CO$, as shown in Figure 2. The effects of water on viscosity, surface tension, and CO_2 solubility are considerable, but its effect on density is weak. Figure 3 illustrates the viscosity at different temperatures and water contents. The viscosity decreases as water content and temperature increases. The viscosity of choline chloride/urea is very high at low temperatures. For example, the viscosity is larger than 1571 mPa·s at 298.15 K for choline chloride/urea with a very small amount of water (0.12%). When the water content increases to 3.61%, the viscosity decreases to 337 mPa·s, which is only one-fifth of the viscosity compared to that with 0.12% water. With increasing water content, the viscosity keeps decreasing, but the drop is not as notable as those at higher choline chloride/urea concentrations.
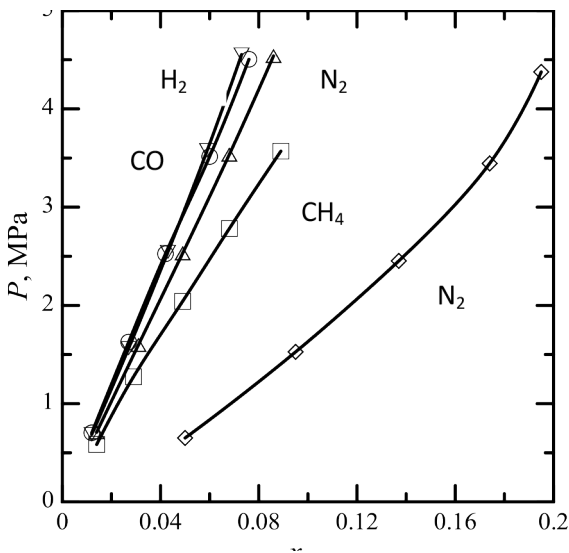
FIGURE 2. *Solubilities of gases in choline chloride/urea at 308.2 K.* ∇, H_2; O, CO; $\triangle$, N_2; $\square$, CH_4; $\diamond$, CO_2; *Curves: correlations.*
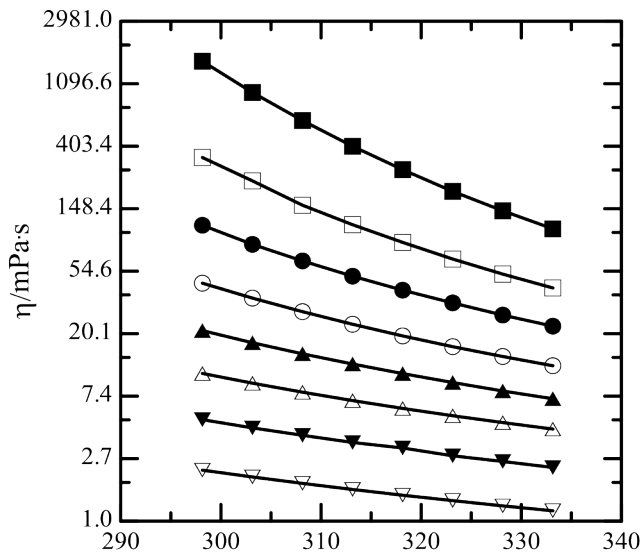
FIGURE 3. Viscosity of choline chloride/urea with water (wt%) at ■, 0.9988; □, 0.9639; ●, 0.9330; ○, 0.8933; ▲, 0.8458; △, 0.7809; ▼, 0.6855; ▽, 0.5015; Curves: correlations.

PROSPECTS

CO_2 recovery is an energy-intensive process, and a large amount of research has addressed it. Ionic liquid-based technology has been proposed as a promising technology to reduce the energy penalty for CO_2 recovery, but the available research is still limited to property measurement, model development, and process simulation. To promote this new technology development and application, an intensive collaboration among the experts from material synthesis, process engineering and simulation as well as industrial partners is required, and fundamental research from data measurement to model development will play an important role in carrying out process simulation and design. There is, however, still a long way to go before this new technology can be properly applied in a specific process.

In addition, deep eutectic solvents have recently been proposed as a promising substitute for traditional ionic liquids. However, the properties are much more limited compared to traditional ionic liquids. However, the lower gas solubility with a similar viscosity compared to traditional ionic liquidsmay be the main factors to overcome in order to substitute the traditional ionic liquids.

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UTILIZATION OF PURIFIED BIO-SYNGAS AND GASIFICATION BY-PRODUCTS

Catalytic Conversion of Syngas to Fuels and Chemicals

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Introduction

Biomass is a renewable resource with significant potential for biochemical and biofuel production. It has recently attracted more interest due to environmental concerns and possible future shortages of fossil oils. In addition to the production of heat and power, thermochemical treatment of biomass yields gases and oils which may be considered as a starting point for the production of chemicals and fuels from purified syngas.

In the HighBio2 project, research activities at Kokkola University Consortium Chydenius have mainly focused on the implementation of work package 3, that is, the use of purified syngas in the development of Fischer-Tropsch (FT) synthesis. This paper considers some aspects of the preparation of FT catalysts and the need for proper characterization of the catalysts.

Fischer-Tropsch synthesis

Fischer-Tropsch synthesis (FTS) was discovered in 1923 by Franz Fischer and Hans Tropsch, two scientists working at the Kaiser Wilhelm Institute in Germany in the 1920s. The process involves the conversion of syngas, a mixture of hydrogen and carbon monoxide, into liquid hydrocarbon fuels

such as gasoline or diesel. FTS needs to be activated by catalysts, and iron (Fe) and cobalt (Co) were used for the first experiments. In the first test, a high yield of oxygenates were observed over iron catalysts, and therefore, catalysts were optimized to obtain longer hydrocarbons chains. FT plants were developed in Germany, and synthetic fuel production soon peaked, especially during World War II. (Dry, 2002; Casci *et al.*, 2009)

Until recently, oil stock and crisis have guided the evolution of Fischer-Tropsch research. During periods of shortage, chemists were encouraged to find new ways of producing liquid fuels. Much information on the process has been collected from the Germans after World War II, but the discovery of oil fields in the Middle East in the mid-1950s enabled fossil fuels to conquer the world market, and FT fuels were no longer advantageous. At the same time, South Africa wanted to promote their huge coal reserves and they developed new FT plants (coal-to-liquid, CTL). The company Sasol enabled the production of FT fuels, and this reduced the effects of the Iranian revolution (South Africa's main oil supplier) and the embargo that was in place due to the country's policy of apartheid, and made South Africa independent of oil. (Dry, 2002; Casci *et al.*, 2009)

Interest in FTS grew with the international crises of the 1970s, and the discovery of huge gas reserves during this period encouraged researchers to study gas-to-liquid process (GTL), in particular. At the end of the 20th century, environmental concerns were growing while awareness about the non-renewable status of fossil fuel such as oil motivated researchers to examine other potential products. The Fischer-Tropsch process thus returned to center stage. Fischer-Tropsch synthesis enables the synthetic gas to be obtained from a large range of hydrocarbon molecules such as paraffin wax, olefins or oxygenates. Depending on the operating conditions, the range of compounds produced varies greatly. The choice of the catalyst is crucial and affects the performance and the productivity of the process (Dry, 2002; Casci *et al.*, 2009).

Physicals parameters in FTS have to be strictly controlled. The reaction is performed at relatively high pressures (20–60 bars), and at high temperatures (200°C–450°C). Two main processing conditions can be identified: low-temperature FT (200°C–250°C), which produces mainly waxes and diesel, and high-temperature FT (350°C–450°C), which produces gasoline and olefins. The gas used for FTS is highly reactive: hydrogen (H_2) is explosive and carbon monoxide (CO) is toxic. Considering these criteria, the Fischer-Tropsch process has to be carried out under strictly controlled conditions and following strict safety rules (Casci *et al.*, 2009).

The Fischer-Tropsch process converts hydrogen (H_2) and carbon monoxide (CO) into aliphatic hydrocarbons. The basic equation can be written as follows:

$$CO + 2H_2 \xrightarrow{\text{Catalyst}} CH_2 + H_2O \qquad (1)$$

The stoichiometric ratio of H_2/CO for this reaction is 2:1. It occurs when this ratio is lower than 2:1. Then water can be added to the reagents to increase the amount of hydrogen and to obtain the ratio sought. The addition of water is called the water–gas shift. The reaction is described below:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

The relationship between H_2 and CO is essential to perform the reaction. However, since gasification of wood-based materials gives a ratio H_2/CO of about 1, the water–gas shift reaction (see Equation 2) has to be used to increase the amount of H_2. If unwanted CO_2 is produced, it is nevertheless profitable to perform this reaction to increase H_2 content and enhance the FTS (Casci *et al.*, 2009).

ACTIVITY AND SELECTIVITY OF FISHER-TROPSCH CATALYSTS

Synthesis gas is obtained by the gasification of biomass followed by proper cleaning steps of the producer gas. This synthesis gas can later be catalytically converted into a number of chemicals, including for those used in the production of traffic fuels by the Fischer-Tropsch process (FTS).

FT catalysts consist of active metals, promoters, and a porous support (see Figure 1). It is well known that transition metals from group VIII – such as nickel (Ni), cobalt (Co), iron (Fe), and ruthenium (Ru) – are active metals in the Fischer-Tropsch catalysis. Of these metals, ruthenium has the highest FT activity, but because of its high price it is used in trace quantities only. An addition of small amounts of ruthenium is known to improve dispersion of the active metal (cobalt) on the support. Metals like ruthenium act as electronic promoters making the reduction of different oxides of the active metals easier. More recently, ruthenium has to some extent been replaced by the much cheaper metal, rhenium (Re). Nickel has a tendency to produce high amounts of methane as a by-product. Iron is also often used in FT catalysts but it requires rather high reaction temperatures, and therefore, cobalt is the most useful metal for FTS.
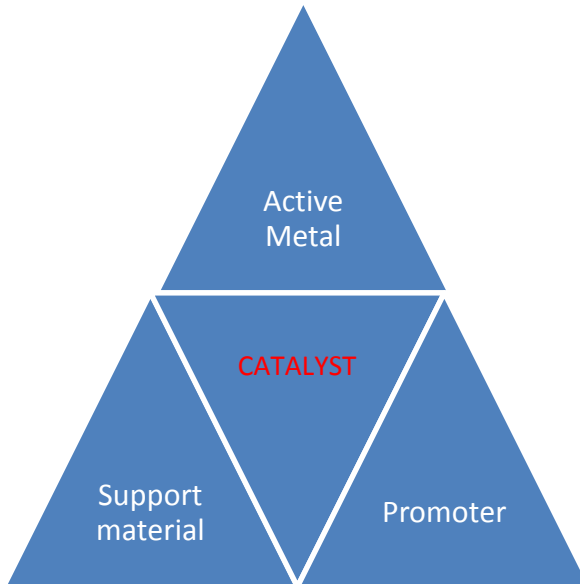
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FIGURE 1. *Components of an active catalyst.*

There are a number of supports used for FT catalysts, such as titanium dioxide (TiO_2), alumina oxide (Al_2O_3) and zirconium oxide (ZrO_2). These supports have a number of common properties, including a large specific surface, pore distribution suitable for the expected end products and high mechanical strength. The supports can be manufactured in different shapes and are today available as powders or compressed and shaped into spheres of different sizes like rings and pellets. The choice of support must be evaluated in each individual case and it is dependent on, among other factors, reactor type and size, water content in the syngas, attrition effects and diffusion-related kinetic problems.

For each catalyst three important parameters must be known in order to use it commercially: catalytic activity, selectivity, and stability. Activity is defined as the mass of products produced by time unit and mass unit catalyst. It tells how much product can be produced by the catalyst. Selectivity is defined as the mass of wanted product in relation to the mass of products totally produced. These parameters must be measured at the conversion level used for the final reaction or at the same level for all catalysts in order to achieve comparable results. Stability is a measure of the long-term activity of the catalyst, and it can be lost by, for example, thermal deactivation, poisoning, or mechanical attrition.

