Global Assessment of Biomass and Bioproduct Impacts
on Socio-economics and Sustainability

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Identification of current and future industrial and small scale conversion chains

WP 3 – Task 3.1

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1   INTRODUCTION

In this report current and future industrial and small-scale conversion chains are identified for a number of biomass feedstock. The report corresponds to task 3.1 and as part of deliverable D 3.1 of the Global-Bio-Pact project (www.globalbiopact.eu).

The following approach is used:
- Biomass can be used for the production of: (1) food and feed, (2) bioproducts, (3) biofuels, and/or (4) energy (heat and electricity). This paper covers conversion chains for the production of biofuels and/or bioproducts, possibly in combination with energy, food and feed production. However, conversion chains solely directed to the production of food and feed fall outside the scope of this report.
- Depending on the structure and composition of the biomass (oil, starch, sugar, lignocellulose) different conversion routes can be used to produce energy (heat, electricity), biofuels, and/or bioproducts. Therefore, a distinction is made between conversion chains based on (1) oil containing biomass, (2) sugar and starch biomass, and (3) lignocellulosic biomass.
- Current biomass conversion technologies are described in chapter 2, covering mainly commercially available technologies. For each conversion technology the (expected) commercial scale of production is described.
- The distinction between small and industrial scale has been made according the following working definition (based on BTG's experience with biomass conversion chains)[1]:
  - micro (household) scale < 1 MW$_{th\ input}$, < 0.25 MW$_{e,\ output}$ and/or < 500 tonnes $_{product}$
  - small scale: 1- 20 MW$_{th\ input}$, 1-5 MW$_{e,\ output}$ and/or < 0.5-10 ktonnes $_{product}$
  - medium industrial scale: 20-200 MW$_{th\ input}$, 5-50 MW$_{e,\ output}$, and/or 10-100 kton $_{product}$
  - large industrial scale: >200 MW$_{th\ input}$, >50 MW$_{e,\ output}$, and/or >100 kton $_{product}$
- Future conversion chains are described using the concept of biorefineries, thereby covering a whole range of integrated biofuel, bioproduct and bioenergy production installations. Different types of biorefineries are described in chapter 3.
- In chapter 4 relevant conversion chains are selected for further analysis in the case studies and in task 3.2 of the Global-Bio-Pact project.

The report has the following purposes:
- Providing the reader with an overview of current and future conversion technologies and their scale of application.
- Offer background information for the selection of the case study on 'Socio-economic impacts of large-scale second generation conversion technologies in EU/North America).

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[1] These capacities are indicative and roughly comparable; for energy applications the electric or thermal capacity can be used; for liquid and solid fuels the capacity can be expressed in kilo tonnes per year. Example: 10,000 tonnes biomass with 15 GJ/ton corresponds to 20 $_{MWthermal\ input}$, or 5 $_{MWe\ output}$ at an electric efficiency of 25% and 7,500 production hours per year.

- Select current and future conversion chains for further analysis in task 3.2 of the Global-Bio-Pact project.

2   CURRENT BIOMASS CONVERSION CHAINS

2.1   Classification of biomass resources

Biomass consists of a large variety of wastes, residues and crops that can be used for the production of solid, liquid and gaseous energy carriers and products.

Biomass can be defined as '*the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste*' (2001/77/EC 2001).

Biomass can be classified according to its sector of origin, like forestry, agricultural and waste sectors; or to the way it is released: main crops, primary harvest residues, secondary processing residues and tertiary residues after end use. In this paper, the following classification based on the composition of the biomass will be used:

- Oil containing biomass
- Sugar and starch biomass
- Lignocellulosic biomass
    - woody biomass
    - grassy biomass

Oil containing biomass
Oil containing biomass includes common agricultural crops like rape, sunflower, and soy, as well as Jatropha, an oil-containing non-food crop that can survive on poor soils under dry conditions. Furthermore, used frying oil, animal oils and fats and fat containing algae can be added to the list. The oils have a high energy content of 32-40 GJ/ton. Traditionally vegetable oils are mainly used for food applications. Oils can also be used as input material for biodiesel production, biogas production and direct combustion.

Sugar and starch biomass
Sugar and starch biomass includes agricultural commodities like sugar beet, sugar cane, corn, wheat, potatoes, etc. Sugar and starch crops have an energy content of 17-18 GJ/ton. Their main application is in food, but technical applications like glue, adhesive, pharmaceutical applications etc. are common as well. Sugar and starch are also commonly used for ethanol production and derived chemicals.

Lignocellulosic biomass
Lignocellulosic biomass refers to plant biomass that is composed of cellulose, hemicellulose, and lignin. Lignocellulosic biomass can be grouped into four main categories:
- wood residues (including sawmill and paper mill discards),
- agricultural residues (including corn stover and sugarcane bagasse),
- dedicated energy crops (including wood plantations and grasses), and

- end-of-life biomass waste (including demolition wood and the organic fraction of municipal waste).

Lignocellulosic biomass is expected to play a key role as cheap input for new conversion technologies for the production of liquid biofuels and bioproducts. It has three primary components: cellulose, hemicellulose and lignin.

- Cellulose has a strong molecular structure made from long chains of glucose molecules.
- Hemicellulose is a relatively amorphous component that is easier to break down with chemicals and/or heat than cellulose.
- Lignin is essentially the glue that provides the overall rigidity to the structure of plants and trees (trees typically have more lignin, which makes them able to grow taller than grasses).

For each main type of biomass the main conversion chains are described for the production of energy, fuels and chemicals. A distinction will be made between small, medium and large scale conversion technologies.

2.2 Biomass conversion chains for oil crops

Main biomass conversion chains for oil biomass are biodiesel and pure plant oil production. They are described in more detail in the following two chapters.

2.2.1 Biodiesel production and application

Figure 1 shows the main inputs and outputs of the biodiesel production process, based on the most common biodiesel production technology called "trans-esterification". In this process, oils and fats are combined with mono-alcohol in the presence of base catalyst to form fatty acid esters (biodiesel).
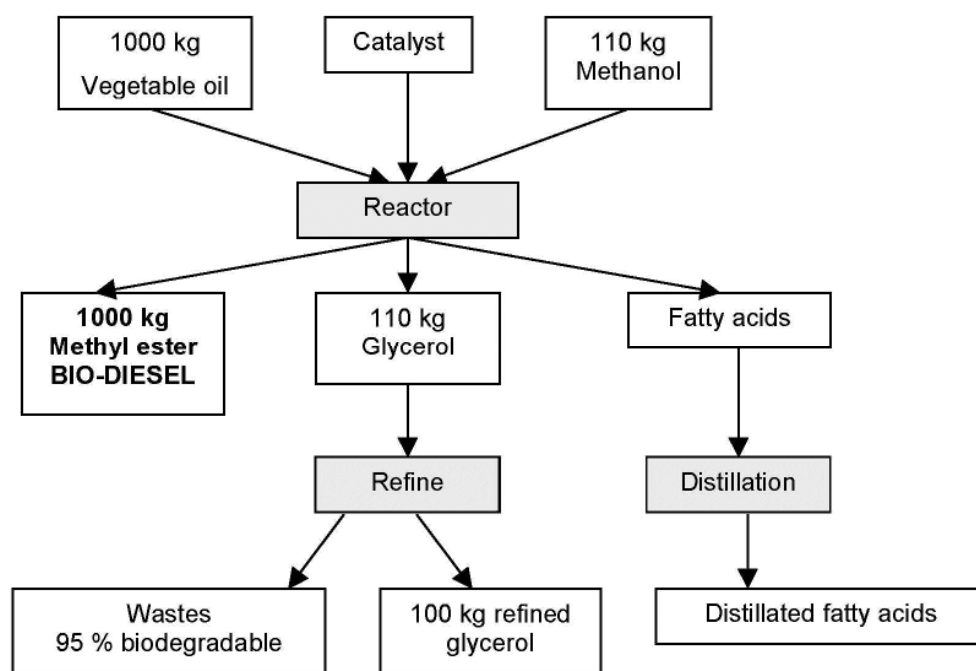
Figure 1 Main inputs and outputs of the biodiesel production process (Source IPTS 2002)

Animal and plant fats and oils are typically made of triglycerides which are esters containing three free fatty acids and the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol is used. The reaction has no other inputs than the triglyceride and the alcohol. Normally, without external input, this reaction will be either very slow or will not happen at all. Heat, as well as an acid or base are used to help the reaction proceed more quickly. It is important to note that the acid or base are not consumed by the transesterification reaction, thus they are not reactants but catalysts. Biodiesel has to be filtered and purified to meet fuel grade specifications required for use in diesel engines.

More detailed descriptions of the biodiesel production process can be found in various publications, like (Mittelbach and Remschmidt 2006), (Schober and Mittelbach 2009), (Knothe, Gerpen et al. 2005), and on websites like www.top-biofuel.org. It is possible to replace fossil diesel by 100% pure biodiesel. However, biodiesel is mainly used for blending with ordinary diesel to meet targets as set in the frame renewable energy policies in many countries.

Biodiesel factories form medium to large scale industrial conversion chains. The capacities can vary between 10-500 ktonnes/year, most of them larger than 30 ktonnes/year. The average plant capacity of biodiesel plants in Europe is 131 ktonnes/year[2].

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[2] Based on FACTBOX-Biodiesel plants across Europe (situation June 2007) http://uk.reuters.com/article/idUKL3037791620070621

Practically all biodiesel is used for transport purposes; most of it is blended with fossil diesel, part of it is sold as 100% biodiesel.

2.2.2 Example: biodiesel from soy

Soy is a leguminosae plant native to East Asia, widely grown for its edible bean which has numerous uses. Soybeans contain about 18% oil and 43-49% protein. Fat-free soybean meal is a primary, low-cost, source of protein for human consumption and animal feeds. Soy vegetable oil is widely used as cooking oil and increasingly used for biodiesel production. The United States, Brazil, and Argentina are the world's main soy producers. In 2010-2011, roughly 50 million tons of soy were produced in Argentina, which is about 20% of the world production. In 2010, about 2.5 million tons of soy biodiesel were produced in Argentine, while in 2005 biodiesel production was still marginal. This illustrates that although soy biodiesel is not Argentina's main soy product, its importance has increased significantly. Soy oil conversion takes place in two main steps, (1) the production of crude soy oil and (2) further refining steps. Both steps are described below.

Production of crude soy oil

Soy oil is present in the soy seed. Harvesting is done mechanically by a combine, it cuts the soy plant with the soy beans and the combine separates the soy seeds from the soy beans. The soy seeds are (mechanically) pressed, and the resulting oil is filtered. Typically, an oil yield of 15-20% is possible. This crude soy oil needs some further purification and the product is refined soy oil. The refined soy oil is further processed to biodiesel and the press cake contains proteins mainly which are used as cattle feed. See Figure 2.

Steps in the crude soy oil production process:
1. The soy crushers buy soy beans from suppliers
2. A pre-treatment such as cleaning, drying and dehulling is necessary prior to oil extraction.
3. The soy beans are crushed and pressed and the crude soy oil is extracted.
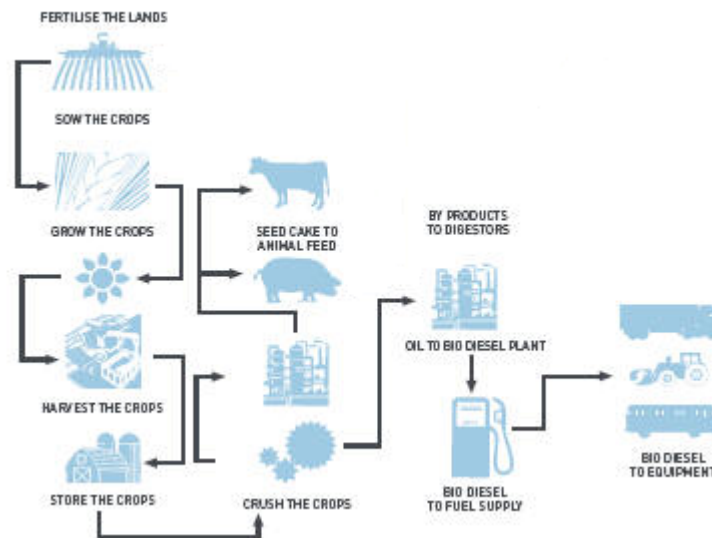4. The press cake is used as cattle feed.

Figure 2 Crude oil milling process
Source: http://www.ecotechbiodiesel.com/questions.htm

Refining of crude soy oil

The crude soy oil still contains many oil-insoluble and oil-soluble impurities that need to be removed. The oil-insoluble materials are removed with filtration and the soluble materials are removed in five steps.

1. Degumming: the phosphatides are removed by adding water or acid.
2. Deacidification: in this step the development of rancid flavors of free fatty acids (FFA) are prefented. The content of these compounds in unrefined soy oil is between 0.6-6%.
3. Bleaching: in this step colorants are removed from the oil and this will extend the storage life of the oil. Usually, an absorbing substance such as bleaching earth, silica gel or activated carbon is added to remove the colorants.
4. Deodorization: in this step odorous substances are removed by steam distillation.
5. Dehydration: in the final step water impurities are removed. Traces of water may decrease the conversion of soy oil into biodiesel.

Biodiesel production

Although refined soy oil can be used as automotive fuels in their pure form, their use does require some serious engine modifications. Alternatively, the oil can be used for biodiesel production. Biodiesel can be used directly in most (modern) diesel engines[3], either in its pure form or blended with fossil diesel. It is produced through the process of transesterification, which is a reaction between refined soy oil (90%) and with methanol (10%). The reaction products are biodiesel (90%) and glycerine (10%).

Biodiesel can be produced from a range of vegetable and animal oils and fats. However, the quality of the biodiesel largely depends on the attributes of the raw material. Fuel stability, ignition behaviour, smoothness of combustion and (in colder climates) winter

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[3] Some (plastic) parts in the engine fuel system can be degraded by biodiesel over time. However, in response to the upcoming biodiesel market, today most manufacturers are using resistant materials.

operability are important fuel characteristics that are dependent on the composition of the oil. There is no single oil that scores perfectly on all attributes, but soy oil comes close to an ideal raw material (Körbitz 2008).

2.2.3 Pure plant oil production and application

Although the name „pure plant oil" (PPO) refers to a vegetable origin like rapeseed, soybean etc., also oils from other resources, e.g. waste oil and animal fat, can be included in this category. Other publication also use the more generic term „straight vegetable oil" (SVO). Like in biodiesel production the oil needs to be extracted followed by refining in order to remove undesirable substances, such as phosphatides, free fatty acids, waxes, tocopherols and colorants. In case of PPO no transesterification process takes place, which makes the PPO production process simpler than the biodiesel production process, and easier to apply on a smaller scale. For an extensive description of the PPO (and biodiesel) production process, please refer to (Rutz and Janssen 2007)

Already in 1900 PPO was used as a fuel to run diesel engines; however, its current application as transport fuel is more limited than biodiesel. Properties of pure plant oil (PPO) largely differ when compared to fossil diesel. For example the viscosity of PPO is much higher, especially at cooler temperatures. This property leads to technical challenges in winter running and when cold starting in conventional engines. Since PPO tends to gum up at colder temperatures, it has been difficult to blend it with conventional diesel fuel. On the positive site, the flashpoint of pure plant oil is significantly higher than that of normal diesel and is therefore particularly safe in storage and transport and easy to handle. Additionally, PPO is biodegradable in a short time in soil and waters and e.g. in Germany, it is not classified in any water hazard class (Rutz and Janssen 2007).

2.2.4 Example 1: Palm oil conversion chains

Palm oil conversion takes place in two main steps, (1) the production of crude palm oil and (2) further refining steps. Both steps are described below.

Production of crude palm oil

In palm oil mills fresh fruit bunches (FFB) are processed into crude palm oil (CPO), palm kernels and - in some of the plants – into palm kernel oil (PKO). Empty bunch ash (soda), fibres, shells and palm oil mill effluent (POME) are the side products of the process. See Figure 3 and the following description based on (Yew 2007). The steps in the process are numbered; the treatments of main by-products after each separation process are indicated with the number followed by "a" (e.g. 7a).
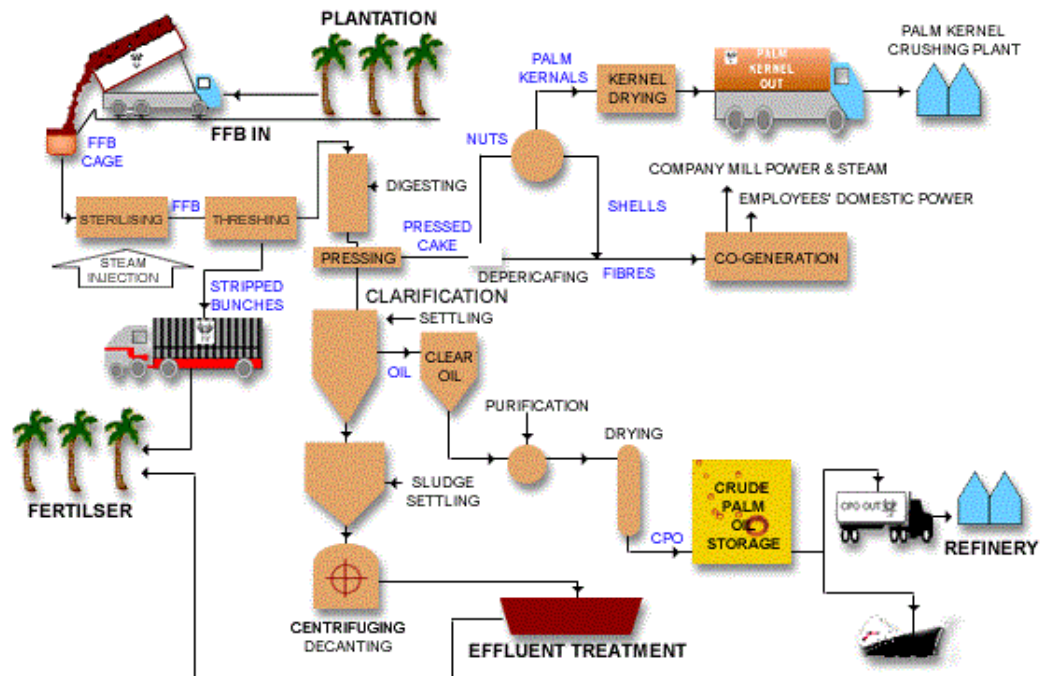
Figure 3 Crude oil milling process
Source: Plots Investment Group http://plotspalmoil.com/plantations.htm

Steps in the crude palm oil production process:

1. The palm oil mill buys fresh fruit bunches (FFB) from their suppliers or harvests the FFBs from own plantations.
2. Filled lorries with FFB are weighed at the weigh-bridge section to ensure that the weight of FFB are match with the document.
3. After weighing, the FFB is graded at the grading section for quality control and also to determine the price of the FFB.
4. FFB are then unloaded into RAMP section.
5. The RAMP unloads FFB into cages that are charged into a sterilizer to cook the FFB. The overall sterilization takes around 85 minutes.

