



OULUN YLIOPISTO  
UNIVERSITY of OULU

Department of Process and Environmental Engineering  
Mass and Heat Transfer Process Laboratory

Master's Thesis

## **Small-scale biomass-to-energy solutions for northern periphery areas**

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Author: Anu Kauriinoja

Supervisor: Riitta Keiski  
Professor

Advisors: Eva Pongrácz  
Docent, D.Sc.(Tech.)

Mika Huuhtanen  
D.Sc.(Tech.)

Department Dep. of Process and Environmental Eng.		Laboratory Mass and Heat Transfer Process Laboratory	
Author Kauriinoja, Anu Elina		Supervisor Keiski, R. Professor	
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<p>Abstract</p> <p>The concern on impacts of global warming and decrease of the conventional fossil fuel sources enhance the interest to renewable energy sources. Biomass, containing all organic material that stems from plants, accounts for about half of the renewable energy used in the European Union. As a very versatile energy source, biomass can be used in transport, electricity and heating. The European Union aims to promote and support all these sectors in the purpose to diversify its energy supply, to increase the share of renewable energy, to reduce reliance on imported energy, and to decrease greenhouse gas emissions.</p> <p>The aim of this thesis was to collect information from technologies suited to energy production from biomass and biomass based waste. Especially the suitability of these technologies for small-scale use in the northern periphery areas was evaluated. Northern rural regions have many special properties considering energy production from biomass. These areas are sparsely populated, insular, and peripheral, and have a harsh climate with long and cold winters. SMEs and local organisations in these regions have a possibility to generate energy on site from their own wastes and by-products, at the scale that is economically viable. On the whole, northern periphery areas have a great potential for biomass and energy production.</p> <p>Biomass can be converted to energy by thermo-chemical, biochemical, mechanical, chemical, or electro-chemical process routes. From these, different thermo-chemical and biochemical conversion technologies are suited to the wide range of biomass while the others have more limitations on the feedstock. Thermo-chemical conversion methods are suited to relative dry woody and herbaceous biomass whereas biochemical technologies can also handle biomass with high moisture content.</p> <p>The most suitable conversion technologies for northern periphery areas are those that produce energy commercially also in small scale and are inexpensive and simple to construct and maintain. Gasification and anaerobic digestion were found to be good technologies with quite dissimilar feedstock requirements.</p> <p>The thesis is done as part of the MicrE project financed by the Northern Periphery Programme. Another output of the thesis is the technology cards which have been done from pyrolysis, gasification, anaerobic digestion, fermentation, and pelletisation. The cards can be used to introduce the different feasible technologies to the local organisations and the enterprises.</p>			
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<b>Tiivistelmä</b> <p>Huoli ilmaston lämpenemisestä ja perinteisten fossiilisten energialähteiden vähentyminen kasvattavat kiinnostusta uusiutuviin energialähteisiin. Biomassa, käsittäen kaiken alun perin kasveista peräisin olevan orgaanisen materiaalin, sisältää noin puolet Euroopan Unionissa käytetystä uusiutuvasta energiasta. Hyvin monipuolisena energialähteenä biomassaa voidaan käyttää liikennepolttoaineiden, sähkön ja lämmön tuotannossa. Euroopan Unionin tavoitteena on edistää ja tukea kaikkia näitä sektoreita tarkoituksenaan monipuolistaa energian hankkimista, kasvattaa uusiutuvan energian osuutta, vähentää riippuvuutta tuontienergiasta ja pienentää kasvihuonekaasupäästöjä.</p> <p>Tämän työn tavoitteena oli kerätä tietoa teknologioista, jotka sopivat energian tuotantoon biomassapohjaisesta jätteestä. Erityisesti näiden teknologioiden soveltuvuus pienen mittakaavan käyttöön pohjoisilla periferia-alueilla arvioitiin. Pohjoisella maaseudulla on paljon erityispiirteitä tarkastellessa energian tuotantoa biomassasta. Nämä alueet ovat harvaanasuttuja, eristyneitä, perifeerisiä ja niillä on ankara ilmasto pitkin ja kylmine talvineen. Näiden seutujen pk-yrityksillä ja paikallisilla organisaatioilla on mahdollisuus tuottaa energiaa omista jätteistä ja sivutuotteista mittakaavassa, joka on taloudellisesti mahdollinen. Kaiken kaikkiaan pohjoisilla periferia-alueilla on suuri potentiaali biomassan ja energian tuotantoon.</p> <p>Biomassa voidaan muuntaa energiaksi termokemiallisilla, biokemiallisilla, mekaanisilla, kemiallisilla tai elektrokemiallisilla prosesseilla. Näistä erilaiset termokemialliset ja biokemialliset konversioteknologiat sopivat suurelle biomassajoukolle, kun taas muilla on enemmän rajoituksia syötölle. Yleisesti termokemialliset konversiomenetelmät soveltuvat suhteellisen kuivalle puu- ja ruohomaiselle biomassalle, kun sitä vastoin biokemialliset teknologiat voivat myös käsitellä biomassaa, jossa on paljon kosteutta.</p> <p>Yleensä sopivimmat konversioteknologiat pohjoisille periferia-alueille tuottavat energiaa kaupallisesti myös pienessä mittakaavassa ja ovat edullisia ja yksinkertaisia rakentaa ja ylläpitää. Kaasutus ja mädätys osoittautuivat sopiviksi teknologioiksi melko erilaisin syöttövaatimuksin.</p> <p>Tämä työ tehtiin osana Northern Periphery Programme -ohjelmaan kuuluvaa MicrE-projektia. Työn tuloksena syntyi myös teknologiakortteja, jotka tehtiin pyrolyysistä, kaasutuksesta, mädätyksestä, fermentoinnista ja pelletoinnista. Kortteja voi käyttää eri toteuttamiskelpoisten teknologioiden esittelyyn paikallisille organisaatioille ja yrityksille.</p>			
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Appendix 5. Pelletisation technology card

## **Preface**

This thesis was made as a part of the MicrE-project (Micro Waste to Energy Business: Micro Energy to Rural Enterprise), which is Northern Periphery Programme Research project. Thesis was done in collaboration with Mass and Heat Transfer Process Laboratory and Thule Institute at the University of Oulu during May to December 2009.

I would like to acknowledge Professor Riitta Keiski for being my supervisor. I would like to thank my advisors, Eva Pongrácz and Mika Huuhtanen, for guidance through my thesis work and for many new ideas and viewpoints. I express my appreciation to them for the opportunity to take part in this interesting project. I would also like to thank co-workers from the laboratory and especially Auli Turkki for all the practical help and useful advice.

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Oulu, December 2009

Anu Kauriinoja

## Abbreviations and Nomenclature

a	year
BFB	Bubbling fluidised bed
CFB	Circulating fluidised bed
CHP	Combined heat and power
CV	Calorific value
d	Day
DME	Dimethyl ether
EC	European Commission
EF	Entrained flow
ESP	Electrostatic precipitator
ETBE	Ethyl tert-butyl ether
EU	European Union
FAME	Fatty acid methyl ester
GJ	Gigajoule ( $10^9$ Joule)
h	Hour
HHV	Higher heating value
IPPC	Integrated pollution prevention and control
kW	Kilowatt
kWh	Kilowatt-hour
LCFA	Long-chain fatty acid
LHV	Lower heating value
MJ	Megajoule ( $10^6$ Joule)
MTBE	Methyl tert-butyl ether
MSW	Municipal solid waste
MW	Megawatt
MW <sub>e</sub>	Megawatt of electrical energy
MW <sub>th</sub>	Megawatt of thermal energy
RCR	Rotating cone reactor
SME	Small and medium enterprises
t	tonne (1,000 kg)
TOP	Torrefaction and pelletisation
VFA	Volatile fatty acid

## 1 Introduction

The interest to renewable energy sources is significantly growing since the concern on impacts of global warming and the decrease of conventional fossil fuel sources. Diversification of Europe's energy supply, increasing the share of renewable energy, reducing reliance on imported energy, and reducing greenhouse gas emissions are the main targets set by the European Union. (EC 628/2005)

Biomass accounts for about half of the renewable energy used in the European Union while the rest is produced by wind power, solar power (thermal and photovoltaic), hydro-electric power, tidal power, and geothermal energy. The term biomass contains all organic material that stems from plants, i.e. all land- and water-based vegetation and all organic wastes. Green plants produce biomass by converting sunlight to sugars and further to plant material through photosynthesis. The energy of sunlight is stored in chemical bonds and released to produce energy by digestion, combustion or decomposition. (McKendry 2002a, EC 628/2005)

Biomass is very versatile energy source and can be used in transport, electricity and heating. The objective of the EU is to promote and support all these sectors. Using biomass in residential and industrial heating has strong traditions and the technology for this kind of energy production is simple and cheap. All kinds of biomass can be used to generate electricity. In combined heat and power (CHP) plants, biomass can produce both heat and power at the same time. Small-scale decentralised biomass plants generating electricity are often quite expensive but have other advantages for the environment and for rural development. (EC 628/2005)

The aim of this study was to get familiar with energy production from biomass based waste and particularly small-scale solutions suitable for the northern periphery areas. Small and medium enterprises (SMEs) and local organisations in rural areas have potential to generate energy on site from their own wastes and by-products, at the scale that is economically viable. This study presents and evaluates different biomass-to-energy solutions feasible to the northern periphery areas.

## 2 Northern periphery

Northern periphery is a large area located in northern Europe. It includes areas from Finland, Sweden, Norway, Ireland, and Scotland, as well as Ireland, and Northern Ireland, Iceland, Greenland, and Faroe Islands as whole, as shown in Figure 1. All these areas are sparsely populated, rural, insular, and peripheral, and have a harsh climate. (NPP 2009)



Figure 1. Northern periphery area (NPP 2009).

Northern periphery areas have special properties considering biomass. In long winter period there is cold and dark, and therefore vegetable based biomass production is limited. On the other hand, long and warm days accelerate the biomass growth in summer time. There are also large, sparsely inhabited areas available for biomass production. Thus, northern rural areas have great potential for biomass and energy production. However, the impact and possible implications of climate change have a

great influence on northern areas and reducing the change is essential but also providing for it is necessary.

The Northern Periphery Programme 2007–2013 is a European Union programme aiming to develop economic, social, and environmental potential of the peripheral and remote communities on the northern margins of Europe. The programme consists of various joint projects. This thesis has been done as a part of the MicrE-project, which is also approved under the Northern Periphery Programme 2007–2013. (NPP 2009)

The priorities of the programme are to promote innovations and competitiveness in remote and peripheral areas and sustainable development of natural and community resources. Co-operation between R&D institutions and SMEs, also transnationally, helps to exchange best practises, increases the capacity for innovation and new innovative products, and strengthens competitiveness. The use of advanced information and communication technologies (ICT) facilitates the development and overcomes the long distances in the Europe's northern periphery. Developing and maintaining transport infrastructure under harsh climatic conditions is also an objective of the programme. (NPP 2009)

Environment is an advantage in the northern periphery areas and one objective of the programme is to strengthen the synergies between environment protection and economic growth in remote regions. Efficient and sustainable management and utilisation of resources and development of small-scale renewable energy solutions facilitate to develop the potential of Europe's northern periphery. In the programme sustainable development in peripheral areas is improved by strengthening urban-rural relations and promoting of natural and cultural heritage. (NPP 2009)

The aim of MicrE-project (Micro Waste to Energy Business: Micro Energy to Rural Enterprise) is to develop small-scale renewable energy solutions for SMEs in the rural northern periphery areas. Especially energy production from by-products and waste materials is under particular attention. MicrE will improve self-sustaining energy production and business as well as reduce adverse environmental impacts. In the project several research groups and companies from the participating NPP countries are doing collaboration in this area. (MicrE 2009)

### **3 Biomass**

Photosynthesis is a process where green plants convert CO<sub>2</sub> in the air, water and sunlight to carbohydrates. Typically photosynthesis converts less than 1% of the available sunlight to the chemical energy used in building blocks of biomass. When the energy stored in chemical bonds is released chemically or biologically, also CO<sub>2</sub> and water are formed. Therefore the process is cyclic. One of the most significant differences between biomass and fossil fuels is the time lag of uptake and release of CO<sub>2</sub>. It takes millions of years to convert biomass to fossil fuels and thus they are not renewable fuels within the time-scale of mankind use. (McKendry 2002a)

The value of a particular type of biomass depends on its chemical and physical properties. Biomass can be converted into three main types of product: electrical/heat energy, transport fuel, and chemical feedstock. The utilisation of biomass has strongly increased over the last decades in the European Union and the ambition is further boosted to the use of biomass instead of fossil resources. (McKendry 2002a, Khan et al. 2009)

#### **3.1 Biomass classification**

There are various different ways for biomass classification. The origin of the biomass and the biomass properties are the main approaches used. Khan et al. (2009) have classified biomass fuels based on the origin of the biomass:

1. Primary residues: By-products of food crops and forest products (wood, straw, etc.),
2. Secondary residues: By-products of biomass processing (food industry by-products, wood industry by-products, etc.),
3. Tertiary residues: By-products of used biomass derived commodities (demolition wood, food wastes, etc.),
4. Energy crops.

The classification can also be based on properties, according to Khan et al. (2009):

1. Wood and woody fuel (hard and soft wood, wood residues, demolition wood, etc.),
2. Herbaceous fuels (straw, grasses, etc.),
3. Wastes (sewage sludge, municipal waste water, etc.),

4. Derivatives (wastes from food industries, etc.),
5. Aquatic (algae, etc.),
6. Energy crops (particularly cultivated for energy purposes).

### **3.2 Biomass characteristics**

The biomass material properties of interest considering energy production can vary widely depending on biomass, but generally the following properties are important to be taken into account (McKendry 2002a, Kelleher et al. 2002):

- moisture content (intrinsic and extrinsic),
- calorific value,
- proportions of fixed carbon and volatiles,
- ash/residue content,
- alkali metal content,
- cellulose/lignin ratio,
- carbohydrate/sugar content,
- lipid/fat content,
- protein content,
- pH.

The type of biomass dictates the most likely form of the energy conversion process. The moisture content is the main character that has to be taken into account when considering the possible processes. In addition, other factors need to be considered in some situations, especially to those forms of biomass that lies midway between the two extremes of 'wet' and 'dry'. For wet biomass conversion processes, cellulose/lignin ratio can play a significant role, while for dry biomass the calorific value, proportions of fixed carbon and volatiles, ash/residue content, and alkali metal content must be taken into account for. Therefore, some biomasses are suitable for nearly all of the potential conversion technologies while others can be used just for a few technologies. (McKendry 2002a)

### **3.2.1 Moisture content**

The moisture content of biomass can vary in a very wide range. Both intrinsic and extrinsic moisture contents have to be taken account. Intrinsic moisture means the moisture content of biomass without the influence of weather effects while extrinsic moisture includes the influence of prevailing weather conditions during harvesting. In general, thermal conversion technologies require low moisture content (typically <50%) while bio-conversion technologies can handle also biomass with higher moisture content. Woody and low moisture containing herbaceous biomasses are the most efficient biomass sources for thermal conversion. (McKendry 2002a, Khan et al. 2009)

### **3.2.2 Calorific value**

The energy content of material denotes the calorific value (CV), or the heat value. That content releases when material is burnt in air. The unit for CV is usually MJ/kg for solids, MJ/dm<sup>3</sup> for liquids, and MJ/Nm<sup>3</sup> for gases. The CV of a fuel can be expressed as the higher heating value (HHV) (also called the gross CV) or the lower heating value (LHV) (the net CV). The HHV is the total energy content that is released in burning in air, and represents the maximum amount of energy potentially exploitable. The LHV excludes the latent heat contained in water vapour, and therefore represents the actual amount of energy recovered. The HHV is independent of the conversion process, while the LHV varies from one conversion process technology to another. (McKendry 2002a, Khan et al. 2009)

### **3.2.3 Proportions of fixed carbon and volatile matter**

The volatile content or volatile matter (VM) of a solid fuel is that portion of gas that is released by heating to 950±25°C for 7 min according to the American ASTM standard. In British and Australian standards the required temperature is 900±5°C. The mass remaining after the release of volatiles and excluding the ash and moisture content is called the fixed carbon content (FC). The VM and FC provide a measure of ease with which the biomass can be ignited and subsequently gasified or oxidised. Usually, biomass has a high volatile content. Volatiles can further divide into gases such as light

hydrocarbons, carbon monoxide, carbon dioxide, hydrogen, moisture, and tars. (McKendry 2002a, Khan et al. 2009, Ward 1984)

### **3.2.4 Ash/residue content**

All chemical breakdowns of a biomass fuel produce a solid residue, which in some cases can be called ash. The ash is the non-combustible inorganic residue that remains after burning. The residue content of biomass affects both the handling and the total biomass-to-energy processing cost. The residue represents the amount of non-biodegradable carbon present in biomass. In biochemical conversion processes, this residue will be greater than the ash content in thermo conversion processes, because the residue represents the recalcitrant carbon which cannot be degraded further biologically but which can be burnt thermally. (McKendry 2002a, Ward 1984)

The ash can cause problems for thermo-chemical conversion processes, and particularly for combustion, because some chemical compounds in the ash can react to form slag. The formation of slag could cause notable operational problems, by decreasing plant throughput and resulting in increased operating costs. Potential utilisation of ash is affected by contaminants. In the case of ash with very low heavy metal content, it can be used as fertiliser. (Khan et al. 2009)

### **3.2.5 Alkali metal content**

Plants require metals to grow. Due to plant biology if the lignin content decreases, the metal content increases. Most of the herbaceous biomass contains silicon (Si), chlorine (Cl) and potassium (K) in high percentages. Potassium is the dominant alkali metal in most biomasses. For thermo-chemical conversion processes, the alkali metal (mainly sodium (Na), potassium, calcium (Ca) and magnesium (Mg)) content of biomass has to be taken into account because the reaction of alkali metals with chlorine and silica present in the ash at high temperatures produces a sticky liquid phase, which can lead to blockages of airways in the furnace and boiler plant and cause corrosion. (McKendry 2002a, Khan et al. 2009, Fahmi et al. 2007)

Alkali metal content in biomass can be reduced simply by leaching with water because alkali metals are largely water-soluble. Also mechanical compression can be used to improve the washing process. Simple washing pre-treatment method removes up to 70% of the alkali metals. After washing the feedstock has to dry before feeding to combustor, gasifier or pyrolyser. The washed feedstock produces also less char than the unwashed feedstock in pyrolysis and gasification processes. (Fahmi et al. 2007, Turn et al. 1997)

### **3.2.6 Cellulose/lignin ratio**

Cellulose, hemicellulose and lignin are called together lignocelluloses, the base of most biomasses and most abundant organic material on earth. The composition of different kind of lignocellulosic biomass is very similar. Cellulose is a long chain of glucose sugar molecules joined together in a crystalline structure. Biomass contains generally 35% to 50% of cellulose. (Wyman 1996)

Hemicellulose is also a long chain of sugar molecules and biomass contains generally 20% to 35% hemicellulose. Unlike cellulose, hemicellulose is usually made up of a mixture of sugars and is often dominated by the five-carbon sugar, xylose. About 65% to 75% of the overall lignocellulosic composition is composed by cellulose and hemicellulose together. A large fraction of the remaining material comprises lignin, which is an insoluble phenylpropene polymer attached to the hemicellulose. Small amounts of ash, soluble phenolics and fatty acids are also present in lignocellulosic biomass. (Wyman 1996, Khan et al. 2009)

Cellulose and hemicellulose can be broken down back to sugars for fermentation, like starch conversion to sugars. The biodegradability of cellulose is much higher than that of lignin. Therefore the proportions of cellulose and lignin in biomass affect significantly in biochemical conversion processes. Hence the highest yields produced by biochemical conversion processes are reached by biomass with high cellulose/hemicellulose content and low lignin content. (McKendry 2002a, Wyman 1996)

### **3.2.7 Carbohydrate content**

Carbohydrates, i.e. molecules containing carbon, hydrogen, and oxygen, are the bulk of the biodegradable material, including mainly cellulose, starch and sugars. 5-carbon and 6-carbon sugars are the most common forms found in plant and animal-based feedstocks, but sugars might have from 3 to 9 carbon atoms per molecule. Starches are long chains of sugar molecules and much easier to break down than cellulose. (Wisbiorefine 2004b)

Carbohydrate content of the biomass influences significantly on biochemical conversion processes, because some carbohydrates can decompose easily while the most complex carbohydrates are difficult or nearly impossible to decompose in the purpose of economic energy production. (Kelleher et al. 2002)

### **3.2.8 Lipid/fat content**

Lipids (or fats) are composed of fatty acids. Especially the content of long-chain fatty acids (LCFAs) need to be taken into account in biochemical processes and, in particular, in anaerobic digestion. LCFAs might be toxic to some micro-organism and therefore inhibit the anaerobic digestion process. LCFAs may also form scum causing problems in the process. (Kelleher et al. 2002, Salminen & Rintala 2002)

### **3.2.9 Protein content**

Proteins are large complex organic materials consisting of hundreds of thousands of amino acid groups. The organic nitrogen released from protein degradation can inhibit biochemical processes. (Kelleher et al. 2002, Salminen & Rintala 2002)

### **3.2.10 pH**

The acidity or basicity of a solution is specified by pH. It is defined as the amount of dissolved hydrogen ions ( $H^+$ ) in a solution described usually at logarithmic scale, which is not absolute scale. Neutral solution is represented at pH 7. Biochemical processes

have a certain pH where their operation is ideal. For example, the functioning of anaerobic digestion process is optimal at pH 7. (Ward et al. 2008)

### **3.3 Characteristics of certain biomasses**

Dividing biomasses to lignocellulosic biomass and other biomass by-products promote to list biomasses with their properties, which might influence on biomass-to-energy processes. Table 1 represents the characteristics of lignocellulosic biomasses and Table 2 the characteristics of other than lignocellulosic biomasses.