The development of catalysts is a time-consuming process including several steps. These steps includes catalyst preparation (wet or dry impregnation, drying, and calcination), characterization by a number of

methods such as ICP (metal content), physisorption of nitrogen according to BET isotherm (pore size and distribution), chemisorption with reactive gases (metal dispersion and crystal sizes), electron microscopic methods SEM and TEM (particle size, crystal size), identification of metal phases (XPS, XRD), and different temperature-dependent methods (TPR, TPO, TPD). Finally, the best candidates for catalysts undergo experiments for activity and selectivity in a laboratory-scale FT reactor (see Figure 2).
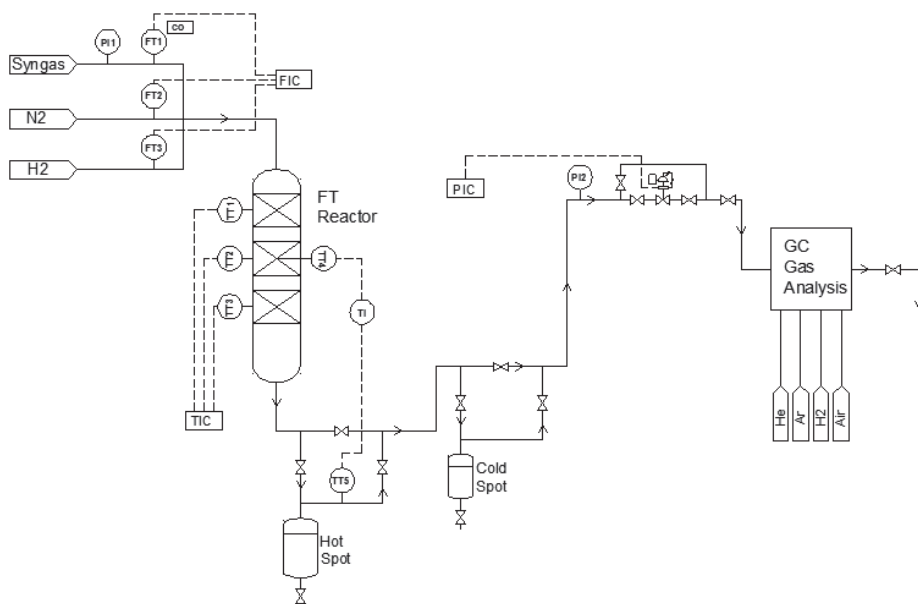
FIGURE 2. *Laboratory-scale Fischer-Tropsch reactor.*

Factors affecting the Fischer-Tropsch reaction include temperature, pressure, the ratio of H_2 to CO, and the size of catalyst particles. Smaller particles, down to a certain particle size, are known to produce higher activity, whereas smaller particles also produce smaller amounts of short-chained, gaseous compounds.

Catalyst development during HighBio2 project

The development of Fischer-Tropsch catalysts and the laboratory-scale FT reactor has been performed at Kokkola University Consortium Chydenius. A large number of catalysts have been prepared with different combinations of active metals, additional metals (promoters), and supports. All the catalysts were characterized as mentioned earlier. One aim of the research

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was to find a suitable preparation method for the catalyst that yields metal crystals small enough to maximize the catalytic activity. To some extent this work has been performed in cooperation with Norwegian University of Science and Technology (NTNU), Trondheim, Norway. A number of measurements, the characterizations and activity as well as selectivity experiments were made at NTNU during Henrik Romar's research visit in autumn 2012. Preliminary results from the interaction between the active metals and support were presented at EuropaCat conference 2013 (http://www.europacatlyon2013.fr). Later these results will also be published in scientific publications.

FIGURE 3. *Effect of additional metals on the reducibility of Co/Al$_2$O$_3$ catalysts. A clear shift of the reduction temperature can be seen when promoters are added. Blue line: Unpromoted Co; red line: Co promoted with rhenium; green line: Co promoted with ruthenium. X-axis: reduction temperature; Y-axis: signal from TC-detector. (Romar et al., 2013)*
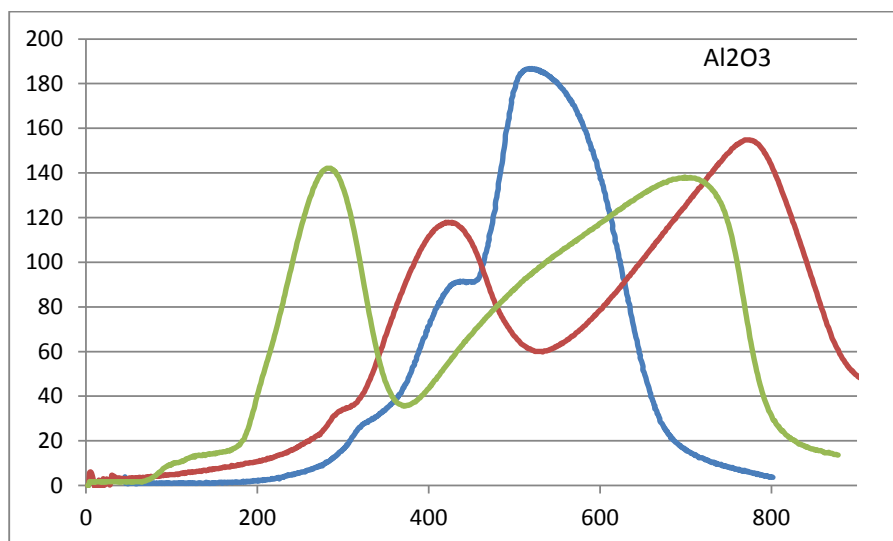
Development of the Fisher-Tropsch reactor

In addition to the development of catalysts for FT synthesis, the FT reactor system has been subject to changes and it was rebuilt a number of times during the HighBio and HighBio2 projects. In early spring 2013, the reactor was completely rebuilt and changed according to the suggestions and new ideas. The whole FT reactor system is now built into a framework of metal tubing that provides more flexibility for future changes.

The gas feed system has been changed to allow much higher reaction pressures. The maximum pressure is now set to be 50 bar with a safety release valve opening at 60 bar. The higher pressure limits for the system makes it possible to perform other catalytic routes from the purified synthesis gas, such as methanol synthesis or dimethyl ether (DME) synthesis. Along with the increase in reaction pressure, the gas feed was changed to a one-bottle mix of syngas instead of mixing the gases with mass flow controllers. This change allows the use of a more exact gas composition between individual experiments.

The most important changes have been made for the collection of reaction products. Both hot and cold pots have been changed in a way that allows much better condensation of the products. Better product condensation results in less risk for contamination of the tubing downstream from the collection points.

Gas analysis was performed with an online gas chromatograph (GC) equipped with double detectors and double separation systems that provide information on the gaseous organic compounds formed and the consumption of individual syngas components. Information obtained from the GC provides a basis for a better understanding of the conversion levels during the experiments and the selectivity of the individual catalysts. Long-term stability of the catalysts can also be determined by the existing reactor system.

The preliminary experiments performed with the modified reactor have been very promising. A single one-week experiment has now very high productivity. These experiments were performed with a conversion ratio around 50% and selectivity for C_{5+} (liquid or semi-solid hydrocarbons), and the results are comparable with the results of commercial FT catalysts.

Conclusions

– FT catalyst testing is time-consuming work, and there is a demand for proper instrumentation in order to make real characterizations of catalysts.
– National and international cooperation is needed in order to increase competence.
– According to the preliminary experiments, the Fischer-Tropsch reactor built at Kokkola University Consortium Chydenius in its present (but maybe not final) configuration seems to be promising.
– Activity and selectivity experiments made on some selected catalysts prepared at Kokkola University Consortium Chydenius have shown high activities and good C_{5+} selectivities, both of which are comparable to commercial catalysts.
– The experiments will continue in order to improve the preparation methods of catalysts. The main goal for the near future is to optimize the metal crystal size of the catalysts.

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Chemical and Physical Activation of Gasification Carbon Residue: Adsorption Studies

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Introduction

In recent years, energy generated from biomass-based heat and power production has become more established due to higher electricity prices and the introduction of green electricity certificates. The use of wood for energy production has many advantages because it is renewable as well as local, and it creates jobs, especially in areas of dispersed development. However, energy generated via biomass gasification produces a solid carbon residue that must be utilized economically. Utilization of carbon residue is part of sustainable power generation from biomass and contributes to a green energy image. In addition, according to Finland´s national legislation of waste material, which is largely based on EU legislation, all kinds of waste must be utilized primarily as material (reuse and recycling) (Waste Act 646/2011). The options available for dealing with waste are described by a waste hierarchy that is derived from five categories: prevention, reuse and preparation for reuse, recycling, recovery (e.g. as energy), and disposal (Directive 2008/98/EC of the European Parliament and of the Council).

   Adsorption is widely applied in the treatment of wastewater as well as in the purification of drinking water and groundwater. Activated carbon is a versatile adsorbent due to its good adsorption properties and its important role as a filter material for the removal of odors, colors, and tastes from liquids and gases. In the future, activated carbon use will increase due to growing concern over environment pollution. Water contamination and limited water resources are a global problem and

therefore powerful purification methods are needed. The preparation of activated carbon typically consumes a significant amount of energy and consequently, preparation is fairly expensive, which may limit its use. Therefore, there is a growing need to derive activated carbon from cheaper and locally available waste materials (Ahmadpour & Do, 1996). Carbon residue from gasification processes typically has a lower specific surface area than commercial activated carbon but its carbon content is high (Kilpimaa *et al.*, 2013). In an adsorption process the specific surface area of the adsorbent must be large (Afkhami *et al.*, 2007) and therefore, the adsorption properties of carbon residue would be more suitable if their specific surface area was also larger.

Activated carbon can be produced from a variety of fossil or biomass based raw materials such as coal, coconut shell, and others (Ahmadpour & Do, 1997). There are also large numbers of studies regarding the preparation of activated carbon from different waste materials, such as peanut husks and cherry stones (Lussier *et al.*, 1994; Ricordel *et al.*, 2001). Basically, there are two processes for the preparation of activated carbon: physical activation and chemical activation. Physical activation is performed, for example, with CO_2 whereas chemical activation uses chemical activating agents. These agents are typically alkali and alkaline earth metals containing substances such as potassium hydroxide KOH, sodium hydroxide NaOH, and zinc chloride $ZnCl_2$, or some acids such as phosphoric acid H_3PO_4 (Ahmadpour & Do, 1996). Chemical or physical activation is required to increase the specific surface area of carbon residue from biomass gasification and thereby enhance its adsorption properties.