6. The sterilized fruit bunches (SFB) are dropped into the thresher hopper and then into the feeder, where the feeder controls the feeding of SFB into the thresher. When the SFB enter the thresher, the thresher separates loose fruits from bunches.

7. Sterilized fruits from the thresher go through a sterilized fruit conveyor and elevator to the digesters. Digesters are filled with ¾ full of sterilized fruits, to soften the fruits before the press.

7a. Empty bunches and un-stripped bunches from the threshing go into a hard bunch crasher. At the hard bunch crasher, un-stripped bunches fall into the cages again for second round sterilization, while the empty fruit bunches (EFB) go into the incinerator for burning into ash; fibre from empty bunches can be used for fertilizer and for fuel at the boiler section.

8 Softened sterilized fruits are pressed to obtain crude oil and press cake.

8a. The press cakes consist of the mixed fibre and nuts and enter into a depericarper drum, where fibres are sucked up to fibre cyclone by cyclone fan, at the same time. Fibres are used as a fuel at the boiler section. Nuts from the depericarper drum go to the polishing drum by elevator to remove fibres from nuts. After the polishing drum, the de-stoner fan sucks fibres from nuts to the fibre cyclone, and nuts go into the nut silos and then into a nut cracker (ripple mill) to get cracked mixtures. These cracked mixtures will go through two winnowing systems (LTDS) for separation. Shells and kernels (cracked mixture) which are not 100% separated at the LTDS, conveyed to clay bath for further separation by using vibrating screen. Wet kernels go to kernel silos for drying, and these dried kernels will then store in kernel bunkers for dispatch, while shells to the boiler as fuel.

9. Crude oil flows into a crude oil gutter and then into a vibrating screen to separate dirt and sludge from crude oil. Dirt and sludge flow into conveyor back to digesters for oil recovery, and crude oil flows into crude oil tank then pumped to the oil room. In the crude oil tank, there is a skimmer to skim the pure oil at the upper layer of the crude oil and straight pump to the pure oil tank. Oil and sludge will underflow at the crude oil tank and pumped to clarifier 1 in the oil room. In the oil room, crude oil from the press is pumped into clarifier 1. Basically, the crude oil will form into 2 layers of oil, the pure oil at the upper layer while the oil plus sludge at the bottom layer. The coil in the clarifier heats up the crude oil to enable the pure oil to merge and float up easily to the top. Pure oil will overflow into a skimmer in the clarifier to the pure oil tank, and oil plus sludge and dirt will underflow to clarifier 2. The same concept applied in clarifier 2, where pure oil will overflow into a skimmer to reclaim oil tank and back to clarifier 1.

9a. The remaining oil, sludge and dirt will underflow to sludge tank then into the sludge siever to remove dirt and sands with bigger particle. Later, sludge and oil are pumped up to the decanter to remove sludge plus dirt, which are also called the decanter cake. Decanter cake used to make fertilizer. The oil and sludge from decanter are then flow into a decanter tank then pumped up to a baffle tank which located on top of the clarifier 2. From baffle tank to sludge separators, hot water added into sludge separators to separate the pure oil from the oil plus sludge. The sludge separators contain hundreds of bowls which piled up and function like a centrifuge. Sludge at the bottom is drained out and pure oil at the top is pumped into a fat oil tank then back into clarifier 1. Sludge and dirt at the bottom of the pure oil tank flows into the reclaim oil tank for recovery by going back into clarifier 1 again.

10. Pure oil from pure oil tank flows into a vacuum dryer with nozzles. These nozzles spray the hot oil into droplets with moisture in a vapour form, the vacuum sucks out the moisture and left the oil in a liquid form. Pure oil, commonly known as crude palm oil or CPO, which is produced from the mill is pumped into storage tanks for dispatch.

Refining of crude palm oil

Crude palm oil (CPO) is further processed by either physical or chemical refining to produce either refined, bleached and deodorised palm oil (RBDPO) or neutralised, bleached and deodorised palm oil (NBDPO). These are subjected to fractionation to obtain the respective liquid olein fraction and the solid stearin fraction. See Figure 4 and the description below based on (Hai 2002). Of the two processes, physical refining is the predominant approach adopted by the refineries as it is simpler, less capital intensive, more efficient and produces a lower effluent load.

Physical or steam refining begins with degumming when the CPO is treated with food grade phosphoric acid or citric acid to remove natural gums in the form of phosphatides, followed by bleaching with activated earth (Fuller's Earth) under vacuum to remove colouring matters as well as to adsorb any metal ions. The treated oil is then heated to 240 - 260 °C under 2-6 mm Hg (MEOMA, 2002) for simultaneous de-acidification and de-odorisation. The free fatty acids are stripped off by live steam and is recovered together with the entrained oil as palm fatty acid distillate. The steam distillation process also removes odours and off-flavors from the CPO ('Deodorisation'). The oil is then cooled to 55°C before polishing. Refined Bleached Deodorised Palm Oil (RBDPO) is the basic oil product sold on the world's commodity markets.

In the *chemical refining process*, the free fatty acids present in CPO are removed by neutralisation with caustic soda (sodium hydroxide), the concentration of the latter being dependent on the quality of the CPO feedstock. This chemical reaction produces neutralised CPO and a soap stock; the latter is separated from the oil by a high-speed separator. The neutralised oil is subjected to earth bleaching to remove colour pigments and metal ions followed by deodorisation - steam distillation under vacuum to remove odoriferous matters such as aldehydes and ketones.
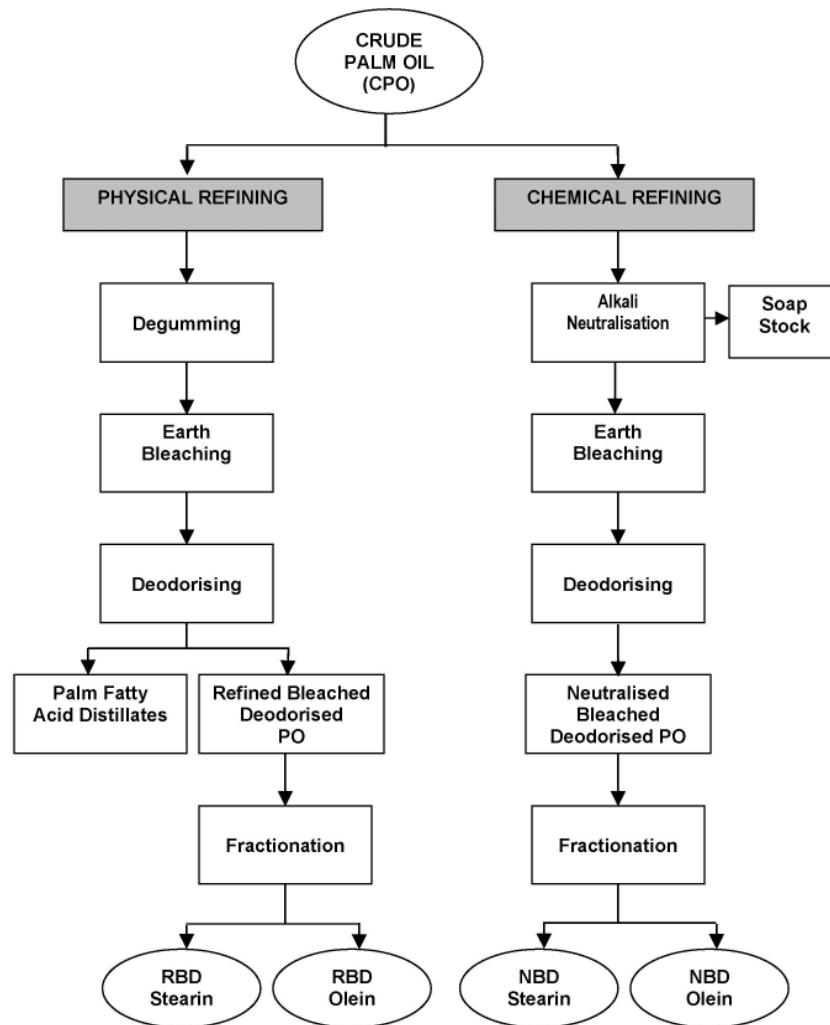
Figure 4 Palm oil refining process Source: (Hai 2002)
PO = palm oil; R = refined; N= Neutralised; B=bleached; D = deodorised

The refined oil contains triglycerides of various compositions and melting points, the main fractions being palm olein and palm stearin. These fractions can be separated by dry fractionation, detergent fractionation and solvent fractionation. Dry fractionation is commonly used whereby the refined oil is allowed to crystallise under controlled temperature and the resultant slurry is pumped through a membrane filter press to obtain the liquid olein fraction and the solid stearin portion. The olein could also be fractionated for a second time ('double fractionation') to produce a 'super olein' and a solid palm mid-fraction (PMF) which is the feedstock for production of specialty fats and other products.

After refining, palm oil possesses all the characteristics required for many uses without hydrogenation. By fractionating palm oil, its uses are further increased. Hydrogenation and inter-esterification increase its uses even further, especially in making specialised and sophisticated edible products. Its versatility makes it a suitable raw material for many applications both in edible and non-edible products. There are several classes of foodstuffs made wholly or in large part from oils and fats. Some of the products include:frying/cooking oils and fats, shortening, Vanaspati (vegetable ghee), margarine

and spreads, and imitation dairy products. Non-food applications of palm oil include soaps, oleochemicals like fatty acids, methyl esters, fatty alcohols, glycerine and epoxidised palm oil.

Table 1 Main applications of palm oil derivates. Source (Salmiah 2000)

Fatty acids	- Medium chain triglycerides for use in the flavour and fragrance industries - Processing aids for rubber products. - Production of candles - Manufacture of cosmetic products from myristic, palmitic and stearic acids - Production of soaps via a neutralisation process - Production of non-metallic or non-sodium soaps
Fatty esters	- Production of pure soap - Alfa-sulphonated methyl esters as active ingredients for washing and cleaning products (anionic surfactants) - Palm-based methyl esters as a substitute for diesel fuel for vehicles and engines
Fatty alcohols	- Fatty alcohol sulphates (anionic surfactants) - Fatty alcohol ethoxylates (nonionic surfactants) - Fatty alcohol ether sulphates (anionic surfactants)
Fatty nitrogen compounds	- Imidazolines with good surface active properties (rust prevention) - Esterquats as softeners
Glycerol (Monoglycerides and Diglycerides)	- Wide range of applications such as a solvent for pharmaceutical products, humectants in cosmetics and tobacco, stabilisers, lubricants, antifreeze, etc.

Biodiesel from palm oil

Like other vegetable oils, palm oil can be used for the production of biodiesel through transesterification into methyl esters. Depending on the design, palm oil based biodiesel plants use either accept crude palm oil (CPO) or refined, bleached and deodorised palm oil (RBDPO). Direct use of CPO requires an additional esterification step while RBDPO can undergo direct transesterification. See Figure 5. CPO's treatment into a good quality biodiesel can take many shapes (using pure chemically-based materials, biocatalysts such as potassium-oxide and sodium-oxide or even microorganisms such as Pseudomonas fluorescens); subsequent transesterification usually involves the use of a sodium methoxide solution, or alternatively a high purity sodium hydroxide solid catalyst (Toh and Koh 2008).

Compared to other oil crops, palm oil is characterized by high amounts of medium-chain saturated and monounsaturated fatty acids. Therefore, the resulting palm biodiesel has a high filter plugging point and cloud point, and is referred to as "summer grade biodiesel". A "winter grade biodiesel" can be produced by either a partial crystallization or a fractional distillation step to remove the C_{16} fraction; the C_{16} fraction can be further hydrogenated to produce a feedstock suitable for the manufacture of MES, a key ingredient in the detergent industry. Both summer and winter palm biodiesel grades are commercially available.
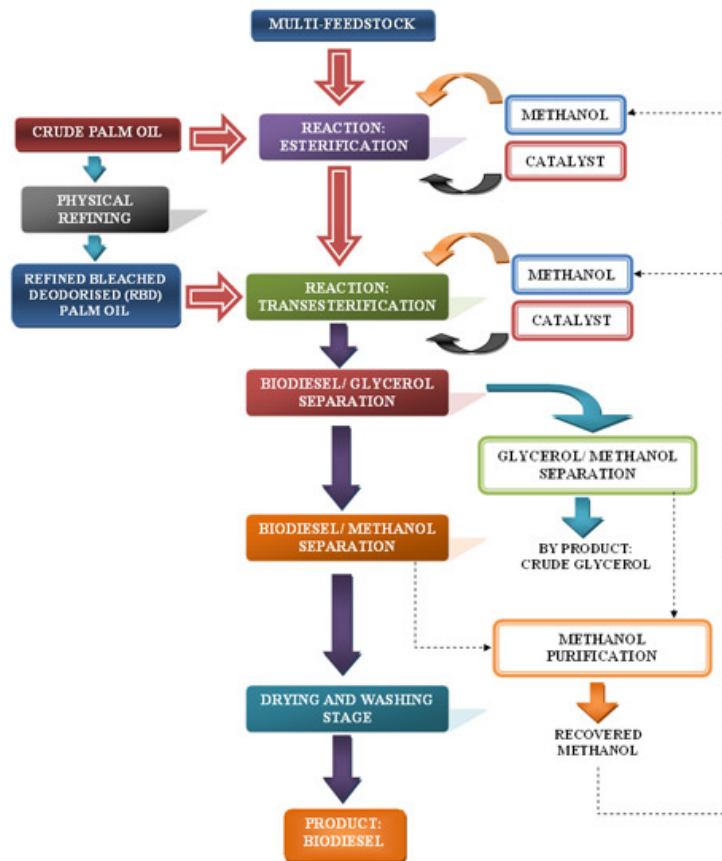
Figure 5 Multi feedstock palm oil biodiesel process flow. Source: www.lipochem.co.my

In recent years, high palm oil prices have stimulated the search for alternative biodiesel feedstock. Palm fatty acid distillate (PFAD) is a potentially valuable low-cost feedstock for biodiesel (Cheah, Toh et al. 2010). PFAD is generated in the fatty acid stripping and deodorization stages of the CPO refining process. Although the basic process for the conversion of high-acid oil feedstock to biodiesel is well known, it has been carried out mainly in small-scale batch-type processes. A breakthrough came in October 2009 with the successful operation of the world's first continuous large-scale 200 MT/day PFAD biodiesel plant (in Sumatra, Indonesia). In this plant, owned by a large Asian based multinational palm oil group, fresh PFAD from the refineries is sent directly to the PFAD biodiesel plant for conversion to biodiesel. The biodiesel yield from this plant approaches 100%, and it fully meets EN (European Standards) specifications. After distillation, the PFAD biodiesel also passes the ASTM Cold Soak Filtration Test, introduced in 2008.

2.2.5   Example 2: Jatropha oil conversion chains

Jatropha oil is present in the jatropha seed kernel. After harvesting, the hulls of the seeds are removed in a de-hulling step. The kernels are (mechanically) pressed, and the resulting oil is filtered. Typically, 75-85% of the available oil is extracted. Both the oil and the by-products (press cake and hull) can be used for energy production or further processing. See Figure 6.
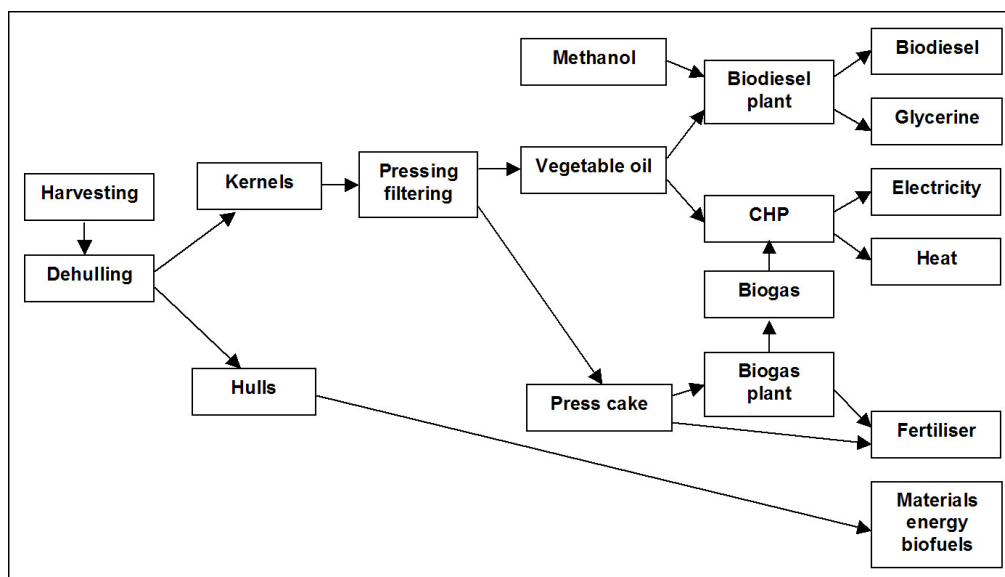
Figure 6 Application of jatropha seeds Source: (Vis, Reumerman et al. 2009)

According to FACT Foundation (the Netherlands) the potential energy production from a jatropha plantation is made up of approx. 35% of energy from oil, 9% of energy in fruit shells and 35% of energy in press cake and oil residues. Thus it can be seen that adding energy use of fruit shells, press cake and oil residues can more than double the energy output, while improving the compost output as well. This makes addition of biogas into a pure jatropha oil model a very interesting new component. Biogas also has the advantage of returning the maximum of organic matter back to the land.