Table 1. Characteristics of lingocellulosic raw materials (Bridgeman et al. 2008, McKendry 2002, Zanzi et al. 2004, phyllis 2009, Ververis et al. 2004).

	Moisture	HHV	Calorific value (LHV)	Fixed carbon content	Volatile matter	Ash/residue content	Alkali metal content	Cellulose	Lignin	Hemi- cellulose
	wt%	MJ/kg	MJ/kg	% dry basis	% dry basis	% dry basis	%, Na and K oxides	wt%	wt%	wt%
Wood (average)	20	20	19	17	68–82	1		40	25	25
Softwood	7–8	21	19	17–19	72–82	1–2	5	35–40	27–30	25–30
Hardwood	3–60	19–20	19	11	47–88	0–2	16	45–50	20–25	20–25
Herbaceous plants/ grasses/straw	3–30	17–19	16–17	11–21	46–83	0–6	12–14	30–50	5–20	10–40

Table 2. Characteristics of biomass by-products and wastes (Preto et al. 2008, phyllis 2009, Salminen & Rintala 2002, Russ & Meyer-Pittroff 2002, 2004, Kuhn 1995, Shilev et al. 2007, Buendia et al. 2008, Arbelia et al. 2006, Nges & Liu 2009, Linke 2006, Parawira et al. 2004, Mshandete et al. 2004).

	Total solids (TS)	Moisture	HHV	LHV	Volatiles	Volatile solids (VS)	Carbo-hydrate content	Lipid content	Lipid content	Protein content	Protein content	pH	Ash content
	%	wt%	MJ/kg	MJ/kg	wt%	% of TS	% of TS	% of TS	wt% dry	wt% dry	% of TS		% dry
Manure	5–47	75–80	14–19	13–18	51–87	60–76	0	3–7	0–3	0–47			11–35
Slaughterhouse wastes	12–45	74	18–23	18–22	64–96	68–97		1–54	54	35	32–91		1–26
Meat processing industry wastes	3–30	70–97				10–60		3–80			15–85	6.2–8	
Poultry industry wastes	5–40	60–95				35–70		15–45			20–30	5.5–6.5	
Dairy wastewater	0.5–7	92–99.5				60–70		5–65			1.5–4.5	5.5–7.5	
Municipal wastewater	0.3–1.5	98.5–99.8				70–80		0.5–14	0.1–0.25	0.01–0.15	5–15	6.0–7.6	
Sewage sludge	4–25	70–95	15	14	54	60–70	0			0		6.8–7.8	35
Potato industry wastes	10–25	78–90				90–95	50–60		0	0.15–2	1.5–2	3.5–4.5	5–10
Food residues /organic domestic wastes	25–90	70–80	16–18	15–17						14			5–35
Fish industry wastes	25–35					50–55		50–75	5–15	3–6		6.5–7	
Fish oil		0.05	40								0		

## 4 Energy production methods

The conversion of biomass into energy can be achieved using various different routes, each with specific pros and cons. The three main categories of conversion processes are thermo-chemical, biochemical, and mechanical. In Figure 2 the routes from biomass to fuels and energy is presented. In addition, sources, processing methods, and products are introduced. (McKendry 2002b)

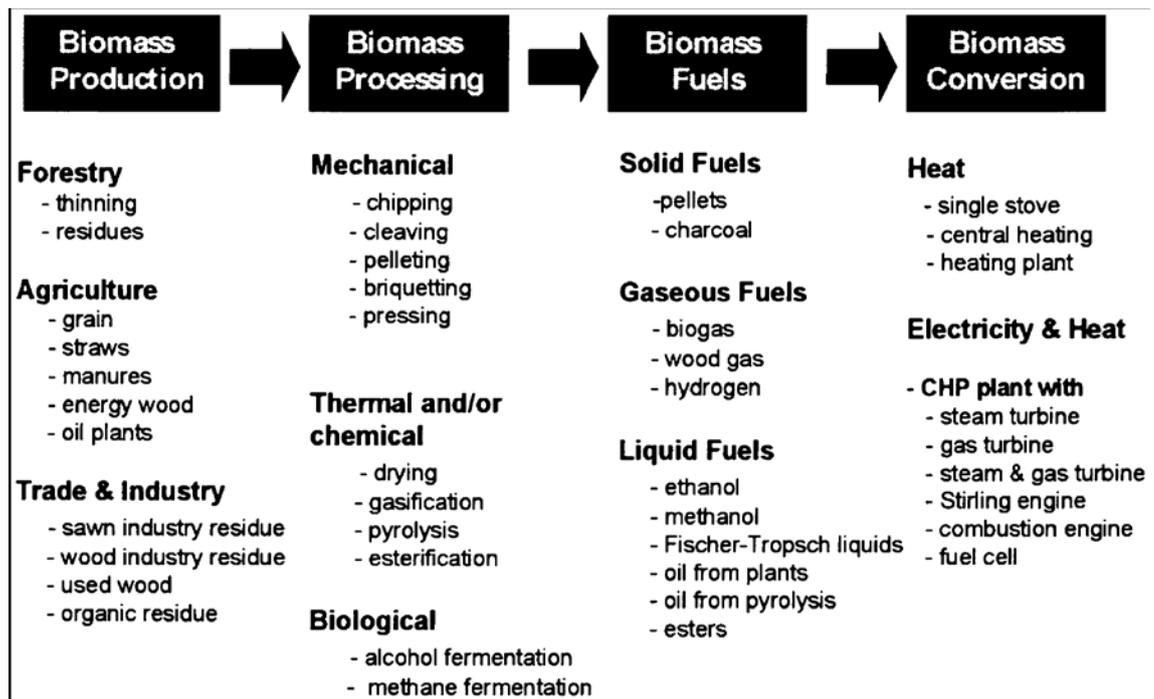


Figure 2. From biomass to energy and fuels (Chum & Overend 2001).

Energy conversion technologies do not produce electricity directly. Table 3 presents main technologies with their products as the primary technology and electricity conversion method as the secondary technology. This chapter as well as the whole study concentrates on primary technologies. The purpose of this study was to consider especially small-scale processes.

Table 3. Conversion technologies of biomass-fuelled CHP systems (Dong et al. 2009).

Primary technology	Secondary technology
Combustion producing steam, hot water	Steam engine; steam turbine; stirling engine; organic rankine cycle (ORC)
Gasification producing gaseous fuels	Internal combustion engine; micro-turbine; gas turbine; fuel cell
Pyrolysis producing gaseous, liquid fuels	Internal combustion engine
Biochemical/biological processes producing ethanol, biogas	Internal combustion engine
Chemical/mechanical processes producing biodiesel	Internal combustion engine

#### 4.1 Thermo-chemical conversion processes

Thermo-chemical conversion processes take place at high temperatures. These processes are combustion, gasification, pyrolysis, torrefaction, and liquefaction technologies. Each of these technologies produces different kinds of products. Figure 3 illustrates these technologies, their intermediate and final products. Torrefaction is not presented in the figure.

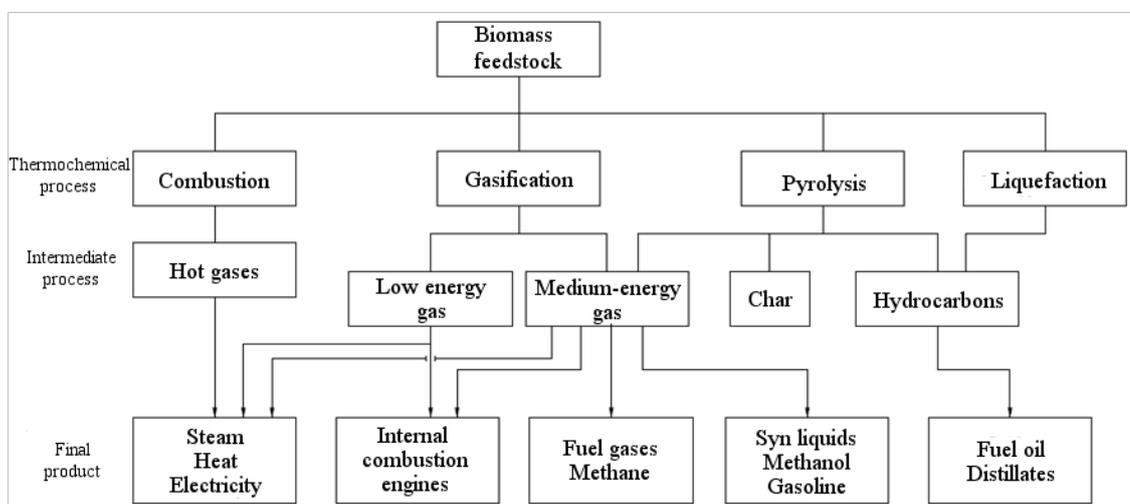


Figure 3. Main thermo-chemical conversion processes, intermediate energy carriers and final energy products (McKendry 2002b).

All thermal concentration processes require different concentrations of oxygen. As can be seen in Figure 4, combustion occurs in an environment with an excess of oxygen, gasification is a partial oxidation process requiring an oxygen concentration slightly below the stoichiometric level, and pyrolysis takes place in the absence of oxygen

(Austerman & Whiting 2007). Also torrefaction occurs in the absence of oxygen while liquefaction takes place in liquid water (Bergman et al. 2005, Behrendt et al. 2008).

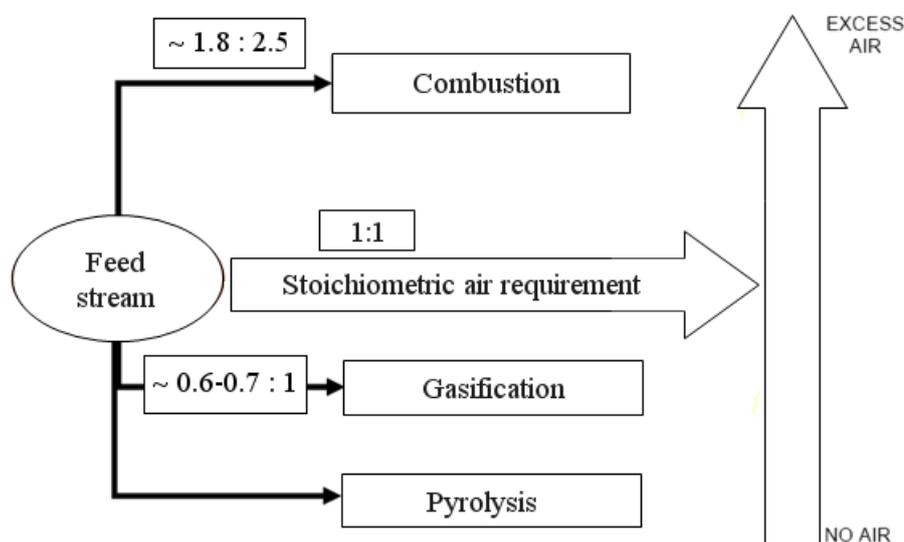


Figure 4. Thermal conversion processes (Austerman & Whiting 2007).

#### 4.1.1 Combustion

Combustion is the oldest and still the most used way to convert biomass to energy. The principle in combustion is direct and complete oxidation in which carbon in biomass is oxidised to carbon dioxide, hydrogen to water, sulphur to sulphur dioxide, and nitrogen to nitrogen oxides. The useful scale of combustion is very large in heat production. In power production the smallest commercial technologies are about 50 kW<sub>e</sub>. However, combustion is a quite ineffective way to generate electricity compared to gasification, and even unfavourable in purpose to produce liquid or gaseous fuels. (Lampinen & Jokinen 2006)

Mass-burn incineration is a large-scale incineration process with typical volumes of wastes between 10 and 50 ton/h. Complete combustion or oxidation takes place in a single-stage chamber unit. Fluidised bed, cyclonic, rotary kiln and liquid and gaseous incinerators are examples of other types of combustion processes. They are usually small-scale and volumes are between 1 and 2 ton/h. (Kelleher et al. 2002)

Bubbling, turbulent and circulating bed types are the main types of fluidised beds. They all are composed of a bed of sand in a refractory-lined chamber through which primary combustion air is blown from the bottom of the chamber. The sand particles are fluidised by adjusting the airflow. The incoming fuel is dispersed rapidly and heated up to ignition temperature. Fluidised beds have high heat-storage and heat-transfer rates. Therefore these bed types permit fast ignition of low combustible wastes. Flow diagram of a power plant is presented in Figure 5. (Kelleher et al. 2002)

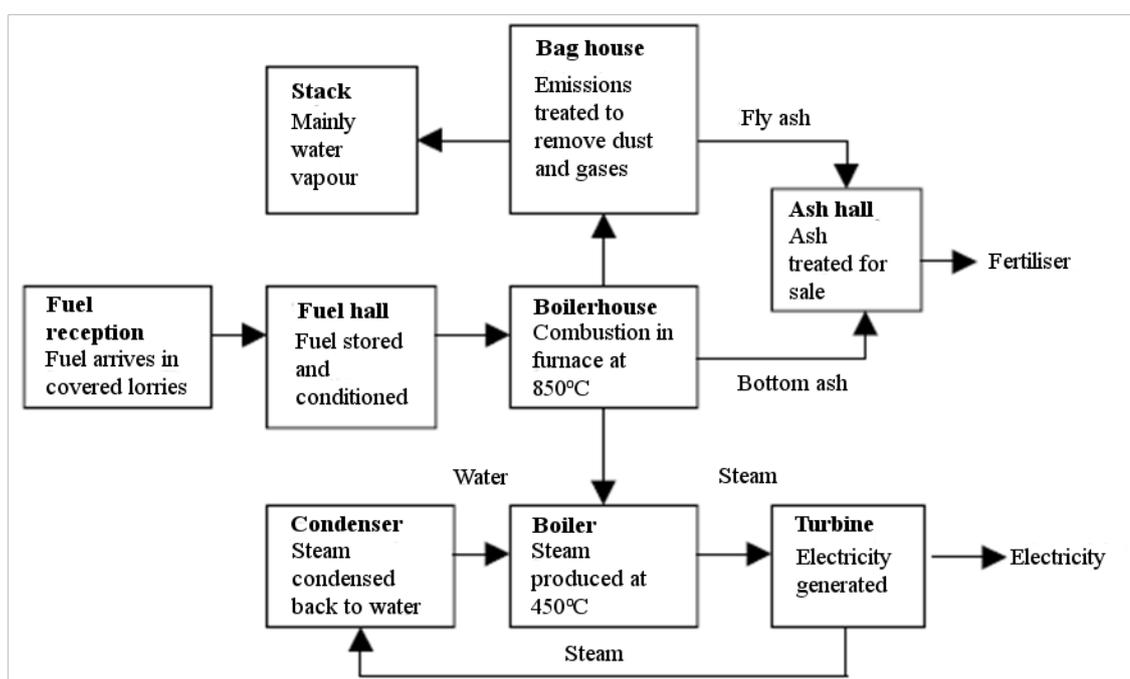


Figure 5. Flow diagram of a power plant (Kelleher et al. 2002).

The moisture content is a significant factor when considering the direct combustion. Also high moisture wastes may burn in a co-incineration plant but the minimisation of moisture content at low cost is apparently desirable. In addition, it is worthy for all combustion techniques. (Kelleher et al. 2002)

Fish oil, a by-product of the fish-processing industry, is produced in large quantities annually. It has similar calorific value to petroleum distillates, especially to diesel, and studies have been carried out for substituting fish oil for diesel. Preto et al. (2008) have investigated the combustion properties of fish oil in conventional combustors and found that fish oil and its blends with fuel oil burn easily in conventional furnaces and boilers.

Such combustors can function on a wide range of fuel quality and impurities cause usually no problems, in contrast to diesel engines. (Preto et al. 2008)

#### 4.1.2 Pyrolysis

Pyrolysis is a process in which organic material is heated at high temperatures in the absence of oxygen. The products are gases, liquids (pyrolysis oil) and solids (char) (Figure 6). Usually the gases are used to produce heat for drying and pyrolysis reactions. Pyrolysis oil, often called as bio-oil, can be used to replace heating oil, or it can be refined to secondary fuels such as crude oil. (Lampinen & Jokinen 2006)

Temperature in the pyrolysis process is between 400–800°C. The characteristics of biomass, the reaction parameters and the pyrolysis method affect the relative portions of pyrolysis products. Pyrolysis can be roughly divided to fast and slow pyrolysis. The slow pyrolysis produces mainly char. The fast and flash pyrolysis processes reach the greatest oil yield and usually have a very high heating rate. The yields of fast pyrolysis are 40–65% of organic condensates, 10–20% char, 10–30% gases, and 5–15% water based on dry feed. The lower heating value of the pyrolysis oil is 15–18 MJ/kg, the gas is around 15 MJ/Nm<sup>3</sup> and the char is around 32 MJ/kg. The char produced in fast pyrolysis is very flammable and therefore the hot char must be handled with caution. (Uslu et al. 2008, Demirbas 2004)

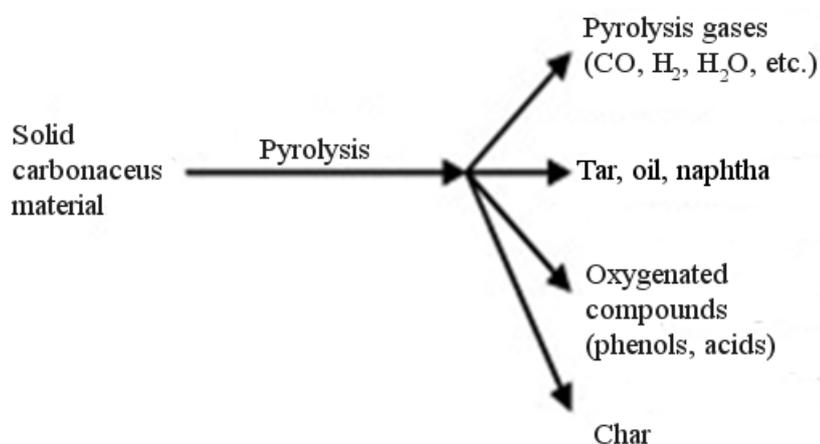


Figure 6. Pyrolysis pathways (Ahmed & Gupta 2009).

Bubbling fluid bed (BFB) pyrolysers are commonly referred to as fluidised beds. Figure 7 illustrates a typical reactor configuration with electrostatic precipitators (ESPs) which are widely used to remove particles from gases. Fluidised bed reactors are a well understood technology which is simple in construction and operation. Their good temperature control and very efficient heat transfer to biomass particles due to high solids density are also advantages. Heating can be achieved in a variety of ways especially in small-scale while some heat transfer methods are not suited to large-scale plants. (PyNe 2009)

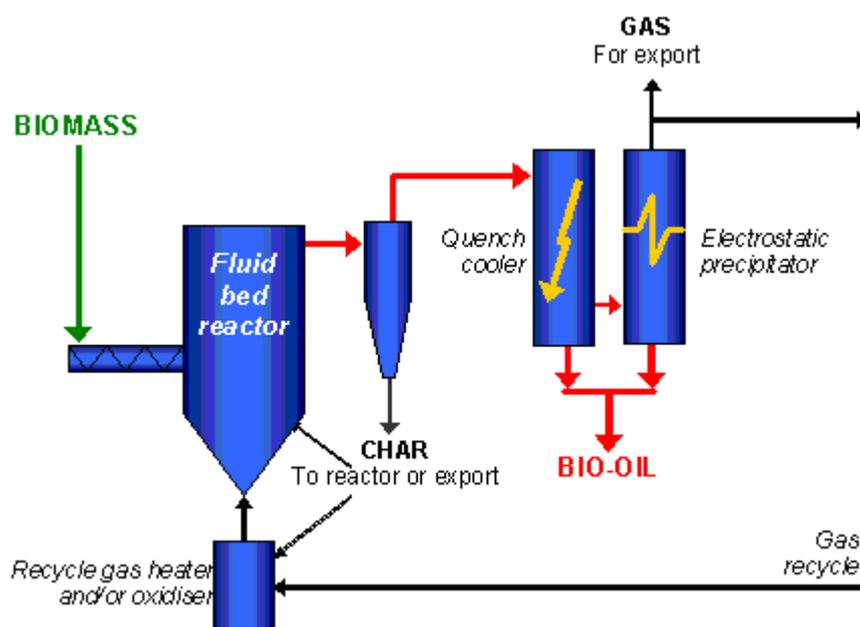


Figure 7. Bubbling fluid bed reactor with ESP (PyNe 2009).