In this study we aimed to develop a utilization application for gasification carbon residue. Figure 1 depicts this development process. First, we determined the physical and chemical properties of carbon residue formed in the gasification process and evaluated the possibility of utilizing the residue directly. If direct utilization proves impossible, carbon residue could be modified to develop suitable utilization applications. During the HighBio2 project, we modified carbon residue from the biomass gasification process using chemical and physical activating agents. To achieve this goal, we studied the effects of different parameters on the activation process of the carbon residue. The parameters we investigated during chemical activation were the chemical agent, the liquid-to-solid ratio of the carbon residue and the chemical activating agent, the concentration of the impregnation solution, and contact time. During physical activation, we examined the activating agent, the duration of activation, and the activation temperature. We used a chemically activated carbon residue as an adsorbent for phosphate and nitrate removal and investigated the influence of adsorption time, initial phosphate or nitrate concentration,

and pH. For reference samples, we used commercial activated carbon and carbon residue without any pre-treatment process.
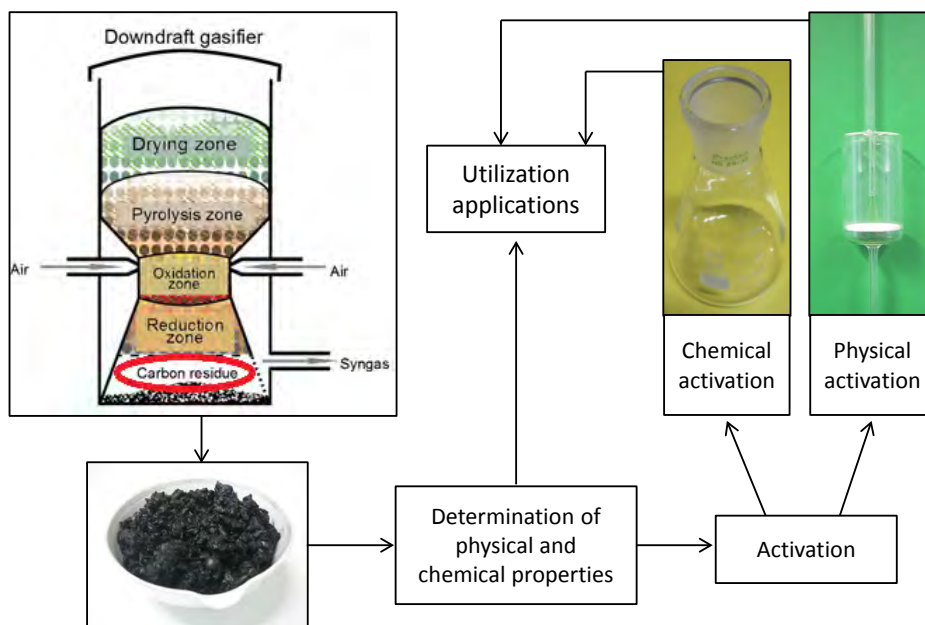
FIGURE 1. *This study aimed to utilize gasification carbon residue directly or after modification as, for example, an adsorbent.*

Preparation of adsorbents

The carbon residue used in the preparation of adsorbents was obtained from a biogasification pilot plant that had a 150 kW downdraft gasifier operating at a temperature of 1000°C. Finnish wood chips (pine and spruce) were used as a fuel for the gasifier at a feed rate of 50 kg h^{-1}. The gasifier had no separate carbon residue collector. The gas produced in the gasifier was washed by a wet scrubber and the carbon residue formed in the process was collected from a water container. Commercial activated carbon (pro analysis quality) provided by Merck was used as a reference sample.

Chemical activation was performed using the wet impregnation method according to the reference (Ahmadpour & Do, 1996). First, carbon residue was dried overnight at 110°C and then washed with a 1 N solution of HCl and H$_2$SO$_4$ (1:1) for 24 hours in order to reduce the ash content. After that, the sample was washed with distilled water and dried overnight at 110°C before being crushed and sieved to achieve particles under 150 µm with

uniform quality. The dried sample was mixed with a chemical activating agent for five minutes (contact time). The carbon residue used in this experiment was treated with 0.1 M hydrochloric acid HCl, 0.1 M sulfuric acid H_2SO_4, 5 M $ZnCl_2$, 5 M KOH, HCl or HNO_3 using a liquid-to-solid ratio (L/S) of 10 (w/w). The mixture of the carbon residue and chemical activating agent was dried overnight at 110°C and activated at 500°C in an air atmosphere for one hour. The resulting products were washed sequentially with 0.5 M HCl for ten minutes using an L/S ratio of 10, hot distilled water and cold distilled water to remove any remaining residual chemicals and organic and mineral matters. Finally, products were dried overnight at 110°C and crushed and sieved again to ensure a particle size of < 150 μm.

Specific surface areas of activated carbon residues were determined in order to evaluate the success of the activation with different activation parameters. Based on the surface area measurements, the highest specific surface area was obtained using 5 M $ZnCl_2$ as a chemical activating agent during the chemical activation process (Kilpimaa *et al.*, 2012). The next step was to examine the effect of activation parameters, such as the L/S ratio of the carbon residue and chemical activating agent, the concentration of the impregnation solution and the contact time between the activating agent and carbon residue by using zinc chloride as the activating agent. These parameters varied as followed: L/S between 4 and 10, concentration between 2 and 5 M, and time between 10 minutes - 6 hours. The highest specific surface area was obtained using a 5 M zinc chloride solution with a liquid-to-solid ratio of 10 and a contact time of 1 hour for the chemical activation.

Physical activation was carried out with two different activating agents, CO_2 and CO. The two parameters investigated during the HighBio2 project were temperature (600 °C and 800°C) and the duration of activation (1 - 3 h). In addition, reference samples were prepared by thermal treatment without an activating agent. In the case of physical activation, the highest specific surface area was obtained using CO_2 as a physical activating agent at 800°C and with an activation duration of 3 hours.

REMOVAL OF NITRATES AND PHOSPHATES
OVER ACTIVATED CARBON RESIDUE

Eutrophication is the term for the enrichment of water bodies with nutrients, such as nitrates and phosphates. Phosphate in wastewater is one of the main factors that leads to the eutrophication and deterioration of water bodies. Wastewaters possess harmful levels of phosphates and

the removal of it before discharge is paramount. Adsorption is a popular method of removing nutrients, especially phosphorus, from effluent by using porous materials such as zeolites. (Bolan *et al.*, 2004; Chen *et al.*, 2006; Huang *et al.*, 2009; Zeng *et al.*, 2004) In addition to phosphate, nitrate can also cause several environmental problems. Nitrate stimulates eutrophication and it has been linked to the outbreak of infectious diseases. Excess nitrate in drinking water may cause methemoglobinaemia, also called blue baby syndrome, in newborn infants. (Feleke & Sakakibara, 2002)

During the HighBio2 project, we studied phosphate and nitrate removal efficiency over chemically activated carbon residue. The effect of pH was studied over a pH range of 4 to 8, and the effect of initial solution concentration was studied at optimum pH with different initial concentrations (25 - 125 mg L^{-1}) of phosphate or nitrate ions. The optimum pH and effect of initial solution concentrations were determined using polyethylene flasks, in which a solution of phosphate or nitrate and adsorbent was mixed together and the pH value of the solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH. This was done after adding the adsorbent to ensure the solution had the correct pH because the carbon residue from the gasification process is clearly alkaline (pH ≈ 9).

The largest removal of phosphate occurred at pH 8 for the carbon residue and activated carbon residue, and at pH 6 for the activated carbon (Kilpimaa *et al.*, 2012). Carbon residue includes nutrients such as calcium, magnesium, and potassium, but chemically activated carbon residue also possesses zinc because its activation is performed by zinc chloride (Kilpimaa *et al.*, 2013). It has been established that high pH and high calcium concentration are advantageous for calcium phosphate precipitation and it can be assumed that zinc phosphate is also precipitated. Precipitation reactions often co-occur with the adsorption process and can thus make it difficult to distinguish these individual processes (Prasad & Mortimer, 2010). In laboratory experiments, the conditions were chosen in such a way that precipitation does not occur. In practice it is insignificant how phosphate removal occurs, i.e. if the mechanism is adsorption or precipitation. The results suggest that the optimal pH for phosphate removal over activated carbon residue was 6, over carbon residue 4 and over activated carbon 6, which were optimal pH values when alkaline conditions were eliminated. The optimal initial phosphate concentration was 25 mg L^{-1} in activated carbon residue and activated carbon. In carbon residue, it was 50 mg L^{-1}. In the case of nitrate removal, the optimal pH values were 6 for activated carbon residue and carbon residue, and 4 for activated carbon. For all adsorbents, 25 mg L^{-1} was the optimal initial nitrate concentration.

The adsorption of phosphate and nitrate on three different adsorbents was investigated as a function of adsorption time (1 min - 24 h) with an

optimum pH and optimum initial concentration. Phosphate removal percentages as a function of time are presented in Figure 2a, which clearly shows that phosphate removal efficiencies increase rapidly with time especially when activated carbon residue was used as the adsorbent. The results presented in Figure 2b also indicate that nitrate removal efficiency increases with adsorption time. Modified carbon residue showed a high adsorption capacity and removal efficiency for phosphates and nitrates.
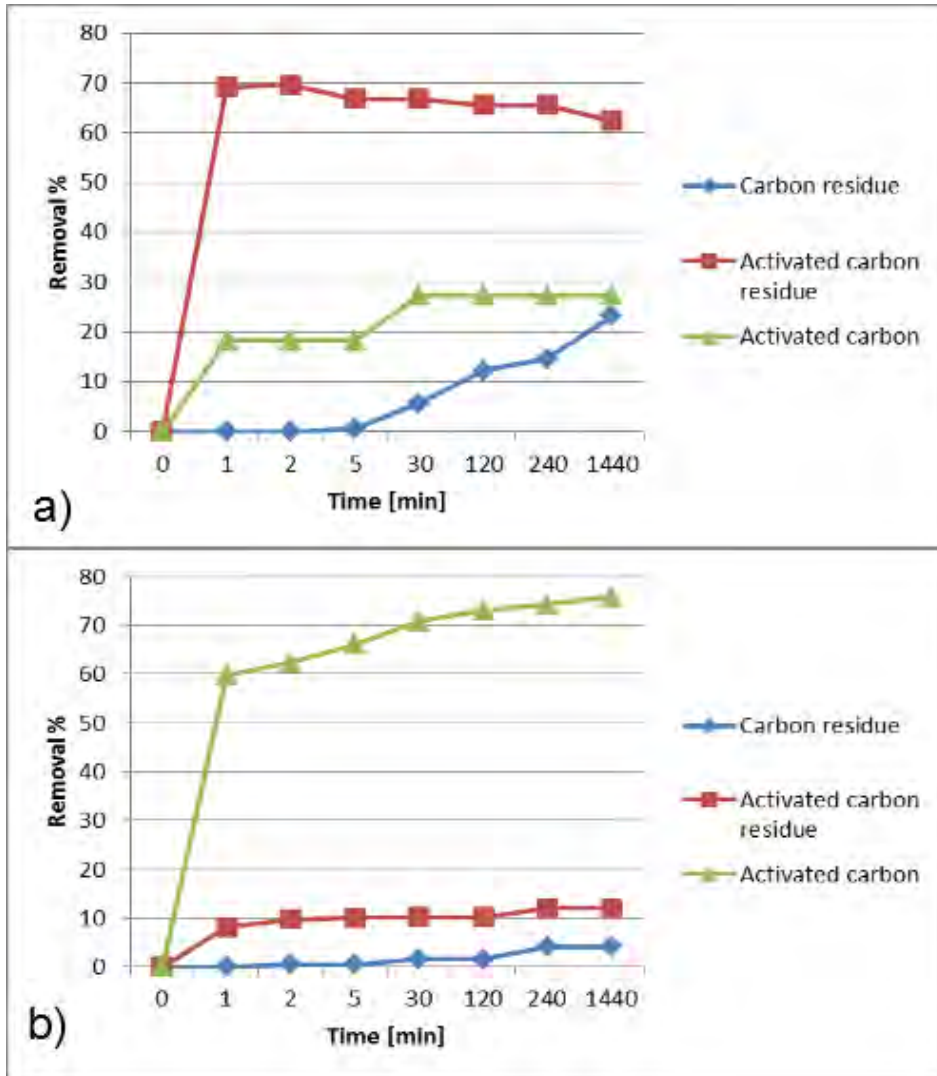

FIGURE 2. *The removal efficiency of phosphate (a) and nitrate (b) as a function of time for different adsorbents.*

Conclusions

Chemically activated carbon residue may be used as a low-cost adsorbent for the removal of phosphates and nitrates in, for example, wastewater treatment. In the case of phosphates, we observed that modified carbon residue has an adsorption capacity that is notably higher than commercial activated carbon. In addition, we found that adsorption capacity is also substantially better for activated carbon residue than it is for carbon residue. This result indicates that adsorption capacity can clearly be enhanced by chemical activation. Gasification carbon residue is an effective and inexpensive adsorbent, and it has the potential to significantly reduce waste streams. This innovation creates possibilities for using this low value by-product in new water treatment applications.