Biodiesel production
Although vegetable oils can be used as automotive fuels in their pure form, their use does require some serious engine modifications. Alternatively, the oil can be used for biodiesel production. Biodiesel can be used directly in most (modern) diesel engines[4], either in its pure form or blended with fossil diesel. It is produced through the process of transesterification, which is a reaction between oil (90%) with methanol (10%). The reaction products are biodiesel (90%) and glycerine (10%).

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[4] Some (plastic) parts in the engine fuel system can be degraded by biodiesel over time. However, in response to the upcoming biodiesel market, today most manufacturers are using resistant materials.

Biodiesel can be produced from a range of vegetable and animal oils and fats. However, the quality of the biodiesel largely depends on the attributes of the raw material. Fuel stability, ignition behaviour, smoothness of combustion and (in colder climates) winter operability are important fuel characteristics that are dependent on the composition of the oil. There is no single oil that scores perfectly on all attributes, but jatropha comes close to an ideal raw material (Körbitz 2008).

Box 2: Jatropha oil attributes

Jatropha oil is a vegetable oil that is, due to its toxicity, unfit for human or animal consumption. It is mainly composed of palmitic, stearic, oleic and linoleic fatty acids (Schultz 2008). Specific physical attributes:

Lower heating value:	39.0 MJ/kg
Density:	0.91 kg/litre
Energy content of 1 litre jatropha oil[5]	35.49 MJ/litre
Energy content of 1 litre jatropha oil	9.86 kWh/litre
Viscosity (at 25 oC):	50 cS
Saponification Number:	192
Iodine Value:	97

Electricity production

Like many vegetable oils, jatropha oil can be used directly for the generation of electricity in (modified) diesel engine – generator sets.

- Since the early 2000s, the use of vegetable oils for the production of combined heat and power (CHP) has increased steadily in Europe. Particularly in the last 2-3 years, many engine plants running on rapeseed and palm oil have been commissioned in for instance Germany, Italy and Belgium. Plant sizes range from below 100 kWe to several dozens of MWe. Also, the use of jatropha is anticipated: a 9 MWe CHP plant on jatropha oil is now under construction in Belgium.
  - In developing countries, the interest in using vegetable oils (particularly locally produced jatropha) for the production of electricity and mechanical power is growing, for example for rural applications. MFC Nyetaa (Mali-Folkecenter Nyetaa) is currently carrying out a variety of projects in 12 villages which will use Jatropha oil as fuel. 3 new projects combine jatropha oil with solar or biogas to have renewable energy hybrid systems. Another recent example is FACT Fuels, which has installed several generator sets in combination with their jatropha cultivation scheme in Mali. A further example is Winrock India, which installed several electricity generator sets running on jatropha oil for electrifying remote villages in Chhattisgarh[6].

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[5] See: www.jatropha.de/p-o-engines/index.html

[6] See http://www.winrockindia.org/act_proj_ene_prom_bio_1.htm.

- In a wider international context, application of vegetable oils in UNDP's Multifunctional Platform (MFP) Programme is a possibility.

Use as a cooking fuel

Experiments with the use of vegetable oils as cooking fuels have led to the development of several types of cook stoves. An example of a modern, efficient stove is the Protos Plant Oil Cooker of B/S/H (Shiroff 2008). This cooker was developed in recent years for application in developing countries. At present, it is being marketed in a number of countries in Asia.

Use for small-scale soap production

Soap is a proven market for jatropha oils in rural Africa. Jatropha oil has good properties for making soap and soap production can be accomplished with minimal investment of supplies and equipment. The jatropha soap is often marketed as a medical soap and can be sold for a good price.

Use of residues

Finding applications for the valorisation of by-products of jatropha production is seen as one of the major challenges to improve the economics of jatropha growing.

- The jatropha press cake that is left after oil pressing has so far been seen as a fertiliser to be returned to the soil. It contains mainly proteins but due to its toxicity it cannot be used as animal feed. Experiments with detoxification, and breeding of non-toxic varieties, are on-going.
- Recent experiments with press cake indicate that it can be used for the production of biogas, through anaerobic digestion. The biogas can be used for energy production; the digester effluent, which still contains all the nutrients in the press cake, can be applied as a fertiliser on the land. MFC Nyetaa is currently carrying out a project in this area in Garalo, southern Mali. First studies by FACT show good economic results.
- Jatropha seed hulls constitute about one third of the seed weight. Experimental work in the Netherlands show that hull can be used as raw material for fibreboard production, wood-plastics composites or as a feedstock for the production of bioenergy of biofuels (Heeres 2008).

2.2.6 Anaerobic digestion

Oils and fats can be used as co-substrates for co-digestion with manure. For more information on anaerobic digestion please refer to section 2.4.6.

2.3 Biomass conversion chains for sugar and starch biomass

The main conversion chain for sugar and starch crops is ethanol production which includes a number of steps including fermentation. Sugar and starch crops can be used for anaerobic digestion as well.

2.3.1 Ethanol production from sugar and starch biomass

Ethanol is generally produced either synthetically from petrochemical feedstock (petroleum) or by microbial fermentation which is applicable to bioethanol production. The process for production of fuel bioethanol from biomass can be broken down to the following steps.

- Feedstock production: harvesting , reception, storage
- Physical pre-treatment: milling
- Saccarification: conversion of starch and cellulose into sugar
- Chemical treatment: dilution of the sugars with water and addition of yeast or other organisms
- Fermentation: production of ethanol in solution with water along with waste and by-products
- Distillation: separation of ethanol
- Dehydration: Removal of the remaining water by molecular sieves (anhydrous ethanol)
- Co-product preparation: Drying of the alcohol free stillage (mash) for high-value animal feed.

The steps in the feedstock-to-ethanol conversion process largely depend on the type of feedstock. Table 2 shows an overview of the ethanol production process for main feedstock types.

Table 2 Ethanol production steps by feedstock and conversion technique

Feedstock type	Feedstock	Harvest technique	Feedstock conversion to sugar	Process heat	Sugar conversion to Alcohol	Co-products
Sugar crops	cane	Cane stalk cut, mostly taken from field	Sugars extracted through bagasse crushing, soaking, chemical treatment	Primarily from crushed cane (bagasse)	Fermentation and distillation of alcohol	Heat, electricity, molasses
	sugar beet	Beets harvested, foliage left on the field	Sugar extraction	Typically from fossil fuel	Fermentation and distillation of alcohol	Animal feed, fertilizer
Starch crops	wheat	Starchy parts of plants harvested; stalks mostly left in the field	Starch separation, milling, conversion to sugars via enzyme application	Typically from fossil fuel	Fermentation and distillation of alcohol	Animal feed (e.g. distillers dried grains)
	corn	Starchy parts of plants harvested; stalks mostly left in the field	Starch separation, milling, conversion to sugars via enzyme application	Typically from fossil fuel	Fermentation and distillation of alcohol	Animal feed (e.g. distillers dried grains), sweetener
	potatoes	Potatoes harvested, foliage left on the field	Washing, mashing, cooking, starch separation, conversion to sugars via enzyme application	Typically from fossil fuel	Fermentation and distillation of alcohol	Animal feed, industrial use
Cellulosic crops	trees	Full plant harvested (above ground)	Cellulose conversion to sugar via saccarification (enzymatic hydrolysis)	Lignin and excess cellulose	Fermentation and distillation of alcohol	Heat, electricity, animal feed, bioplastics, etc.
	grasses	Grasses cut with regrowth	Cellulose conversion to sugar via saccarification (enzymatic hydrolysis)	Lignin and excess cellulose	Fermentation and distillation of alcohol	Heat, electricity, animal feed, bioplastics, etc.
Waste biomass	Crop residues, forestry waste, municipal waste, mill waste	Collected, separated, cleaned to extract material high in cellulose	Cellulose conversion to sugar via saccarification (enzymatic hydrolysis)	Lignin and excess cellulose	Fermentation and distillation of alcohol	Heat, electricity, animal feed, bioplastics, etc.

Source: (Rutz and Janssen 2007)

Sugar-to-Ethanol Process

The simplest way to produce ethanol is the sugar-to-ethanol production. Sugar crops like sugar beets or cane contain substantial amounts of (six-carbon)[7] sugars which can be fermented directly to ethanol. Although fungi, bacteria, and yeast microorganisms can be used for fermentation, the specific yeast Saccharomyces cerevisiae (Bakers' yeast) is frequently used to ferment glucose to ethanol. Theoretically, 100 grams of glucose will produce 51.4 g of ethanol and 48.8 g of carbon dioxide.

In Brazil and in most tropical countries which produce ethanol, sugar cane is the most common feedstock for ethanol production. In these countries the costs of ethanol production from sugar cane are among the lowest of any biofuels.

Figure 7 Sugar cane and sugar beet harvest

Starch-to-Ethanol Process

A large portion of starch based bioethanol is produced from the starch component of grain crops, primarily corn and wheat in the US and wheat and barley in Europe. Starch molecules are made up of long chains of glucose molecules which have to be broken into simple glucose molecules (saccharification). Therefore starchy materials require a reaction of starch with water (hydrolysis). Typically hydrolysis is performed by mixing the starch with water to form slurry which is then stirred and heated to rupture the cell walls. During the heating cycle, specific enzymes are added, which break the chemical bonds. Organisms and enzymes for starch conversion and glucose fermentation on a commercial scale are readily available. The starch-to-ethanol process is shown in Figure 8. In conventional starch-to-ethanol processes, only the starchy part of the crop plant is used. Section 3.4.3 describes a biorefinery process using the whole starch crop.

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[7] Six-carbon sugars are much easier to convert to ethanol than five carbon sugars. See also chapter 3.5.1 on ethanol production from lignocellulosic biomass.
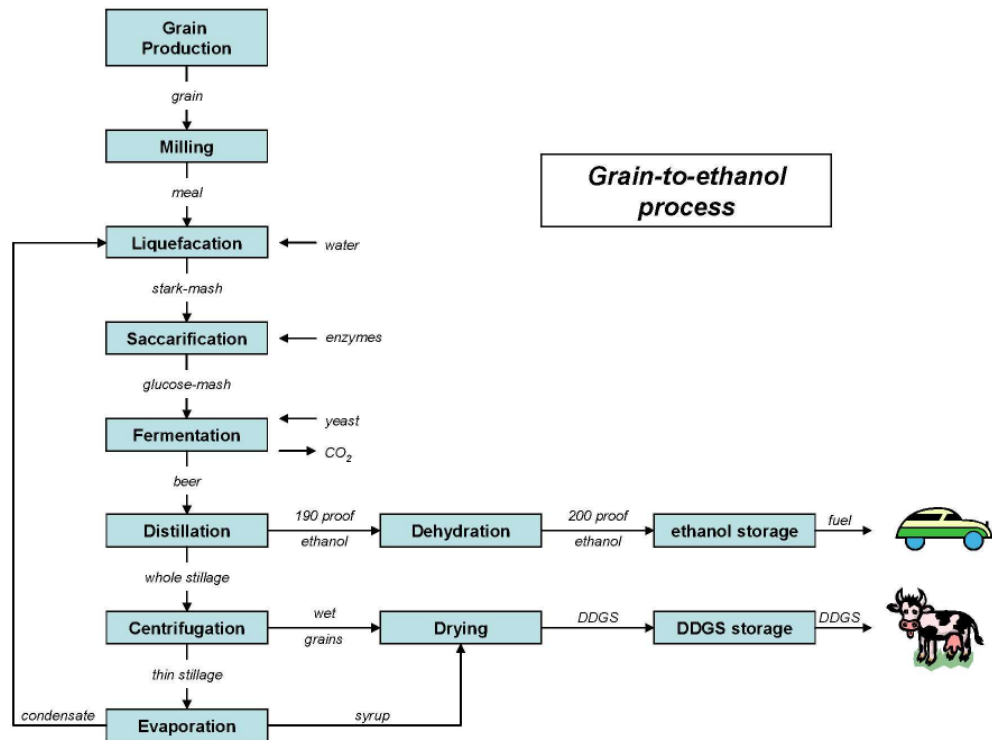
Figure 8 Grain to ethanol process. Source: (Rutz and Janssen 2007)

Ethanol - industrial versus small scale conversion chains

Although plant capacities vary widely ranging from 1.5 - 500 mln. litres/year, ethanol production is generally speaking a large scale business. The average capacity of European wheat/starch ethanol installations is 152 mln. litres/year; the average capacity of sugar/juice based ethanol production units is 132 mln litres/year[8]. In the USA most of the ethanol production plants are corn based, their average capacity is 192 mln litres/year[9]. The small scale initiatives (1.5 - 10 mln litres/year) mainly concern ethanol based on less common feedstock such as cheese whey, C-starch, seed corn, milo, brewery and beverage waste (as well as pulp and other lignocellulosic feedstock).

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[8] Based on 2010 data from ePURE http://www.epure.org/statistics.php?id=5

[9]Based on 2010 data from EPAC Ethanol Producers And Consumers http://www.ethanolmt.org/plants.html

2.3.2   Example: ethanol production in Brazil and Costa Rica

In Brazil and Costa Rica, sugar cane is used as feedstock for ethanol. As of late 2007, sugarcane fields occupied about 7.8 million hectares in Brazil, or about 2% of all arable lands available in the country. The yearly yield of sugar cane in season 2008/09 was 569 mln tonnes of sugar cane, resulting in 31 mln tonnes of sugar, 18 mln m^3 of hydrous ethanol and 9.3 mln m^3 of anhydrous ethanol (UNICA 2011). This makes Brazil the number one producer of sugarcane in the world, followed by India, Thailand and Australia. Costa Rica has a much smaller yield of 4.1 mln tonnes of sugar cane in 2009 (FAOSTAT 2011). Main production regions are South-Central Brazil, where close to 90% of overall production is concentrated, and the Northeast, which accounts for the remainder. There are two harvests per year, which allows Brazil to produce sugar and ethanol year round for both the internal market and for export.

Sugar cane processing units can be divided into mills that produce only sugar, mills with distillery plants that produce sugar and ethanol, and independent distillery plants that produce ethanol only. If used in ethanol production only, each ton of ground sugarcane would result in 89 litres of hydrated or 85 litres of anhydrous ethanol today; if used exclusively in sugar production, each ton would yield 118 kg of sugar and 10 litres of ethanol from the molasses. It should be noticed, however, that under normal market operation the Brazilian average yield is 71 kg of sugar and 42 litres of alcohol per tonne of crushed sugarcane (Kaltner, Azevedo et al. 2005). Below the process scheme to produce ethanol (without sugar production) is illustrated.

The sugar cane is harvested by cutting the cane stalk mechanically or by hand; subsequently the stalks are taken from the field and transported to the processing facility. It takes two main steps from feedstock to ethanol. First, the sugars are extracted from the feedstock and second, the sugars are converted by fermentation and distillation into ethanol. See Figure 9 for all necessary steps.

Steps from feedstock to ethanol fuel:
1. The ethanol production facility receives sugar cane from the production fields.
2. It is first cleaned of dirt and any other extraneous material that may be present.
3. It is than chopped or shredded to change the harvested material to a fibrous material ready for sugar extraction.
4. During the milling process, the sugars (in form of juice) are squeezed out and the leftovers (fibrous materials) are called bagasse which is used as fuel for the processing facility.
5. The juice is then pasteurized, partially evaporated and centrifuged into syrup, or molasses.
6. The easiest method to produce ethanol from sugar is the sugar-to-ethanol production. Yeast is added to the syrup (sugar) and these organisms transform the six-carbon sugars (mainly glucose) to glucose. The formed products are ethanol and carbon dioxide.
7. The mixture of ethanol and yeast is centrifuged (distilled), the yeast is extracted from the ethanol and the end product is the biofuel ethanol.
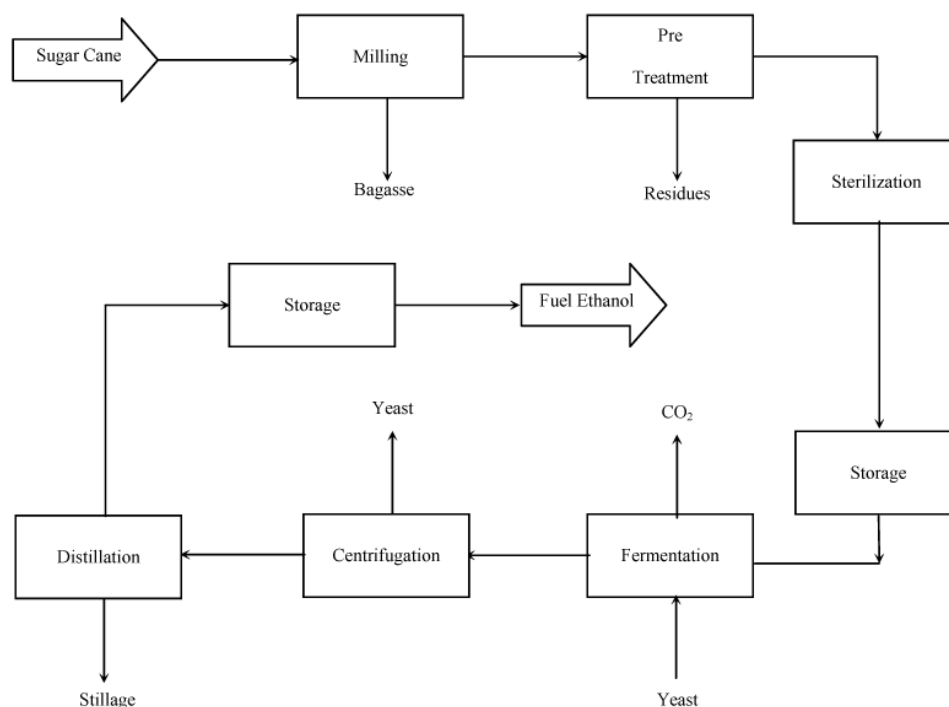
**Figure 9: Process flow ethanol production from sugar cane
(source: http://www.proceedings.scielo.br)**

Uses of residues

- Bagasse is the fibrous material that is leftover after the milling process. It contains a lot of energy which is burned in boilers for steam production and used for power and heat generation.
- Molasses: sugar cane molasses is a common ingredient in baking, often used in baked goods such as gingerbread cookies. Furthermore it can be used for ethanol production as well.