Fluidised bed pyrolysis reactors give good and consistent performance with high pyrolysis oil yields (usually 70–75% from wood on dry basis). Feedstock particle sizes of less than 2–3 mm are required to achieve high heating rates and the rate of particle heating is generally the rate limiting step. The fluidising gas flow rate controls residence time of solids and vapours and the time is higher for char than for vapours. Rapid and effective char separation is significant because char acts as an effective vapour cracking catalyst at fast pyrolysis reaction temperatures. (PyNe 2009)

Circulating fluidised bed (CFB) and transported bed reactor systems have many similar features than BFB reactor systems except that the residence time for the char is almost the same as for vapours. Gas and char are also in better contact with each other due to

the higher gas velocities which can lead to higher char content in the produced bio-oil. A typical CFB reactor configuration is presented in Figure 8. The CFB technology is widely used in the petroleum and petrochemical industry and is suitable for very large throughputs. Heat needed in a pyrolysis reactor is usually from recirculation of heated sand from a secondary char combustor, which can either be a bubbling or circulating fluidised bed. The rotating cone reactor (RCR) systems have many similarities to the CFBs except that the sand and feedstock transport is boosted by centrifugal forces operating in a rotating cone. (PyNe 2009)

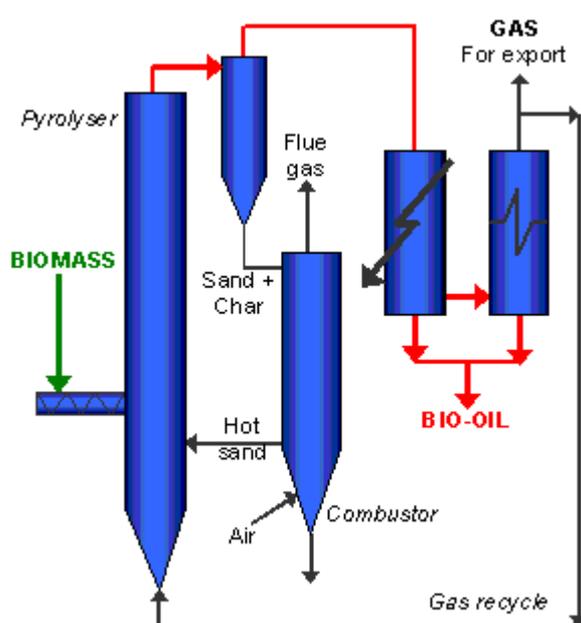


Figure 8. Circulating fluid bed reactor (PyNe 2009).

Ablative pyrolysis reactors are notably different compared to the other methods of fast pyrolysis. In all the other methods, the rate of heat transfer through a feedstock particle limits the rate of pyrolysis reaction and, therefore, small feedstock particles are required. Ablative reactors can handle also large particles and there are no upper limits to the size that can be processed. In ablative pyrolysis heat is transferred from the hot reactor wall to feed material that is in contact with it under pressure. As the material is mechanically moved forward, the residual oil film both provides lubrication for successive particles and also rapidly evaporates to give pyrolysis vapours. (PyNe 2009)

The rate of reaction in ablative systems is strongly affected by pressure, the reactor surface temperature and the relative velocity of feedstock on the heat exchange surface.

The high pressure is achieved due to centrifugal or mechanical forces. The limiting factor in the ablative process is the rate of the heat supply to the reactor rather than the rate of heat absorption by the pyrolysing feedstock as in other reactors. (PyNe 2009)

Fast pyrolysis of biomass is on demonstration stage in power production. Fluidized and transported bed reactors have proven reliable to produce bio-oil with relatively high yields. Also other reactor types such as ablative, rotating cone and vacuum reactors are conceivable. Bubbling fluidised bed reactor is commercially available with the capacity of 20–400 kg/h and circulating fluidised bed reactor with the capacity of 20–1,700 kg/h. Thus, these pyrolysis systems are suited for small scale use. Table 4 presents different pyrolysis technologies and their characteristics. (Uslu et al. 2008)

Table 4. Different pyrolysis systems and some reactor characteristics (BTG 2009, PyNe 2009).

Technology	Status	Oil yield (%)	Complexity	Feed size	Equipment size	Scale-up
Fluidised bed	Demo	75	Medium	Small	Medium	Easy
CFB	Pilot	75	High	Medium	Large	Easy
EF	None	65	High	Small	Large	Easy
RCR	Pilot	70	High	Small	Small	Medium
Ablative	Lab	75	High	Large	Small	Hard
Screw reactor	Pilot	60	Low	Medium	Small	Medium
Vacuum	On hold	60	High	Large	Large	Hard

One of the main disadvantages of fluidised bed reactors is their requirement for very small feedstock particle size (1–2 mm). Ablative reactors can handle feedstock sizes up to 20 mm but they have other drawbacks. Vacuum reactors produce very clean bio-oil but with relatively low bio-oil yields (30–45%). A rotating cone reactor is based on mixing of biomass feedstock with hot sand near the bottom of the cone. Currently it is scaled up to 200 kg/h as a pilot plant. The energy yield of fast pyrolysis process is around 66%. (Uslu et al. 2008)

Capital cost of a pyrolysis plant with the capacity of 25 MW<sub>th</sub> is in the range of 4.5–11.5 M€ The production cost is around 75–150 €/tonne of product (6–12 €/GJ) when the feedstock cost is excluded. If the capital cost increases 40% the production cost increases with around 12%. Therefore the pyrolysis process is capital-intensive. Smaller

scales are favourable compared to torrefaction. The specific investment cost does not decrease any longer above 20–25 MW<sub>th</sub> input for the pyrolysis (Figure 9). (Uslu et al. 2008)

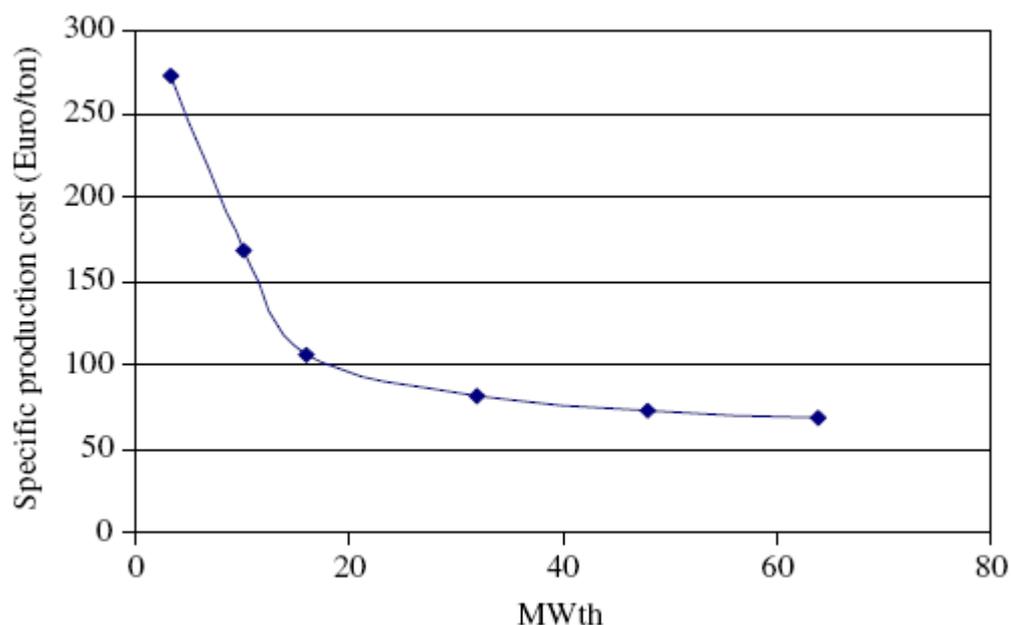


Figure 9. Scale effect on bio-oil production costs (Uslu et al. 2008).

Pyrolysis oil is suited to liquid fuel feeding systems which may need to be adjusted depending on the bio-oil characteristics. The quality of the bio-oil influences the combustion efficiency outstandingly. The main characters are viscosity, water and solids (mainly char) content, bio-oil raw material, bio-oil age and amount of methanol addition (up to 10% wet). In general, bio-oil contains approximately 25% water. Bio-oils acidity with pH of about 2.5 may also cause problems. (Uslu et al. 2008, Evans 2007)

Methanol addition into pyrolysis oil improves the quality of oil and decreases particulate emissions. The high water content of bio-oil makes the ignition complicated and the high viscosity may cause blockages of the burner pipe. Pre-treatment of bio-oil can be needed before combustion. Pre-treatment consists of filtering and pre-heating. The prevailing biomass pre-treatment, sizing, is not needed in the case of bio-oil. (Uslu et al. 2008, Zhang et al. 2007)

### 4.1.3 Gasification

In gasification, biomass is converted by partial oxidation at high temperature into a gas mixture called product gas or syngas. The product gas can be used as a fuel in internal combustion (IC) engines or gas turbines. Gasification technology can be used for heat and power production beginning from 1 kW<sub>e</sub> micro-scale applications. (Lampinen & Jokinen 2006)

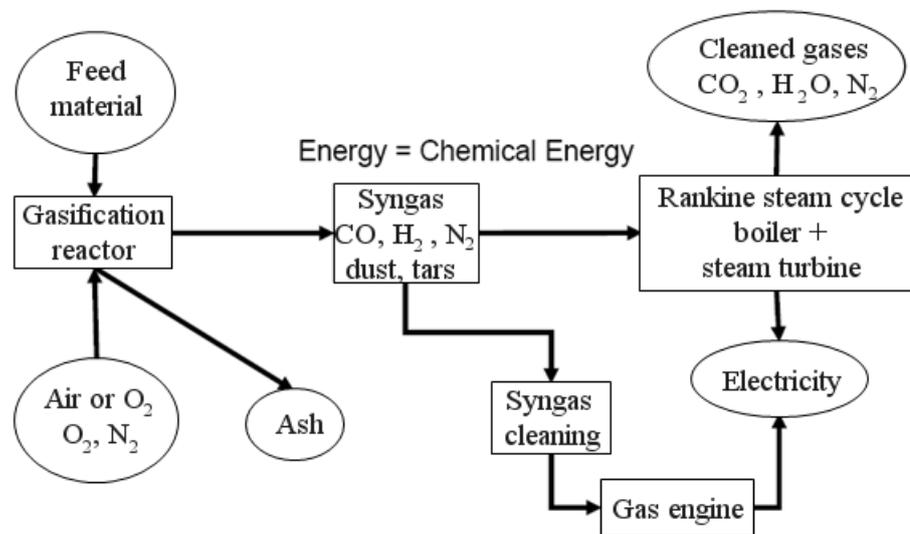


Figure 10. Schematic representation of a gasification process (Austerman & Whiting 2007).

In Figure 10 the gasification process and electricity generation from syngas is presented. Partial oxidation in the reactor occurs with air, pure oxygen, oxygen enriched air, or by reaction with steam. Using air as the oxidant is the cheapest option and results in product gas with a relatively low energy content. The product gas contains up to 60% nitrogen and the lower heating value is 4–6 MJ/Nm<sup>3</sup> while oxygen gasification gives a product gas with the lower heating value of 10–18 MJ/Nm<sup>3</sup> but requires an oxygen supply which is expensive. (Austerman & Whiting 2007, McKendry 2002c)

Various parameters have an influence on the gasification process reactions and the distribution of products. For example, feedstock particle size and particle size range, moisture content, mode of gas-solid contacting, pressure, heating rate, temperature and temperature profile, and residence time may have to be taken into account. Table 5

presents the different design and configurations that have been developed for gasification reactors. Only few of these are fully commercialised, particularly the fixed bed (updraft and downdraft) and the fluidised bed designs. (Austerman & Whiting 2007)

Table 5. Gasifier reactor types and their mode of gas-solid contact (Austerman & Whiting 2007).

Reactor type	Mode of contact
<b>Fixed bed</b>	
Downdraft	Solid moves down, gas moves down, i.e. co-current
Updraft	Solid moves down, gas moves up, i.e. counter-current
Co-current	Solid & gas move in same direction, e.g. downdraft, but both can move up
Counter-current	Solid & gas move in opposite directions, e.g. updraft, but flows can be reversed
Cross-current Variants	Solid moves down, gas moves at right angles, i.e. horizontally Stirred bed; two stage gasifier
<b>Fluidised bed</b>	
Bubbling bed	Relatively low gas velocity, inert solid stays in reactor
Circulating bed	Inert solid is elutriated, separated and re-circulated
Entrained bed	Usually there is no inert solid; has highest gas velocity of lean phase systems; can be run as a cyclonic reactor
Twin reactor	Steam gasification and/or pyrolysis occur in 1st reactor, and product char is transferred to the 2nd reactor, where it is combusted to heat the fluidising medium for re-circulation. A bubbling fluidised bed is typically used as the combustor
<b>Moving bed</b>	
Variants	Mechanical transport of solid, usually horizontal. It is typically used for lower temperature processes such as pyrolysis
<b>Other</b>	
Rotary kiln	Gives good gas-solid contact
Cyclonic or vortex reactors	Employ attrition and abrasion with high particle velocities to effect high reaction rates

The fuel is introduced into the gasifier (see Figure 11) via the drying zone where hot gases (<250°C) are drying the biomass. The biomass is heated in the pyrolysis zone at high temperatures (400–650°C) in the absence of oxygen. Volatile compounds of biomass are separated from the char in this zone. Combustion reactions happen in the oxidation zone (900–1200°C), where heat is produced for the endothermic pyrolysis and gasification reactions. Inside the reduction zone product gas is formed through various reactions. The tar content of the gas is decreased in thermal treatment at temperatures higher than 850°C. (McKendry 2002c)

Downdraft gasifiers and bubbling beds (BFB) are used primarily in small-to-medium scale applications while the updraft gasifiers are used typically in medium-to-large scale. Circulating beds (CFB) are employed in large scale applications. Figure 11 represents the schematics of updraft and downdraft gasifiers and Figure 12 the schematics of BFB and CFB reactors. (Austerman & Whiting 2007)

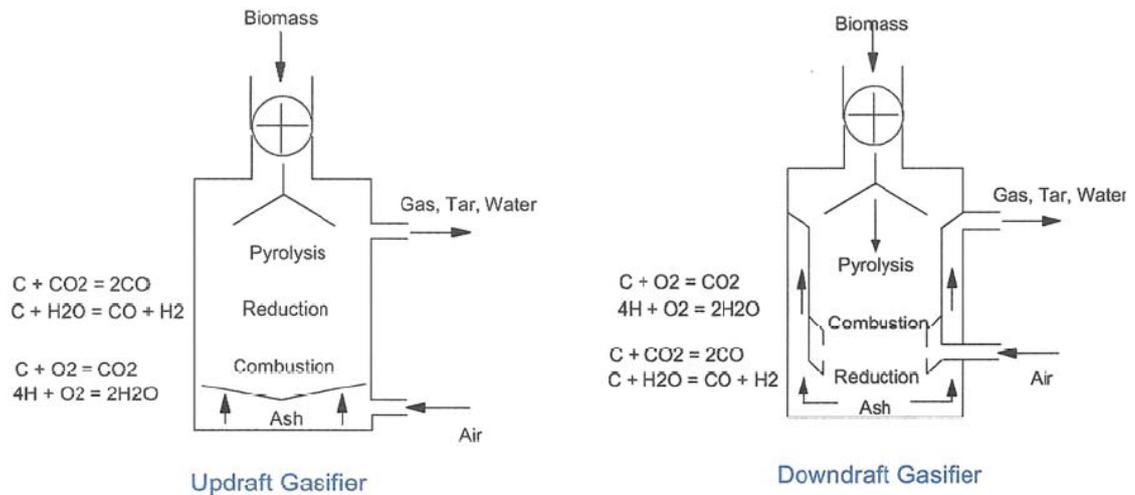


Figure 11. Schematics of fixed bed gasifiers (Austerman & Whiting 2007).

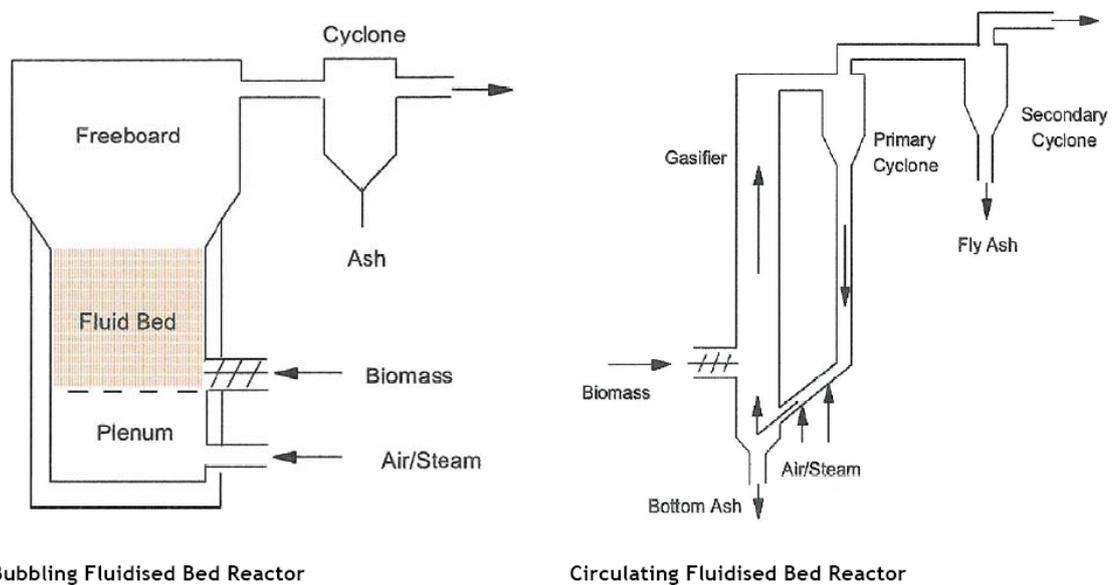


Figure 12. Schematics of fluidised bed reactors (Austerman & Whiting 2007).

A major technical challenge for biomass gasifiers is tar carryover. Entrained flow (EF) gasifiers produce tar free product gas, but feed material requires energy-consuming size reduction as a pre-treatment process. In EF gasifiers the particle size of feed material should be <math><0.1\text{--}0.4\text{ mm}</math>. Downdraft gasifiers have low tar production but they also

require uniform sized feed. Updraft gasifiers are less sensitive to the size variation and moisture content of the feed material. However, updraft gasifiers have high tar content in product gas and thus downstream catalytic tar cracking may be needed. (Austerman & Whiting 2007, McKendry 2002c)

In small-scale applications the downdraft gasifier is the best choice for combined heat and electricity production. The potential advantage of a downdraft gasifier is the fact that the pyrolysis products flow co-currently through the hot combustion and gasification zones, where most of tars are decomposed and oxidized. Therefore, the product gas of an ideally working downdraft gasifier can be used as a fuel in an IC engine after simple filtration and cooling. Possible utilizations for side product, ash, are as a fertilizer or as an additive to construction materials. (Kurkela 2002)

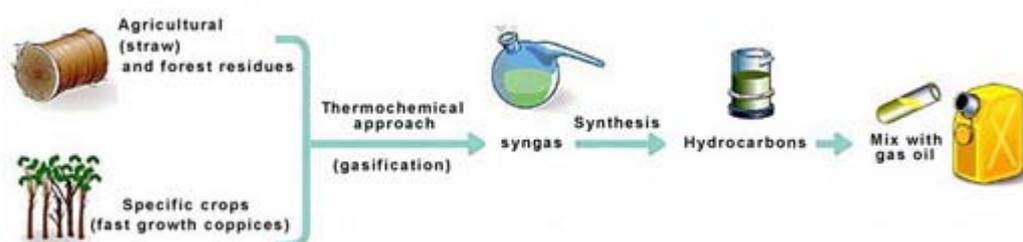


Figure 13. Production of hydrocarbon fuels via gasification and synthesis (IFP 2009).

The gas produced in the gasification process can be further utilised in two different ways. In the first approach, the ‘raw’ product gas can be combusted to produce a hot flue gas from which steam and then electricity is generated within an integrated Rankine Cycle. In the second approach, direct production of electricity by the utilisation of the ‘cleaned’ syngas in gas engine is possible. (Austerman & Whiting 2007)

Most of the existing gasification systems use ‘raw’ product gas to generate energy either in boilers or by co-firing the gas in power stations and cement kilns. However, the thrust of current development is towards ‘cleaned’ syngas utilisation, and most of the new companies in the market are offering CHP technology based on gas engines combined with heat exchangers in the engine exhaust stream. (Austerman & Whiting 2007)

#### 4.1.4 Torrefaction

Torrefaction is a possible pre-treatment method before gasification or combustion. Generally, torrefaction means roasting lignocelluloses containing biomass at a temperature range between 230–280°C in the absence of oxygen and at atmospheric pressure. Woody and herbaceous biomasses are the main feedstock for the torrefaction process presented in Figure 14. The process consists of biomass crushing and drying, torrefaction, product cooling and combustion of torrefaction gas which produces the necessary heat for drying and torrefaction. A utility fuel may also be used when the torrefaction gas contains little energy. During torrefaction the biomass dries completely and loses its tenacious structure. The torrefied biomass is coloured brown or dark brown depending on the process temperature and the parent biomass. (Bergman et al. 2005)

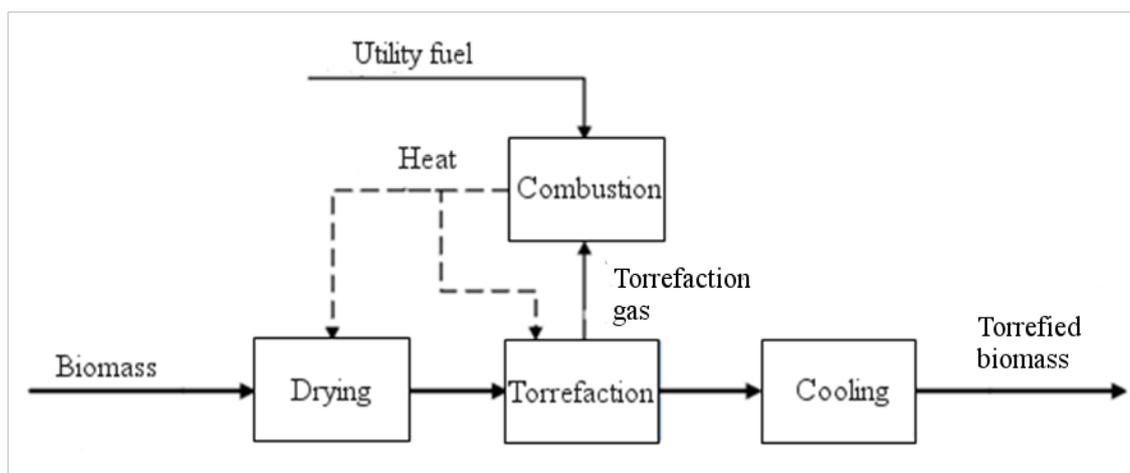


Figure 14. Torrefaction production plant (Bergman & Kiel 2005).