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Biodegradation of Organic Pollutants in Condensing Water from Wood Chip Gasification

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Introduction

Biomass used as a source of renewable energy includes plant material from photosynthesis, such as algae, trees, and crops. The energy is stored with chemical bonds to carbohydrates. When the biomass is processed chemically or biologically, the energy stored in the chemical bonds can be utilized. The carbon dioxide produced is then available to produce new biomass. In this way the carbon dioxide is absorbed and returned for a cycle of new growth (McKendry, 2002).

Water in wood samples can exist in two places: in the cell cavity as free water or as absorbed water in the cell walls (Bousquet, 2000). The chemically bound water in the cell walls is attached to cellulose with hydrogen bonds and it is more difficult to remove in the drying process than the free water from the cell cavities (Thuvander *et al.*, 2002)

Condensing water: what is it?

Water in wood chips is vaporized during gasification and some organic components are distilled along with it. The amount of condensing water is dependent on the moisture content of the gasified wood chips and the temperature. This wastewater is typically a very heterogenic solution, containing organic components such as tars and small organic acids. This wastewater should be purified before sewering. A water sample taken

from the gasifier is usually yellow and muddy, sometimes even dark. It contains some solid material that can be dissolved with organic solvents, such as DMSO (dimethylsulfoxide) and ethanol.

COMPOSITION OF POLLUTANTS IN CONDENSING WATER

In order to identify the organic pollutants in condensing water from gasification processes, it was extracted for analysis by two different methods. First, the solution was diluted with DMSO and examined with gas chromatography mass spectrometry (GC-MS). Another extraction was done with 1,2-dichloroethane and both water and solvent phases were examined with GC-MS. The organic compounds found before any treatment of condensing water were small organic acids, phenols, phenantrene, anthracene, naphthalene, biphenylene, dibenzofuran, pyrene, fluorine, and their derivatives. After extraction the main components left in the condensing water were mainly phenols. Table 1 presents the metal contents of the condensing water and some limit values for sewage. Based on the results of the samples studied, the metal contents were not so high that they should be removed from the condensing water.

TABLE 1. **Typical metal contents of the raw condensing water sample and the average limit values for drainage. (Kouvolan Vesi)**

	Metal limit value [mg/L]	Metal measured value condensing water [mg/L]
As	0.1	<0.04
Hg	0.01	<0.5 [µg/L]
Ag	0.2	Not measured
Cd	0.01	<0.01
Cr	1.0	<0.03
Cu	2.0	0.06
Pb	0.5	<0.04
Ni	0.5	<0.02
Zn	3.0	0.04
Sn	2.0	<0.04

Biodegradation

The biodegradation of organic material in condensing water was measured with the BOD (Biochemical Oxygen Demand) OxiTop® Control technique (Roppola, 2009). This technique is based on small pressure changes in the airspace of the sample container. In the biodegradation reaction the sample biodegrades due to the presence of bacteria that consume oxygen in their respiration reaction. In some way, it resembles the respiration of higher life forms. The reaction produces carbon dioxide, water, new biomass, and ammonia. In the reaction the carbon dioxide forms the same mole amount as oxygen is consumed. The pressure change emerges when the carbon dioxide formed is absorbed into NaOH (sodium hydroxide) pellets. The water that forms enters the liquid phase or absorbs into the NaOH pellet in the upper part of the sample container. Two moles of water is formed in biodegradation reaction when one mole of oxygen is consumed.

The biodegradation reaction is represented by the equation:

$$C_xH_yO_zN_w, O_2, \text{Bacteria} \rightarrow CO_2, H_2O, NH_3, \text{Biomass}, \text{Energy}$$

The BOD OxiTop Control system contains the sample bottles, the NaOH holder in the neck of the bottle, constant stirring with a magnet, and the measuring head. The controller is separate, and it is used to start the measurement and read the values. The equipment provides 360 measuring points for every measurement and it can be monitored in real-time during measurement. The results can be transferred to the computer directly (Prokkola *et al.*, 2012).

FIGURE 1. *OxiTop Control system for biodegradation measurements in solution.*
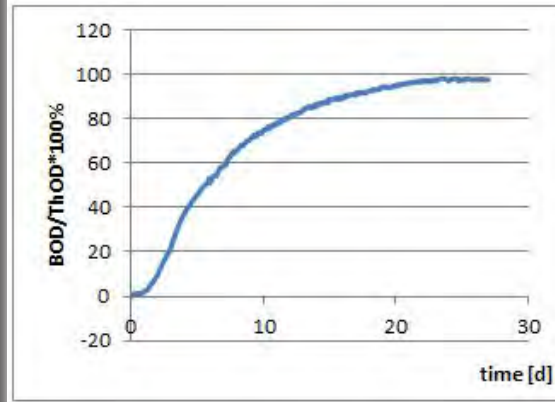
FIGURE 2. *Biodegradability development in the oil sample in OECD 301F standard conditions (T = 20°C)*

Purification methods

The purification of raw water was tested with different methods. Filtering was performed with activated carbon, carbon residue from the biogasification process, and ash granules that were prepared from combustion ash. The activated carbon removed a portion of the impurities but the carbon residue and ash granules did not adsorb any substances. Electrocoagulation and aeration were also tested and based on preliminary experiments these purification methods were not functional for condensing water. On the contrary, the chemical oxygen demand (COD) value increased with all methods other than activated carbon filtering, probably due to the dissolution of some metals or organic matter during the process.

Different oils and solvents were also tested for the extraction of impurities from the water samples. The result was that the dirty/used motor oil, biodiesel, and rape seed oil all caused a water-oil emulsion after extraction both in water and oil phases. Extractions were also performed with kerosene, pentanol, and hexanol. These produced better results than the oils that were first tested. The third time the extractions were tested with lamp oil (almost the same as kerosene), pure motor oil, diesel oil, and fuel oil. These also gave good results.

Filtering the samples

A packed column with activated carbon (provided by Merck) and gasification carbon residue was used for filtering the samples. The column was packed as follows:

1. Glass wool
2. Sand 6.25 g
3. Activated carbon + sand mixture 20.4 g
4. Sand 16.2 g
5. Glass wool

The test was then repeated using carbon residue from the biogasification process instead of the activated carbon. The water was discharged upward. Before the test the system was rinsed with deionized water for about an hour. The flow rate with deionized water was 26 ml/min. The flow rate of the sample was 2 ml/min through the activated carbon and the carbon residue from the biogasification process. A faster flow rate (29 ml/min) with the carbon residue from the biogasification process was also tested. Activated carbon and carbon residue were dried at 105 °C overnight and then crushed and screened under 150 µm. The surface area from BET[1] measurement was 603 m^2/g for activated carbon and 37.9 m^2/g for the bio ash (carbon residue), which indicates the adsorption potential of the material. The purification efficiency was clearly dependent on the surface area and carbon content of the filtration material (Kilpimaa *et al.*, 2013).

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1 Brunauer–Emmett–Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

Electrocoagulation of condensing water

Electrocoagulation is a water and wastewater treatment technology that combines the advantages of coagulation, flotation, and electrochemistry. Electrolysis is a process in which oxidation and reduction reactions take place when electric current is applied to an electrolytic solution. Electrocoagulation is based on dissolution of the electrode material used as an anode. This so-called sacrificial anode produces metal ions that act as coagulant agents in the aqueous solution in situ. At its simplest, an electrocoagulation system consists of an anode and a cathode made of metal plates, both submerged in the aqueous solution being treated. The electrodes are usually made of aluminum, iron, or stainless steel (SS), because these metals are cheap, readily available, proven effective, and non-toxic. The initial pH of the condensing water was 8.7. Electrocoagulation was tested and even the added salt did not help the current power to rise, which indicates that the treatment was not successful for the purification of condensing water (Kuokkanen *et al.*, 2013).

Aeration of the sample

Aeration with compressed air was performed with small bubble aeration. The air was pressed through pumicite that splits the air current into smaller bubbles and intensified the aeration. Bubbling time was five hours. The COD value increased the most during this treatment, because the water is vaporized during aeration and therefore concentrates the sample solution. (MTB, 1999)

Extraction with oils and solvents

Extraction with oils was also tested. The oils tested included used motor oil, biodiesel, and rapeseed oil. These experiments were not successful, because in the water phase and the oil phase a water-oil emulsion formed and the degree of purification of organic material in the condensing water was minimal, at least without further processing of the emulsion (Kuokkanen *et al.*, 2013). The two alcohols—heptanol and hexanol—were tested as extractants and the result was clearly better than other methods. Purification was tested with kerosene (paraffin) and the result was also good. The amounts used in extraction were 100 ml of wastewater and 10 ml of the extraction agent. Smaller amount of solvent was also tested: 5 ml of solvent and 150 ml of wastewater. TOC (Total Organic Carbon) values

were measured from these purified waters. The purification efficiency was the best with extraction by kerosene. Pentanol and hexanol were also good extractants. The pure motor oil was as good as others extactants, but there were three phases at the end. First was the water phase, second was a white solid material and third was an oil phase. The disposal of this phase was so difficult that motor oil was not used further. The others can be disposed of through burning. The result was that the motor oil, biodiesel, and rape seed oil all caused a water-oil emulsion in both phases. Diesel oil and fuel oil also were tested and the results were not as good as using kerosene extraction.

FIGURE 3. *Extracted condensing waters from wood chips from biogasification with kerosene (1 and 2), pentanol (3 and 4) and hexanol (5 and 6).*

Oxidation of samples by UV light and hydrogen peroxide

The combination of UV (Ultra Violet) light and hydrogen peroxide were tested and the result was that it is not suitable as a purification method for these kinds of waters. The amount of hydrogen peroxide consumed was quite large and the flow rate was 200 ml/min.

Discussion

In the preliminary experiments, the activated carbon was the only functional treatment that gave clearly better results than the other tested treatment methods mentioned above. However, activated carbon filtration purified only a part of the organic matter. It was also the only treatment method that lowered all COD (chemical oxygen demand), DOC (dissolved organic carbon), and BOD (biological oxygen demand) values. After other

purification methods, the COD values increased. One of the reasons for the increased DOC and COD values after aeration may be due to the evaporation of the water in the sample and thus sample concentrating during treatment. The filtering of the materials may raise the COD values due to the metals dissolving into the sample. The DOC values after treatments remained at the same level as they were at the beginning of the process. No treatment affected pH or electrical conductivity. The seven-day degree of biodegradation was 2 % for raw water and between 5 % and 17 % for filtered samples. The degree of biodegradation of the sample after aeration was 3 % and after electrocoagulation it was 10 %. These results were not repeatable. Variation, for example, in the sample's degree of biodegradation degree after filtration through ash granules was large.
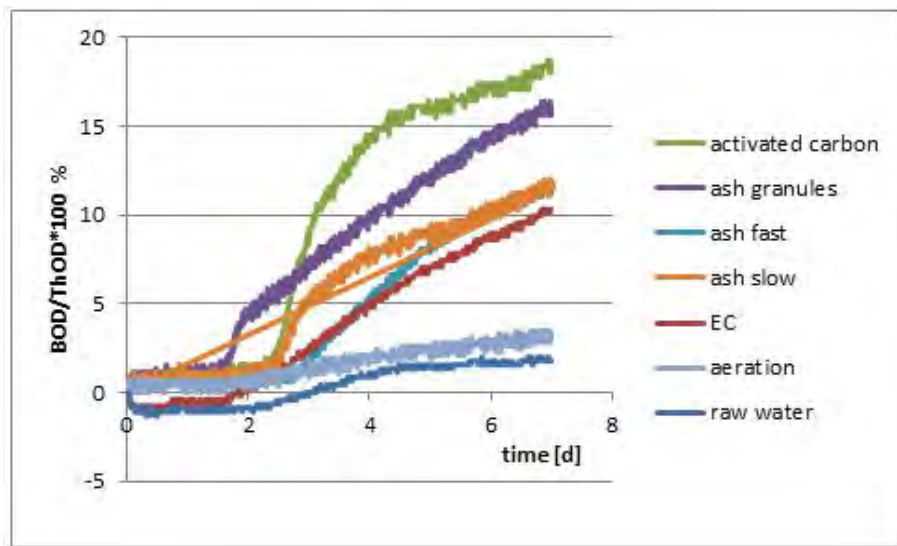
FIGURE 4. *The degrees of biodegradation of the raw water sample and after preliminary treatments. Values are mean values of two repetitions.*

The extractions gave better results than other listed treatments. The DOC value decreased to one-tenth. The best extractants were pentanol, hexanol, and kerosene. The extractions will be performed again with at least two other samples and the most effective one will then be selected for practical use. The capacity of extractants should also be tested. These results are promising for practical application in the future.