2.3.3 Anaerobic digestion

Sugar and starch biomass such as corn can be used as co-substrates for co-digestion with manure. For more information on anaerobic digestion please refer to section 2.4.6.

2.4 Biomass conversion chains for lignocellulosic biomass

A large number of technologies exist for the conversion of lignocellulosic biomass. Lignocellulosic biomass can be directly converted into energy by combustion. Other thermochemical processes such gasification, pyrolysis, or carbonisation allow the production of intermediary products such as syngas, pyrolysis oil and charcoal that could be combusted for energy or used for the production of materials, fuels and or chemicals. Anaerobic digestion results in a methane rich biogas that can be regarded as an intermediate product as well. Ethanol production by fermentation of lignocellulosic biomass is challenging; a key characteristic of lignocellulosic biomass is that it is

naturally resistant to being broken down into their constituent parts, particularly in comparison to first-generation biomass feedstock such as sugar starch or vegetable oil.

The above mentioned conversion chains are described in the sections below, i.e. combustion, followed by the main thermochemical processes that produce intermediate products (gasification, pyrolysis and carbonisation) as well as the biochemical process of anaerobic digestion.

2.4.1 Combustion

Biomass combustion is the most common biomass conversion technology, applied on household and industrial levels since ancient times. Over the last decades, modern biomass combustion technologies have emerged like fully automated pellet boilers, co-firing, and efficient combined heat and power production from a large variety of biomass resources. Biomass combustion is used to generate heat, electricity or mechanical energy. After combustion only flue gas is generated, and - besides ash - no by products are produced. The following common combustion technologies can be distinguished on small (household), medium (larger buildings and industry) and large (power sector) scale:

- Biomass combustion on household level (heat only)
  - o Charcoal stoves (cooking in developing countries)
  - o Barbeque stoves (leisure use)
  - o Fireplaces for wood blocks (low efficient, usually only for leisure use)
  - o Wood block stoves and boilers
  - o Wood pellet stoves and boilers.

- Biomass combustion for (non) residential buildings and industrial sector (heat and/or electricity)
  - o Wood pellet boilers for houses and block heating
  - o Wood chips boilers for block heating
  - o Wood chips and straw boilers for district heating (and electricity production)
  - o Boilers for industrial heat (and electricity) production using sawdust, wood chips, bark, black liquor, straw, etc.
  - o Boilers for electricity production using wood chips, straw, etc.
  - o Gas engines for the production of electricity and heat from biogas (from anaerobic (co)digestion of manure, waste water and industrial organic residues)
  - o Gas engines for the production of electricity from landfill gas.

- Biomass combustion in the traditional power sector
  - o Co-firing of biomass pellets (wood, straw, other) and torrefied biomass (wood) in coal fired power plants
  - o Co-firing of liquid fuels (palm oil, fats) in power plants.

After the right pre-treatment (especially drying and sizing) practically all biomass can be combusted for energy generation. The most common biomass types for heat and electricity production are chipped, pelletised or carbonised wood. Compared to many other solid biomass types such as straw and other agricultural residues, wood has a

relatively low content of elements like chlorine and alkalies that can harm the conversion equipment during combustion. Nevertheless combustion of agricultural residues such as straw, bagasse, rice husks is also common practice.

For more information on combustion and co-combustion see for instance (Loo and Koppejan 2008); Also IEA task 32 on Combustion and Cofiring (http://www.ieabcc.nl/) is worth visiting. For more information on pellets see for instance the Pellet Handbook of (Obenberger and Thek 2010).

2.4.2 Gasification

Biomass gasification is an endothermic thermal conversion technology where a solid biomass fuel is converted into a combustible gas. A limited supply of oxygen, air, steam or a combination serves as the oxidising agent. The product gas consists of carbon monoxide, carbon dioxide, hydrogen, methane, trace amounts of higher hydrocarbons (ethane), water, nitrogen (with air as oxidant) and various contaminants, such as small char particles, ash, tars, higher hydrocarbons, alkalis, ammonia, acids, and the like. For firing the product gas in a boiler simple de-dusting of the product gas in a cyclone is sufficient, while for other applications such as gas engines, turbines and upgrading for biofuel/chemical production, various degrees of tar removal and extensive gas cleaning is needed.

Different types of gasifier designs can be distinguished:
- Fixed bed: downdraft, updraft, crossdraft
- Fluid bed: bubbling, circulating (CFB), twin-bed
- Entrained flow
- Stage gasification with physical separation of pyrolysis, oxidation and/or pyrolysis zones.

The following main applications can be distinguished:
- Gasification for heat production
- Fixed bed gasifiers for power or CHP production from biomass
- Co-firing gas from biomass in existing power plants
- Fluid bed gasification for power production
- Syntheses gas production for liquid (transportation) fuels. Synthesis gas differs from producer gas as it contains only CO and H_2 and is usually produced with oxygen as gasification agent.

Industrial versus small scale applications
Biomass gasification can be applied at very small scale (fixed bed at household level) up to extremely large scale as applied in refineries (entrained flow). See Figure 10.
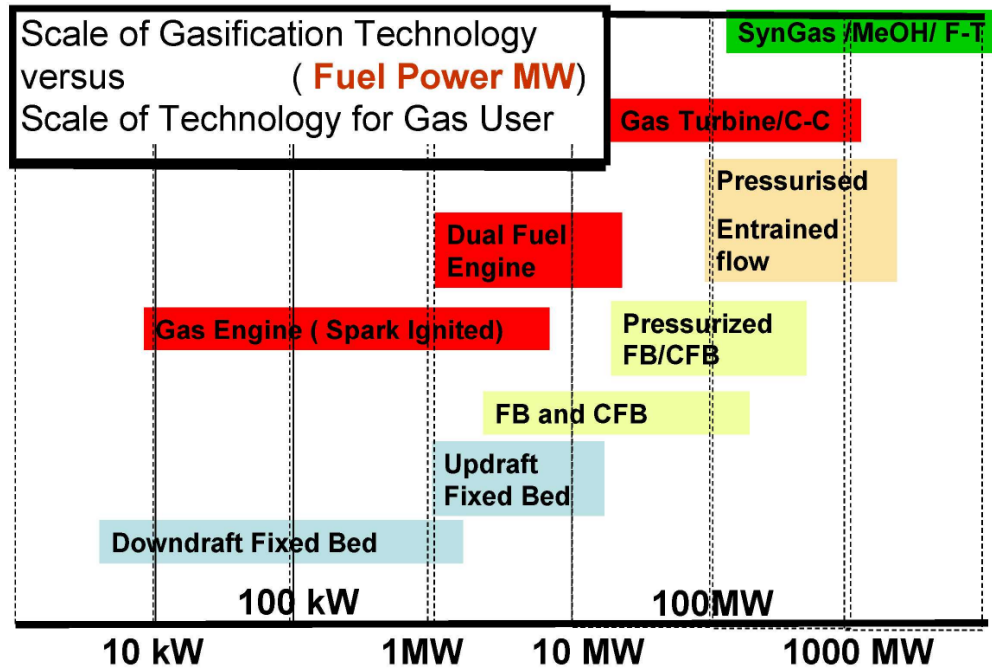
Figure 10 The scale of gasification technologies and applications. Source: (Rensfelt 2005)

At small scale, gasification is usually implemented for heat, or combined heat and power production (e.g. in rural electrification projects) up to a few MW. Small scale gasifiers combined with a gas turbine or engine can reach significantly higher electric efficiencies than small scale steam cycle combustion systems. At the medium to large scale, the market segment may change to co-firing, IGCC and/or syngas production for a wider variety of products. An entrained flow gasifier does not encounter large size restrictions and its capacity can easily reach several hundreds of MW, which could be combined with Fischer-Tropsch liquid production. Many gasification concepts are currently under demonstration and evaluation. An excellent source for more information is the Handbook Biomass Gasification (Knoef 2005); furthermore it is worthwhile to check IEA Task 33 on thermal gasification of biomass[10].

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[10] http://www.gastechnology.org/webroot/app/xn/xd.aspx?it=enweb&xd=iea/homepage.xml

2.4.3 Pyrolysis

Fast pyrolysis is a process in which organic materials are rapidly heated to 450 - 600 °C in absence of air. Under these conditions, organic vapours, permanent gases and charcoal are produced. The vapours are condensed to pyrolysis oil. Typically, 50 - 75 wt.% of the feedstock is converted into pyrolysis oil.

Pyrolysis transforms difficult-to-handle biomass of different nature into a clean and uniform liquid, called pyrolysis oil. Not only woody biomass, but also agricultural residues such as empty fruit bunches can be converted into pyrolysis oil. Pyrolysis oil can be used for the production of renewable/sustainable energy and as a building block for the production of chemicals. Its energy density is four to five times higher than the original solid material, which offers important logistic advantages.
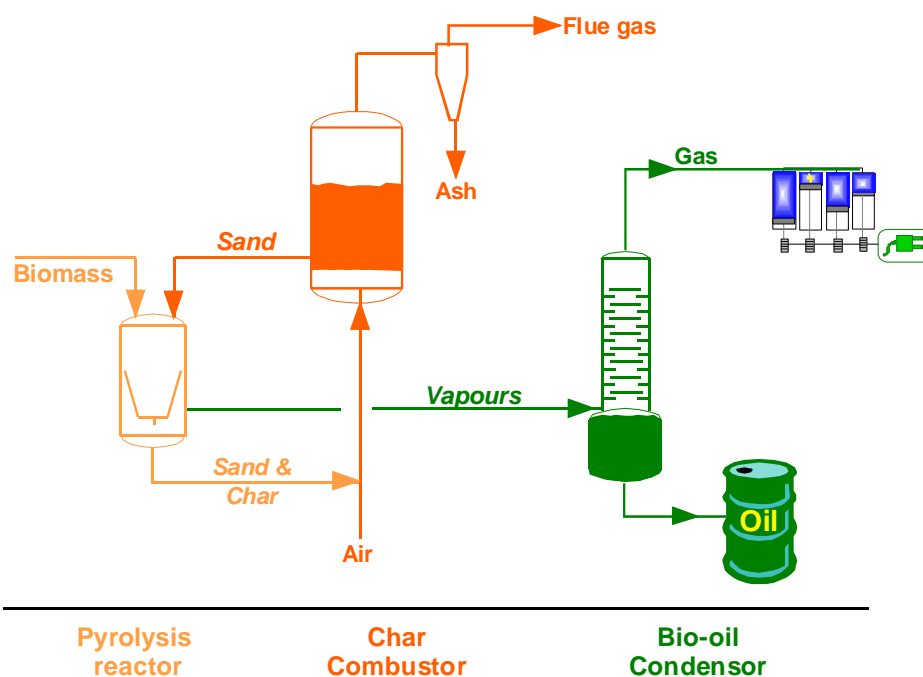
Figure 11 BTG's fast pyrolysis process. Source: BTG

Pyrolysis oil production is in its demonstration phase. BTG works on the development of a 5 ton/hour input pyrolysis unit that can produce 26,000 ton/year pyrolysis oil in Hengelo, the Netherlands. In 2005, a 2 ton/hour plant was delivered to a client in Malaysia. Generally speaking pyrolysis oil production is viable at production rates of 20,000 - 50,000 pyrolysis oil per year, which requires an input of 30,000 - 75,000 tonnes of dry biomass, which is comparable with medium sized biomass plants. Pyrolysis oil knows various applications, from heat boilers for block, district and industrial heat to large scale biorefineries and co-refining in existing fossil refineries.

For more information one could refer to (Bridgwater, Czernik et al. 1999), IEA Task 34 on Biomass Pyrolysis (http://www.pyne.co.uk) and company websites such as www.btgworld.com and www.btg-btl.com.

2.4.4 Carbonisation

Charcoal production from wood is the most common carbonisation technology, but also agro residues like cotton stalks can be carbonised and further upgraded to household fuels. The main applications for carbonised wood are cooking (in developing countries) and barbeque use. In some countries like Brazil, carbonised wood is used in steel making. Also specialities such as activated carbon for filters and medicine are made of charcoal.

Figure 12 Charcoal production with Beehive kilns in Brazil. Source: BTG

The production of charcoal can be performed in earth or metal kilns, or in more advanced installations that allow the full use of the energy rich vapours that are released. The scale of production ranges from a few m^3 up per batch up till installations that can produce 1,500 tonnes/unit per year. Large wood plantations and charcoal companies can use multiple charcoal installations in parallel, but their total production capacities are usually well below 100,000 tonnes/year. The technologies are mature and found all over the world. The World Bank and FAO report regularly on the impacts of charcoal production for household use. For a charcoal handbook see for instance (Krishnan and Robinson 1999).

2.4.5 Torrefaction

Torrefaction is a partial carbonisation process at temperatures of 200-400°C, making the biomass 'crispy', comparable with roasting of coffee beans. The torrefied biomass is suitable for co-firing in coal-fired power plants. Compared to carbonised biomass, a higher percentage of the initial energy content of the biomass stays in the product. Torrefaction is a relatively novel concept; the first demonstration plants have been built in the Netherlands; the capacity of facilities is medium sized (60,000 ton/year) and seen the application of the torrified products in power plants, up-scaling to large production plants >100 kton could be anticipated. For more information see for instance

http://www.dutchtorrefactionassociation.eu/ and company websites such as http://www.topellenergy.com. IEA task 32 'biomass combustion and cofiring (http://www.ieabcc.nl/) also covers torrefaction.

2.4.6 Anaerobic digestion

Anaerobic digestion is the production of a methane rich biogas from wet biomass sources like manure, kitchen and garden waste, wastewater, etc., or from dedicated energy crops such as from corn silage. The biogas can be used for heat and power generation using gas engines, or upgraded for use in the natural gas grid.

Main anaerobic digestion approaches include:
- Manure digestion
- Manure co-digestion with additional materials (co-substrates)
- Digestion with dedicated energy crops
- Digestion of kitchen and garden waste
- Landfill gas extraction
- Anaerobic waste water treatment
- Micro digestion units for cooking (developing countries)

All approaches are mature and commercially available. In most cases the biogas is used for electricity production with a gas engine and generator set, resulting in a considerable electric efficiency of 30-40%. In case of manure digestion, the heat of the engine is used to keep the digester in an optimal temperature range and excess heat can be used for heating buildings, or drying. If no nearby heat users are available, as often the case with landfill gas extraction, the excess heat is lost. The biogas can be used for heat only applications as well, including cooking on biogas. Upgrading of biogas to 'green gas' for use in the natural gas grid is in its early commercial phase; it can also be used to fuel cars.

Figure 13 Small scale anaerobic digestion installation. Source BTG

Manure co-digestion allows the use of a wide range of co-substrates like sugar/starch biomass (corn, food waste), oil containing biomass (e.g. used frying oil), and lignocellulosic biomass such as grasses. Woody biomass is not suitable as a co-substrate for anaerobic digestion. The scale of most digestion technologies is in the range of 10 kW_e up till 5 MW_e, which is relatively small. Sometimes small biogas grids are used to collect biogas from multiple manure (co)digesters.

More information can be found in the German Biogas Praxis (Eder and Schulz 2006), which is known by experts. English speaking readers could for instance consult the Complete Biogas Handbook (House 2006) as well as websites such as http://www.biogas-info.co.uk or the Biogas Handbook of the BiG>East project (www.big-east.eu) (Al Seadi 2008).

2.5 Conclusion

The overview of current industrial and small-scale biomass conversion chains can be summarised in a Biomass Technology Combination Matrix as presented in Table 3. In principle, all biomass feedstock could be combusted for energy generation, but lignocellulosic biomass is preferred from an economic point of view.

Table 3 Current conversion chains for oil, sugar and lignocellulosic biomass

	Oil containing biomass	Sugar and starch containing biomass	Lignocellulosic biomass
Combustion	++	++	++
Gasification, pyrolysis	-	-	++
Carbonisation, torrefaction	-	-	++
Anaerobic digestion	++	++	-
Fermentation – ethanol	-	++	+
Transesterification - biodiesel	++	-	-

Note: ++ = common combination; + = possible combination - = not common combination

Gasification, pyrolysis, carbonisation and torrefaction are strongly linked to solid lignocellulosic biomass sources. Anaerobic digesters can use a range of feedstock, except woody biomass. Obviously, transesterification and production of pure plant oil is linked to oil containing biomass; and fermentation to sugar and starch crops. Ethanol production through fermentation of lignocellulosic crops is challenging but could potentially result in high yield of ethanol from a wide range of feedstock.