Torrefaction can also be called as mild pyrolysis. The smoke producing components and water are removed and the remaining solid product has approximately 70% of the original weight and 80–90% of the initial energy content. Thus, torrefaction improves the fuel quality. The hydrophobic nature of torrefied biomass remains unaffected when immersed in water. Torrefaction increases the fixed carbon content and energy density with both time and temperature. However, temperature has more influence on the torrefaction process than residence time. Torrefied biomass can be used to replace coal as fuel, for example, in domestic cooking stoves, residential heating, compacted fireplace logs and barbecue briquettes in commercial and domestic use. It can also be

mixed with coal and co-fired in a pulverized coal boiler. (Zanzi et al. 2004, Felfli et al. 2005)

The calorific value of the torrefied biomass is greater than the fresh biomass since biomass loses more oxygen and hydrogen compared to carbon. During torrefaction, dehydration reactions occur, which make the torrefied biomass very dry because of the destruction of OH groups, and the moisture uptake remains very limited. In addition, non-polar unsaturated structures are formed causing the hydrophobic nature for the torrefied biomass. The torrefied biomass has porous structure with a high volumetric density which makes it fragile and easy to grind or pulverize. (Uslu et al. 2008)

Three main polymeric structures are the basis of woody and herbaceous biomass. In general, these structures, i.e. cellulose, hemicellulose and lignin, are called lignocellulose. Identical reactions occur for each polymer, but the reaction temperatures differ, hemicellulose being the most reactive. Below 250°C, the devolatilisation and carbonisation are limited, while above 250°C they are extensive. Cellulose is the most thermo-stable compound and only limited devolatilisation and carbonisation may occur at torrefaction temperatures. The thermo-reactivity of lignin is between hemicellulose and cellulose. Hemicellulose fractions can be different in different kind of biomasses. Deciduous wood has been observed to be more reactive than coniferous wood in torrefaction. (Prins et al. 2006, Bergman & Kiel 2005)

Mass and energy yields vary for different biomasses in the same operation conditions due to the different polymeric structure, reactivity and content of extractives and lipids. Hence, each type of biomass has to carry out its own set of operation conditions to obtain similar product qualities. In torrefaction, the residence time is quite long, from 5 to 90 minutes and, therefore, the influence of particle size is rather insignificant. For example, woodchips sized 2 cm can be torrefied without heat transfer limitations. (Bergman & Kiel 2005)

Biomasses have usually higher atomic O/C and H/C ratios than fossil fuels such as coal, as presented in Figure 15. The high O/C ratio fuel in gasification makes the process relatively inefficient compared to the gasification of coal. Torrefaction lowers the O/C ratio of biomass which improves gasification efficiencies and increases the product

heating value by ca. 5–25%. Charcoal requires much higher temperatures to be produced and thus the torrefied biomass differs much from charcoal. Torrefaction decreases the moisture content from typically 10% to 0–3% and the content of volatiles from near 80% to 60–75%. (Prins et al. 2006)

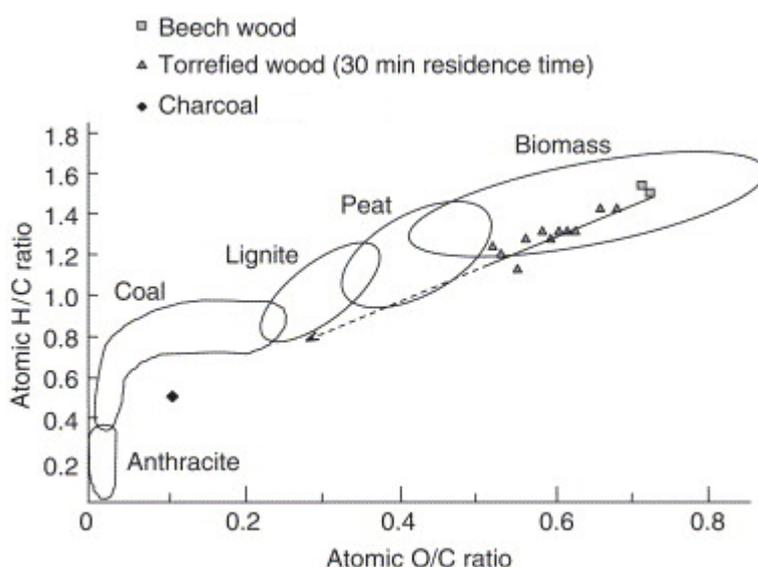


Figure 15. Composition of beech wood and torrefied beech wood in van Krevelen diagram (Prins et al. 2006).

Biomass is not an ideal fuel for gasifiers due to the high O/C ratio, the low heating value, the high moisture content and the high energy requirements for size reduction. Torrefaction makes biomass more attractive to gasifiers, improving the fuel characteristics. Only a few research studies exist upon biomass gasification via torrefaction. Prins et al. (2006) have investigated the overall efficiencies of circulating fluidized bed (CFB) gasifier and entrained flow (EF) gasifier. They considered the integrated torrefaction and EF gasifier as a promising method to improve the efficiency of the biomass gasification process. (Prins et al. 2006)

Wood based biomass is mainly used in the researches related to torrefaction. Some researchers, for example Jones et al. (2008), have also investigated herbaceous biomass such as wheat straw, which is an agricultural residue, and reed canary grass which is an energy crop. In addition, they compared these biomasses to woody biomass (willow). As a result, willow is found to have significantly lower amount of hemicellulose but higher amount of cellulose and lignin, compared with reed canary grass and wheat

straw. The mass loss and increase in energy content were higher when the hemicellulose content was higher. (Bridgeman et al. 2008, Jones et al. 2008)

Electricity requirements for size reduction are 50–85% smaller for torrefied wood compared with fresh wood. The oxygen content of torrefied wood is lower than that of fresh wood. Thus the torrefied wood produces more H<sub>2</sub> and CO in gasification process compare to the parent wood. However, the difference is quite small. CO<sub>2</sub> and CH<sub>4</sub> yields do not differ between the wood and the torrefied wood. Gasification is more completed at higher temperature than 1200°C. Gasification of torrefied wood produces more char and that char contained more residual carbon and less ash, in comparison to the gasification of fresh wood. The char from torrefied wood is also less reactive than that from wood. (Couhert et al. 2009)

Torrefaction is not yet a widely used commercial technology and it has not been developed to the stage of technical demonstration. The statement of torrefaction to upgrade biomass for large-scale co-firing with coal is still in the “proof-of-concept” phase. The technical demonstration at larger capacity needs the feasibility evaluation of different possible technologies, and then commercial demonstration for the chosen technology. Accordind to Bergman and Kiel (2005), the next phase of development of torrefaction is the technical demonstration, which is planned in the near future. Uslu et al. (2008) have evaluated the specific investment costs in contrast to the scale of the torrefaction plant (Figure 16). (Bergman et al. 2005, Bergman & Kiel 2005, Uslu et al. 2008)

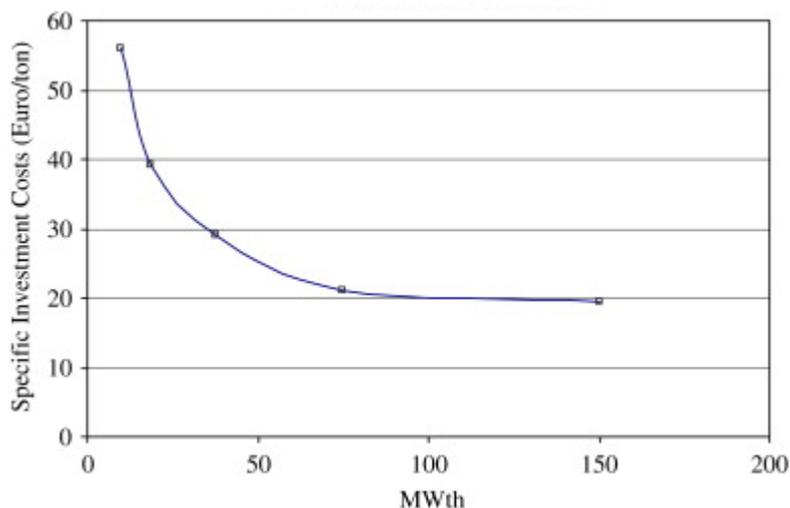


Figure 16. Scale effect on torrefied investment costs (Uslu et al. 2008).

#### 4.1.5 Liquefaction

In direct liquefaction, the biomass is converted to a liquid form at high temperature and high pressure using hydrogen or water. Catalytic hydrocracking, i.e. Bergius process, is the most applied type of direct liquefaction, initially developed about 100 years ago in Germany for liquefaction of coal. Compared to pyrolysis, liquefaction has greater yield and the liquid product has higher energy content and lower oxygen content, which makes the final product more stable. Albeit the oxygen content in the liquefaction product oil is significantly lower than in the original biomass, the oxygen content is still way too high to use the product oil as a gasoline or diesel fuel substitute and downstream processes are required. (Lampinen & Jokinen 2006, Behrendt et al. 2008)

The vegetable oil hydrogenation process can also be categorised as a liquefaction process though the processes are quite dissimilar with oils compared to lignocellulosic biomass. The vegetable oil hydrogenation process involves the reaction of vegetable oil with hydrogen (usually oil derived) in the presence of a catalyst. The resulting product is a straight chain hydrocarbon. (Evans 2007)

A large variety of reactor types and process conditions have been applied for direct liquefaction of biomass as well as pyrolysis and gasification of biomass. Direct liquefaction can be classified into different reaction paths and reaction conditions, for example (Behrendt et al. 2008):

- Solvolysis,
- Aqueous medium (acidic, basic or neutral hydrolysis),
- Organic medium,
- Thermal decomposition under reducing atmosphere.

In general, the conversion of lignocellulosic biomass into liquid hydrocarbons comprises with only little exceptions the following steps (Behrendt et al. 2008):

1. Pre-treatment of feedstock,
2. Slurrying the feedstock within a liquid carrier,
3. Heating the slurry to reaction conditions,
4. Addition of reducing gas (e.g.  $H_2$  or  $H_2/CO$ ) at elevated pressure,
5. Main reaction,
6. Product separation, and
7. Solid-liquid separation and recovery of solvent.

Catalysts, which might be used, are typically added to the slurry.

These engineering process steps of liquefaction correspond to the following chemical steps (Behrendt et al. 2008):

1. Solvolysis of the feedstock,
2. De-polymerisation of the main components of biomass (i.e. cellulose, hemicellulose, and lignin),
3. Chemical and thermal decomposition of monomers and smaller molecules leading to new molecular rearrangements through bond ruptures, dehydration, and decarboxylation,
4. Degradation of oxygen containing functional groups in the presence of hydrogen.

The de-polymerisation of cellulose and hemicellulose in aqueous media can be regarded as relatively well known because a massive knowledge base from sugar and pulp and paper industries exists. Characteristic for the de-polymerisation of cellulose and hemicellulose is the great number of different degradation products with a multiplicity of oxygen containing groups. From these functional groups very few are able for further direct reduction by cleavage of carbon dioxide. Hence, the presence of hydrogen is essential for the degradation of functional groups and to avoid re-polymerisation. The de-polymerisation of lignin in a solvent leads to numerous different substituted phenols.

As in the case for cellulose and hemicellulose the absence of hydrogen quickly leads to re-polymerisation of the products. (Behrendt et al. 2008)

The gaseous, liquid, and solid yields of liquefaction of biomass depend on various parameters, which can be classified into chemical and physical parameters. Chemical parameters are, for example, the lignin content of the biomass, the solvent, the catalyst, and the atmosphere, and physical parameters are the temperature, the mass ratio of solvent to biomass, the concentration of the homogeneous catalyst, and the residence time. (Behrendt et al. 2008)

## **4.2 Biochemical processes**

Biochemical processing techniques can also be called ‘wet’ processing techniques. Considering high-moisture materials, such as manures, thermo-chemical conversion processes consume more energy than is produced. Therefore it is more economical to use a biochemical conversion process, i.e. fermentation or anaerobic digestion. (McKendry 2002a)

In biological conversion, micro-organisms convert biomass to biofuels. The processing of biomass occurs by using either one of two different microbiological methods: anaerobic digestion and fermentation. Also composting is a biological conversion process but it produces only some heat and no electricity or biofuels. (Lampinen & Jokinen 2006)

### **4.2.1 Fermentation**

Crops and plants with high sugar or starch content, such as sugar beet, corn, and potato, are suitable and easily exploitable for the feedstock of fermentation reaction, which is presented in Figure 17. Also other biomasses, like wood and straw, can be utilised after acid or enzyme treatments. This route is presented in Figure 18. In a fermentation process, microbes (usually yeast or bacteria), or less frequently fungi, split organic matter producing typically alcohol as a final product. (Lampinen & Jokinen 2006)

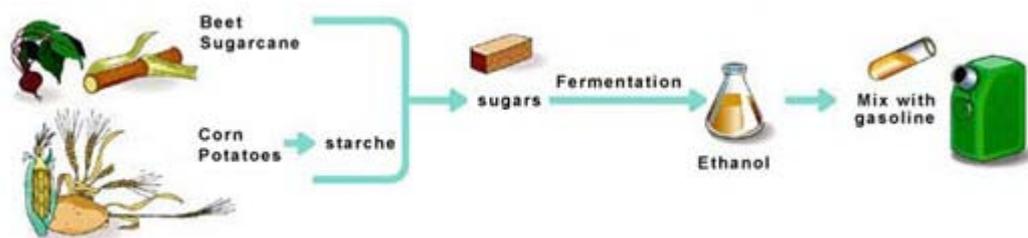


Figure 17. Fermentation of sugars and starch (IFP 2009).

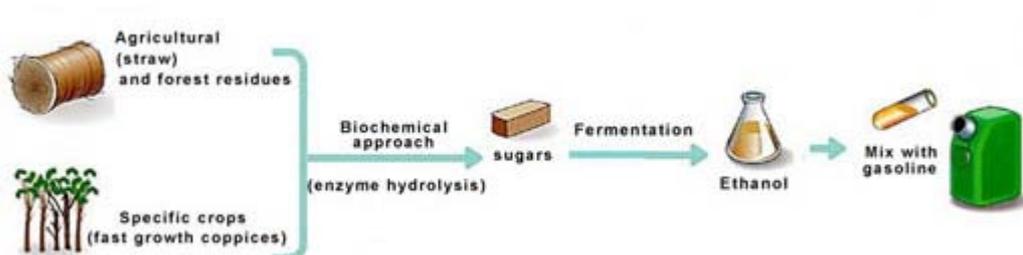


Figure 18. Fermentation of lignocellulose based raw materials (IFP 2009).

The first-generation biofuels from agricultural crops are produced commercially, and the industry is growing throughout the world. Although the fermentation technology is mature, there is still extensive research, development and innovation occurring. Second-generation biofuels from wood and wastes (i.e. lignocellulosic material) are more promising in the long term since they do not use materials suited for food. Second-generation biofuels are still more expensive than the first-generation biofuels and no significant contribution from second-generation biofuels has materialised yet. Various companies and research groups work intensively to produce second-generation biofuels commercially. (EC 628/2005)

Ethanol is the most common compound produced through commercial fermentation, because of its versatility as transportation fuel and fuel additive. Ethanol has various favourable properties which boost its use as a desirable fuel compared to gasoline, such as high heat of vaporisation, low flame temperature, greater gas volume change, high specific energy, and high octane. Ethanol fuelled engines produce lower emissions of particulates, oxides of nitrogen and aromatics than conventional gasoline fuelled engines. (Wyman 1996)

Ethanol as a blend in gasoline improves fuel quality and reduces the need to use other fuel additives, such as toxic benzene. On the other hand, ethanol has about two thirds of

the energy density of gasoline. Ethanol from sugar cane is produced commercially in Brazil for use in 22% ethanol/gasoline blend and as a pure fuel. Corn starch is used as the feedstock for most commercial ethanol production plants in the United States. (Wyman 1996)

In addition to ethanol, butanol is being developed for the use as a fuel substitute. BP (in collaboration with British Sugar and DuPont) and Green Biologics are planning to make butanol from cereal derived feedstocks. Butanol can be used as both gasoline and diesel substitutes, it can use the existing supply infrastructure, and it suits well to current vehicle and engine technologies. Also development of a new fuel substitute called furanics is ongoing. Avantium, a spin-off enterprise from Shell, has developed a catalytic process to make furans from hexose containing materials. (Evans 2007)

Sugars containing one or two molecules can be fermented. When they exist naturally in plants, these sugars can be released by simple pre-treatment that includes chopping or crushing, and washing with hot water. Before fermentation, the plant material must be removed. Starch molecules are too large to ferment directly. The cell walls and husks of grain and other starch feedstocks must be first opened to make the starch accessible. The starch must also be separated from other portions of grain feedstock. (Wisbiorefine 2004b)

Generally, wet and dry milling processes are used to produce ethanol from starches. Starch must be broken down to sugars of one or two molecules by hydrolysis process before fermentation. Historically, acids have been used to hydrolyse the starch at temperatures of 150 to 200°C. Since the 1960's, the use of specialised enzymes, like  $\alpha$ -amylase, instead of acids to break the starch into smaller molecules has become more popular. Acid hydrolysis might be combined with enzyme hydrolysis. In hydrolysis process, starch is liquefied in the presence of acid and/or enzymes, and then saccharified by treating with another enzyme to smaller, fermentable sugars. (Wisbiorefine 2004b, Elander & Putsche 1996)

Also cellulose and hemicellulose compounds in lignocellulosic biomass must be broken down to simple sugars by hydrolysis before fermentation. Lignin must be separated from cellulose and hemicellulose by chemical and other means because lignin is not

fermentable. Enzymatic hydrolysis techniques seem the most promising methods for reducing costs while improving yields, even though concentrated acid and dilute acid hydrolysis technologies have long industrial histories. Figure 19 illustrates a generalised lignocellulose fermentation process flow diagram with recycle loops. (Wisbiorefine 2004a, Wyman 1996, Keller 1996)

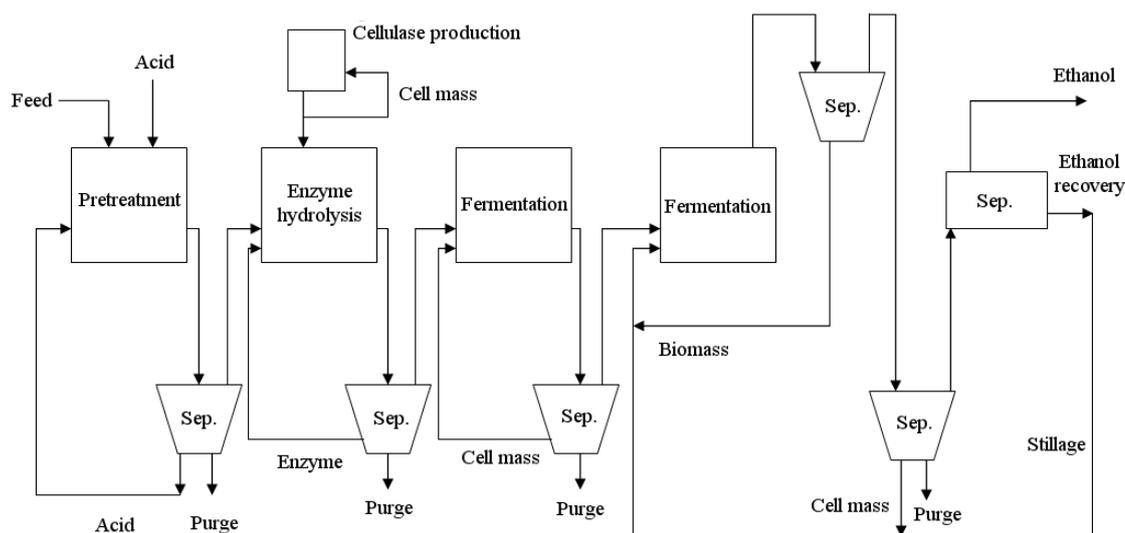


Figure 19. Example of used fermentation process for lignocellulosic feedstocks. Sep. is an abbreviation for separation. (Keller 1996)