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RAW MATERIAL REQUIREMENTS OF GASIFICATION AND BIOREFINERY PROCESSES

High Quality Wood Chips for Gasification

Ulf-Peter Granö, Finland

Introduction

The quality development of small-scale production and processing of biomass for local and regional consumers requires research and monitoring. Small-scale solutions improve employment prospects for rural workers in energy production and processing. Active small businesses and energy cooperatives are needed in the harvesting, handling, and processing of local energy commodities for local and regional consumers.

To successfully produce high-quality final products, a few aspects should be considered across the entire value chain:

- Choose good-quality energy wood to ensure low amounts of bark
- Properly utilize the natural drying process to save drying costs
- Use powerful, well-built equipment that can provide high-quality energy wood
- Integrate activities with processes such as gasification of biomass and small-scale CHP units
- Cooperate with local energy cooperatives and entrepreneurs
- Prefer customers in the local area and the local region

The appropriate combinations and good application of the elements listed above can help achieve a higher utilization rate of energy wood and side products. A higher rate then contributes to the reduction of waste and unused by-products while also reducing environmental impact.

FIGURE 1. *Smooth and fine wood chips*   *Uneven and poor wood chips.*

QUALITY OF ENERGY WOOD IMPORTANT FOR GASIFICATION

Recently there has been a significant increase of interest in procuring the best quality wood chips for processing. Getting the best raw material requires that each stage and instance of handling in the process be carried out with the best practice available.

There are two basic methods for managing energy wood from the forest.

1. Handling fresh chips by chipping recently delimbed trees next to a forest road.
2. Handling the delimbed wood and chipping after natural drying in the field.

Forest machine harvesting and natural drying

Harvesting energy wood is performed with efficient machinery, which is nowadays often equipped with a multi-tree handling (MTH) unit for multi-stem handling and multi-stem delimbing.

FIGURE 2. *The MTH unit for multi-stem delimbing. Photo: John Deere (*<u>www.deere.se</u>*)*

Connecting weighing equipment to an energy-harvesting unit can facilitate the calculation of the amount of harvested energy wood. Crane-tip mounted scales make it possible to determine the amount of energy wood that is harvested or forwarded with a forest tractor, a harvester, a forwarder or a harwarder.

FIGURE 3. *A crane-tip mounted scale for weighing of energy wood.*

Chipping fresh wood chips

The handling chain for chipping green wood chips requires that fresh wood material be used within a limited time, especially during the warm season. Microorganisms directly trigger the degradation process, resulting in temperature rise, humidity increase, and unhealthy mold dust (fungal spores).

For the production of quality chips, all branches and green parts should be left in the forest. After chipping, the material should be dried by an efficient drying process and then temporarily stored under a roof before the chips go to further processing.

Drying fresh chips

Drying fresh wood chips directly after harvesting, when the moisture content is between 45% and 55%, means that a very large amount of water must be removed to reach a moisture content below 15% to 25%, as many of the gasification plants may require. There are many different types of wood dryers to choose from. Effective options for better drying quality include rotary drum dryers, bin dryers, tower dryers, and belt dryers.

FIGURE 4. *Natural drying in the field in an open area. The energy wood must be covered before the autumn rains begin.*

Final drying of field-dried wood

After chipping, naturally field-dried energy wood has a moisture content between 25% and 40%. Drying should achieve a moisture content below 15% to 20%, therefore the final drying process must be performed correctly.

In order to achieve moisture content below 20%, preheated air needs to be used. It requires an efficient dryer that can utilize waste heat to keep the drying costs down. For a small chip producer it often means that the drying plant will be built adjacent to a local district heating plant.

Quality energy wood requires quality throughout the handling chain

To achieve and maintain a sufficient supply of high-quality wood chips, the various work and management, from harvest to processing, must be carried out in a satisfactory manner. The quality of the energy wood that reaches the processing plant depends on the quality of the wood materials, as well as on the quality of work in different parts of the handling chain of the biomass.

General guidelines

Some general guidelines for the management of energy wood materials from harvesting to processing:
– Prevent the energy wood material from contamination by soil, dust, and other contaminants during harvest and transport.
– Remove the nutrient-rich green parts during harvest (e.g., branches, needles, and leaves).
– Sort the energy wood materials by quality at an early stage.
– Choose a good location for the natural drying and storage, where contamination can be avoided and drying can be done in the best way.
– Cover energy wood stacks stored for natural drying before the autumn rains.
– Avoid making large quantities of damp wood chips for long-term storage. Moist wood chips easily get moldy. In addition to degradation of the chips' energy potential, mold spores easily spread into the environment.
– Minimize the risk of mold in damp wood chips by starting the final drying early.
– Protect dried energy source from precipitation by storing it under a roof.
– Minimize the potential for soil moisture to moisten an already dried wood material.

A well-prepared storage location provides good conditions for effective drying of energy wood.

FIGURE 5. *MTH multi-stem delimbed downy birch provides excellent energy wood for quality chips.*

Chipping energy wood

The effective coordination of the chipping process for energy materials requires a careful driver and effective chipping equipment. Substandard or poor quality material should be sorted out before chipping.

FIGURE 6. *Large, tractor-driven chippers operated by an experienced entrepreneur often produce better chip quality.*

Transportation

Avoid exposure to impurities at all handling stages: during the transport of energy wood materials from the forest to the field drying location, during transport of wood chips to the storage location, and during transport to final drying from the chipping location. Contamination and unwanted contact with the ground can easily occur during loading and from tractor tires.

Logistics and final drying

Well-planned loading and removal of wood from the chip dryer improves the handling. Final drying is accomplished with minimal energy losses and achieves uniform moisture content of the dry wood chips, which ensures higher quality.

Storage of dried chips

After the wood chips are dried, they must be stored under a roof in a dry place where water cannot enter. If drying is done in batches, a larger buffer silo for wood chips is needed before transportation to the processing plant. Otherwise, there can be problems when a steady supply of wood chips exists.

Effective field drying

Experience and knowledge show that field drying can reduce moisture content to 25%–30% with the right choice and extra effort. Here are some guidelines:
– Choose an open, airy space for drying and storage.
– Ensure that air can circulate under the stack of energy wood, supported by the right size logs.
– Cover the woodstack before the autumn rains.
– Utilize the dry weather during the summer season for efficient drying.
– Do not let snow and water get into the stack during the removal of energy wood and chipping.
– Old and overyear wood material should be burned as wood chips. It should not be used for further processing.

SOME EXAMPLES OF LOGISTICS FOR BIOMASS

To ensure the availability of good biomass for the gasification of wood chips, smooth logistics and efficient supply chain management are needed. Good logistics depends on the type and quality of wood materials used in the gasification. The general guideline to follow is as follows: the cleaner and more homogeneous the wood material is, the easier the purification process after gasification will be.

During start-up, the following must be considered: the availability of wood materials and the main purpose of the producer gas or biosyngas (bio-SNG). If the product gas is directly burned in the local combined heat and power (CHP) unit, the requirements for the purification of the gas are lower. Other uses of the product gas increase the demands for purity and gas quality.

Harvesting, handling, and pre-treatment or processing of the biomass from forests can be done in many different ways, depending on the seller and the buyer. The biggest differences in the handling chain often depend on who the customer is. Customers can be major ones, such as power plants, or local ones, such as energy co-operatives.
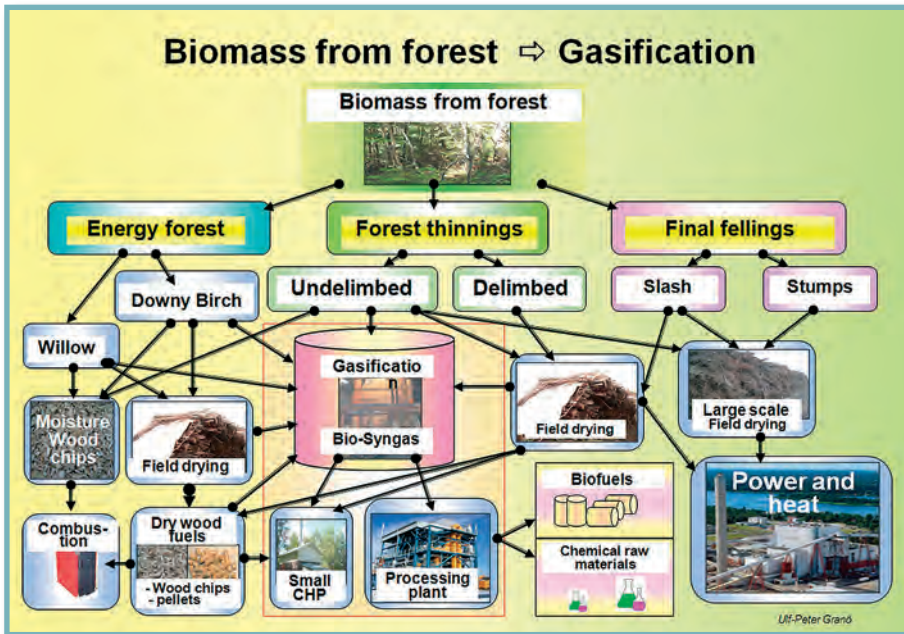

FIGURE 7. *Simplified overview of the routes biomass can take: from the energy forest, forest thinnings, and final fellings.*

For small-scale gasification in rural areas, the primary question is choosing the right way to combine the gasification plant with the local CHP unit for producing both heat and electricity to make most of biosyngas (i.e., wood gas) from the gasification. Depending on the type of gasification facility and the technology, the biomass more or less requires final drying before the wood chips can be used for gasification after chipping and drying.

Biomass from forest thinnings

Final fellings often require larger equipment because the wood is thicker and a high amount of larger trees are included. In contrast, harvesting and processing biomass from thinnings requires only the smallest harvester models.

