Overview of Biobased production processes and their environmental impacts

An initial exploration

RIVM

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SUMMARY

On behalf of RIVM, RHDHV conducted a study to explore the environmental impact related to biobased production processes. The report provides an overview of the main biobased process routes that can be distinguished for producing biobased substances:
1. hydrolysis/fermentation;
2. transesterification/hydrogenation;
3. anaerobic digestion;
4. algae;
5. gasification;
6. pyrolysis.

For two selected biobased products, a comparison is made of the environmental impact with the conventional production route based on fossil fuels: 1) bioethylene, and 2) glycerol.
In general, one of the associations with biobased processes is that these are inherently "environmental friendly". This report shows the results of a first exploration on the environmental risks of biobased processes, showing that also biobased production processes often require catalysts and/or auxiliary chemicals. Therefore, biobased production does not mean by definition a "green production process". Among the six biobased process technologies, three routes are based on the use of micro-organisms (hydrolysis/fermentation, anaerobic digestion, algae), and generally speaking these processes have less environmental releases in terms of amounts and toxic compounds and are more energy friendly, due to the moderate process conditions necessary for living organisms to operate. The three other biobased process routes (transesterification/hydrogenation, gasification and pyrolysis) are chemical processes using bio-feedstock instead of fossil feedstock, but are process wise comparable to the conventional route in terms of releases to the environment.

In general, biobased production processes take place at more moderate temperatures than fossil based processes, so energy wise usually the biobased process is expected to be more energy efficient. But more detailed analysis is needed, as the fossil based production routes often make part of highly optimised (petro-)chemical production complexes, which might sometimes make that the fossil production route is more energy efficient than the biobased route. However, in this stage, not many biobased production takes place at an industrial scale yet, and over time, when more biobased processes come into operation, also the biobased production can be expected to evolve into more (energy) efficient processes.

Within the framework of this project, no biobased production of biobased chemicals that substitute priority substances were identified to be operational in The Netherlands yet. Most biobased production routes take place at moderate process conditions with such auxiliary materials that it is not likely that priority substances will be formed during the process, except for the high temperature processes of pyrolysis and gasification.

Bio-ethylene is an example of one-to-one substitution of fossil-based ethylene. Comparison of the environmental risks show that the environmental emissions of the fossil-based route are relatively large compared to the biobased production route.

Glycerol is produced as a by-product from the production of soap as well as from biodiesel. The conventional production is also from a renewable source. Due to the increased availability of glycerol more applications of glycerol as raw material are currently being developed, for example, potentially leading to functional replacement of prioritised petrochemical plasticisers. It may also serve as a one-to-one replacement of propylene for the production of the building block epichlorohydrin (which is a priority substance itself). The comparison in environmental risks shows that the biodiesel route, due to the use of methanol, leads to a higher emission to air than the production by saponification. Otherwise, the processes are more or less similar and so are the environmental emissions and potential environmental risks.

In developing policy on biobased processes, it is recommended to take into account the environmental aspects of biobased processes as well, as in some cases the biobased production process might have considerable environmental consequences as well. It is advised to conduct more in depth studies to determine <u>quantitatively</u> the environmental aspects of biobased production routes and compare these with the conventional routes. The outcomes are useful to support the environmental policy development in this field. As in future more biobased production processes are expected to take place at industrial scale, the introduction of Best Available Techniques (IPPC/IED) in biobased processing might be a useful instrument to guarantee that the design and operation of biobased industries is according best available techniques, both managerial and technical.

Key words:

Biobased economy, biobased processes, environmental aspects, chemicals, priority substances

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Annexes:

Annex A: List of biobased products and priority substances (ref. Van Helmond – annex 2).

1 INTRODUCTION

1.1 Background

One of the tasks of the RIVM is to identify the potential impacts on the environment and public health from new technological developments in science and society. The biobased economy is one of these developments that may lead to potential major improvements in the way we use the available resources. At the same time, continuous attention is needed to monitor whether parts of these developments really lead to a more sustainable situation.

In this study we focus on biobased production of chemicals. The biobased production of chemicals covers a broad spectrum of technologies. It is important to be able to distinguish between the different kinds of biobased production lines and subsequently to know what specific environmental issues are linked to these individual processes. This information will give focus to discussion points about, for example, the (non)applicability of the current REACH framework for biobased production processes, but also to the weighing of various environmental and sustainability factors in overall decision-making processes (see below).