The first stage of hydrolysis may contain hemicellulose hydrolysis with dilute acids (using <1% sulphuric or other acid solution) to break it down into its component sugars. The second stage is hydrolysis of cellulose, either through additional dilute-acid processing, or the use of biobased enzymes. Bio-based enzymes, called cellulases, are proteins that break cellulose down into glucose. Liquid, simple sugars must be recovered from each stage and neutralised before the following fermentation process. Enzymatic options are developed rapidly and have a great potential of achieving lower production costs than acidic fermentation. (Wisbiorefine 2004a, Wyman 1996)

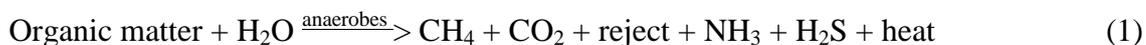
In fermentation processes, sugar concentration must be adjusted, nutrients such as nitrogen source added, and temperature and pH controlled to be optimal. Then, micro-organisms digest simple one and two molecule sugars to produce energy and chemicals they need to live and reproduce, and give off by-products such as carbon dioxide, hydrogen, and ethanol. Production rates are low by chemical refinery standards, and

living organisms may be sensitive to impurities including the by-products that inhibit the action of organisms. (Wisbiorefine 2004b)

Crops and plants that release fermentable sugars leave plant residues which might be utilised, for example, as energy production purposes, as animal feed, or which can be converted into other bio-based products. Residual cellulose and lignin left over from hydrolysed lignocellulosic biomass can be used as boiler fuel for electricity or steam production. Purified lignin can also be converted into valuable chemicals or fuels. The fermentation process releases gases such as carbon dioxide that can be captured for sale. Ethanol separation processes result in wastewaters which have a high biological oxygen demand and require a treatment. (Wisbiorefine 2004a, Wisbiorefine 2004b, Wyman 1996)

#### 4.2.2 Anaerobic digestion

Anaerobic digestion can be used to produce bioenergy from fast decomposed biowastes such as manures, slaughterhouse wastes, industrial and domestic biowastes, and wastewaters. Also herbaceous biomass, grasses and plant residues can be utilised. Anaerobic digestion occurs in a reactor in the absence of oxygen, and it is based on decomposing of organic matter by anaerobic bacteria. The product of this treatment is biogas which mainly consists of methane and carbon dioxide. Equation 1 presents the anaerobic digestion process and its main products. (Lampinen & Jokinen 2006, Kelleher et al. 2002)



The biogas can be used to produce heat and power, or it can be purified to be used as transportation fuel in vehicles. Anaerobic digestion is also suited to produce hydrogen, but this technology is not yet commercially available. (Lampinen & Jokinen 2006, Kelleher et al. 2002)

There are three main groups for reactor design: batch reactors, one-stage continuously fed systems, and two-stage (or sometimes multi-stage) continuously fed systems. Batch reactors are the most simple. In one-stage continuously fed systems all the bio-chemical

reactions occur in one reactor, and in two-stage continuously fed systems the hydrolysis/acidification and acetogenesis/methanogenesis processes are separated. (Ward et al. 2008)

Anaerobic digesters are also divided into wet and dry reactor types. The schematic figure of the wet reactor is shown in Figure 20. If the total solids value is 16% or less, the reactor is known as the wet reactor. Minimum total solids value for the process is about 4%. In dry reactors the total solids value is between 22% and 40%. The reactors between dry and wet are called semi-dry reactors. The dry and semi-dry reactor technology is mainly used with municipal solid waste and vegetable wastes, whilst the wet reactors are suitable for many types of manure. (Ward et al. 2008, Renewable Energy Association 2009, Kelleher et al. 2002)

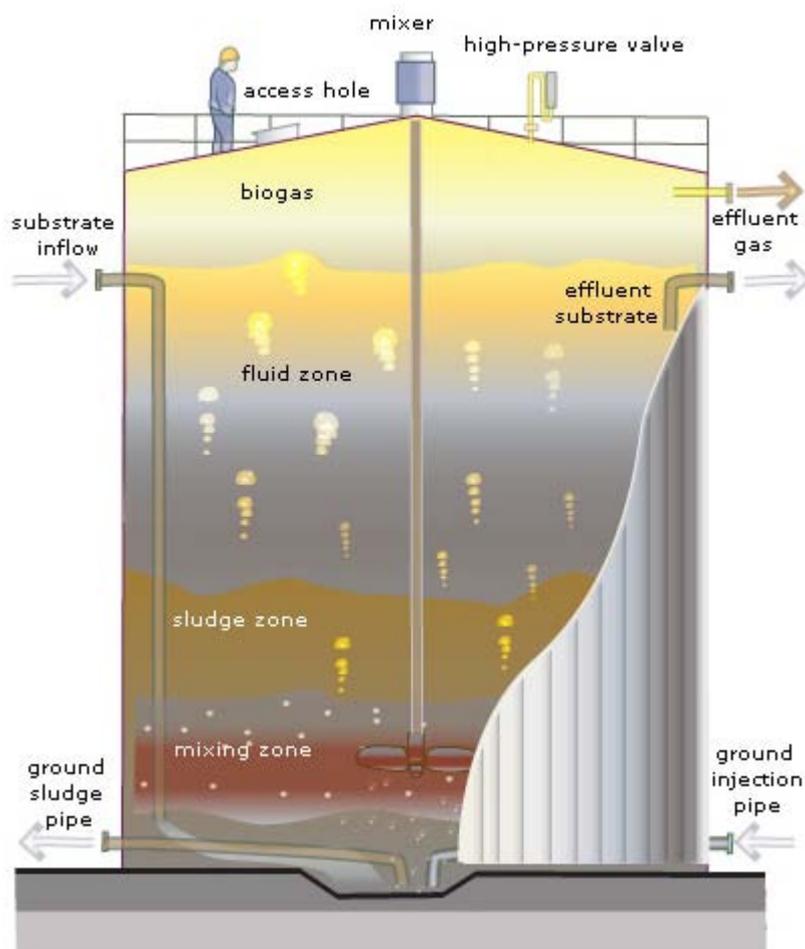


Figure 20. Schematic of a wet reactor (Renewable Energy Association 2009).

Mixing ensures efficient transfer of organic material for the active microbial biomass. It also releases gas bubbles trapped in the medium and prevents sedimentation of denser particulate matter. Therefore a certain degree of mixing is required. However, excessive mixing can reduce biogas production. According to Ward et al. (2008) the reason for this is unclear, but it might have something to do with the formation of anaerobic granules. The type of mixer depends on the total solids value. A screw is used in some pilot scale dry reactors while propellers are commonly used with wet reactors. (Ward et al. 2008)

Reducing the amount of micro-organisms washed out of the digester can enhance the operation of a digester. Anaerobic filters and sludge blankets are in use in the treatment of wastewater. Microbial support materials have shown to improve methane yields compared to support free digester. The support material can be either inert or degradable. Experiments have been made with straw, glass, plastic, rock wool, polyurethane foam, loofah sponge, clay minerals, activated carbon, and porous stone. (Ward et al. 2008)

Anaerobic digestion can occur at psychrophilic temperatures below 20°C but the reactions are very slow and hence it is rarely used. Mesophilic and thermophilic temperatures, with optima at 35°C and 55°C, respectively, are generally used in most reactors. Thermophilic reactors can usually manage a shorter retention time. The difference in methane yields between mesophilic and thermophilic reactors depends partly on the feedstock, and is not very significant when taking into account the increased energy requirements for maintaining the high temperature. Also rapid degradation of fatty acids at thermophilic temperatures may cause problems. (Ward et al. 2008)

The ideal pH for anaerobic digestion is 7. For methanogenesis process, ammonia is toxic above pH 7 and volatile fatty acids and hydrogen below pH 7. However, the optimum pH of hydrolysis and acidogenesis is between pH 5.5 and 6.5. The main advantage of two-stage reactors is separation of the hydrolysis/acidification and acetogenesis/methanogenesis processes. (Ward et al. 2008)

Wastes containing high amounts of proteins and lipids can cause problems to the anaerobic digestion process. Therefore, in the anaerobic digestion of solid slaughterhouse waste the effects of long-chain fatty acids (LCFAs) and ammonia need to be taken into account. The degradation of LCFAs may be the limiting step because of the slow growth of LCFA-consuming bacteria and because the degradation of LCFAs requires low  $H_2$  partial pressure. The easily accumulating LCFAs may also cause problems because of their toxicity to anaerobic micro-organisms, especially acetogens and methanogens. LCFAs can also form floating scum. The floating LCFAs may influence their toxicity and bioavailability and cause fouled gas collection pipes and scum overflow. (Salminen & Rintala 2002)

LCFAs are surface-active compounds and the unionised form of LCFAs adsorbs first to the microbial cell surface, which cause inhibition. The concentration affects both LCFA adsorption and inhibition, as well as various other factors. Unsaturated LCFAs with 18 carbon atoms and saturated LCFAs with 12–14 carbon atoms are the most inhibiting compounds to the anaerobic digestion process. LCFAs' toxicity to methanogens is synergistic, which commonly means that the presence of another LCFA increases the toxicity. (Salminen & Rintala 2002)

Ammonia from protein degradation can cause troubles because unionised ammonia inhibits anaerobic micro-organisms, especially methanogens. Unlike ammonia ions, unionised ammonia can easily diffuse across the cell membrane, causing toxicity. Sulphide can increase ammonia inhibition. On the other hand, e.g. poultry feather degrades poorly under anaerobic conditions since they are based on keratin, a fibrous protein. (Salminen & Rintala 2002)

Thermophilic digestion is typically more effective than mesophilic with a view to destroy pathogenic bacteria, parasites, and viruses. EU-legislation requires a certain treatment for animal by-products before the utilisation. (Salminen & Rintala 2002)

Ionisation of ammonia is a function of pH and temperature, and increasing pH and temperature higher the free ammonia concentration remarkably. In thermophilic conditions the free ammonia concentration is higher than in mesophilic conditions, which could explain more serious inhibition in thermophilic digestion, compared to

mesophilic digestion, when using feedstock rich in proteins and lipids. In anaerobic digestion of animal by-products, the highest specific methane yields are achieved when the by-products are at high dilution. Usually higher temperatures result in higher bacterial growth rates and metabolic activities but in the case of anaerobic digestion of animal by-products, thermophilic digestion results in lower biogas yields and a more stressed process. Thus mesophilic temperature is a better choice for anaerobic processes operating with high N loadings. (Hejnfelt & Angelidaki 2009)

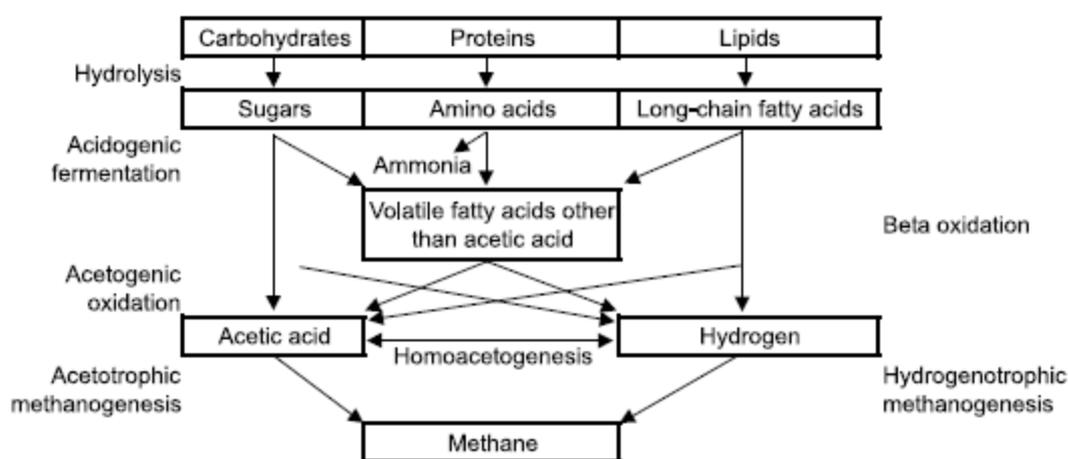


Figure 21. Anaerobic digestion pathways (Salminen & Rintala 2002).

Different kinds of micro-organisms are enclosed in the various steps of anaerobic degradation (Figure 21). In the process fermentative bacteria hydrolyse proteins to polypeptides and amino acids. Lipids are hydrolysed to long-chain fatty acids (LCFAs) and glycerol via  $\beta$ -oxidation and polycarbohydrates to sugars and alcohols. Secondly fermentative bacteria change the intermediates to volatile fatty acids (VFAs), hydrogen ( $H_2$ ), and carbon dioxide ( $CO_2$ ). The by-products of amino acid fermentation are ammonia and sulphide. Hydrogen-producing acetogenic bacteria metabolise LCFAs, VFAs with three or more carbons, and neutral compounds larger than methanol to acetate,  $H_2$ , and  $CO_2$ . Eventually methanogens convert acetate,  $H_2$ , and  $CO_2$  to methane and  $CO_2$ . (Salminen & Rintala 2002)

Organic acids are intermediates of anaerobic digestion. They are microbial substrates, improve microbial growth and deplete soil oxygen, causing immobilisation of soil nitrogen. Similarly with ammonia, organic acids are possibly phytotoxic for plants. Ammonia and organic acids can inhibit the growth of plants, especially the germination

and root growth. Organic acids have been shown, for example, to cause ion loss from roots. Both the unionised ( $\text{NH}_3$ ) and ionised ( $\text{NH}_4^+$ ) form of ammonia may influence on plant growth though the inhibition mechanisms are different. To ensure the maturity of anaerobically digested material, aerobic post-treatment may be needed. It decreases the content of volatile inhibitors such as ammonia and organic acids, but it also results in a remarkable loss of nitrogen through the volatilisation of ammonia. (Salminen et al. 2001)

There is probably no full-scale anaerobic digester, which treat only solid slaughterhouse wastes. However, numerous anaerobic digestion plants use co-digestion of different industrial organic wastes, including solid slaughterhouse wastes, and agricultural wastes. Co-digestion of wastes with variable characteristics is a good way to dilute toxicants and to improve the nutritional value and moisture content. Much more common than anaerobic treatment of solid slaughterhouse wastes is anaerobic treatment of slaughterhouse wastewater. As early as in 1968 in Leeds, the UK, slaughterhouse wastewater was treated in an anaerobic plant. Co-digestion of various organic wastes has not only been viable but there was also a superior biogas yield from the treatment of combined waste as opposed to the digestion of the wastes on their own. Also biomass that is unsuitable for digestion may co-digest with another material. (Kelleher et al. 2002, Salminen & Rintala 2002)

Local circumstances influences outstandingly on the cost of anaerobic digestion. Construction and labour costs, possibilities of energy recovery, treatment capacity, energy prices, taxes, energy purchase tariffs, land price, markets, and prices of digested material may affect the total costs of anaerobic digestion. Capital investment is usually higher in an anaerobic digestion plant than in a composting plant. On the other hand, anaerobic digestion produces biogas which can be used for energy production. (Salminen & Rintala 2002)

### **4.2.3 Composting**

Composting is an aerobic biological process in which micro-organisms convert biodegradable organic matter into a humus-like product. Composting of organic wastes has a long history and it is still popular and environmentally friendly way to treat

wastes. The composting process destroys pathogens, converts ammonia to stable organic forms, reduces the volume and improves the nature of the waste. Temperature, oxygen supply, moisture content, pH, C/N ratio, particle size and degree of compaction are the main factors for the effectiveness of the process. Composted organic wastes are good fertilizers and when returned into the soil they also improve soil structure. (Imbeah 1998)

If the biomass is too wet for direct composting, co-composting with a bulking agent like straw, sawdust, peat, or litters is usually possible. They have been shown to accelerate the composting process and have made the processes odour-free. In general, bulking agent also work as a carbon source, which is always required in composting process. (Imbeah 1998)

Temperature and aeration rate are the most important factors in a successful composting process. The metabolic heat generation of micro-organisms maintain the suitable temperature while temperatures more than 60–65°C would destroy almost all micro-organisms and stop the process. The temperature can be controlled by adjusting the amount of oxygen available to the micro-organisms. Aeration in composting piles can be arranged by turning the pile, by forced aeration using pumps, or by passive aeration in which air is allowed to passively flow through the pile. (Imbeah 1998)

Figure 22 illustrates generalised temperature and pH changes during the composting process. At the beginning of the process, biological decomposition is started by mesophilic microbes which causes temperature to increase. The acidic metabolism products of mesophilic bacteria from decomposition of sugars, starches and fats cause the pH decrease. At the temperature of 40°C, thermophilic period begins and the decomposition of organic matter is very efficient. Proteins start to decompose at thermophilic temperatures releasing free ammonium nitrogen which increases the pH of the compost. (Rämö 2008)

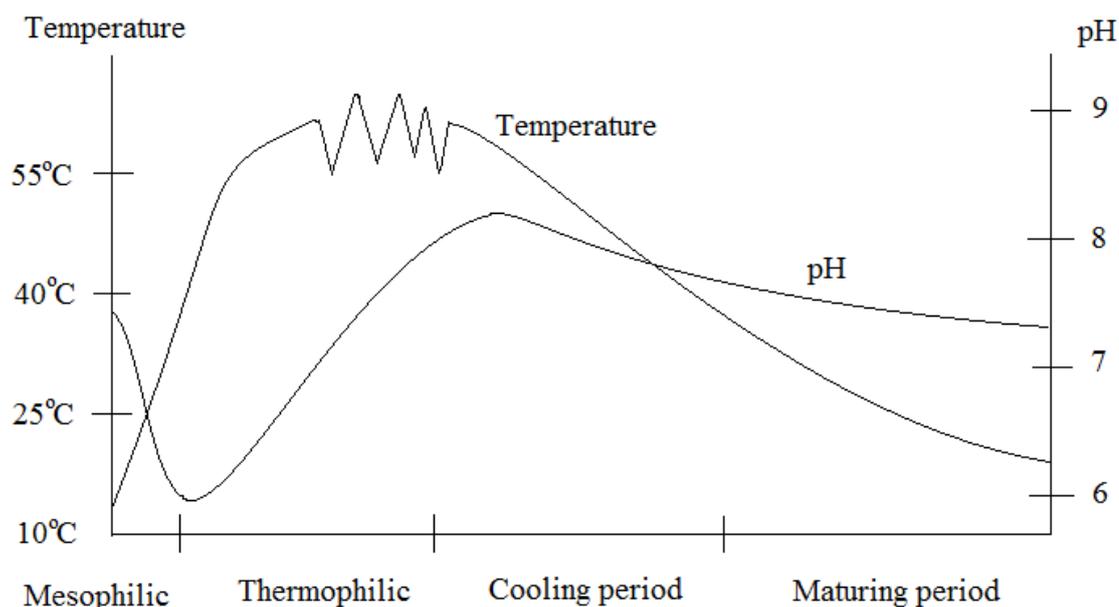


Figure 22. Temperature and pH changes during composting process (Rämö 2008).

When the temperature rises above 70°C microbes die and the production of heat stops. The temperature decreases slightly and the microbes activate again and start to produce heat. When easily decomposed organic matter is utilised, the temperature starts to decrease and the cooling period begins. The ammonia nitrogen in biomass is converted to soluble nitrate nitrogen and the pH stabilises. The maturing period begins when the temperature decreases close to ambient temperature. The composting material converts to humus soil with low biological activity. The maturing period takes about some months depending on the original feed material. (Rämö 2008)

Composting is implemented in either windrows or reactors. Poultry slaughterhouse wastes, including screenings, flotation tailings, grease trap residues, manure, litter and feather are generally treated by composting. However, releases to air, water and land from the process may be a problem, particularly in windrow composting. (Salminen & Rintala 2002)

Loss of nitrogen and other nutrients during composting, equipment and labour costs, odour and land use are the main disadvantages in a composting process. A low C/N ratio promotes large ammonia losses. The moisture content affects the decomposition rate and the tendency to stabilise significantly. Therefore the moisture content should be maintained between 40% and 60% to achieve a successful composting process.

Different kind of amendments such as natural zeolites, clay or  $\text{CaSO}_4$  can be added to compost to improve the process and to reduce the loss of  $\text{NH}_3$ . (Kelleher et al. 2002)

### **4.3 Mechanical conversion**

Solid and liquid biofuels can be produced by mechanical conversion. Splitting and pressing of solid bioenergy sources to pellets, briquettes, straw bales, etc. are much used conversion methods. At the same time, the energy density increases. However, densification of solid biomass is a fairly expensive process and its cost addition to fuel is significant. Liquid biofuels can be produced by mechanical extraction of oil plants and used directly but are more suitable to engine use as after-processed. (Lampinen & Jokinen 2006, Khan et al. 2009, Hossain & Davies 2010)

#### **4.3.1 Pelletisation**

Pelletisation is a process in which biomass is dried and compressed under high pressure into cylindrical extruded pieces with a diameter of 6–10 mm and height of 10–20 mm. Pellets have a higher energy density (approximately  $1,100\text{--}1,500 \text{ kg/m}^3$ ) and a smaller volume compared to raw biomass like wood chips. Therefore pellets are more efficient to store and transport, especially in long distances. In pelletisation, the amount of dust produced is minimised and pellets offer a uniform and stable fuel. (Uslu et al. 2008, Kuokkanen 2009)

Maximum 3–20 mm feedstock particles and moisture content about 10–25% are the main requirements for pelletisation. Cutter dust, plane chips, and saw dust are the most used raw materials but also other wood and wood residues as well as herbaceous crops and grasses can be used. The moisture content of pellets is typically 7–12% and the ash content less than 1–3% depending on the feed material. In the pressing process, presented in Figure 23, the feedstock is first heated to  $50\text{--}100^\circ\text{C}$  to soften the lignin and adjust the moisture content optimal, and then the mechanical densification occurs at  $150^\circ\text{C}$ . (Uslu et al. 2008, Kuokkanen 2009)

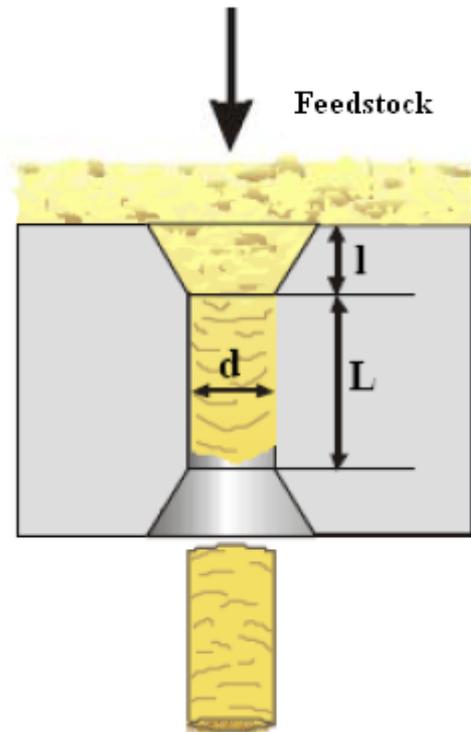


Figure 23. Pellet press (Kuokkanen 2009).