The quality of biomass feedstock deteriorates quickly if degrading fungi, bacteria, and insects are allowed to rapidly proliferate during storage. The risk of degradation can be reduced by pre-drying and proper storage.
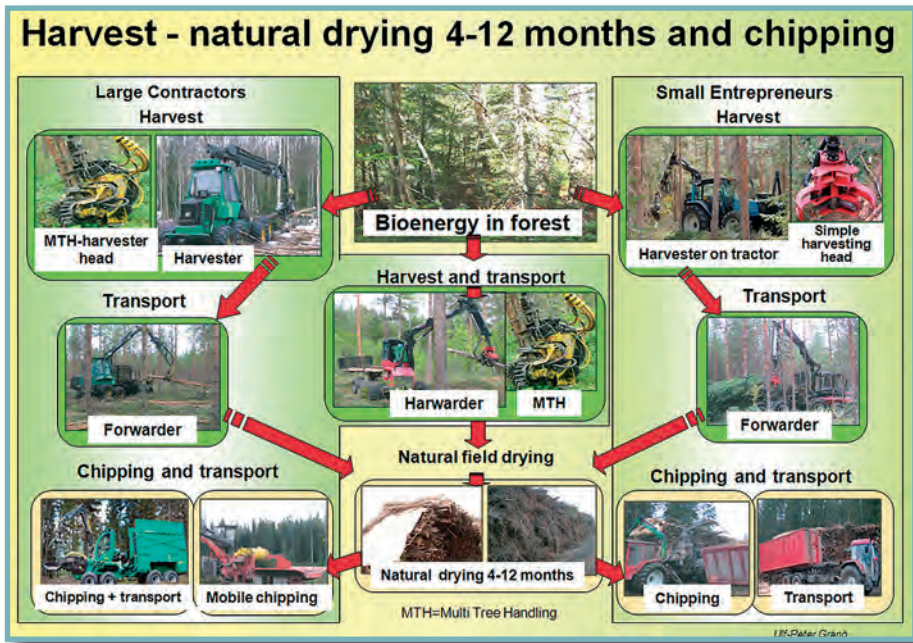

FIGURE 8. *Examples of machines and equipment in the forest harvesting chain.*

Natural drying of energy wood

Natural air drying is the best option to eliminate the high humidity in the energy wood material. By ensuring that the material is properly protected before the autumn rains, the material stays drier and at least 5% lower humidity of the wood material can be achieved compared to an uncovered stack of energy wood.

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FIGURE 9. *A well-made coverage for energy feedstock produces drier end product. Depending on the conditions, the moisture content of the energy wood can be below 30% (moisture).*

EQUIPMENT FOR CHIPPING AND CRUSHING BIOMASS

To use biomass from forests for small-scale heating or small CHP units, the material has to be chipped or crushed. For small users, the wood fuel is normally in the form of wood chips.

Small or large energy entrepreneurs?

Development in rural areas has shown that a range of machine work services are increasingly delivered by contractors. This also involves the large-scale forestry machine work. Harvesting and transportation of roundwood and energy wood, slash bundling, chipping, and other actions are performed by small and large contractors. The small contractors are often local one-man businesses.
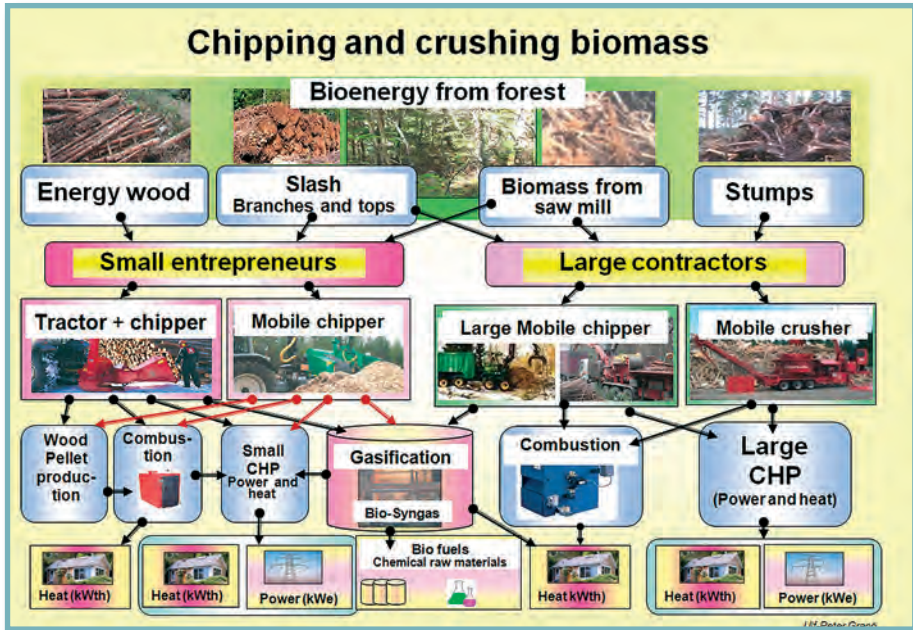
FIGURE 10. *Overview of alternative routes for biomass from forest, through chipping / crushing, and processing. Bioenergy for heat or for electric power and heat. Bioenergy, as feedstock for biofuel or the chemical industry.*

FIGURE 11. *Examples of differences between small and large contractors. Large contractors have often chips equipment with capacities of over 150 m³/h. Large mobile crushers are mainly used in connection with large power plants to, for example, crush stumps and demolish wood.*

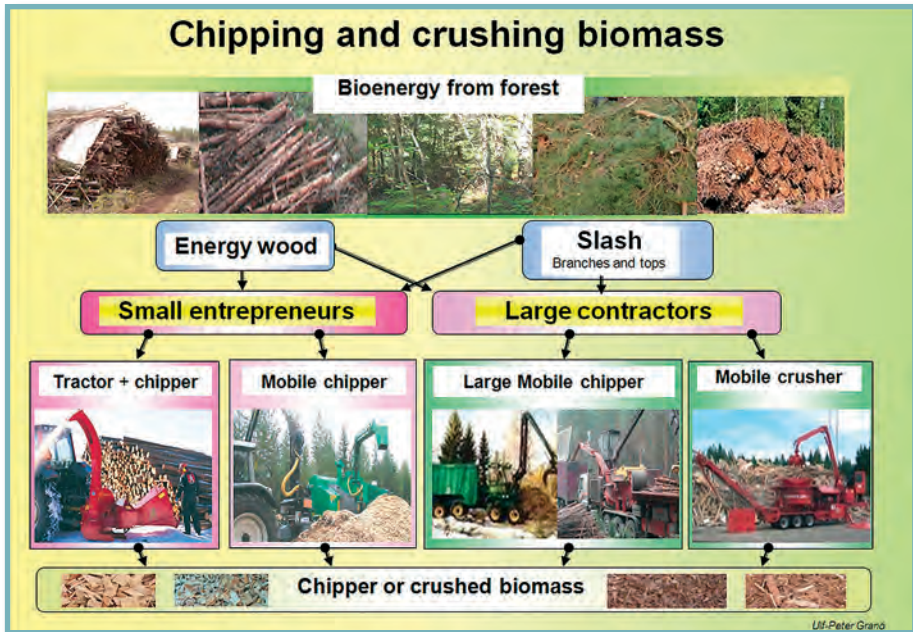## Examples of the ways for producing biofuels from wood

Type of action	Biofuel raw materials		Handling		Type of wood fuel
Final fellings (for regeneration of forest)	Slash (Branches and tops)	Fresh	Harvesting - Collecting	Chipping	Green wood chips
			Harvesting - Bundling	Chipping	Green wood chips
				Field drying + chipping	Brown wood chips
		Harvesting - Field dried	Collecting	Chipping	Brown wood chips
			Bundling	Chipping	Brown wood chips
Thinning and clearing in young forest stands	Energy wood, whole trees	Fresh	Harvest -Direct chipping	at harvest	Green wood chips
			Harvesting -forwarding	Chipping	Green wood chips
			Harvesting -forwarding	Field drying + chipping	Brown wood chips
			Harvesting - Bundling	Field drying + chipping	Brown wood chips
	MTH delimbing	Fresh	Harvesting -forwarding	Field drying + chipping	Quality wood chips
	Energy wood		Harvesting -forwarding	Field drying + combi-splitter	Firewood
Short rotation Energy forest (downy birch)	Energy wood	Fresh, whole energy woods	Harvest -Direct chipping	at harvesting	Green wood chips
			Harvesting -forwarding	Chipping	Green wood chips
				Field drying + chipping	Brown wood chips
	MTH delimbing	Fresh	Harvesting -forwarding	Field drying + chipping	Quality wood chips
	Energy wood		Harvesting - Bundling	Field drying + chipping	Brown wood chips
Bioenergy forest, Growing willow	Energy fuels	Fresh	Harvesting - Collecting	Chipping	Green wood chips
			Harvesting - Bundling	Field drying + chipping	Brown wood chips
Stumps	Energy fuels	Fresh	Collecting stumps	Field drying and crushing	Brown crushed wood

MTH = Multi Tree Handling   MTH delimbing = MTH for multi-stem delimbed   Ulf-Peter Granö

FIGURE 12. *Different fuel qualities can be produced from various materials by a range of methods in the subsequent handling.*

Good quality energy wood makes it easier to achieve a high-quality final product. The most important guideline for energy wood is to utilize natural air drying and prevent bacteria and fungi from attacking the wood material. By properly protecting the stack of energy wood before the autumn rains, material that is at least 5 percentage points drier can be achieved.

FINAL DRYING OF WOOD CHIPS FOR GASIFICATION

For the gasification of biomass, most types of small-scale gasifiers need some kind of drying of wood chips to achieve a moisture content below 20% to 25%. However, there is some promising research on new gasification reactors that use wood chips with moisture levels of 25% or higher.

Utilizing natural field drying

To achieve high-quality energy wood, the natural drying process should be favored. The best drying period is during the summer months because of higher temperatures and lower humidity.
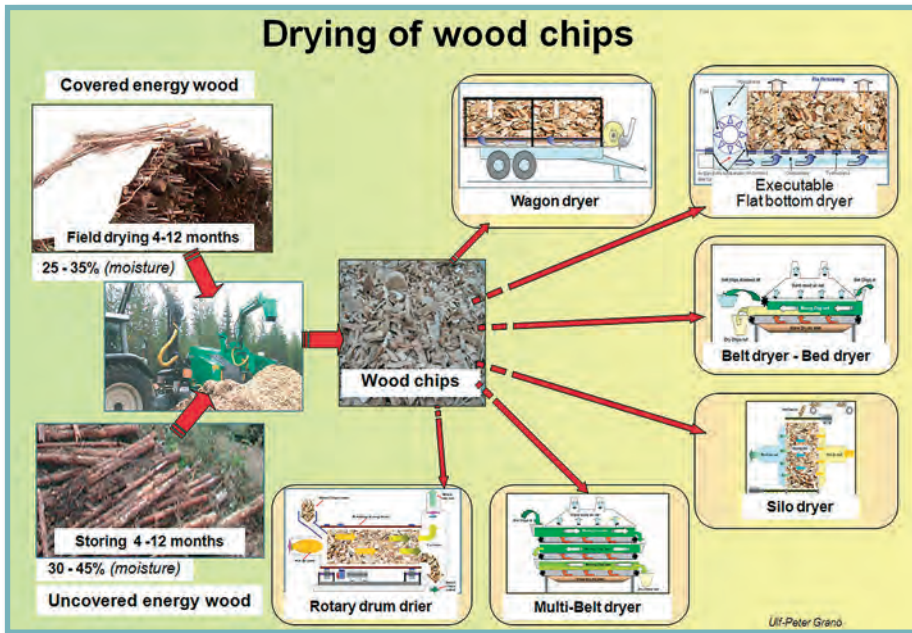

FIGURE 13. *Overview of different dryers for small-scale drying small-scale, carried out by smaller entrepreneurs or energy co-operatives (energy co-op).*

The worst period for drying is the rainy autumn months when the humidity is high. Especially if the energy wood stack is uncovered, several percentage points of dryness are easily lost to higher moisture content.

Different types of materials are used to cover the wood. They range from tarps that can be used for several years to covers made of kraft paper. The use of kraft paper covers has increased because they are easy to handle and can be fed into the chipper at chipping.