The scale of production of the current conversion chains is summarised in Table 4. Basic physical properties of the feedstock and final products influence the common scale of production. Table 4 shows that ethanol production from sugar and starch crops and biodiesel production from oil have the largest scale of production, while conversion technologies for lignocellulosic feedstock such as combustion, gasification, pyrolysis, carbonisation and torrefaction are often applied in the range of the small and medium scale applications. It has to be kept in mind that raw biomass feedstock such as wood and agricultural residues have a higher bulk density and are available in smaller quantities than oil seeds and sugar/starch crops from large scale agriculture. This could affect the

expected scale and feedstock of future lignocellulosic feedstock refineries. Nevertheless the wood based paper and pulp industry operates at a large scale. The future possible size of lignocellulosic ethanol production could therefore be estimated by studying the paper industry.

Table 4 Scale of production of current biomass conversion technologies[a]

	Small scale	Medium scale	Large scale
Electric output	<5 MWe	5-50 MWe	>50 MWe
Thermal input	<20 MWth	20-200 MWth	>200 MWth
Production capacity	<10k ton/year	10-100 kton/year	>100 kton/year
Combustion	++	++	+
Gasification	++	+	+
Pyrolysis	+	++	-
Carbonisation	++	+	-
Torrefaction	+	++	+
Anaerobic digestion	++	-	-
Fermentation (sugar/starch)	+	++	++
Transesterification	-	++	++

Note: ++ = common capacity range; + = possible capacity range but less common; - = not common capacity range

[a] The capacities are indicative; for energy applications the electric or thermal capacity can be used; for liquid and solid fuels the capacity can be expressed in kilotonnes per year. Example: 10,000 ton biomass with 15 GJ/ton corresponds to 20 $MW_{thermal\ input}$, or 5 $MW_{e\ output}$ at an electric efficiency of 25% and 7500 production hours per year.

For several reasons anaerobic digesters are usually small scale applications. First of all, only part of the incoming biomass can be converted into biogas which means that, compared to other conversion chains, relatively large input quantities of biomass are needed. Consequently, this leads to higher transport costs and a lower radius from which the (wet) biomass can be collected. Secondly, the voluminous biogas cannot be stored and needs to be used almost directly; and last but not least the electric efficiency of biogas combustion in gas engines is already high, which reduces the need to scale up.

All mentioned existing conversion chains can play a role in future conversion chains, mainly as part of different biorefinery concepts, which are presented in the next chapter.

3   BIOREFINERIES

In this chapter various conversion routes are presented that might have an important future role as 2nd generation biofuel and biomaterial production processes. These conversion routes are usually presented as 'biorefineries'. In this chapter, definitions and classifications of biorefineries are presented, followed by a selection of biorefineries relevant for oil containing biomass, sugar/starch biomass and especially lignocellulosic biomass based conversion routes.

3.1   Definition of biorefineries

The term biorefinery is a popular concept nowadays and, depending on the type of activity and stakeholders involved, different definitions for biorefinery are currently used. (Ree and Annevelink 2007) present the following examples of definitions of biorefineries.

- A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass. The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum (NREL 2007).
- A biorefinery is a cluster of bio-based industries producing chemicals, fuels, power, products, and materials.
- A biorefinery is an overall concept of a promising plant where biomass feed stocks are converted and extracted into a spectrum of valuable products (DOE 2007).
- Biorefinery is the separation of biomass into distinct components which can be individually brought to the market either directly after separation, or after further (biological, thermo chemical/chemical) treatment(s) (Elbersen 2003).
- Biorefining is the transfer of the efficiency and logic of fossil-based chemistry and substantial converting industry as well as the production of energy onto the biomass industry (Kamm, Gruber et al. 2006).
- Biorefineries are integrated bio-based industries, using a variety of technologies to produce chemicals, biofuels, food and feed ingredients, biomaterials (including fibres) and power from biomass raw materials (EU Eurorefinery Euroview 2007).
- Addition of pure plant oil into traditional oil refineries (Shell 2007).
- Biorefinery is efficient use of the entire potential of raw materials and by-streams of the forest-based sector towards a broad range of high added-value products (by co-operation in between chains) ((Biorefinery Taskforce FTP 2007).
- A biorefinery is an integrated cluster of bio-industries, using a variety of different technologies to produce chemicals, biofuels, food ingredients, and power from biomass raw materials (Europabio, 2007).

Following (Ree and Annevelink 2007), the following definition as provided by the IEA Bioenergy Task 42 on Biorefineries, will be used in this report.

> Biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy.

3.2   Types of biorefineries

Just as with crude oil refineries, the feedstock - biomass - is separated and refined to produce various fuels and products in a biorefinery. Biorefineries are not new. An existing example is a modern sugar factory that can fine-tune the plant to produce either more bio-ethanol or more sugar. Another example is the starch hydrolysis plant, for the production of among others glucose, which can be used for the production of many chemicals and products such as ethanol, acetic acid, etc.
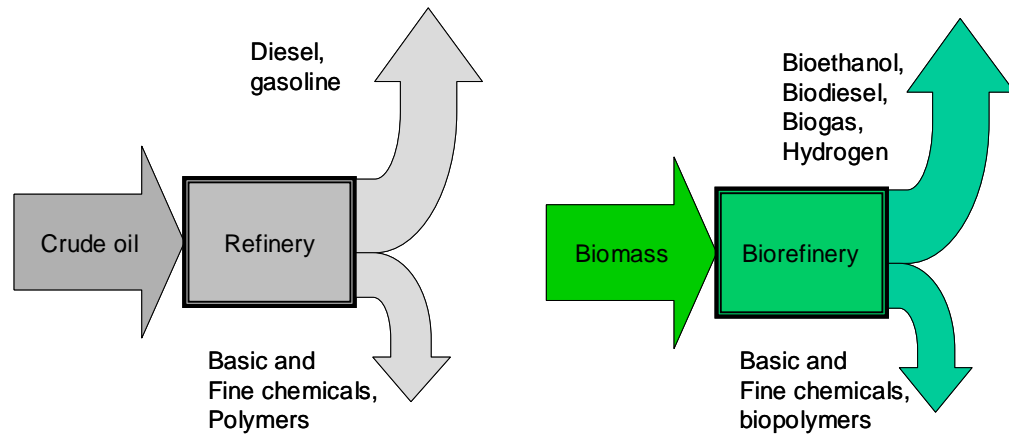

Figure 14 The biorefinery concept. Instead of crude oil, biomass is upgraded and refined to produce a variety of fuels and materials. (Kamm, Gruber et al. 2006).

Biorefineries come in all shapes and sizes and there are many classifications possible. Among others, classifications can be based on:
- Raw material input (ligno-cellulosic biomass, aquatic biomass, etc.),
- Type of technology (thermo-chemical treatment, microbial degradation, etc.),
- Status of technology (conventional vs. advanced, 1st and 2nd generation), and
- Main (intermediate) product (syngas, sugar and lignin platform).

The following general classification, presented by (Kamm, Gruber et al. 2006) is often used nowadays:
- **Conventional biorefineries** - many existing industries make use of biorefinery concepts, like for instance in the sugar, starch, vegetable oils, feed, food, pulp and paper industries and the traditional biofuel industry.
- **The lignocellulosic feedstock biorefinery (LCF)** - where "nature-dry" biomass, such as wood and other cellulose-containing biomass is first separated into cellulose, hemicellulose and lignin, after which further processing can take place.
- **Thermo-chemical biorefineries** - where thermo-chemical technologies are used like pyrolysis or gasification to produce an intermediary product that can be refined thermo-chemically into a portfolio of value added products. A specific type of thermo-chemical biorefineries makes use of the existing fossil oil based petrochemical infrastructure.

- **Two platform biorefinery** - Here two platforms are distinguished; the sugar platform and the syngas platform. The sugar platform is based on biochemical processes, and the syngas platform is based on thermo-chemical conversion.
- **Whole crop biorefinery** - this concept uses raw materials such as cereals or maize. The straw may be utilised as in an LCF biorefinery, the seed may be converted to starch, or grinded to meal, followed by further processing.
- **Green biorefineries** – where "nature wet" biomass such as green grass are converted to various products using microbial degradation.
- **Marine biorefinery** - in which aquatic biomass (algae) are treated by cell disruption, product extraction and separation into, for instance, lipids and "algomass".

Relevance of biorefinery types for different biomass types

In section 2.1 three main types of biomass were identified:
- oil containing biomass,
- sugar and starch biomass and
- lignocellulosic biomass (wood/straw and grass).

In the next sections biorefinery types relevant for these types of biomass are highlighted.

3.3 Biorefineries for oil containing biomass - the oleochemical industry

Vegetable and animal oils and fats are used in food, feed and other applications including cosmetics, shampoos, soaps, detergents, pharmaceutical products, paint, inks, industrial lubricants, plastics, waxes, candles, etc. (see for instance http://www.apag.org/oleo/index.htm). The oleochemical industry can be regarded as 'conventional biorefineries' responsible for the production of the above mentioned non-food non-feed applications.

The production of biodiesel from plant oils can also be regarded as part of the oleochemical industry. However (part of) the traditional oleochemical industry opposes the subsided use of oils and fats for transport fuels since it has led to considerable market distortions. In particular the drop in glycerine price induced by the increased biodiesel and subsequent glycerine production has hit the European oleochemical industry.

On-going research is focused on the use of oleochemical building blocks in order to increase the percentage of non-petroleum based components in various applications (Kamm, Gruber et al. 2006) (Vol II, p 295-300). It is however questionable how far these developments should be regarded as new biorefinery activities separate from the existing oleochemical industry.

For further information on the oleochemical sector see for instance the handbook of (Gunstone and Hamilton 2001) and (Kamm, Gruber et al. 2006).

3.4 Biorefineries for sugar and starch biomass

Upgrading of sugar and starch biomass is mainly performed in 'conventional biorefineries', but also new developments can be observed. In the next sections sugar-based and starch based biorefineries are presented as well as the -starch crop based-whole crop biorefinery concept.

3.4.1 Sugar based biorefinery

Sugar mills operating in Brazil and other countries are large units functioning as autonomous industrial complexes. Their main products are sugar, fuel ethanol and bagasse. These systems can be regarded as 'conventional biorefineries' and have been described in section 2.3.1. The combined sugar and ethanol production, which is common in Brazil, could be called sugar-based biorefinery.
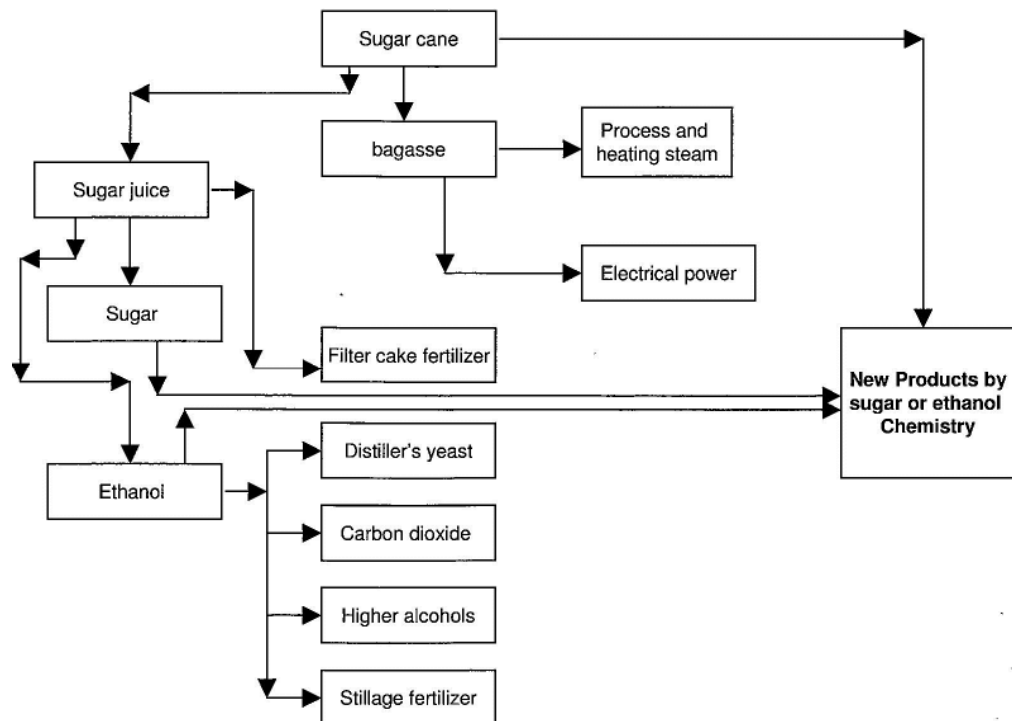

Figure 15 Sugar cane processing to sucrose, ethanol, by-products and new products. Source (Kamm, Gruber et al. 2006)

One interesting application is the production of poly-3-hydroxybutyrate (PHB), an environmentally degradable material belonging to the polyhydroxyalkanoates (PHA) family. PHB is a bioplastic that can be processed as a conventional thermoplastic in most industrial transformation processes including extrusion, injection, and thermopressing. It is fully biodegradable under the conditions of industrial waste composting sites (Kamm, Gruber et al. 2006). PHB is slightly more biodegradable than polylactic acid (PLA) - the most widely used bioplastic, and has a wider range of applications ranging from stiff packaging to highly elastic materials for coatings (Evans 2010).

PHB is produced in an aerobic fermentation process in which the sugar carbon source is converted into a biopolymer by means of the microorganism *Ralstonia eutropha*.

Recovery of PHB in biomass from fermentation involves several complex steps, for example microorganism cell breakdown, removal of impurities, and purification of the final product. For more information see (Kamm, Gruber et al. 2006) (Vol I, p 212-223)

Production of PHB can be integrated in a sugar and ethanol mill; the milling season lasts 180 days whereas PHB facilities could work all year round, meaning that the sugar input (medium quality standard sugar) needs to be stored. The required thermal energy and power could be supplied by the combustion of bagasse. The investment costs of a 10 kton PHB plant is estimated at 38 mln USD. The estimated production costs of integrating a PHB plant with an existing sugar mill are lower than those of a standalone PHB plant (Kamm, Gruber et al. 2006) (p 223).

No commercial sugar cane based PHB production plant was found yet. However, Telles, a joint venture of Metabolix and Archer Daniels Midland (ADM) has completed the initial phase of construction of a 50,000 ton/year corn based PHA manufacturing plant in Clinton, Iowa. This first ever large-scale PHA manufacturing facility will allow a range of PHA polymers to be produced and commercialized in large volume markets (Evans 2010).

3.4.2 Starch based biorefinery

Starch is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. It is the most important carbohydrate in the human diet and is contained in such staple foods as potatoes, wheat, maize (corn), rice, and tapioca (cassava).

Potato starch

Potato is the most important tuber used for industrial isolation of starch. Potato has the advantage that the extraction process is simpler than processes used for cereals, because it is not necessary to swell or mill them or prepare a dough. The disadvantages are the lower starch content of tubers and the large quantity of fruit water produced. Examples of (potato) starch based products are paper (mainly paper sizing), building additives (such as starch ethers for the dry mortar industry), adhesives (such as wallpaper, paper sack, envelop, billposting adhesives), textile (warp yarn sizing agents), etc. (see for instance www.avebe.com).

Corn starch

In the processing of corn based starch, a general distinction is made between traditional dry milling and wet milling.

Dry milling ethanol production plants work by grinding the grain to flour. The flour is then fermented to produce ethanol. Ethanol is separated off, and the residue (the "sillage") is then dried to get DDGS "dried distillers grains with solubles", which is used as cattle fodder. The CO_2 released during fermentation is captured and sold separately (see drawing).
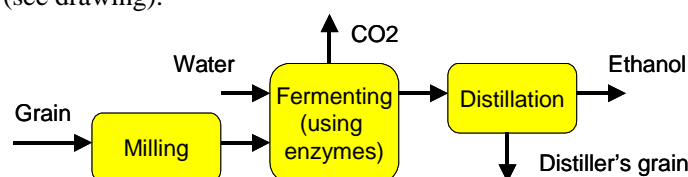
In the w*et milling* process, grain is first soaked in water and sulphurous acid and 'steeped' for 1 to 2 days. It is then separated into its four basic components: starch, germ, fibre and protein. A metric tonne of corn grain yields, on average, 684 kg starch, 237 kg corn gluten feed, 45 kg gluten meal (60% protein) and 34 kg corn oil in a typical wet milling operation (Kamm, Gruber et al. 2006). Each component can be further processed to yield products. The greatest portion of the wet milled corn starch is converted to ethanol or syrup. The extent of hydrolysis determines whether a corn syrup (20-70 dextrose equivalent[11] (DE)) or dextrose syrup (94-98 DE) is produced. Converting 95 or higher DE glucose syrup provides the refiner with three options. It can be refined as dextrose or 95 DE corn syrup, fermented to ethanol, or isomerised to high fructose corn sweetener (HFCS). In the USA the most widely used varieties of high-fructose corn syrup are: HFCS 55 (mostly used in soft drinks) and HFCS 42 (used in many foods and baked goods). In the USA, HFCS is among the sweeteners that have primarily replaced sucrose (table sugar).
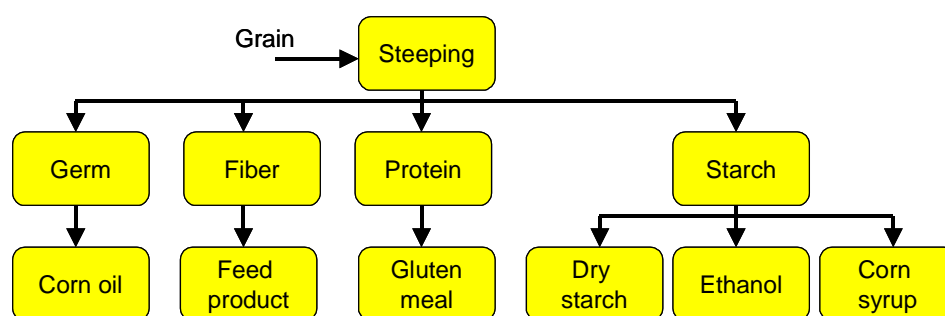
The dry milling process is commonly used for the production of ethanol. It is cost effective, and capital expenditures are limited. Wet milling requires more investments, but the plant is more flexible, and a bigger portion of the grain is used to produce a variety of products. Although both processes can be regarded as 'conventional biorefineries', the development of the wet milling process with its flexible outputs is seen as exemplary for future biorefineries.