Pelletisation is a commercial technology. In Europe, Finland and Sweden are the leading countries in pelletising technology. Pelletisation typically consists of drying, milling (grinding), pelletising, and cooling, as presented in Figure 24. The produced pellets have a lower heating value in the range of 16–18 MJ/kg. Thermal efficiency of the process is around 94%. When the utility fuel is included the efficiency is around 87%. The investment cost is in the range of 0.15–0.25 M€MW<sub>th(input)</sub> and the production costs vary depending on the production scale, as presented at Figure 25. (Uslu et al. 2008)

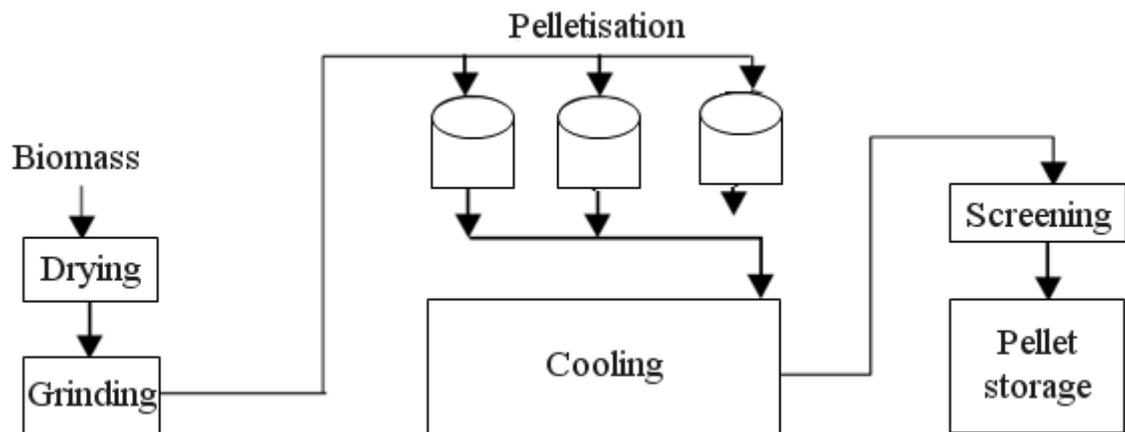


Figure 24. Diagram of a pellet producing process (Uslu et al. 2008).

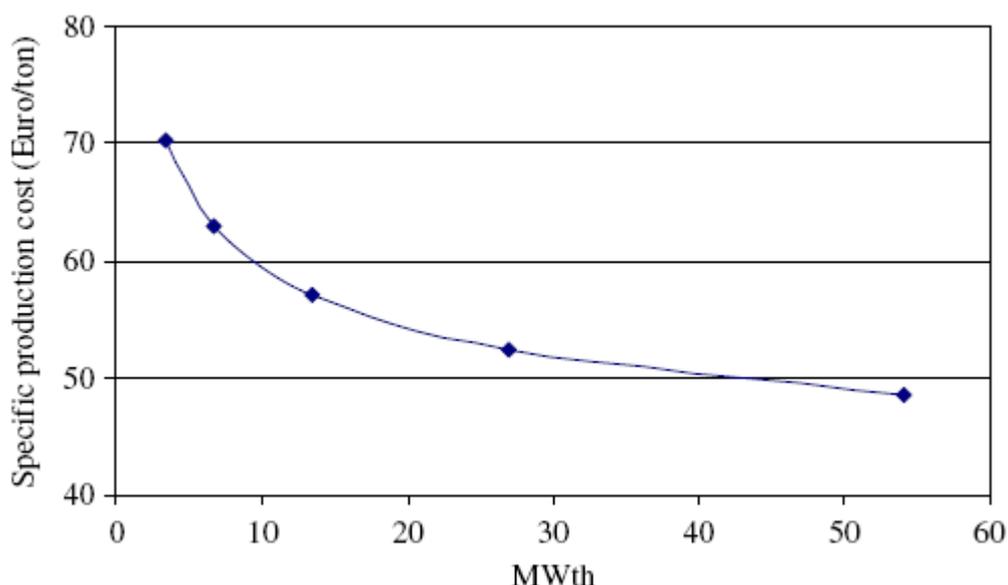


Figure 25. Scale effect on pellet production costs (Uslu et al. 2008).

#### 4.3.2 Mechanical extraction

Liquid biofuels can be produced from oil plants (such as rape) or algae by mechanical extraction and settling. Received oil can be used as raw in compression ignition engines. Methods to modify the oil properties more suitable for engine use include, for example, pre-heating of the oil to reduce viscosity, blending with fossil diesel, or addition of oxygenates and emulsification. Also modifying the engine parameters and maintenance schedule can be done to improve combustion, to reduce harmful emissions and to avoid adverse impacts to the engine performance. The oil can also be refined via transesterification to biodiesel (chemical conversion). (Lampinen & Jokinen 2006, Hossain & Davies 2010, McKendry 2002b)

#### 4.4 Chemical conversion and electro-chemical conversion

Chemical conversion, reforming and reformulation means numerous chemical processes in which source materials could be treated to fuels and additives which are better suited for utilisation. For example ethyl tert-butyl ether (ETBE) can be produced from ethanol, and methyl tert-butyl ether (MTBE) and dimethyl ether (DME) from methanol. Steam reforming is a versatile conversion process in which methanol, hydrogen and syngas can be produced from methane. (Lampinen & Jokinen 2006)

By esterification, plant oils, animal fats, waste fats and greases as well as pine oil and other wood oils can be processed to biodiesel-fuels suitable for diesel engines. However, animal fats have not been studied to the same extent as vegetable oils. The esterification process reduces oils viscosity and unsaturation and makes oils more suitable for engine use without any engine modification. Both biodiesels and plant oils can be used in other engine types, gas turbines, and heaters instead of heating oil. (Lampinen & Jokinen 2006, Hossain & Davies 2010, Ma & Hanna 1999)

The fatty acid methyl ester (FAME) process is the most commonly used method to convert vegetable oil into a biodiesel. The meaning of the process is to lower the viscosity of the oil. Vegetable oils react with an alcohol (typically methanol is used) in the presence of a potassium hydroxide or sodium hydroxide catalyst (see Figure 26). The methanol used is typically derived from natural gas. The transesterification reaction removes glycerol from the oil leaving three long-chain hydrocarbons which can be used as diesel. (Evans 2007, Ma & Hanna 1999)

Glycerol is a by-product from the FAME process. It is contaminated with excess methanol and a spent catalyst but it can be purified for industrial or pharmaceutical quality glycerine. Also conversion to chemicals is being developed for glycerine. The FAME process is relatively mature technology and a number of providers are available, for example Lurgi, BDI, and Axens. Currently the process is small-scale technology but there is a move towards large-scale production. (Evans 2007)

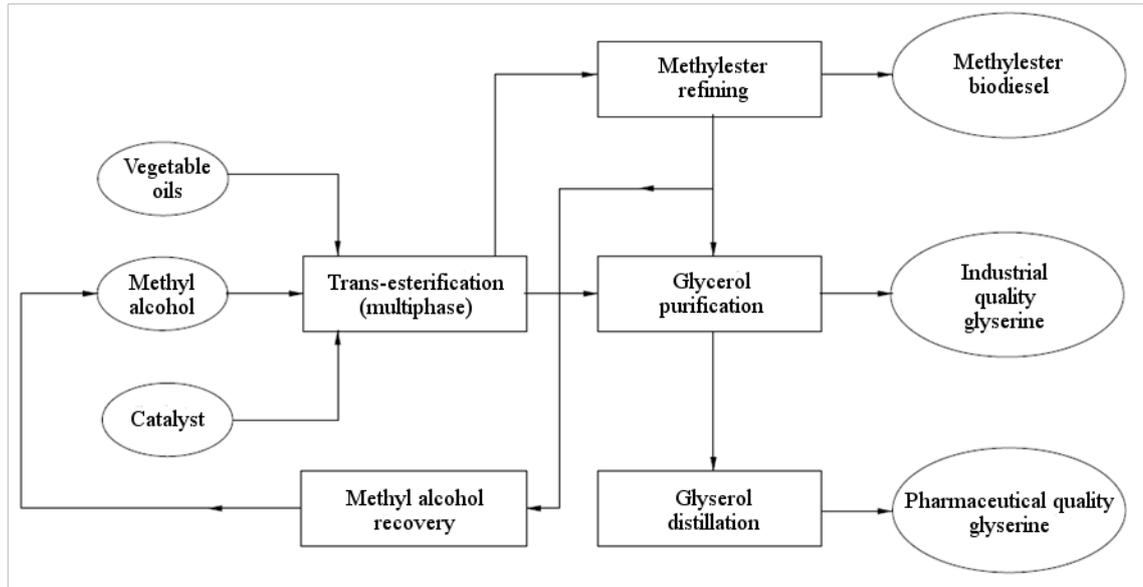


Figure 26. Production of methylester bio-diesel and glycerine (McKendry 2002b).

In electrolysis, hydrogen could be manufactured from water using electricity. Electrolysis can also be used to break down many other compounds than water. Electrolysis enables very pure (over 99.9%) hydrogen manufacturing in all scales. Hydrogen can be used as fuel in special vehicles. If the electricity is generated from bioenergy, the produced hydrogen is bio-hydrogen. Hydrogen can also be produced by using many other methods. Electricity is the most versatile fuel. (Lampinen & Jokinen 2006, Lampinen 2009)

## 5 Legislation

This chapter reviews the main directives in EU legislation relating to energy production and wastes. Only EU legislation is reviewed because MicrE project has participants in several EU member states.

The Waste Framework Directive (WFD) encourages prevention, recycling and recovery of waste, as well as the use of recovered materials and energy. WFD aims to reduce production of wastes, as well the amount of wastes to dispose in landfills. WFD also requires that waste treatment facilitates need to obtain permits from competent authorities. The protection of human health and the environment against harmful effects caused by collection, transport, treatment, storage and tipping of waste are the fundamental objectives relating to waste management. (DIR 2006/12/EC)

According to the IPPC Directive (integrated pollution prevention and control directive), as well as environmental policy of the EU in general, the environment has to be protected as a whole, especially by preventing, reducing and, as far as possible, eliminating pollution as well as ensuring prudent management of natural resources. The objectives and principles are in compliance with the 'polluter pays' principles and the principle of pollution prevention. (DIR 1996/61/EC)

The Landfill Directive aims at the reduction of biodegradable wastes disposed in landfills in order to reduce the production of methane gas from landfills and thus combat global warming. The Landfill Directive is in effect since 1999 and, according to it, Member States should have set up a national strategy for the implementation of the reduction of biodegradable waste going to landfills. (DIR 1999/31/EC)

The Biofuel Directive promotes the use of biofuels or other renewable fuels for transport in order to reduce the dependence on fossil oil in the transport sector. However, the legislation on fuel quality, vehicle emissions and air quality should not be detracted in any way. As well, sustainable farming and forestry practices should be maintained. (DIR 2003/30/EC)

Sustainable energy is also promoted by the Directive on the promotion of electricity produced from renewable energy sources in the internal energy market. According to the Directive, in force since 2001, all Member States should be required to set national targets for the consumption of electricity produced from renewable sources. The use of electricity from renewable sources helps also to meet Kyoto targets. (DIR 2001/77/EC)

According to the regulation laying down health rules concerning animal by-products not intended for human consumption, some animal by-products are prohibited to be utilized before certain treatment. The treatment depends on the category of the animal by-product. Three categories are defined: category 1 for high risk material (part of infected animals, international catering etc.), category 2 for high risk animal by-products (diseased animals, manure and digestive tract content), and category 3 for low risk material (catering residues, meat, precooked foods, etc.). All of these three category materials can be directly disposed as waste by incineration in an incineration plant. (REG 2002/1774/EC)

Category 1 material is not allowed to be treated in composting or biogas plants under any circumstances. Category 2 material cannot be used as feedstock in composting and biogas plants, unless they have first been rendered to 133°C and 300 kPa for 20 min according to the EU pressure-rendering standard (sterilization). Category 3 material must be treated at least at 70°C for 1 h in a closed system. (REG 2002/1774/EC)

The Directive on the incineration of waste sets strict limitations to prevent the negative impacts on the environment. Plants treating only vegetable waste from agriculture and forestry, vegetable waste from the food processing industry, wood waste with the exception of halogenated organic compounds or heavy metals contained wood waste, or animal carcasses are excluded from the scope of the directive. Also experimental plants used for research and treating less than 50 tonnes of waste per year are excluded. (DIR 2000/76/EC)

## 6 Downstream processes

Most of the technologies presented in this work need after-treatment processes. This chapter presents downstream processes for pyrolysis, gasification, fermentation, and anaerobic digestion. Combustion, torrefaction, composting, and pelletisation are left out from this chapter, mainly because they do not require after-treatment. Torrefaction and pelletisation are pre-treatment methods.

Liquefaction is not presented here either because there are several different liquefaction processes each requiring special after-treatment processes before the product oil can be used as a fuel. These downstream processes are introduced shortly after each liquefaction process in the Industrial applications chapter.

### 6.1 Downstream processes of pyrolysis

Pyrolysis process conditions have significant influence on the composition of the produced oils. Pyrolysis oils typically suffer from poor thermal stability and cause corrosion to engines. Generally, bio-oil is a difficult product to be used or upgraded directly. Figure 27 presents different options for pyrolysis oil after-treatment and upgrading. (Soltes 1988, McKendry 2002b, Evans 2007).

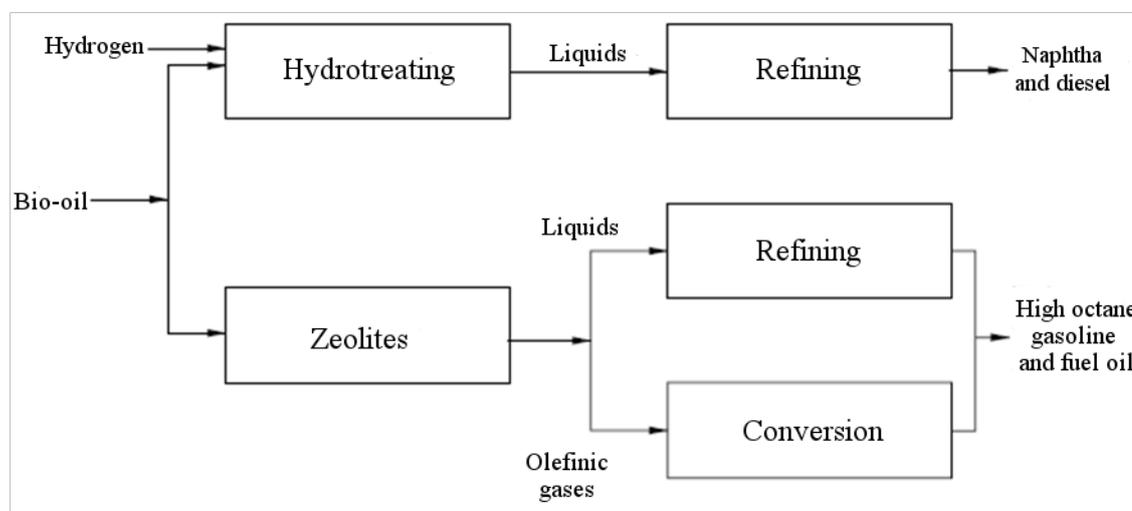


Figure 27. Bio-oil upgrading (McKendry 2002b).

The pyrolysis oils can be primary phenolic and then hydrotreating is necessary to remove oxygen. Single ring phenolics and cyclic ketones present in the oils can be upgraded through deoxygenation to hydrocarbon fuels. Heavier, higher molecular weight products such as the polycyclic aromatics need also to be hydrocracked. A number of catalysts have been tested. Initially, typical petroleum hydrotreating or hydrocracking catalysts at high pressures have been used but more recently acidic zeolites at lower pressures have gained interest. (Soltes 1988, McKendry 2002b)

## **6.2 Downstream processes of gasification**

Feedstock, reactor configuration, and used oxidant influence remarkably on the quality of syngas produced in the gasification process and when the contaminants forming is prevented in a feasible way, there might be no need to after-treat the syngas. However, the prevention of contaminants is not always possible, in which case downstream processes are needed.

Usually particulates and tars are the most significant contaminants which have to be removed. Depending mainly on the gasifier, tar content varies from about 0.5 to 100 g/m<sup>3</sup> when most applications of syngas require tar content of 0.05 g/m<sup>3</sup> or less. Also alkali compounds, nitrogen-containing compounds and sulphur may cause problems. (Austerman & Whiting 2007, Han & Kim 2008)

Solid phase materials in syngas, called particulates, consist typically of inorganic ash which is derived from mineral matter in the feed material. Cyclones, filters (ceramic, baffle, fabric), electrostatic precipitators (ESPs), and scrubbers (water, venturi) remove particulates effectively from syngas and are widely used. (Han & Kim 2008)

Vaporised tars will condense either onto cool surfaces or as aerosols, which could lead to fouling or blockage in the fuel lines, filters, turbines, and engines. Therefore, tar removal is needed in systems where syngas is compressed prior to use, such as gas turbines. ESPs and wet scrubbers have been used widely for tar removal from gas streams in coal and coke processing plants. Also catalytic tar destruction, thermal cracking and plasma (Pyroarc, Corona, Glidarc) techniques are being developed. (Austerman & Whiting 2007, Han & Kim 2008)

Though scrubbers, filters, cyclones, and ESPs remove tars effectively and quite inexpensively, they can only remove or capture the tar from syngas and the energy in tar is lost. Some of these systems also produce a lot of contaminated water which creates a disposal problem. Thermal cracking systems decompose tar very effectively but operation costs are high due to high temperature. Catalyst cracking can operate at very low temperature. However, there are still shortcomings. The commercial Ni-based catalysts, which are extensively applied in the petrochemical industry, and dolomite are deactivated significantly by carbon deposition. Alkali metal catalysts are easily sintered. (Han & Kim 2008)

Mineral matter in feedstock contains generally high levels of alkali salts, which can vaporise when temperature is above 800°C and further deposit on cooler downstream surfaces. These alkali vapours condense to form sticky particulates (<5 µm) or aerosols. High temperature removal of alkali compounds is possible using ceramic filters or packed bed filters employing activated bauxite. (Austerman & Whiting 2007)

Removal of ammonia from syngas can be done to avoid conversion to NO<sub>x</sub> when the syngas is combusted. Catalytic destruction or wet scrubbing techniques can be used to ammonia removal. Sulphur compounds, typically H<sub>2</sub>S but sometimes also COS (carbonyl sulphide), can be formed in the gasifier and this poses technical challenges. H<sub>2</sub>S could be oxidised to SO<sub>2</sub> in a thermal device downstream. (Austerman & Whiting 2007)

### **6.3 Downstream processes of fermentation**

Generally, as much as 50–70% of the total production cost in first-generation fermentation processes can be due to downstream processing. However, intensive research has improved the efficiencies to usually less than 50% of the total costs. The low final concentration in the water broth, the complex mixture of cellular materials and chemicals in the final broth, and the purity required from the final product are the main reasons for high costs. (Wisbiorefine 2004b, Elander & Putsche 1996)

Distillation is an energy-intensive separation process used to separate two liquids by taking advantage of their difference in boiling point temperatures. The formed fractions

can further be purified by a second distillation. Although distillation is conventional and formerly very widely used, it is not effective separation process for fermentation products. Therefore, lower cost, lower energy separation techniques are being developed and used. (Wisbiorefine 2004b, Elander & Putsche 1996)

Other recovery methods include precipitation, other chemicals-based techniques, and diverse types of membrane separation. Membranes, engineered barriers with special properties, restrict the transport of various chemicals in a selective manner. Transport through the membrane may be driven by convection, diffusion, electric charge (electrodialysis), pressure, temperature, or concentration differences. Membranes can provide significant energy savings compared to distillation. (Wisbiorefine 2004b)

Pervaporation is quite a new membrane-based technology. It is used to separate and concentrate volatile compounds from a liquid mixture by selective permeation through a non-porous membrane into a vacuum permeate stream. Pervaporation is a promising technology to separate volatile compounds (e.g. dewatering liquid biofuels) cost-effectively. (Wisbiorefine 2004b)

## **6.4 Downstream processes of anaerobic digestion**

The main contaminants in biogas are hydrogen sulphide, ammonia, carbon monoxide, siloxanes, water, and particulates. In addition to odour, hydrogen sulphide can cause corrosion problems in gas engines because the SO<sub>2</sub> produced in combustion of the biogas containing can create an acidic environment in the presence of moisture. There are numerous proven and commercially available technologies for H<sub>2</sub>S abatement including chemicals-based systems using ferric chloride as an additive and systems using biological techniques. Ammonia can be removed by catalytic destruction or wet scrubbing techniques if necessary. (Austerman et al. 2007, Austerman & Whiting 2007)

Moisture reduces the calorific value of biogas and affects adversely the gas engine performance. Simple condensers are commonly used for moisture removal, especially in anaerobic digestion plants which are used to generate electricity. Particulates from the anaerobic digestion process and more notable from combustion air accelerate engine

wear. Simple filters can be used to reduce the particle load to gas engines. (Austerman et al. 2007)

Siloxanes are a subgroup of compounds containing Si-O with organic radicals bound to silicon. Feedstocks containing silicon can generate siloxanes which have a negative influence on gas engines. Siloxanes are a problem mainly in anaerobic digestion plants processing municipal solid waste. Siloxanes abatement techniques are less development and available than H<sub>2</sub>S abatement techniques and seldom used in small-scale plants processing only biomass. (Austerman et al. 2007)

## 7 Industrial applications

Several enterprises develop and market different kind of industrial applications of the technologies presented earlier in this work. Gasification and anaerobic digestion are commercially most mature technologies and numerous enterprises offer different kind of these applications. Large scale pyrolysis and fermentation applications are also offered commercially but the technologies are less mature. Torrefaction and liquefaction are not yet fully-commercial technologies. Industrial applications of these technologies are presented in this chapter.