Experiments have shown that a well-made cover for energy wood decreases the moisture content by 5 to 10 percentage points compared to wood without a cover. A poorly covered stack of energy wood and a stack without a cover after drying can have a moisture content of 35% to 45%, while a covered stack of energy wood after the end of drying time can have a moisture content of 30% to 35%. With optimal storage and covering conditions, the moisture content can be decreased below 30%, therefore resulting in high-quality energy wood.

SMALL CHP PLANTS FOR WOOD BIOMASS

The technology of small power plants (CHP) is currently undergoing rapid development. It is now possible to utilize forests as a bioenergy source in different types of small and medium-sized power plants. The basic fuel can be wood chips or pellets. In Central Europe there is significant interest in small CHP plants using biomass as a fuel. Small CHP units are between 30 kWe and 500 kWe in size (kWe = kilowatts of electricity). The development of small CHP plants is based on several principles, some of which will be briefly discussed in the following sections.

Main technologies for small CHP units

Small- and medium-sized co-generation technology is primarily based on the following:

- **ORC technology**
- **Stirling engines**
- **IC engines** (gas engines) – *requires biomass gasification*
- **Microturbines** – *requires biomass gasification*
- **Fuel cells** – requires *biomass gasification*

Organic Rankine Cycle (ORC) units manufactured in Europe

The Italian firm Turboden is among the leading manufacturers of ORC units. For the past 30 years, they have worked with ORC systems for small power plants. They have built over 250 ORC units in Central Europe and several are currently under construction. The Turboden ORC units range in size from 200 kWe to 2.5 MWe.

FIGURE 14. *Turboden ORC plants are factory installed on the platforms, and during the assembly in the CHP plant they are connected together and to the boiler. The ORC-CHP plant in the picture is in Toholampi, Finland, and the power output is 1.3 MWe. Photo: Turboden.it*

Stirling engines mainly in use for small CHP installations

Stirling engines are developed, for example, in sizes ranging from 9 kWe to 75 kWe. These Stirling engines are mainly for boilers, with the size range between 100 kW and 800 kW. For good heat transfer and high efficiency, the Stirling engine's heat transfer surfaces should be kept clean. To make cleaning easy, only product gas (biosyngas) from gasified wood fuel should be burned in the boiler. During the burning of biosyngas, the soot formation is low compared to wood chip combustion.

FIGURE 15. *Stirling engine 35 kWe, before assembly. The heat transfer device is visible on the cylinder head. Photo: Stirling.dk*

Microturbine

In the last ten years, the development of microturbines for biogas and wood gas biofuels has taken off. Different sizes of microturbines are available and have been in use for many years for natural gas, especially in remote locations where no power lines for electricity exists. As an example, ISET in Germany has been working on development projects to follow up Capstones microturbines in sizes from 30 kWe to 500 kWe.
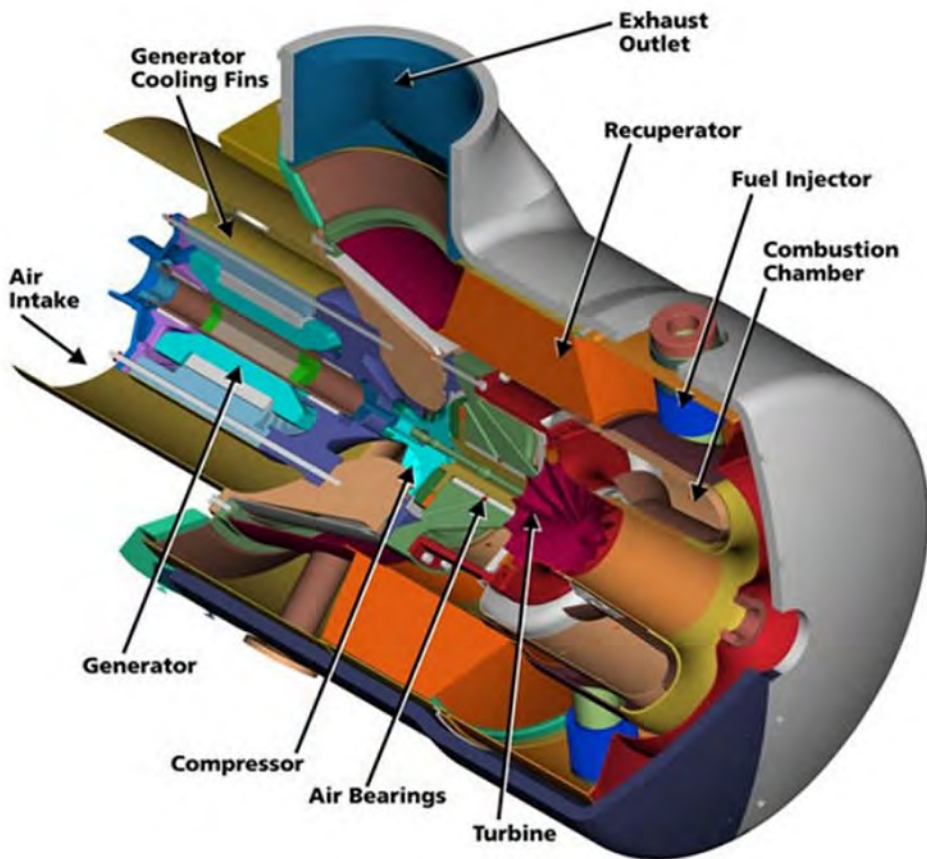

FIGURE 16. *Microturbine equipped with a generator from Capstone, which can use purified biogas or wood gas. Microturbine units are usually below 200 kWe in size. Photo: Capstoneturbine.com*

Some advantages of microturbines:

– Compact with smooth execution
– Low maintenance costs
– Low noise level
– Easy to install, requires no strong foundation

Biogas and biosyngas used in microturbines must be purified well, also of moisture, and the gas needs to be compressed. A microturbine can withstand hydrogen sulfide (H_2S) better than the piston engines.

IC gas engine (piston engines)

Large IC gas engines for natural gas have been used in power generation for some time, including as reserve units for hospitals and other buildings. Small CHP units with gas piston engines fueled with natural gas or biogas have been used in several areas where electricity is not otherwise available. It is possible to modify and install different types of IC gas engines so they can utilize biogas or biosyngas fuels.

FIGURE 17. *IC gas engine (piston engines). Example of a piston engine in a CHP unit, a 20-cylinder Jenbacher gas engine. Photo: ge-energy.com (Jenbacher)*

Future promises fuel cells for biosyngas

In the near future, biosyngas from gasified wood chips can be used as fuel for CHP units with fuel cells. The company MTU CFC Solutions GmbH in Germany manufactures fuel cells that can use biogas and biosyngas after thorough purification. CHP units with fuel cells in sizes around 250 kWe are already in operation, but mainly for natural gas.

FIGURE 18. *Installation of a fuel cell stack at a MTU CFC plant in Germany. Photo:* www.mtu-online.com

Many different development opportunities available

Development of small-scale processing of biomass will continue in many different ways. The most important starting point for small-scale processing is to process and refine bioenergy feedstock near the place where it is available for local and regional customers.
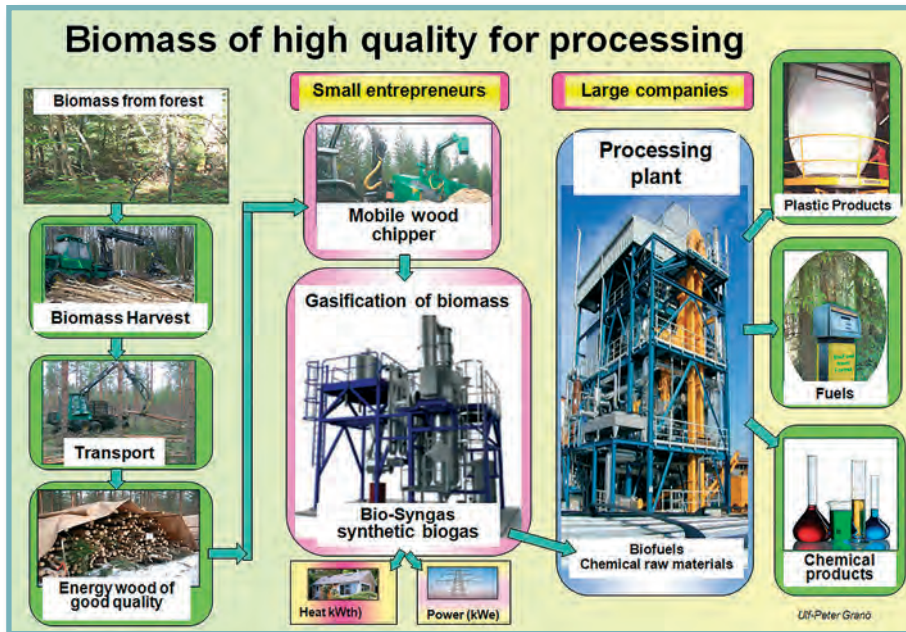
FIGURE 19. *Final high-quality products are more easily obtained from high-quality biomass.*

The better the cooperation between different local actors, such as energy co-operatives, the easier it is to achieve the objectives of biomass processing for energy. An excellent gateway to start cooperation might be a local heating unit for a few farms, businesses, schools, or a local heating unit in the village. The next step in development may be to simultaneously produce electricity but also to integrate with other biomass processing activities.

The goal should always be to strive for as good quality of wood biomass feedstock as it is possible to procure from the forest. Lower quality wood biomass as well as logging residues and logging slash can be advantageously transported to large consumers who have custom boilers that can utilize material with high bark and small branch content. In addition, these large consumers also often have a flue gas purification process. In the future, biomass gasification in small-scale units will make it possible to produce raw materials in gas and liquid form for further processing by the fuel and chemical industries.

To ensure the best possible end products, the energy wood collected from forests must be high quality. The same applies to the rest of the chain: all the work and equipment used in harvesting, handling, and processing of bioenergy feedstock must be also high quality.

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Raw Material Requirements of Biorefinery Processes

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The raw material quality requirements of future biorefineries may differ from the current requirements of the forest industry. Different raw material characteristics may be desirable for different types of biorefineries, and the industry can be expected to strive to acquire raw material with a high value for their process at the lowest possible cost (Figure 1). This paper reports on work that aims to identify relevant parameters for characterizing the raw material and to describe the key characteristics that are relevant for different biorefinery processes.
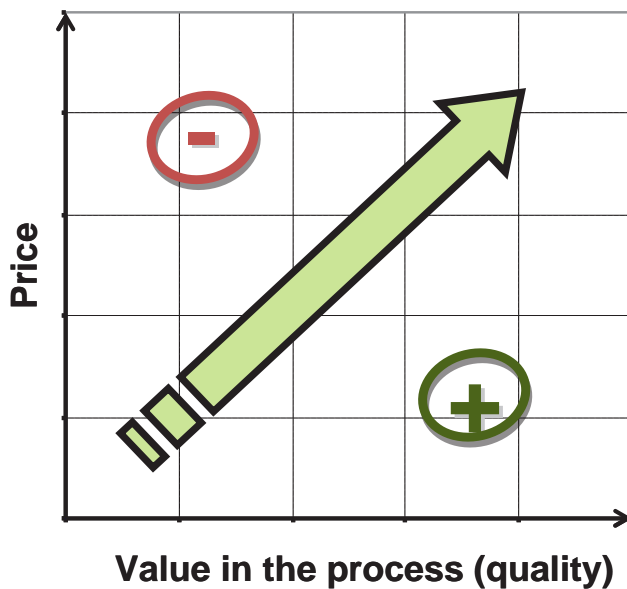
FIGURE 1. *Feedstock price versus value of the feedstock in an industry process. The industry can be expected to seek to acquire feedstock with high value for their process at a low price. There is likely to be a trade-off between low price and high value.*

The main products of the conventional forest-based industry fall into three categories: solid wood products (sawn wood, wood-based panels), fiber products (paper, paperboard, tissue), and bioenergy (fuels for heat and power applications). The industry is dominated by sawmills and pulp and paper mills, whereas wood-based panels and bioenergy are generally produced from processing and forestry residues. The raw material quality requirements for these conventional industries have been described by, for example, Lundqvist and Gardiner (2007). However, the concept of biorefining has not been well defined, but the term is typically used to describe a set of practices different from the traditional one used in the forest industry. The proposed descriptions of biorefining typically focus on the fractionation of the raw material into different components, the diversification of the mix of products that are produced, the integration of energy and material flows connecting several processes, the upgrading of side streams and the optimization of the value produced from the raw material. For this paper, we have selected processes that could be central to future biorefineries. The processes have been grouped into chemical, biochemical, and thermochemical processes. We have also included upgrading of solid fuels by pelletizing.