Furthermore, starch can be upgraded by:
- plasticization (co- and mix-polymerization, compounding with other polymers)
- chemical modification
  - etherification into carboxymethyl starch
  - esterification and re-esterification into fatty acid esters via acetic starch
  - splitting reductive amination into ethylenediamine, etc.,
  - hydrogenative splitting into sorbitol, ethylene glycol, propylene glycol, and glycerin
- bio-technological conversion into poly-3-hydroxybutyric acid (PHB).

Like in case of the oleochemical industry, the development of these new products, will be based on and developed largely by the existing starch processing industry.

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[11] The Dextrose Equivalent (DE) is a measure of the total dry reducing sugars in the syrup calculated as dextrose and expressed as a percentage fo the total dry substance of the solution.

3.4.3 Whole crop milling biorefinery

When the upgrading of starch is combined with the upgrading of lignocellulosic feedstock (straw) at the same site, it is called 'whole crop biorefinery'. The whole crop milling biorefinery is based on dry or wet milling of starch biomass such as rye, wheat, and maize, in which also the lignocellulosic fraction (straw) is applied in a lignocellulosic biorefinery:

- The grain will deliver starch, and derived products.
- The straw (a mixture of chaff, nodes, ears and leaves), represents a lignocellulosic feedstock, and may be further be processed in a lignocellulosic feedstock biorefinery, following biochemical and/or thermochemical pathways (see section 3.5).

The first step is the mechanical separation into a grain and straw fraction; where the portion of grain is approximately 20 wt% and the portion of straw is 80 wt%. Both streams will be further processed separately. Both fractions can be processed further to result in a portfolio of end products. See Figure 16.
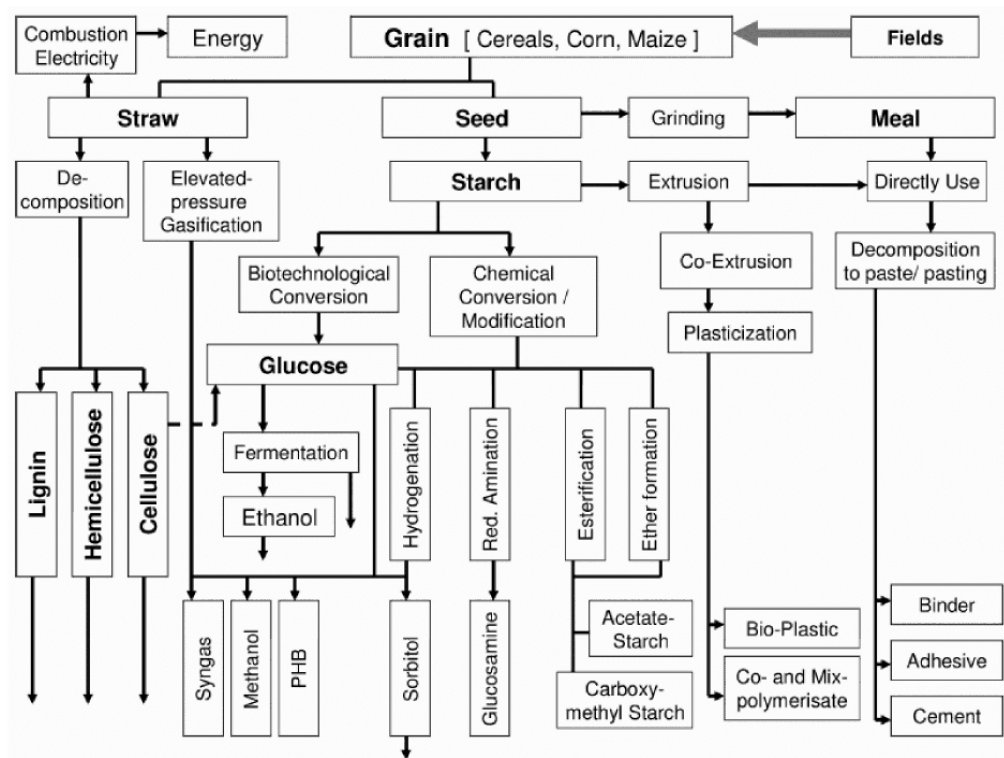

Figure 16 Potential products from a whole crop biorefinery (Kamm, Gruber et al. 2006)

Many dry and wet milling plants can be regarded as 'conventional biorefineries', in which various starch based products are produced. It is expected that this existing large industry will develop toward the whole crop biorefinery concept. The starch part of the feedstock competes with food.

3.5 Biorefineries for wood/straw based lignocellulosic biomass

The following main routes exist for the processing of lignocellulosic biomass:

- *A biochemical pathway*, in which enzymes and other micro-organisms are used to convert cellulose and hemicellulose components of the feedstocks into sugars prior to their fermentation to produce ethanol and/or other products (see section 3.5.1). In addition the lignin fraction of the biomass can be recovered and used for biochemical production (see section 3.5.2)
- A *thermochemical pathway*, where pyrolysis/gasification technologies produce a synthetic gas from which a wide range of fuels and chemicals can be produced (see section 3.5.3)
- A *hybrid pathway* when a combination of thermochemical and biochemical treatments is applied to one fraction (section 3.5.4.).
- With elements of both main routes another pathway can be described, the '*two platform biorefinery*', in which the cellulose and hemicellulose fractions are biochemically upgraded (the sugar platform), and the lignin fraction upgraded in a thermochemical way (syngas platform) (see section 3.5.5).

Status and scale of production

An excellent overview of current biochemical, thermochemical and hybrid lignocellulosic biorefinery projects and their status can be found on (Bacovsky, Dallos et al. 2010), and also accessible through http://biofuels.abc-energy.at/demoplants/projects/mapindex.

number of projects in certain size ranges sorted by technology

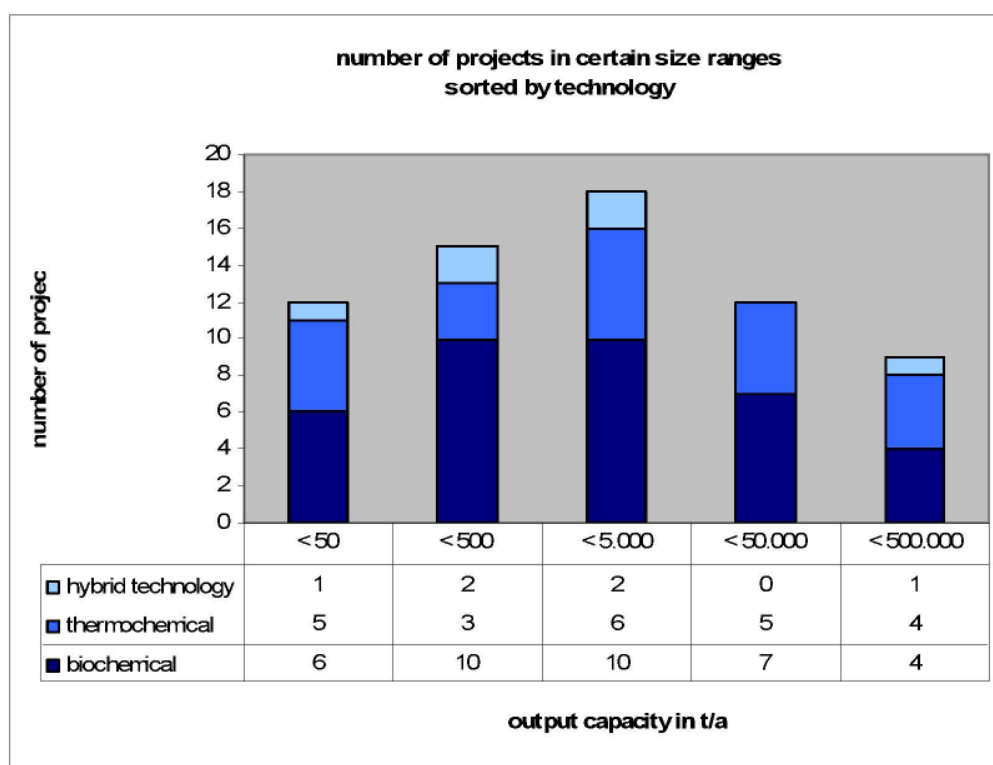| number of projec	<50	<500	<5.000	<50.000	<500.000
☐ hybrid technology	1	2	2	0	1
■ thermochemical	5	3	6	5	4
■ biochemical	6	10	10	7	4

output capacity in t/a

Figure 17 Number of biorefinery project in certain capacity ranges sorted by technology. Source (Bacovsky, Dallos et al. 2010)

(Bacovsky, Dallos et al. 2010) collected information on 66 projects, of which 37 were classified to use a biochemical pathway, 23 a thermochemical pathway and 6 a hybrid pathway. Figure 17 shows that most of these projects (45 out of 66) are small scale, 12 are medium scale and 9 large scale projects. Figure 18 shows that a large part of the small plants are operational, while most of the medium and large scale plants are planned but not yet operational. This clearly shows that the lignocellulosic biorefineries are in the pilot and demonstration scale.

number of projects in certain size ranges sorted by status

	< 50	< 500	< 5.000	< 50.000	< 500.000
☐ planned	2	0	2	8	8
☐ under construction	2	3	5	2	1
☐ operational	8	12	11	2	0

output capacity in t/a
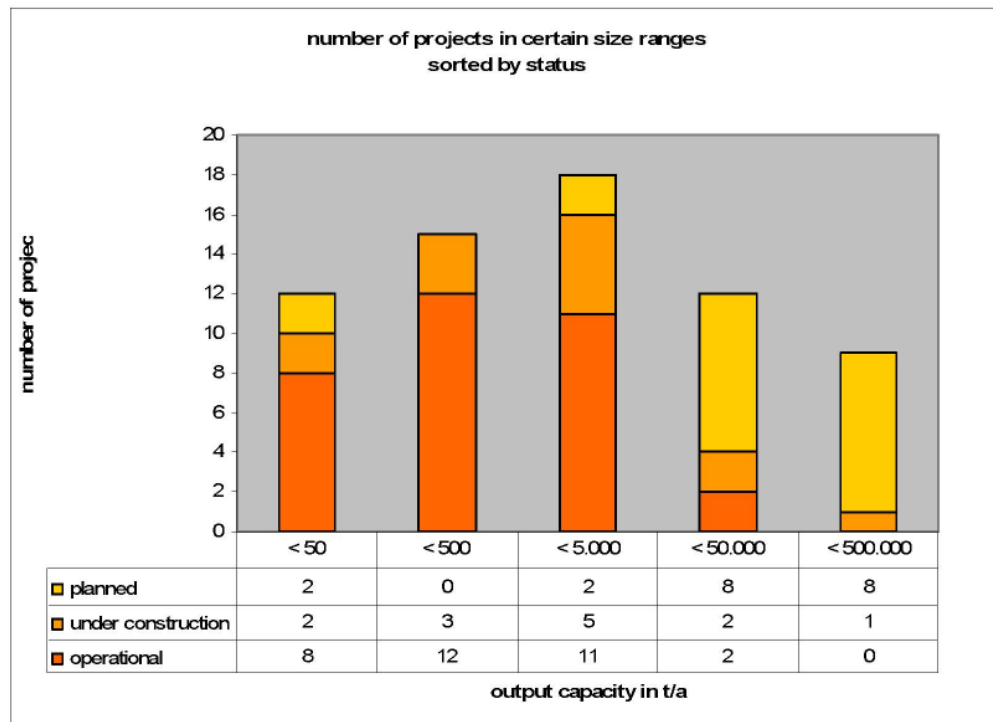
Figure 18 Planned, under construction and operational lignocellulosic biorefinery projects. Source: (Bacovsky, Dallos et al. 2010)

3.5.1   Biochemical biorefinery - lignocellulosic ethanol production

Lignocellulosic feedstock biorefineries are based on the fractionation of lignocellulosic-rich biomass sources into the intermediate output streams cellulose, hemicellulose and lignin, which can then be further processed into a portfolio of bio-based end-products, materials, chemicals, fuels and power and/or heat. See Figure 19.

Figure 19 Potential products from a lignocellulosic feedstock biorefinery (Kamm, Gruber et al. 2006)

Although various possibilities exist, most research is focused on the production of *ethanol* from both the cellulose and hemicellulose fractions (this section) and the utilization of the lignin fraction (section 3.5.2).
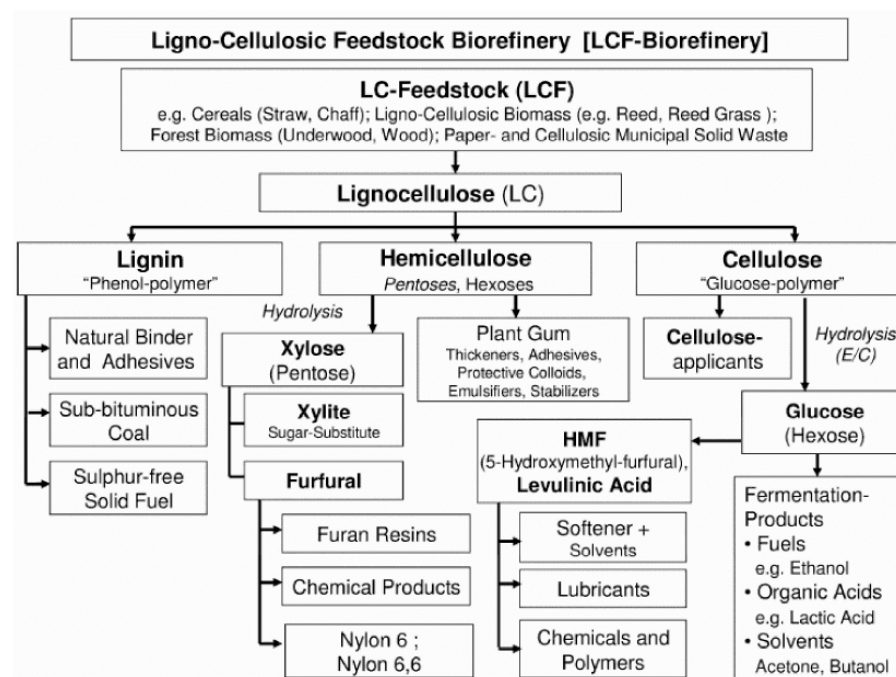
Ethanol production from cellulose and hemicellulose

Lignocellulosic biomass consists of three main components: cellulose, hemicellulose and lignin. Producing ethanol from lignocellulosic biomass depends on converting the complex cellulosic and hemicellulosic carbohydrates into simple sugars which are fermented to ethanol by a variety of microorganisms. The cellulose contains hexose (C-6) sugars; the hemicellulose contains hexose (C-6) and pentose (C-5) sugars. Table 5 shows the carbohydrate composition of different lignocellulosic feedstock.

Table 5 Carbohydrate composition of different lignocellulosic feedstock

	Carbohydrates					
	Cellulose	Hemicellulose/ polyoses				
		Hexosans		Pentosans		
Plant name	Glucan (%)	Mannan (%)	Galactan (%)	Xylan (%)	Arabinan (%)	Lignin (%)
White wood	46.5	11.6	1.2	6.8	1.6	26.7
Douglas fir	43.46	10.76	4.66	2.77	2.67	31.3
Oak	40.63	1.97	1.22	19.19	0.36	23.91
Aspen	45.97	2.10	7.9	17.74	1.23	20.30
Maize cob	34.0	0.5	1.0	14.0	1.7	13.1
Wheat straw	37.0	0.3	6.5	18.9	5.6	13.6
Resulting sugar type	D-glucose (Hexose)	D-mannose (Hexose)	D-galactos (Hexose)	D-Xylose (Pentose)	L-arabinose (Pentose)	

Source: based on (Kamm, Gruber et al. 2006), vol 2, p 109

Depending on the feedstock, next to the conversion of C-6 sugars, the conversion of C-5 sugars of the hemicellulose is essential to achieve high ethanol conversion rates. The biochemical conversion of lignocellulosic biomass into ethanol consists of three main steps:

1. pre-treatment: sizing, removal dirt, releasing cellulose from hemicellulose and lignin
2. (hemi) cellulase-mediated hydrolysis of (hemi)cellulose into sugars (C-5 and C-6)
3. fermentation of C-5 and C-6 sugars into ethanol.

These steps can be carried out with varying degrees of consolidation and are described below.

Pretreatment

Due to the strong bonds of the ligno-cellulose structure, pretreatment processes are generally severe and represent a significant cost element of the whole pathway. The aim of the pretreatment is to open up the cellular structure of the biomass by removal of the lignin fraction, so that the cellulose and hemicellulose can be exposed to enzymatic hydrolysis, and to avoid the release of other components toxic for the hydrolysis process. Woody biomass pretreatments that are under investigation include (1) one stage steam explosion, (2) two stage steam explosion in the presence of SO_2 or sulphuric acid, (3) ammonia fibre explosion (AFEX), (4) dilute mineral acid, and (5) organosolv delignification. Steam explosion under mildly acidic conditions is currently the state-of-the-art pretreatment technology. Laboratory testing has shown that the recovery of C-5 and C-6 sugars and lignin from softwood after steam-explosion pretreatment can be significantly lower than for agricultural residues or hardwoods such as poplar. This problem is one of the primary drivers for assessing alternative pretreatment methods for softwoods. More information on different pretreatment methods is summarised in (Sims and Taylor 2008) (p 46-50).