However, all of these technologies are seen quite novel, unproven technologies with associated high capital costs, and the number of fully operating reference plants is relatively limited worldwide. On the other hand, combustion and composting are very old, common and well-known technologies but quite ineffective in energy generation. They as well as pelletisation are not presented in this chapter.

There are no clear definitions how small small-scale is. It depends on the conversion methods and regulations in different countries among others. According to Dong et al. (2009) small-scale combined heat and power (CHP) systems mean systems with an electric capacity less than 100 kW<sub>e</sub> and micro-scale CHP with electric capacity less than 15 kW<sub>e</sub>. In a small modular biopower project funded by the National Renewable Energy Laboratory of the United States (2000) small biomass-to-electricity systems were defined as systems with capacities of 5 MW and smaller.

Although plants with capacities of few MW are sometimes called as small, these plants are industrial size. Upreti & van der Horst (2004) have studied a failed development project of a biomass electricity plant in the UK. Ambient Energy Ltd. planned a 5 MW state-of-the-art wood gasification plant in the rural area but had to give up the plans because of local opposition. Local people opposed the plant since it would give rise to odour, dust, noise and emission nuisances, steam 117 million litres of water per year into the atmosphere, which might have damaged nature and caused general health impacts. There would also be huge increase in heavy goods vehicles in road and negative effects on property prices in the area. (Upreti & van der Horst 2004)

A same kind of opposition, generally called the ‘not-in-my-back-yard’ attitude, took place also opposing other planned plants in other parts of the UK. The central government strongly supports biomass energy development, aiming to achieve the Kyoto target and slow down global warming and climate change. People in rural areas are afraid of the harmful effects of the industrial sized plants and proposed that industrial estates in towns are more suitable location to these plants. (Upreti & van der Horst 2004)

## **7.1 Industrial applications of pyrolysis**

There is only a small number and limited scale of existing pyrolysis oil production units in the world. However, the development in the fast pyrolysis technology is rapid.

Ensyn has developed Rapid Thermal Process (RTP)<sup>TM</sup> technology for the production of pyrolysis oils from biomass. The company has build and commissioned seven commercial RTP<sup>TM</sup> plants in Canada and the United States and the technology can be classed as fully commercial. The largest plant in operation can process feedstock of 100 tonnes of dry residual wood per day and Ensyn is currently developing plants 5–10 times that size. In RTP<sup>TM</sup> the feedstock material is rapidly heated to 500°C and then cooled within seconds. The process has relatively high yield of bio-oils, about 75%. In addition to bio-fuels, Ensyn also produces several bio-chemicals from produced bio-oils. (Ensyn 2009)

BGT-BTL’s technology is initially based on the rotating cone reactor (RCR) and the company has further improved and optimised the concept. Figure 28 illustrates the process. The bio-oil yield is about 70%. According to the company pyrolysis plants’ with a feedstock capacity of 2 t/h and 5 t/h are commercially available and plants with a capacity of 10 t/h and more will be available in the near future. However, these plants are demonstration or pilot plants and BTG-BTL has not constructed any fully commercial plant. (BTG 2009)

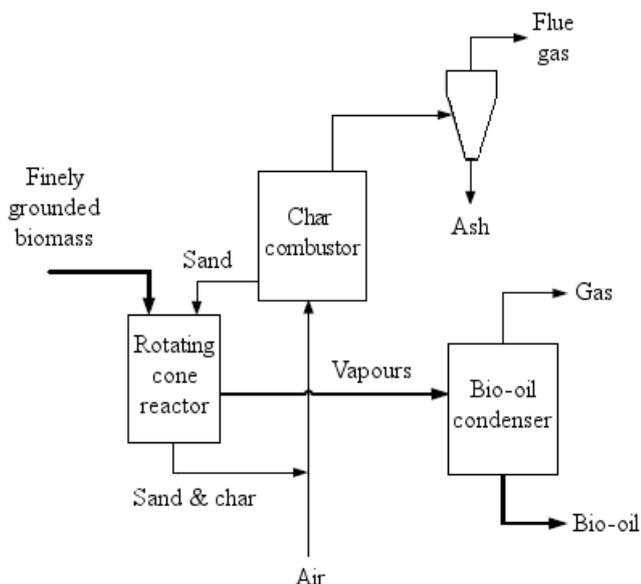


Figure 28. BTG fast pyrolysis technology (Evans 2007).

Dynamotive Energy Systems Corporation has a patented bubbling fluidised bed reactor technology for pyrolysing biomass. The company has developed bench-scale plants, feedstock capacity of 15 t/d pilot plant, and 130 t/d and 200 t/d commercial plants located in Canada. In the process 1–2 mm particle size and <10% moisture content feedstock is heated to 450–500°C in the absence of oxygen. Char is separated from produced gases in a cyclone. Then the gases are quickly cooled in a quench tower and condensed bio-oil is collected. The non-condensed gases are returned to the reactor to maintain the process heating. Hard and soft wood as well as lignocellulosic biomass from other plants and agricultural residues have been tested as a feedstock material for the process and depending on the feedstock composition the yields are 60–75% bio-oil, 15–20% char, and 10–20% non-condensable gases. (Dynamotive 2009)

Dynamotive has also developed an upgrading technology for refining bio-oil into mobile fuels. The first stage in this technology is hydroreforming of bio-oil to liquid that can be used in blends with hydrocarbon fuels as an industrial fuel. The hydroreformed oil contains still about 10% oxygen and needs further treatment to convert it to motor fuel grade products. Therefore, the second stage is further hydrotreating the oil with a commercial catalyst to produce transportation grade hydrocarbon fuels. (Dynamotive 2009)

## 7.2 Industrial applications of gasification

Commercial heat gasifier applications were recorded first in 1830. In 1880, the producer gas was used to generate electricity and, during World War II, there were millions of biomass gasifiers for heat, power or vehicle fuel production globally. However, the availability of relatively inexpensive petroleum fuels has slowed down the development of gasifiers in recent decades and though several gasifier manufactures sell small-scale biomass gasification systems, the actual number of such commercial units installed is quite small. In recent years, most of the gasifiers in operation are located in India and China where they are used for power generation from wood and rice husk. (Stassen 1995)

Gasification is a commercial and mature technology and there are numerous companies working in that area and offering various gasification concepts. However, the number of reference plants in operation in biomass gasification is quite limited and, generally, there are only few commercial technology providers focusing on small-scale biomass gasifiers. Table 6 presents some gasification technology suppliers and the technology they offer.

In addition to the companies presented in Table 6, CHOREN Industries has patented a three-stage gasification process named Carbo-V<sup>®</sup>. In the process dried and shredded biomass is feed into a low temperature (400–500°C) gasifier where it is broken down into tar-rich volatiles and solid char. The second-stage of the process is a high temperature gasification of volatiles. The ash particles melt at temperatures above 1400°C and long chain hydrocarbons are broken down to CO and H<sub>2</sub> resulting in tar-free gas. In the third stage of the Carbo-V<sup>®</sup> process, the pulverised char is blown into the hot tar-free gas from the second stage of the process. The char and the gas react endothermically in the gasification reactor and are converted into a raw synthesis gas. After dust removal the gas is fed via a gas shift reactor to a scrubber to wash out contaminants such as sulphur and chlorine. (CHOREN 2009)

Table 6. Some gasification technology suppliers with their technology type and scale (Austerman & Whiting 2007).

Supplier	Country	Scale	Technology
AHT Pyrogas Vertriebs	Germany	50–500 kW <sub>e</sub>	Fixed bed (proprietary design)
Babcock & Wilcox Vølund	Denmark	200kW <sub>e</sub> –10MW <sub>e</sub>	Fixed bed (updraft)
Biomass Engineering	UK	250 kW <sub>e</sub> modules (3MW <sub>e</sub> maximum)	Fixed bed (downdraft)
Energy Products of Idaho	USA	6 MW <sub>e</sub>	Bubbling fluidised bed
Eqtec Iberia	Spain	250kW <sub>e</sub> –150MW <sub>e</sub>	Bubbling fluidised bed
Host	Netherlands	30kW <sub>e</sub> –5MW <sub>e</sub>	Fixed bed and circulating fluidised bed
ITI Energy	UK	1.5–1.9MW <sub>e</sub>	Fixed bed (proprietary design)
Martezo Renewable Energy	France	70kW <sub>e</sub> –1MW <sub>e</sub>	Fixed bed (co-current)
PRM Energy Systems Inc.	USA	225kW <sub>th</sub> –1MW <sub>e</sub>	Fixed bed (updraft)
ProCone Gasification System	Switzerland	>2.5MW <sub>e</sub>	Fixed bed (various designs)
Puhdas Energia Oy	Finland	250–1000kW <sub>e</sub>	Fixed bed (downdraft)
Repotec Umwelttechnik	Austria	2–5MW <sub>e</sub>	Circulating fluidised bed
Xylowatt	Belgium	300kW <sub>e</sub> (+multiples thereof)	Fixed bed (downdraft)

The synthesis gas can be then used as combustible gas for producing steam, heat and electricity. The other way is to use Fischer-Tropsch synthesis to convert the gas into liquid hydrocarbon fuels. CHOREN commissioned a plant producing 15,000 t/a of synthetic biofuel in 2007 in Germany. Currently they are optimising the process and planning an industrial-scale plant with an annual capacity of 200,000 t of synthesis biofuel. (CHOREN 2009)

### 7.3 Industrial applications of torrefaction

In France the company Pechiney built a demonstration plant in 1987 to produce a reduction agent for the production of aluminium, but the plant suffered from low energy efficiency and was closed in the beginning of the 1990's for economic reasons. The Pechiney process had 12,000 t/a production capacity, the required capital investment nearly 3 M€ and the total production costs over 100 €/t. This reactor technology is expensive and it has poor scale-up characteristics, and the developing of this kind of

torrefaction technology is finished. However, the Pechiney plant can be considered as state-of-the-art of torrefaction technology. (Bergman et al. 2005)

Torrefaction combined with pelletisation may assist logistics problems observed with untreated biomass. Torrefaction and pelletisation (TOP) process produces high energy density containing pellets. These pellets have energy density in the range from 15 to 18.5 GJ/m<sup>3</sup>, compared with wood pellets range 8 to 11 GJ/m<sup>3</sup>. Therefore the transportation cost can be reduced significantly compared to wood pellets, especially in long distance transportation. TOP pellets may be used for house-heating applications made for wood pellets, but there is no research of their suitability for them. (Bergman & Kiel 2005)

The TOP process is under development at ECN in the Netherlands. The commercial scale is expected to be 60,000–100,000 t/a of product while the general wood pelletisation scale is 80,000–130,000 t/a. The scale up characteristics of drying limits the total process scale up. The total capital investment of the TOP technology for a capacity of 60,000 t/a of product is estimated to be 5.5 to 7.5 M€ and the total production costs 40 to 50 €/t TOP pellets. (Bergman & Kiel 2005)

The Pechiney process was indirectly heated while the TOP process is based on direct biomass heating and recycled hot torrefaction gas. The hot gas is re-pressurised and heated after each cycle. The TOP process may also use a utility fuel when the torrefaction gas contains little energy. The TOP process is approved to be very promising for torrefaction. (Bergman & Kiel 2005)

## **7.4 Industrial applications of liquefaction**

Direct liquefaction of biomass is not yet fully-commercial technology though several demonstration and pilot plants exist and there has been intensive research in this area. The PERC process (Pittsburgh Energy Research Center) is a wood chips using liquefaction process developed after the crude oil crisis. The residence time in the process is 10 to 30 min, temperature from 330 to 370°C, and pressure about 200 bar. The process requires a gas mixture consisting of CO<sub>2</sub> and H<sub>2</sub> produced by gasification

of biomass. The development of the PERC process is abandoned because of economic reasons. (Behrendt et al. 2008)

The LBT process (Lawrence Berkeley Laboratory), also developed after the crude oil crisis, starts with the hydrolysis of biomass with sulphuric acid. The liquefaction takes place at pressures from 100 to 240 bar and temperatures between 330 and 360°C. Alkali carbonate is added to produce hydrogen in the presence of water and CO<sub>2</sub> (water gas shift reaction). The product oil is a liquid material similar to bitumen. The development of this process has been abandoned because of economic reasons. (Behrendt et al. 2008, Behrendt et al. 2006)

The BFH process (Bundesforschungsanstalt für Forst- und Holzwirtschaft) was developed in the 1980s and based on catalytic hydrogenolysis using hydrogen, catalysts, and oil. A fast heating of the aqueous solvent and a fast cooling of the reaction mixture is enabled by the reactor system consisting of 3 linked autoclaves. Hydrogen as the reducing agent and oil recycled from the hot gas separator is dosed to the first autoclave. The resulting products are fed to the hot gas separator and then charged into the cooling system to expand. Palladium is used as a catalyst. The development of the BFH process was stopped due to the better prospects of using flash pyrolysis. (Behrendt et al. 2008, Behrendt et al. 2006)

Hydrothermal upgrading (HTU) process is a promising method to convert biomass into biofuel. The process is specially designed for wet organic materials, such as residues from agriculture, forestry, food processing industry, since no drying of feedstock is needed. The process occurs in liquid water in a temperature range of 300–350°C and a pressure range of 10–18 MPa (100–180 bar), with a reaction time of 5–15 minutes. The product of the HTU process is biocrude with the lower heating value of 30–35 MJ/kg. The oxygen content of the feedstock material is reduced from 40% to 10–15% during the process, and the removed oxygen ends up in CO<sub>2</sub>, H<sub>2</sub>O and CO. (He et al. 2008, Goudriaan et al. 2000, Naber et al. 1999)

After the HTU reactor, water and gases need to be separated from the produced biocrude. Furthermore, the biocrude will separate into light and heavy fractions by flashing or extraction. The heavy fraction can be co-combusted in coal or oil fired

power stations. The light fraction contains no minerals and can be upgraded by catalytic hydrodeoxygenation (HDO) and then used as high quality transport fuel. (Goudriaan & Naber 2005, Koppejan 2004)

The basis of the HTU research carried out in the 1980's in the Shell Laboratory in Amsterdam, The Netherlands, and continued in the 1990's with financial support from the Dutch Government. Shell has also made the HTU process a registered trademark, HTU<sup>®</sup>. A pilot plant has been operated with the feedstock of 10 kg/h (dry basis), which means 100 kg/h on wet basis, and the production of biocrude is about 8 kg/h. The commercial demonstration plant with capacity of 10,000 t(dry basis)/a should have started in Amsterdam in 2009, and HTU diesel is expected to be commercial shortly. (Goudriaan et al. 2000, Naber et al. 1999, Goudriaan & Naber 2005)

The DoS (Direct Liquefaction of Organic Substances) process was developed by Hochschule für Angewandte Wissenschaften Hamburg. It is a one-step bottom phase crack process for lignocellulosic biomass working under a pressure of about 80 bar and at temperatures between 350 and 500°C. The DoS process is based on fast pyrolysis followed by solvolysis into product oil. Vaporous product oil is separated from water over the gas/vapour phase and after condensation, gas separation and expansion, it is fed to the cascade distillation for fractionation. A DoS pilot plant is under construction. (Behrendt et al. 2008, Behrendt et al. 2006)

A patented B/M process for biomass to produce liquid hydrocarbons using a catalyst was developed by Stefan Bothur in 1999. The process is based on solvolysis. The process pressure is about 6 bar and the temperature about 200°C and biomass is treated in a melt of potassium carbonate hydrate (30% water). The process mainly consists of decomposition of molecules, disproportioning, and salification of the functional groups. The solution consists of ions of organic salts. Organic compounds are separated using a column. (Behrendt et al. 2008, Behrendt et al. 2006)

The LTC process (Low Temperature Conversion) has been developed by Stadlbauer at the Giessen-Friedberg University of Applied Science. The process operates in the absence of oxygen at atmospheric pressure and temperatures between 350–400°C in the presence of a catalyst. Sewage sludge, meat and bone meal, tar sands, animal fats and

fat residues, and plastic material have been applied as feedstock. The process utilises a heterogeneous catalytic reaction between organic gases from the biomass and the catalyst. The product oils have comparable physical and chemical properties as diesel fuel. (Behrendt et al. 2008)

Liquefaction processes for certain plastics have also been developed. Ozmoenergy/Ozmotech Pty Ltd. has patented a conversion process producing 'Thermofuel' from plastics and heavy oils. The capacity of their plant is 10–40 t/d and it can produce about 1 dm<sup>3</sup> of oil from 1 kg of plastics. Gossler Envitec GmbH uses a heterogeneous catalyst at ambient pressure to produce oils from plastic waste in two pilot plants. The first plant has a capacity of 3,000 t/a in Korea and the second plant 3,500 t/a in Germany. Clyvia Technology GmbH has designed the CL500 process to convert plastics to oils at a pilot plant with a capacity of 4,000 t/a since mid 2006 in Germany. (Behrendt et al. 2008)

Maybe the most advanced of the available vegetable oil hydrogenation processes is the NExBTL process developed by Neste Oil. Annually 170,000 tonnes of diesel producing plant has been in operation since 2007 in Finland. In the process, fatty acids from vegetable oils and animal fats are hydrotreated in a high pressure two stage process over conventional hydrodesulphurisation catalysts. The NExBTL diesel product is a paraffinic hydrocarbon which is free of oxygen and aromatics compounds. (Evans 2007)

## **7.5 Industrial applications of fermentation**

First-generation biofuels are produced commercially in several plants throughout the world. In Brazil ethanol production from sugar cane is common, while in the USA corn and other starch crops are used for ethanol production. In Europe wheat and other grain crops are common raw materials for producing ethanol. However, food crops are not most sustainable feedstock for biofuels production and investments in second-generation biofuels production is growing. (Wyman 1996, Abengoa Bioenergy 2008)

The first demonstration plant producing second-generation biofuels was taken in operation by Iogen Corporation in Canada in 2004. The plant is designed to produce clean-burning cellulosic ethanol fuel using agricultural residues, mainly wheat straw, as

feedstock. At full capacity, the feedstock is about 20–30 tonnes per day and cellulosic ethanol production is about 5,000–6,000 dm<sup>3</sup> per day. For a month in 2009, a 10% cellulosic ethanol blend had been sold to the general customers at a retail service station. (Iogen Corporation 2009)

In the Iogen process (Figure 29), biomass is first pre-treated via modified steam explosion process. The pre-treatment increases the surface area, improves ethanol yields, and reduces overall costs. Then, in enzymatic hydrolysis, cellulose is converted into glucose with the assistance of cellulase enzymes. In ethanol fermentation the sugars are converted into ethanol, and the produced ethanol is then distilled using conventional technology to meet the high quality requirements. Energy efficient heat integration, water recycling, and co-product production are included to make the overall process efficient and economic. (Iogen Corporation 2009)