Stakeholder Survey

We surveyed the existing knowledge about raw material quality requirements for biorefineries through a review of technical and scientific publications and through contacts with stakeholders. A questionnaire was used as the basis for acquiring information from stakeholders. A number of stakeholders were contacted and interviewed. The questionnaire was also emailed to a number of stakeholders. However, none of the stakeholders who received the questionnaire by email only responded.

Results

Some general observations can be made. First, since many of the biorefinery technologies are still in a development stage, there is no complete picture of their respective raw material requirements in industrial-scale applications. Some of the ongoing development work specifically aims at adapting the processes so that they can accept a wider range of feedstock qualities. Thus, there are no definite, fixed, raw material quality criteria that have to be met. Rather, it is a question about the trade-off between a stricter feedstock specification and a more complex process. It is also a question of where it is most efficient to perform feedstock preparation to adapt it to a specific process – at the place of manufacture or along the supply chain. A given process can often be adapted to handle specific feedstock problems, but variations in feedstock properties may be more difficult to handle. This difficulty means that a cost-efficient supply of a clean, homogenous, well-characterized feedstock would become a priority for the industry. Additionally, properties that affect the transportation, storage and feeding of the feedstock are important in most applications. In these aspects, cost per unit energy content would become a key parameter for biorefineries that produce energy products such as solid and liquid fuels, heat and electricity. For biorefineries based on sugar chemistry, the cost per unit mass of sugar molecules, as well as the composition of the sugars, would become important (e.g., cellulosic ethanol production via the biochemical route).

Forest feedstock contains a huge variation of small-volume substances that could potentially be utilized for high-value chemical products. Certain parts of the tree, such as the knots, are richer in these substances. However, commercial developments within this area are scarce, and the present study has so far not been able to draw any general conclusions regarding feedstock requirements for these high-value chemical applications. The requirements will probably be highly specific to the individual application.

Table 1 summarizes the influence of key raw material properties on important biorefinery processes. The information in the table draws on a report by Väisänen (2010), along with the stakeholder interviews. In the following sections, we briefly define and describe the biorefinery processes included in our summary.

Chemical processes

In chemical processes, biomass components are separated or dissolved through the application of organic or inorganic chemicals. The processes can, for example, be alkaline, such as the kraft pulping process or acidic, such as the sulphite pulping process. Chemical pulping (kraft and sulphite) has been used for the production of pulp for paper, but other products are possible from the fiber fraction as well as from other streams. For example, sulphite pulping can yield a pure cellulose pulp with ethanol, biogas and lignin as co-products. The cellulose can be used in the production of textiles through the viscose process. Other chemical processes have been suggested, but they are not discussed in this article. The chemical composition of the feedstock may influence the performance and yield of the processes. Particle size, shape, and porosity affect the impregnation of the feedstock by process chemicals as well as the reaction rate.

Biochemical processes

Biochemical processes apply enzymatic processes to chemically convert the feedstock. An example is the hydrolysis of polymeric sugars (cellulose and hemicelluloses) into monomeric sugars through enzymatic treatment and the subsequent fermentation of the sugars into ethanol by microorganisms. Important raw material properties include the molecular composition (especially in the sugars content and type of sugars), properties that affect the accessibility of the enzymes or microorganisms to the substrate, and the tendency of the feedstock to produce unwanted substances that inhibit biochemical reactions in the process.

THERMOCHEMICAL PROCESSES

Thermochemical processes include torrefaction, a pre-treatment process performed at a relatively low temperature in the absence of an oxidizing

medium, to obtain a compact and brittle solid material; pyrolysis performed at a higher temperature in the absence of an oxidizing medium, typically with a liquid as the main product, which can replace fuel oil or be upgraded to other fuels or chemicals; gasification performed at high temperature, with a limited supply of oxidizing medium to produce a gas that can be used for conversion into fuels and chemicals or for heat and power production; and combustion for heat and power applications. The heating value, moisture content, the ash content and the ash properties are, in general, relevant for thermochemical processes. The particle size affects the reaction rate, which is a key parameter.

Pelletizing

Small particles are pressed through a die with holes to form pellets of a desired dimension. The process requires a relatively dry feedstock with adapted particle size. The energy requirements of the pelletizing process and the physical durability of the pellets are affected by the raw material properties. The intended end-use of the pellets determines the quality requirements.

TABLE 1. Summary of key raw material properties' influence on important biorefinery processes.

	Feedstock composition	Physical properties	Other
Chemical pulping	The cellulose fibers are typically the desired component of the feedstock, but also lignin, hemicelluloses, and extractives may be utilized for co-products. Extractives such as resin may cause problems, especially in sulfite pulping. These problems can be reduced by adjusting the process conditions. Bark and impurities are detrimental for pulp quality and need to be removed.	Typically, stemwood chips are used. Knots and branchwood are generally undesirable. For the efficient impregnation of chemicals, chips should not be too dry, and the moisture content should be known for process control. Fiber properties, such as length, thickness, etc., may be very important, depending on the application. For textile cellulose applications, fiber properties are less important.	The particle size should be homogenous to control process conditions. Moisture variations are tolerable, but process optimization is easier with stable moisture content. While some heterogeneity in, for example, fiber properties may be beneficial, uniformity over time is important to maintain a constant product quality. Removal of bark and impurities is essential.
Hydrolysis	The content and composition of sugars is important. For fermentation to ethanol, glucose is preferred, followed by other hexoses. Pentoses are more difficult to ferment. There are three main groups of fermentation inhibitors: Furans (sugar degradation product); acids, especially acetic acid (mainly from hemicelluloses); and phenols (probably from lignin). Lignin is in general undesirable as it lowers sugar yields and has a negative effect on enzymatic hydrolysis. Extractives may also cause some problems in the process. Hydrolysis is relatively insensitive to impurities. Sand and rocks cause wear on equipment.	Moisture is not a big problem in ethanol production. However, the feedstock should not be too dry. Small particle size is in general desirable, but various sizes, such as chips and sawdust can be used. Fine materials may cause problems in filtering operations.	The particle size should be homogenous to control process conditions. Moisture variations are tolerable, but process optimization is easier with stable moisture content. Bark may cause problems according to some sources. Some sources say that bark and logging residues can be handled.

	Feedstock composition	Physical properties	Other
Torrefaction	All organic matter is of interest. High share of easily volatilized substances lowers the yield. Relatively insensitive to impurities. However, the amount of impurities and ash etc. affects the end product quality. The quality requirements depend on the intended end use.	The material needs to be pre-dried before entering the torrefaction process (to ~10%). The particle size is not so critical. Chips (10x20x40 mm) are good. A high share of fines may create dust problems. Oversized material may give feeding problems.	Homogeneity in particle size and other properties is beneficial for process optimization, because it becomes easier to achieve a homogeneous degree of torrefaction.
Pyrolysis	Impurities are detrimental to the pyrolysis process. Rocks and metal parts must be removed. High levels of extractive substances in the raw material reduce the yield. The effect of impurities in large-scale applications has not yet been totally clarified.	Pyrolysis processes require moisture content to be below 10%. Variations in moisture are generally also a problem. In fast pyrolysis, particle sizes should be small (<3mm).	A homogenous feed is desired. Variations in the feed properties cause undesired variations in the end products' properties.

	Feedstock composition	Physical properties	Other
Gasification	The ratio between oxygen, hydrogen, and carbon in the feedstock affects the gasification process and should preferably be known. Catalytic conversion of the gas into fuels or chemicals is negatively affected by sulphur, phosphor and alkali metals. Gas turbines are less sensitive but corrosion and erosion may be problems. For indirect gasification, more volatile substances and less coke are desirable. Ash content and properties are important. Low ash melting point is a problem in FB gasification. Impurities may cause jams in feeding equipment. Metals are detrimental because they cause the corrosion of equipment and the sintering of bed material in FB gasifiers. The content of, for example, active silicon, phosphor, and calcium affects the ash melting behavior. Clay minerals may reduce potassium-related problems.	Moisture levels should be below 10%–20% for syngas production (depending on gasification technology). EF gasifiers require lower moisture content than FB gasifiers do. Drying is often needed and could preferably be integrated with the gasification process. The desired particle size depends on gasification process, but, in general, the size must not vary much. EF gasifiers require a powder-like feed (particle size typically lower than 0.5 mm) but large fractions of too fine material may also cause problems. FB gasifiers are more tolerant to feed quality changes and larger particle sizes (up to 50 mm for BFB gasifiers). Materials that are too fine may cause problems, especially in BFB gasifiers, while CFB gasifiers are less sensitive.	Raw material homogeneity is very important in gasification processes. The moisture level affects the consumption of the gasification agent, which must be carefully controlled. EF gasification is particularly sensitive to particle size variations. Feeding, especially to pressurized reactors, may be problematic. Bulk density is one important parameter. For the EF process, it is crucial to grind the feed into a suitable powder. Factors that affect the grindability, such as moisture content, are important. Less fibrous material, such as bark and torrefied materials, may be easier to use.

	Feedstock composition	Physical properties	Other
Combustion	A high heating value is desired, but also the ash content and ash characteristics are of interest. Combustion is relatively insensitive to impurities, although both ash and non-wood components are undesirable. Metals, salts, and large rocks may cause big problems. The sensitivity to impurities and ash properties vary with the combustion technology. Grate boilers tolerate impurities well in comparison to other combustion methods.	Higher moisture content gives a lower heating value to the raw material, which is generally unfavorable, but large-scale combustion technologies are relatively insensitive to moisture content. Particle size is not crucial for large-scale combustion technologies, but should preferably be known, so the process can be adapted. Very small particles – fines – may cause problems.	Fluctuations in the raw material feed may lead to high levels of unwanted emissions from the combustion. Some raw material variability can be accepted but abrupt changes are difficult to handle. Variations may also cause feeding problems. In general, grate boilers are more sensitive to particle size variations than BFB boilers.
Pelletizing	Lignin is beneficial for pellet production while high concentrations of extractives may be unfavorable. The acceptable ash content varies with the end use. Household pellet boilers and stoves generally require low ash content, and thus low bark content in the feedstock. Impurities such as sand and rocks can be very detrimental to pelletizing equipment.	The ideal moisture content for the pelletizer is around 10%. The material may have to be dried or wetted. Particle sizes to should not exceed 60% of the pellet diameter (typically 6–10 mm). For the drying process, a small particle size is beneficial. The desired particle sizes may also vary with the end use. Smaller particle sizes are preferred when the pellets are crushed into dust before end use.	Variations in particle size and moisture content cause severe problems in drying and pelletizing. Uneven moisture content of the dried material and plugged die holes in the pelletizer may be the result. The desired properties are to a large extent governed by the intended end-use of the pellets.

Nomenclature: EF: entrained flow, FB: Fluidized bed, BFB: Bubbling fluidized bed, CFB: Circulating fluidized bed

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