Enzymatic hydrolysis

Hydrolysis is a chemical process in which a certain molecule is split into two parts by the addition of a molecule of water, in this case the production of sugars from cellulose by either acid hydrolysis or enzymatic hydrolysis:

- *Acid hydrolysis* can be applied to convert cellulose to sugars. Using sulphuric acid to hydrolyse lignocellulosic fibres into sugars has not been very economical. Processes that hydrolyse fibres with dilute acid and pressure have tended to degrade too much of the hemicellulose sugars before they can be fermented into ethanol, causing low yields. The other option, using concentrated acid at low pressures, requires purchasing and then recycling expensive quantities of acid.
- *Enzymatic cellulose* hydrolysis processes are of interest because enzymes exclusively catalyse specific reactions. Therefore, different from acidic hydrolysis, there are no side reactions or by-productions and the hydrolysis can potentially be performed with yields approaching 100%. Enzymatic hydrolysis of conventional starchy feedstocks has already replaced acid hydrolysis in modern ethanol facilities.

Cellulase is a group of enzymes that cellulose converts to glucose. Efficient enzymatic hydrolysis of cellulose requires the synergistic activity of three groups of enzymes (Sims and Taylor 2008):

- Endo-β-1,4-glucanases are enzymes that hydrolyse accessible regions on cellulose chains and split the chains to provide sites for other enzymes to interact.
- Cellobiohydrolases act on these sites and begin to remove successive cellobiose units (i.e. two joined glucose units).
- β-glucosidase is a specialised enzyme that hydrolyses cellobiose to glucose.

Commercial cellulase preparations are typically deficient in β-glucosidase so require supplementing in order to relieve product inhibition caused by accumulation of cellobiose and other soluble sugars. This adds to the already substantial cost for enzymes. Substantial efforts are made to reduce the total enzyme costs, including enzyme production costs, pretreatment methods that reduce enzyme use and enzyme recycling.

Fermentation

Fermentation of glucose (C-6) to ethanol is not difficult provided there is an absence of inhibitory substances such as furfural, hydroxyl methyl furfural, or natural wood derived inhibitors such as resin acids. For more than 20 years research activities have been directed towards the development of improved micro-organisms for the fermentation of the pentose (C-5) sugars. For cost effective processing, such organisms must be able to co-ferment both glucose and pentose sugars together. Significant progress has been made in engineering such micro-organisms, and pentose fermentation has been achieved on ideal substrates. Their sensitivity to inhibitors and the production of unwanted by-products remain serious problems yet to be overcome if these systems are to become commercially viable. Most of the current lignocellulosic ethanol production units convert only the hexose sugars into ethanol.

Status and scale of production

Ethanol production from lignocellulosic biomass is in its demonstration phase. Whilst the costs for lignocellulosic feedstocks themselves are expected to be lower than for oil, sugar and starch crops, the difficulty of converting these feedstocks to liquid fuels means that the conversion technologies are prone to being more expensive than current conversion technologies. Several initiatives can be found in Europe and especially the USA. Because of the demonstration character, the plants are generally smaller than sugar/starch ethanol plants.

(Bacovsky, Dallos et al. 2010) provide a recent overview of (planned) demonstration units which have capacities of 50-500,000 tonnes/year. The information can also be accessed through a map on http://biofuels.abc-energy.at/demoplants/projects/mapindex. For more information regarding the process please refer to (Kamm, Gruber et al. 2006). Also (Sims and Taylor 2008) provide an excellent overview of the status of a.o. lignocellulosic ethanol production.

3.5.2 Biochemical biorefinery – lignin utilization

Lignin represents a considerable proportion of the structural components of plants. It accounts for approximately 10-12% of some short annual plants and up to 30% and more for some coniferous trees. Most lignin in the chemical pulping industry is burned in chemical recovery boilers. Nevertheless, most experience with lignin recovery is build up by the chemical pulping industry. Significant commercial markets, totalling over one million tonnes per year, already exist for lignins that have been recovered from chemical pulp mills. The value of lignin in these markets is generally an order of magnitude higher than its fuel value. Furthermore lignin from some types of biorefineries will most probably have better performance characteristics and be of greater commercial value for its chemical properties than lignins from existing chemical pulping operations (Kamm, Gruber et al. 2006) (Vol 2, p 165).

Traditional lignin products from paper mills
In paper mills the cellulose is separated from the remaining hemicellulose and lignin fraction, forming black liquor in the kraft process or red/brown liquor in sulphite pulping, from which lignin fractions can be obtained. The main commercial lignin types are lignosulfonates from sulphite pulp mills, and - to a lesser extent - thiolignins from Kraft pulping processes.

Lignosulfonates are recovered from the spent pulping liquids (red or brown liquor) from sulfite pulping. The most widely used industrial process is the Howard process, in which 90–95% yields of calcium lignosulfonates are precipitated by adding of excess calcium hydroxide. Lignosulfonate can be used for road dust suppression, feed pellet binders and animal feed additives. More advanced applications of lignosulfonates, promoted by the larger mills, are its use as dispersants, emulsifiers and surfactants. Borregaard LignoTech produces 400,000 tons of lignosulfonates per year while the total market is below 800,000 tonnes/year. Because of the steadily declining number of sulphite pulp mills, the amount of available lignosulfonates has also declined (Kamm, Gruber et al. 2006) (Vol 2, p 173).

Today vast quantities of lignin are processed in the kraft pulping industry, probably more than 70 million tonnes per year, but of this amount more than 99% is burned in chemical recovery furnaces. The recovery of kraft lignin from black liquors is neither simple nor inexpensive. MeadWestvaco is the main producer of kraft lignins. The total production of kraft lignin is estimated to be below 100,000 tonnes/year (Kamm, Gruber et al. 2006) (Vol 2, p 170). Kraft lignin finds applications as rubber reinforcers, activated carbon, carbon black substitutes, phenolic resin components, and as raw materials for the production of methylsulfonates (competing with lignosulfonates).

Lignin from biorefineries
The options for lignin recovery from biochemical biorefineries depends mainly on the type of pretreatment. The various fibre explosion processes open up the tight structure of the fibre to expose cellulose more for enzymatic attack. In the subsequent enzymatic hydrolysis, the presence of lignin reduces the efficiency of the process as the cellulase tends to bind with the lignin. Therefore, after the initial explosion stage, lignin extraction from the pre-treated material is often included, usually with hot ethanol or hot alkali.

The organosolv process combines pretreatment and (hemicellulose and) lignin removal in one step. It involves treatment of the raw lignocellulosic material with an aqueous organic solvent (frequently ethanol) at temperatures in the range of 180-200 °C, in which most of the hemicellulose and lignin is hydrolysed and dissolved in the liquor. Following washing of the remaining solid fibre, the residual lignin is a minor part of the finely disrupted material. The lignin is separated from the "black" liquor and other components can be extracted as well in further steps as shown in Figure 20.
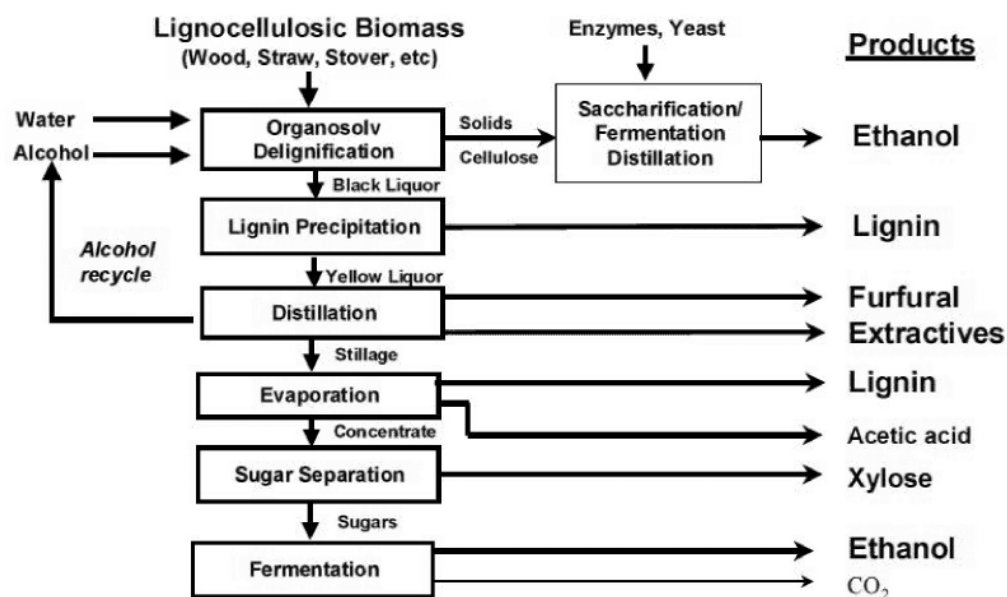

Figure 20 The Lignol modified organosolv biorefinery process. Source (Pye, Rushton et al. 2007)

Recent interest in environmentally friendly chemical pulping has encouraged the investigation and development of organosolv pulping. Various organosolv processes have been proposed and investigated over the last twenty-five years or so. These include the Alcell process, using ethanol; Acetosolv, using acetic acid; Formacell, using formic acid; pulping with phenol; and the Organocell process using methanol.

The Alcell process, developed by Repap Enterprises Inc, during 1987–1997, is perhaps the most commercially advanced of the ethanol-based organosolv pulping processes. The Alcell pulping process was operated in a pre-commercial demonstration plant at Repap's Miramichi pulp and paper mill in New Brunswick, Canada. This plant, with a design capacity of 30 tonnes of pulp per day, operated intermittently from 1989 to 1996 and produced more than 3,700 tonnes of organosolv lignin. This lignin was in the form of a dry powder and was sold in supersacks containing approximately 800 kg each. All of the lignin produced at the plant was sold commercially during the time the plant operated, except for some minor portion that was used for internal study and development purposes. Unfortunately, with the financial collapse and consequent breakup of Repap in 1997, this plant was closed, but the technology has since been acquired by Lignol Innovations Corporation of Vancouver, Canada, and is now being commercialized as a biorefinery technology with the cellulose fraction being used for ethanol production instead of pulp (Kamm, Gruber et al. 2006) (Vol 2, p 179).

Lignin recovery is also addressed by other biorefinery process developers, including hybrid options, like lignin recovery from pyrolysis oil.

Applications of lignin from biorefineries

One of the most important applications of lignin is the replacement of phenol-formaldehyde (PF) resin applications. PF is produced by reacting phenol and formaldehyde in the presence of an acid or alkaline catalyst. Since phenol is now produced almost exclusively from benzene instead of from coking operations, increases in crude oil prices cause a significant rise in the cost of raw materials and a consequent increase in the prices for phenolic resins. The manner of substituting lignin for PF-resins can vary from a simple blending of dry powder lignin with dry powder phenolic resin to the use of organosolv lignin as a primary phenolic component during the manufacture of the resin. Table 6 shows the main present applications of PF in which lignin could play a role as a substitute. The degree of substitution varies and depends on the specific application and R&D efforts. Already in 1995, when Repap was preparing to construct a 450 tonne per day Alcell pulp mill at Atholville, New Brunswick, several studies were commissioned to identify marketing strategies for the 56,000 tonnes of organosolv lignin output from this mill. These studies clearly showed that several hundred thousand tonnes of lignin per year could be easily sold at that time for an average price close to the price of PF resins. Lignosulfonates and thiolignins have been marketed for incorporation into phenolic resins for some time, but they do not appear to have met with significant acceptance by the resin industry.

Table 6 Applications for phenol-formaldehyde resins

PF- Application	Current market size (tonnes/year)	
	USA	World
Panel board adhesives	550,000	1.2 mln
Thermoset resins for moulded products	55,000	200,000
Friction materials	27,000	> 120,000
Foundry resins	55,000-60,000[a]	150,000
Insulation materials	110,000	-
Decorative laminates	100,000	300,000

[a] North America

Lignin from biorefineries can also serve as an anti-oxidant, for instance in animal feed supplements, rubber products and lubricant industry. It could also be used in markets currently served by lignosulfonates, i.e. in concrete admixtures, dye dispersants, asphalt emulsifiers, agricultural applications, and as dispersants for herbicides, pesticides and fungicides. See (Kamm, Gruber et al. 2006) (Vol 2 p 181-199).

3.5.3 Thermochemical biorefinery

Most thermal biorefineries are based on a combination of gasification, gas cleaning and upgrading and fuel synthesis.

Gasification

In most thermochemical biorefineries dry lignocellulosic feedstock is subjected to a severe heat treatment in the presence of a controlled amount of air (or oxygen) so that gasification takes place. Compared to 'ordinary' gasification, the product gas or syngas is used for fuel/chemical production instead of conventional heat and/or power production. In some applications pyrolysis is used as a pretreatment before gasification. Gasification techniques applied are quite equally split between fluidised bed gasifiers and entrained flow gasifiers (Bacovsky, Dallos et al. 2010). Generally the fluidised bed gasifiers are built smaller than entrained flow gasifiers.

Gas cleaning and upgrading

The gas needs to be cleaned for the prevention of corrosion, erosion and deposits in the process lines as well as prevention of poisoning of catalysts. Typical components that need to be removed are dust, alkali metal compounds, tar, sulphur compounds, nitrogen and chloride compounds. After that the gas can be upgraded, for instance by a water-gas-shift reaction, gas reforming and removal of inert gas fractions (mainly CO_2).

Fuel synthesis

Starting from the syngas several fuel processing pathways are possible, such as Fischer-Tropsch synthesis, methanol synthesis, and production of synthetic natural gas (SNG). Ethanol production can be produced from producer gas following either a thermochemical or a microbiological pathway.

Fischer-Tropsch synthesis

Fischer-Tropsch synthesis is a catalysed chemical reaction in which carbon monoxide and hydrogen are produced from the gasification of a solid feedstock such as coal or woody biomass into a range of liquid hydrocarbons. Typical transition metal catalysts are based on iron and cobalt.

Useful reactions give alkanes $(2n+1) H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$

The process was developed in 1923 by Prof Franz Fischer and Dr. Hans Tropsch. In the 1940s 600,000 t/yr of liquid fuels were made from coal in Germany from coals. South Africa built three coal-to-liquid SASOL plants in the 1980s using the FT process to convert coal to gasoline and diesel. Shell has operated a commercial FT-diesel plant in Malaysia since 1993. It uses natural gas as a feedstock to produce primarily low sulphur diesel fuels and food-grade wax (Sims and Taylor 2008).

Similar conversion technologies can be applied to biomass-derived syngas. However, before catalysis the raw syngas must be cleaned in order to remove inhibitory substances that would inactivate the catalyst. Volatile tars as well as sulphur, nitrogen and chlorine

compounds should be removed. The ratio of hydrogen to carbon monoxide in the syngas may need to be adjusted and the CO_2 by-product may need to be removed.

Synthetic natural gas production
Methanisation is a highly exothermal reaction in which carbon monoxide, carbon dioxide and hydrogen are converted into methane and water. The reaction is catalysed typically by nickel oxide catalysts under pressure of 20-30 bar. The formation of carbon (coking) is a possible undesired side reaction of this process. Cleaning and upgrading of the obtained gas is required for increasing the methane content and reaching natural gas quality, which consists of 98% methane. For this upgrading primarily the drying, desulphurisation and the separation of methane and carbon dioxide is necessary.

Alcohol (Methanol, ethanol, and higher alcohols) production
Higher alcohol synthesis (HAS) is performed by the use of catalysts. The catalytic HAS transformation of the syngas to alcohols is typically performed in fixed bed reactors. The optimization of heat removal is of particular interest because the process is highly exothermic. The gas cleaning needs to be adjusted to the requirements of the catalysts. This way of ethanol production may be seen as alternative to lignocellulosic ethanol production.

Status and scale of production
Of the 28 thermochemical biorefineries presented by the overview of IEA task 39[12] ten are operational, of which five pilot plants, four demonstration plants and one commercial plant (Range fuels, Georgia, United States). This shows that commercial operation of these technologies is challenging. A basic technical challenge is that most biomass based syngas is considerably more heterogeneous than natural gas based syngas leading to resulting variations in quality, while the input gases must be relatively clean in order for the synthesis processes (e.g. FT, SNG) to function in a commercially viable way. Most economic studies have indicated that deployment of large scale commercial plants is required to gain the necessary cost reductions from both economies of scale and learning experience for these processes.

3.5.4 Hybrid biorefineries

Hybrid biorefineries make use of a combination of thermochemical and biochemical approaches. Examples are
- Gasification followed by fermentation of the resulting gaseous mixture of carbon monoxide, hydrogen and carbon dioxide.
- Fast pyrolysis followed by hydrolysis and/or fermentation of anhydrosugars found in the resulting pyrolysis oil.

Gasification and fermentation
The microbiological production of alcohols is a fermentative process based on the utilisation of hydrogen, carbon monoxide and carbon dioxide. Besides alcohols such as ethanol and butanol other chemicals such as organic acids and methane can be obtained.

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[12] http://biofuels.abc-energy.at/demoplants/projects/mapindex

The main advantage of the microbiological process is the mild process conditions compared to thermochemical ethanol synthesis. Due to the lower sensitivity of the used microorganisms towards sulphur, the gas cleaning costs may be significantly reduced. Moreover there is a higher reaction specificity for a product than in case of inorganic catalysts which is combined with the high tolerance towards the CO/H_2 ratio (no gas shift reaction is needed). The main disadvantage is the limited gas to liquid mass transfer rate requiring specific reactor designs (Bacovsky, Dallos et al. 2010).