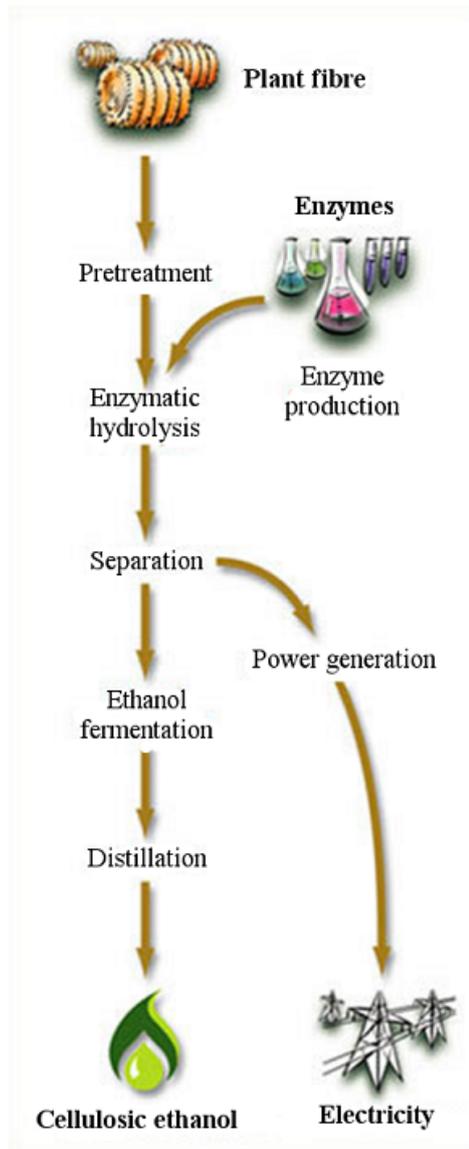


Figure 29. Iogen's cellulosic ethanol demonstration plant: the process. Lignin is used for power generation. (Iogen Corporation 2009)

Etek Etanolteknik AB (nowadays The SEKAB Group) opened a pilot plant for technology development of ethanol production from cellulose raw material in 2004 in Sweden. Softwood residues from harvesting or from sawmills are the main feedstock. The plant has a feedstock capacity of 2 tonnes of dry substances per day and yield of ethanol is about 400–500 dm<sup>3</sup> per day (which is about 150,000 dm<sup>3</sup> per year). Diluted acid hydrolysis process in two steps or diluted acid combined with enzymes in a third step have shown the high yields of ethanol. (Fransson & Lindstedt 2005)

The planning of a commercial production plant is in the process. The capacity of the plant was set to about 75,000,000 dm<sup>3</sup> of ethanol per year, while the investment costs

were calculated to about 120 million Euros. The investment costs of the present pilot plant was about 16 million Euros and the annual running cost about 1.5–2 million Euros. The produced ethanol is not yet sold on the market. The solid residue from the process is mainly lignin, which can be used as fuel for gas turbines or as an incineration additive. Advantages of the residue are low alkali content and high energy value, 6.2 MWh/odt. (Fransson & Lindstedt 2005)

Abengoa Bioenergy commissioned a commercial demonstration plant using agricultural residues, mainly wheat straw, as a feedstock in 2008 in Spain. The plant is integrated to existing fermentation plant using crops, mainly wheat, as a feedstock. The processing capacity is 70 tonnes biomass per day as feedstock and the plant produce about 5 million dm<sup>3</sup> of ethanol per year. In the process, the biomass feedstock is first milled and cleaned, and then pre-treated with a catalyst and steam. After that biomass is digested by enzymes to release sugars, and fermented by yeast to ethanol and carbon dioxide. After distillation the produced ethanol can be used as high quality fuel, and the solid residue can be utilised as animal feed or to recover chemicals, for example. (Abengoa Bioenergy 2008)

In Finland, St1, together with VTT, has developed and patented an Etanolix<sup>®</sup> concept, which basis is a small-scale bioethanol production from food industry wastes and side streams locally. 85% bioethanol is produced from certain food industry wastes and side streams in several plants. Concentration to 99.8% ethanol takes place in a dehydration plant in Hamina, and after that bioethanol is ready to be blended with gasoline. (St1 2009)

The first plant using this concept opened in 2007 in Lappeenranta utilising by-products from local bakery and confectionery industries. The capacity is about 5,000 tonnes of dough as a feedstock, producing bioethanol about 1 million dm<sup>3</sup> annually. In 2008, St1 opened bioethanol plants in Närpiö and Hamina. The plant capacity in Hamina is 5,000 t of bakery wastes and side streams as a feedstock and production of bioethanol is 1 million dm<sup>3</sup> yearly. The plant in Närpiö is integrated to a local potato flake factory and uses its wastes and side streams as a feedstock. The capacity of the plant is 20,000 tonnes of potato wastes producing 1.4 million dm<sup>3</sup> bioethanol per year. (St1 2009)

In 2009 St1 is opening bioethanol plants in Vantaa and in Lahti. The plant in Vantaa will utilise bakery wastes producing around 1 million  $\text{dm}^3$  bioethanol yearly. The plant in Lahti is integrated to a beverage factory and uses its wastes and side streams. St1 is also constructing a Bionolix™ concept plant in Hämeenlinna. The plant will be using 15,000 tonnes municipal biowastes as a feedstock and producing 1 million  $\text{dm}^3$  bioethanol annually. St1 is also developing technologies which can utilise cellulosic raw material, for example straw and other agricultural residues, municipal solid waste (MSW), and various packaging wastes. (St1 2009)

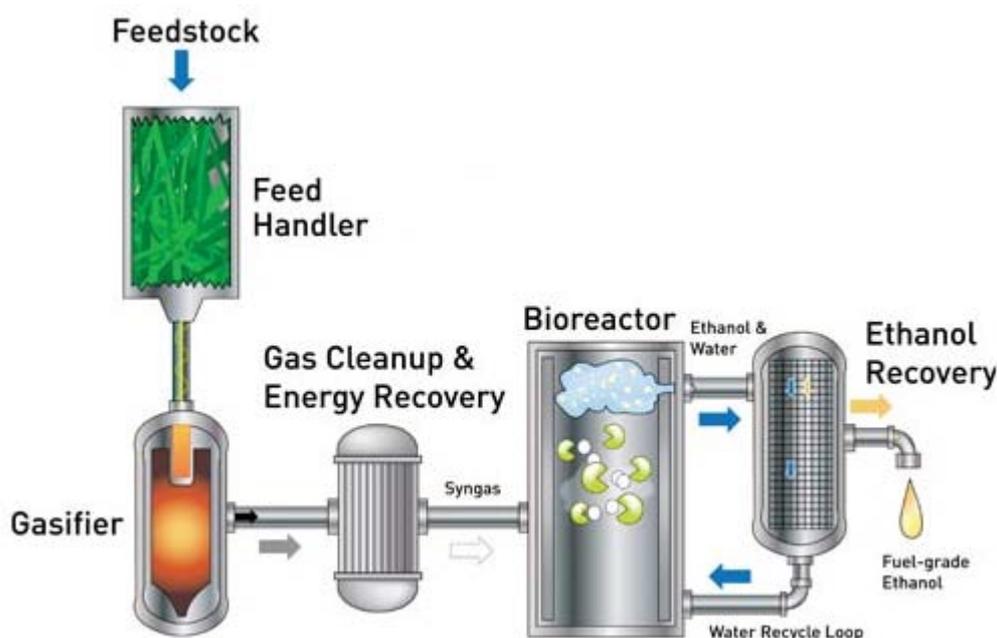


Figure 30. Combined gasification and fermentation process (Corskata 2009).

Corskata has a slightly different approach for fermentation of lignocellulosic raw materials. Using gasification as a pre-treatment method which breaks the chemical bonds, micro-organisms convert the resulting syngas into ethanol (Figure 30). Costly enzymatic pre-treatment is not needed because of the gasification pre-treatment, and fermentation can occur at lower pressures and temperatures reducing operational costs. The resulting ethanol is recovered from the solution using membranes. Corskata is commercialising the technology. (Corskata 2009)

## 7.6 Industrial applications of anaerobic digestion

Anaerobic digestion technology was originally developed for low solids applications in the wastewater treatment sector. Currently more than 2000 anaerobic digestion facilities are operating with sewage sludge as the primary feedstock. That represents the largest share of installed capacity around the world while wastewater from industrial processes is the second largest share. Over the past decade there has been a growing interest towards the use of anaerobic digestion for certain types of commercial, industrial, and municipal solid wastes. (Austerman et al. 2007)

Austerman et al. (2007) have made a list from certain anaerobic digestion technology providers for biomass feedstocks (Table 7). The list is suggestive, mainly because the development goes very fast. Enterprises in the list may have changed their names, merge with other enterprises, their technology is not fully commercialised, or they may have ceased trading, for example. In the list the enterprises that concentrate only on wastewater treatment are not presented.

Table 7. Anaerobic digestion technology providers (Austerman et al. 2007).

Company	Country	Company	Country
AAT Abwasser- & Abfalltechnik	Austria	Krieg & Fischer	Germany
Active Compost	UK	Krüger	Denmark
ADI Systems	Canada	Larsen Engineering	USA
Agri Waste Technology	USA	Lipp	Germany
Agri-Biogassystems	USA	Linde KCA	Germany
Alkane Biogas	UK	Lotepro Environmental Systems	USA
Alpha Umwelttechnik	Switzerland	MAT Müll- und Abfalltechnik	Germany
AnDigestion	UK	MCX Environmental Energy Corp.	USA
ARCADIS	Netherlands	MT-Energy	Germany
ArrowBio	Israel	Nelleman, Nielsen & Rauschenberger (NNR)	Denmark
Bedfordia Biogas	UK	Newbio NBE	USA
BEG Bioenergie	Germany	NIRAS	Denmark
Bekon Energy Technologies	Germany	Novatech	Germany
BioFerm	Germany	Oaktech	UK
Biogas Nord	Germany	Onsite Power Systems	USA

Table 7 continues...

BiogaS int	Netherlands	Organic Power	UK
Bioplan	Denmark	Organic Resource Technology	Australia
Bioplex	UK	Organic Waste Systems	Belgium
Bioscan	Denmark	OrgaWorld	Netherlands
Biotech Sistemi	Italy	Oswald Green	USA
Biotechnische Abfallverwertung (BTA)	Germany	Oswald Schulze	Germany
Brouwers BioEnergy	Netherlands	Paques	Netherlands
BRV Biowaste Technologies	Switzerland	Pinnacle Biotechnologies Int.	USA
Burmeister & Wain Scandinavian (BWSC)	Denmark	PlanET Biogastechnik	Germany
Cambi	Norway	Projectrör	Sweden
CG Jensen - AN biotech	Denmark	Proserpol	France
Citec	Finland	Purac AB	Sweden
Clarke Energy / Clarke Haase	UK	Purac Ltd	UK
DSD Gas und Tankanlagenbau	Germany	RCM	USA
EcoCorp Inc.	USA	RefCom	USA
Eco-Technology JVV (EcoTec)	Finland	Ros Roca	Germany
Energy Group Jutland	Denmark	Risanamento Protezione Ambiente	Italy
Enpure	UK	Reliant Technical Services, RTS	UK
Entec Umwelttechnik	Austria	Schmack	Germany
Entek BioSystems	USA	Schradenbiogas	Germany
Enviro-Control Ltd	UK	Schwarting Umwelt	Germany
Environmental Energy Corp.	USA	Sharp Energy	USA
Farmatic Anlagenbau	Germany	Seghers Keppel	Belgium
Farmatic Biotech Energy	Germany	Strabag	Austria
Farmatic Biotech Energy UK	UK	Sustainable waste systems	UK
Gas & Technology Institute (GTI)	USA	Super Blue Box (SUBBOR) Recycling Corp.	Canada
GBU	Germany	Thöni Industriebetriebe	Austria
Global Renewables	Australia	TBW	Germany
Greenfinch	UK	Umwelt Technik Süd	Germany
Grontmij Vandenbroek International	Netherlands	Unisyn Biowaste Technology	USA
Haase	Germany	Valorga	France
Harvestore Deutschland	Germany	Van Boekel Zeeland BV	Netherlands

Table 7 continues...

Hese	Germany	Vinci	France
Horstmann	Germany	Weda UK	UK
Ibtech	Mexico	Wehrle Umwelt	Germany
Ionics Italba SpA	Italy	Weltec	Germany
ISKA	Germany	Xergi	Denmark
Jysk Biogas	Denmark	YIT	Finland
Kompogas	Switzerland		

Table 8 lists some enterprises providing anaerobic digestion technology. The scale ranges from laboratory scale to over 200,000 tonnes feedstock per year. Table 8 also indicates if the technology they are offering is based on wet or dry, mesophilic or thermophilic, and 1-stage or 2-stage technology. Generally, wet, mesophilic, single-stage anaerobic digestion systems are the most common.

Table 8. Some anaerobic technology providers with offered technology types (Austerman et al. 2007).

Company	Wet	Dry	Mesophilic	Thermophilic	1-stage	2-stage
ArrowBio	Yes	-	Yes	-	-	Yes
BEKON	-	Yes	-	Yes	Yes	-
Biogas Nord	Yes	-	Yes	Yes	-	Yes
Bioscan	Yes	-	Yes	Yes	Yes	-
BTA	Yes	-	Yes	Yes	Yes	Yes
BWSC	Yes	-	Yes	Yes	Yes	-
Citec	Yes	-	Yes	Yes	Yes	-
Greenfinch	Yes	-	Yes	-	Yes	-
Haase	Yes	-	Yes	-	-	Yes
Hese	Yes	Yes	Yes	Yes	Yes	-
Kompogas	-	Yes	-	Yes	Yes	-
Linde	Yes	Yes	Yes	Yes	Yes	-
MT Energie	Yes	-	Yes	-	-	Yes*
Organic						
Power	Yes	-	Yes	-	-	Yes*
OWS	-	Yes	-	Yes	Yes	-
RCM	Yes	-	Yes	-	Yes	-
Ros Roca	Yes	-	Yes	-	Yes	-
Schmack	-	Yes	Yes	Yes	-	Yes
Valorga	-	Yes	Yes	Yes	Yes	-
Weda-GB	Yes	-	Yes	-	Yes	-
Xergi	Yes	-	Yes	Yes	-	Yes

\*multi-stage

Kuittinen & Huttunen (2009) have collected information from biogas reactor plants which have been in operation in Finland at the end of 2008. According to them, altogether 33 landfill biogas recovery plants, 15 biogas reactor plants at different municipal wastewater treatment plants, 8 biogas plants at different farms, 3 biogas plants treating organic solid wastes, and 3 biogas plants at different industrial wastewater treatment plants operating in Finland. (Kuittinen & Huttunen 2009)

Industrial wastewater treatment plants are at Chips Oy Ab in Godby, at Apetit Suomi Oy in Säkyliä, and at Stora Enso Oyj in Kotka. Chips Oy Ab has a potato processing factory the wastewaters of which are digested anaerobically in 2,000 m<sup>3</sup> biogas reactor, with most of the produced biogas being utilised in heat production while a small part is flare combusted. Apetit Suomi Oy has a food processing factory with anaerobically functioning wastewater treatment plant. The biogas is sold for steam production purposes for a power plant. Stora Enso's paper mill in Kotka has treated biomass in anaerobic wastewater treatment plant. (Kuittinen & Huttunen 2009)

Biogas plants treating organic solid wastes at the end of 2008 are in Mustasaari, Laihia, and Vehmaa. In Stormossen plant in Mustasaari 14,400 t of sewage sludge and 9,000 t of biowastes are treated annually in an anaerobic digestion plant to produce biogas for heat and power generation. Also biogas from the old Stormossen landfill is piped to a heating plant. Laihia town owns a 310 m<sup>3</sup> biogas reactor plant. The plant uses 300 t source segregated municipal biowastes, 1,000 t sewage sludge, 1,000 t malt sludge from malt factory, and some grain drying waste. (Kuittinen & Huttunen 2009)

Biovakka Suomi Oy is a company which offers anaerobic digestion plants for producing biogas from organic solid wastes, manures, and sludges. Biovakka's biogas plants exist already in Vehmaa and in Turku, and several new plants are planned. Vehmaa plant, started in 2004, treats manure as the main feedstock and smaller amounts of municipal and industrial biowastes. Turku plant uses sewage sludge as raw material and has been operated since 2009. The capacity of each plant is 4 MW and 120,000 tonnes feedstock per year. Currently the biogas is used to produce heat and electricity but biogas upgrading to pure methane and utilising as vehicle fuel is under development. (Biovakka 2009)

## 8 Technology cards

For the purposes of the MicrE project, technology cards were made reviewing the main technologies which are commercially available and on scale fitting the northern periphery area. The technology cards are represented in Appendices 1–5. These cards can also be used to introduce different workable technologies to the enterprises and local organisations.

The cards have been made for the following technologies: gasification, pyrolysis, anaerobic digestion, fermentation, and pelletisation. Combustion was left out because it is a common and well-known technology. Also torrefaction, liquefaction, and composting were left out. Torrefaction is more a pre-treatment and large-scale technology, liquefaction is a demanding large-scale technology, and composting, while a very common and widely used, is not appropriate to efficient energy production.

Each card represents the main issues from the technology in the general part. There are also pictures which explain the technology. On the reverse side of the cards, technical specifications are listed. Each card should express input (i.e. feedstock), output (products and by-products), process requirements and characteristics, and possible uses for products and by-products. In addition, scale, production costs, and safety issues may be marked.

The main characteristics from combustion, pyrolysis, gasification, torrefaction, liquefaction, fermentation, anaerobic digestion, and pelletisation are presented in Table 9.



Table 9. Characteristics of biomass-to-energy technologies (Austerman et al. 2007, Austerman & Whiting 2007, Behrendt et al. 2008, Bergman & Kiel 2005, McKendry 2002c, Soltes 1987, Uslu et al. 2008, Ward et al. 2008 & Wisbiorefine 2004b, Kelleher et al. 2002).

	Combustion	Pyrolysis	Gasification	Torrefaction	Liquefaction	Fermentation	Anaerobic digestion	Pelletisation
Input (limiting factors)	Moisture <50%	Moisture <45% Ash <25%	Moisture <45% Ash <15%	Moisture <50%	Presence of hydrogen	Homogenous input, Nutrients, pH, Moisture	Total solids 4–40%	Moisture <25% Particle size <20mm
Temperature	>800°C	400–800°C	650–1200°C	230–280°C	200–500°C	15–60°C	Optimum 35°C or 55°C	150°C
Pressure	Atmospheric	Atmospheric	Atmospheric	Atmospheric	6–240 bar, depends on catalysts	Atmospheric	Atmospheric	Depends on input
Oxygen requirements	Excess of oxygen	Absence of oxygen	Partial oxidation	Absence of oxygen	Absence of oxygen	Depends on microbes	Absence of oxygen	Ambient
Output (useful)	Heat	Pyrolysis oils	Syngas	Torrefied biomass	Oils	Alcohol	Biogas	Pellets
Output (others)	Ash	Gases, char	Char	Gases	Gases, solid residue	Reject, gases, water	Reject, water	Dust
Purification of the product	No	Oxygen removal	Particulates and tars removal	No	Oxygen removal	Water removal	Moisture removal	Dust removal

## 9 Discussion and conclusions

The aim of this study was to collect information from different biomass-to-energy solutions and evaluate their suitability to small-scale energy production in northern periphery areas. Also technology cards were made for this purpose.

The conversion of biomass to energy can be done via thermo-chemical, biochemical, mechanical, chemical, or electro-chemical process routes. From these the mechanical, chemical and electrochemical conversion technologies are suitable only for few biomass materials. Different thermo-chemical and biochemical conversion technologies are appropriate to the wide range of biomass. For relatively dry wood and herbaceous biomass thermo-chemical conversion methods are most applicable. Biomass with a high moisture content can relatively ineffectively be converted into energy in the thermo-chemical techniques and the biochemical conversion technologies are more suitable.

Combustion is an ancient and very common technology for heat production purposes but not effective to generate electricity in small scale. Fuels can not be produced from biomass through direct combustion either. Pyrolysis is going to be commercial in large scale but there are still various problems. The product, pyrolysis oil, is challenging to upgrade to the quality of transport fuel. The oil can be used for combined heat and power production but the overall efficiency of the pyrolysis process is quite low.

Gasification has long been a commercial technology but the number of gasification plants in operation is currently quite limited. The product gas can be used to combined heat and power production or as transportation fuel in special vehicles, or it can be processed further to liquid transportation fuels. Torrefaction is a quite new technology and, at the present, there is no commercial plant in operation. Few research groups are planning torrefaction plants but the commercial scale of torrefaction plant seems to be relative large. However, torrefaction is a pre-treatment technology and can not directly produce heat, electricity or transportation fuels.

Liquefaction is a quite demanding large scale technology with high temperatures and pressures. Using catalysts will reduce temperature and pressure needed in the process. Heat, electricity and transportation fuels can be produced via liquefaction.

Fermentation from first-generation raw materials is a commercial technology but competes with food production. Second-generation fermentation from wood and herbaceous raw material starts to be commercial technology in large scale. The produced alcohol can be used for heat and power production and preferably as transportation fuel. Anaerobic digestion is a fully commercial technology and is suited well to energy production from biomass based wastes. The produced biogas can be utilised as transportation fuel or via heat and power production.

Composting is a widely used and common technology also in small scale but produces only a little heat and therefore is not suitable for energy generation. Pelletisation is a commercial and used method to densify woody and herbaceous biomass for lower transportation and storing costs.

Generally, the conversion technologies producing energy in small-scale and being commercial at the present are most suitable for the northern periphery areas. Also inexpensive and simple construction is an advantage. Occasionally plants with capacities of few MW can be defined as small-scale but these plants are industrial sized and thus people in rural areas are frequently opposed to the plants.

Gasification and anaerobic digestion are, in general, the most suitable technologies for northern periphery conditions, each with different feedstock requirements. Anaerobic digestion is excellent technology to produce energy from wastes easily also in very small scale while gasification is maybe a slightly more demanding technology in small-scale with special feedstock requirements.

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