Biorefineries based on fast pyrolysis

Fast pyrolysis is a process in which organic materials are rapidly heated to 450 - 600 °C in absence of air. Under these conditions, organic vapours, permanent gases and charcoal are produced. The vapours are condensed to pyrolysis oil. Typically, 50 - 75 wt.% of the feedstock is converted into pyrolysis oil. The pyrolysis oil is a mixture of many compounds, of which the main components are:

- acids, aldehydes, sugars and furans from the carbohydrate fraction (cellulose and hemicellulose)
- phenolic compounds, aromatic acids and aldehydes derived from the lignin fraction.

There are several possibilities for acquiring upgraded products from pyrolysis oil, as shown in Figure 21. A strong point of pyrolysis oil is that it can be produced relatively near the biomass source and transported to a larger biorefinery for further upgrading.
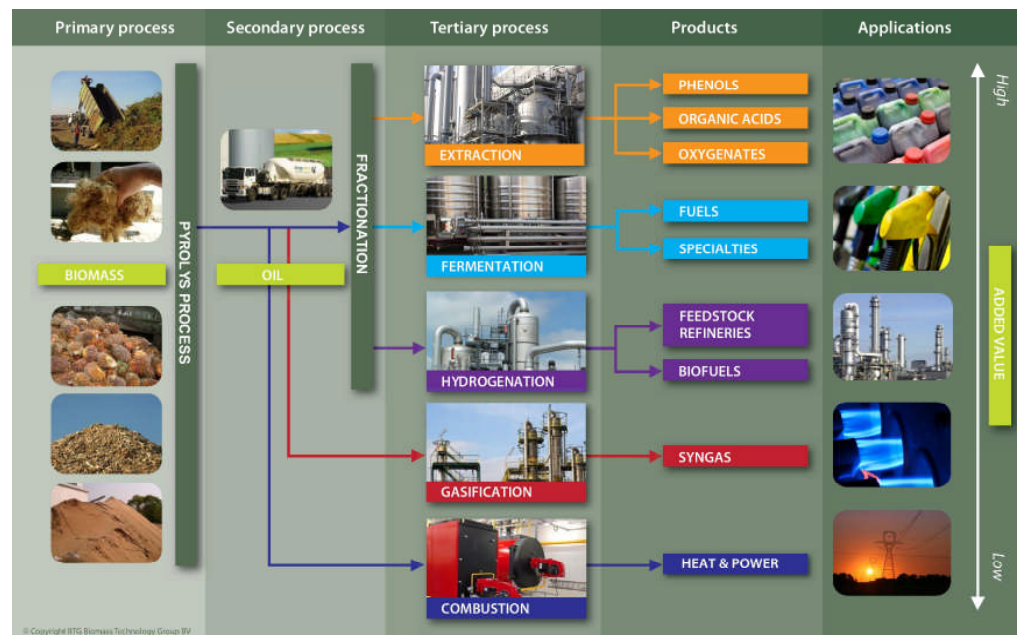

Figure 21 biorefinery options based on pyrolysis of biomass (BTG 2010)

One promising upgrading option is hydrogenation, in which the pyrolysis oil is prepared for the use in conventional refineries. The upgrading process primarily involves oxygen removal by hydro-treatment followed by hydrocracking after which co-processing in conventional refineries is possible. The market for conventional fuels and chemicals is large; even a few percent of co-processing in a conventional refinery would involve large volumes of upgraded pyrolysis oil.

3.5.5 Two platform concept biorefinery

The two platform concept biorefinery is based on fractionation of biomass into mainly a sugar (cellulose and hemicellulose) and a lignin fraction (Figure 12):

- The sugar fraction (cellulose and hemicellulose) will be biochemically converted using a so called "sugar platform" into a portfolio of potential bio-products, such as: materials, chemicals, and fuels.
- The lignin fraction (and the residues from the biochemical process) will be thermo-chemically converted using a so called "syngas platform" into a syngas for the potential production of a spectrum of bio-based products, including power and/or heat, to meet the internal process power and heat requirements.
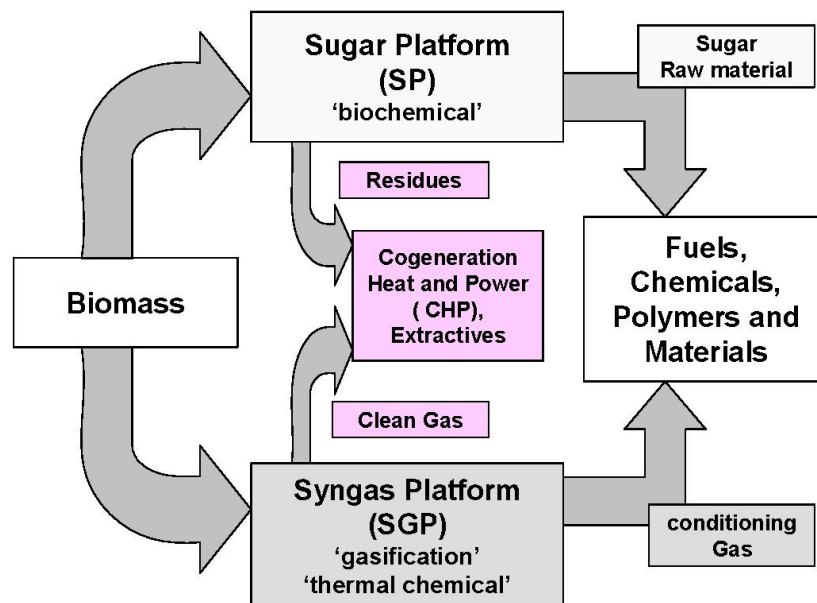

Figure 22 Two platform concept biorefinery (Kamm, Gruber et al. 2006)

3.6 Biorefineries for grassy lignocellulosic biomass - green biorefineries

Like other lignocellulosic biomass green plants, such as grass, alfalfa, immature grain etc. contain cellulose, hemicellulose and lignin fractions. However, in comparison with other vegetable biomass green plants are characterised by a high content of aqueous cell juice with carbohydrates of low molecular weight, a large amount of enzymes (proteins) for photosynthesis and a relatively low content of lignin in the cell walls.

Green biorefineries are based on traditional technologies of green forage preservation, leaf-protein extraction, chlorophyll (pigment) production, and modern biotechnological and chemical conversion methods. All technological concepts of green biorefineries include the separation of the cell juice from the plant framework. Both fractions are subjected to different biotechnological and physiochemical conversion methods. See also Figure 17.

The green biorefinery concept differs from the others because fresh biomass is processed. This means that specific points of interest have to be taken into account, e.g. rapid

primary processing or use of preservation methods (i.e. silage or decomposition) is necessary to prevent degradation of the harvested materials. Three main primary fractionation methods can be distinguished:

- direct wet fractionation
- silage production followed by wet fractionation
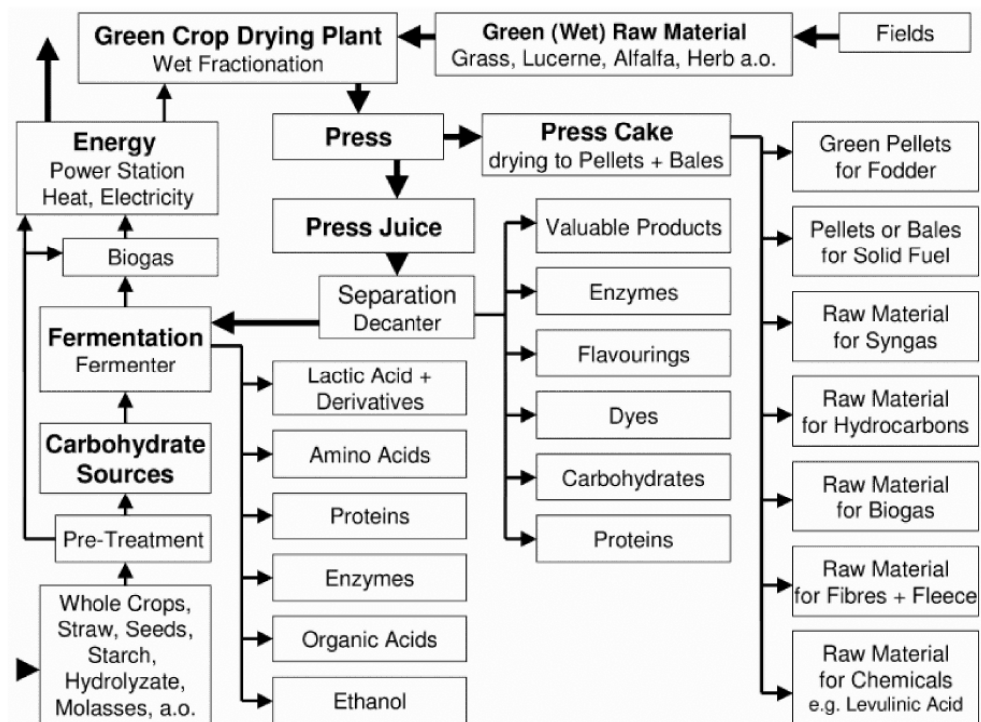- (enzymatic, hydrolytic, or thermal) decomposition followed by fractionation.

Figure 23 Potential products from a green biorefinery (Kamm, Gruber et al. 2006)

Subsequently, various treatments like heat, treatment with organic and inorganic acids, acid anaerobic fermentation, centrifugation, and gel filtration into a leaf nutrient concentrate and brown juice can be used to obtain the different components, such as proteins, lipids, glycoproteins, lectins, sugars, free amino acids, dyes (cartotenes), enzymes, lactic acids, minerals and other materials can be obtained. The main markets are in protein recovery for animal feed, preparation of amino acid mixtures for nutrition, and use of lactic acid for bioplastics, chemicals etc.

The press-cake (fibre) fraction can be pressed into pellets for fodder or biofuels or used for biogas production. Furthermore, upgrading to fibre products is possible for applications such as insulation materials, fibre boards, pulp and paper. Finally, applications known from woody lignocellulosic biorefineries could be applied such as hydrolysis and fermentation for ethanol production, lignin utilisation, etc.

Status and scale of production

Green biorefineries are still mainly in the pilot plant phase. The pilot plants in Utzenaich (Austria) and Brandenburg (Germany) focus on lactic acid recovery. In Switserland a demonstration plant provides a grass fibre insulation product on a commercial basis. In the Netherlands several initiatives are under development, amongst others directed to

protein recovery and fibre utilisation. Given the logistics of this (low) density feedstock, it is expected that future commercial green biorefineries will have a medium scale of 10,000 - 100,000 tonnes per year.

3.7 Conclusion

Figure 24 gives a schematic overview of the main steps from raw biomass to products, showing the different platforms.
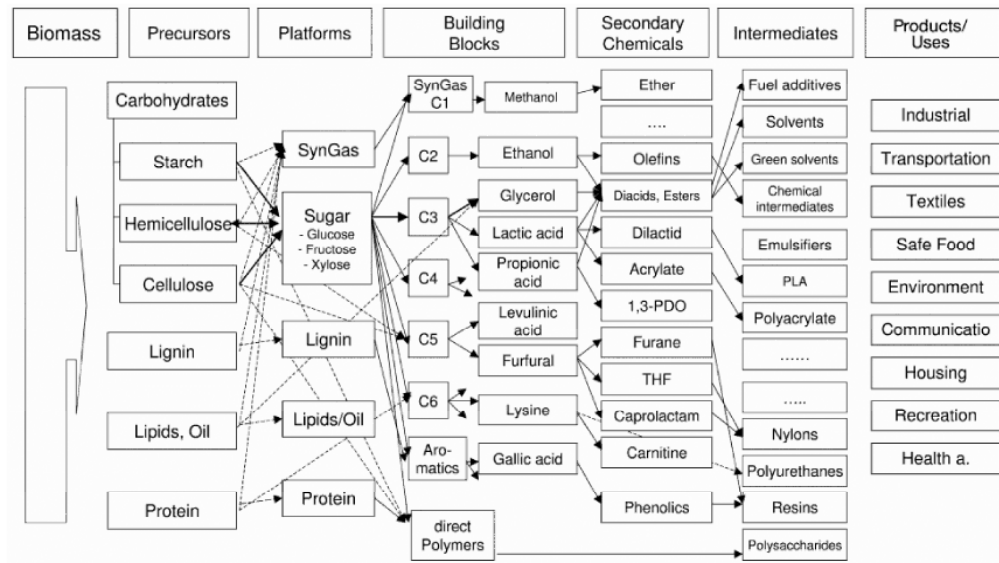
Figure 24 Schematic overview flow chart: biomass to products (Kamm, Gruber et al. 2006)

Table 6 gives an overview of the biorefinery types that were investigated in this chapter together with the feedstock, products, predominant technology, phase of development and the (expected) commercial scale. Small scale means an annual output below 10 ktonnes; medium scale between 10-100 ktonnes; and large scale means > 100 ktonnes. The two platform concept and whole crop biorefinery were not presented since they are based on the other concepts.

Table 7 Summary of biorefinery concepts and main phase of development

Type of biorefinery	Feedstock	Products	Predominant technology	Main phase of development	(Expected) scale[a]
Oleochemical industry	Vegetable and animal oils and fats	Cosmetics, shampoos, soaps, detergents, paint, inks, lubricants, etc.	Fat splitting, hydrogenation, concentration, distillation, refinement, etc.	Commercial	Medium to large
Sugar based	Sugar cane, beets	New products by sugar or ethanol chemistry, like bioplastics (PHB)	Microbiological polymerisation	Pilot, demo	Small to medium
Starch based	Potato	Paper (sizing), building additives, adhesives, etc.	Chemical modification: etherification, esterification, splitting	Commercial	Large
	Corn	Corn or dextrose syrup, sweeteners (HFCS)	Wet milling, hydrolysis, isomerisation.	Commercial	Medium to large
	Starch biomass	Bioplastics, PHB, modified products (PHA)	Plasticization, chemical modification	Pilot, demo	Medium
Biochemical – ethanol production	lignocellulosic biomass: e.g. straw, miscanthus, wood	Ethanol	Pre-treatment, chemical or enzymatic hydrolysis, fermentation, separation	Demo	Medium to large
Biochemical - lignin utilisation	Spent sulphite pulping liquids (red or brown liquor)	Lignosulfonates (feed pellet binders, dust surpression, dispersants, elmulsifiers, surfactants)	Lignin precipitation. In Howard process by addition of excess calcium hydroxide	Commercial (declining, because of decline in sulphite pulping mills)	Medium
	Lignin fraction of lignocellulosic biomass	Replacement phenol formaldehyde resin applications	Organosolv delignification, lignin precipitation	Pilot, demo	Medium
Thermochemical	lignocellulosic biomass	Diesel, petrol, synthetic natural gas, alcohols	Gasification, gas cleaning and upgrading, catalytic synthesis (SNG, FT, HAS)	Pilot, demo	Large
Hybrid	lignocellulosic biomass	Ethanol, alcohols, acids, methane	Gasification/pyrolysis, fermentation	Pilot	Medium
Green biorefineries	wet biomass: green grasses and green crops	Lactic acid, bioplastics	Fractionation in juicy and fibre fraction, various microbiological and biochemical treatments to obtain the components. Fibre upgrading.	Pilot	Small to medium

[a] Expected annual output at commercial scale: small: <10 ktonnes/year; medium: 10-10 ktonnes/year; large: >100 ktonnes/year

4 SELECTION OF CHAINS FOR FURTHER ANALYSIS

The following selection criteria for selecting conversion chains for further analysis of socio-economic impacts are used:

- The input biomass is widely available;
- The input biomass of biorefineries is not competing with food/feed crops;
- There is a realistic prospect that the biorefinery technology will become commercially available between, say, now and 2025.
- The market for the end products is promising; and the total market volume large.

Based on these selection criteria, a preliminary assessment of the presented current and future industrial and small-scale conversion chains has been made. Table 8 provides a summary matrix. BTG has not the intention to judge on the presented technologies. However, the approach makes a justified choice of the main conversion technologies for further analysis possible.

Table 8 Summary of conventional conversion technologies and future biorefineries and their main phase of development

Concept	Availability feedstock	No competition with food/feed	State of development	Market perspective	Selected
Biodiesel production	+	--	++	++	√
Pure plant oil production	+	--	++	+	
Anaerobic digestion	+/-	+/-	++	+	
Ethanol from sugar/starch crops	+	--	++	++	√
Combustion lignocellulosic biomass	++	++	++	++	
Gasification lignocellulosic biomass	++	++	+	+	
Pyrolysis woody lignocellulosic biomass	++	++	+	+	
Carbonisation/torrefaction lignocellulosic biomass	++	++	+	+	
Oleochemical industry	+	-	++	++	
Sugar based biorefinery	+	--	+/-	+	
Starch based biorefinery	+	--	++	+	
Biochemical lignocellulosic biorefinery (bioethanol & lignin utilisation)	++	++	+/-	+	√
Thermochemical lignocellulosic biorefinery	++	++	+/-	+	√
Hybrid lignocellulosic biorefinery	++	++	-	+	√
Green biorefineries	+	-	-	+	

Conventional biodiesel from oil crops and ethanol production from sugar and starch crops have been selected because of their relevance and impact in current production systems including competition (for land) with food and feed production. Combustion has been selected as it is the most important current biomass conversion technology for heat and power production. Much is known about the socio-economic impacts as well. For the future conversion technologies, the lignocellulosic biorefinery concepts have been selected. They are seen as solutions to the current bioliquid production chains, having

lower claims on agricultural land and having higher energy yields at lower carbon and energy inputs, compared to oil, sugar and starch based biorefineries.

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