In this explorative study on biobased chemicals, the key biobased processes are being described, and for each production route the environmental impact is identified. For two selected chemicals, a comparison is made between the biobased process route and the "conventional" process based on fossil feedstock.

The focus is on environmental aspects such as emissions to air, water and production of waste. Other production related environmental aspects like safety issues (fire, explosion) and annoyance (noise) are indicated as relevant environmental impacts in the overview of biobased processes (chapter 2), but not discussed in the more detailed analysis of selected processes in chapter 3. Consumer health risks, as well as occupational health risks are not considered in this study. Also sustainability items like impact on water resources, land usage or energy efficiency are not taken into account in this study. However, it is important to keep in mind that these sustainability factors are important in order to come to a more complete conclusion on the differences in sustainability between biobased production versus the conventional fossil oil based production.

The environmental aspects are not only related to the use of auxiliary chemicals and/or the potential formation and emissions of chemical substances, but also to the application and potential release of enzymes, wild type or GMO yeasts, bacteria and microalgae.

1.2 Aim

The aim of this study is to provide an overview of the existing types of biobased production processes and their technologies. For each process step the environmental impact is being identified. For two selected production routes, the environmental risks are elaborated in more detail.

More specific, this report provides answers on the following questions:

1. Production processes and emissions:
■ What are the emissions to air, water and via waste and their type of potential impact on the environment (chemical substances and biological agents/GMO)?
■ What type of auxiliary substances, catalysts, etc. are being applied in biobased production processes, that can be emitted to the environment, and/or if there is potency for *de novo* formation of hazardous chemical or biological agents?

2. Exposure routes and protective measures:
■ For two selected "example-substances" the REACH 'emission release categories (ERC) and emissions" during the production phase have been determined. A comparison is being made between the biobased production route versus the conventional fossil oil based route.
■ What measures are being applied in the biobased process routes to protect the environment, and are these different from those required under the currently existing environmental legislation and regulations?

1.3 Scope of the study

The scope of this study has been defined as follows:

Biobased processes: first-second-third generation biomass
In the biobased economy a differentiation is made between so called 1st generation feedstock (currently feed and food products), 2nd generation feedstock, based on left over biomass that is not in competition with feed and food, and 3rd generation (algae). In this study we focus on 2nd and 3rd generation feedstock, and not on existing 1st generation biobased production processes like ethanol production out of sugar, beer breweries etc. The reason is that the challenge and opportunities of biobased production of chemicals is in the fact that biomass feedstock is being used that is not in competition with food/feed production and using modern bio-conversion technologies.

Biomass – production process combinations
Biobased production processes for the chemical industry, based on biomass as a feedstock instead of fossil oil. Also processes in which the micro-organism is the unit of production and/or the product are taken into account, as is the case, for example, with some uses of algae.
The production of substances that can be used as a fuel for energy are taken into consideration, like bio-ethanol. The process of energy production is not part of this project (like combustion of wood biomass in a power plant).

Phase of development of the technology
As a starting point, the focus was on existing production facilities in the Netherlands or surrounding countries, or installations that are expected to be operational on an industrial scale in the next five years period. It appeared that currently in practice the amount of biobased processes of chemicals at an industrial scale is rather limited, and some of the process routes are not present at all yet or expected to present within a five years period at an industrial scale (like algae).

So this criterion has at the end not been applied to select processes for further detail comparison between the biobased and conventional route.

Selection of substances

For two selected substances the biobased production process has been described more in detail in terms of environmental risks. For these substances, the biobased route has been compared with the conventional route based on fossil oil. These substances have been selected from the list in the RIVM-rapport "Biobased alternatives for priority substances" (Van Helmond, RIVM, 2013, annex 2). The selection procedure is further described in section 3.1.

Production phase

The focus of this study is on the <u>production phase</u> of a biobased substance and not on the phases of usage and the waste stage of the product. The production of the raw biomass material ("feedstock") and the transportation of this biomass to the location of the production facility are out of the scope of the study, although these items are relevant for drawing conclusions on the overall level of sustainable production.

Other exclusions

As mentioned in the introduction, sustainability items not directly related to environmental risks (toxicity), like impact on water resources, land usage and energy efficiency, are not taken into account.

Legal and permitting aspects are out of the scope of this project. In general, the same legal framework and requirements are applicable to industrial biobased production processes as for regular industrial activities to limit and control emissions to the environment.

1.4   Methodology

The project starts with an overview of the various combinations of biomass (primary feedstocks) with biobased process routes. These can be organised into six main production routes using different type of technologies (conversion routes).
Each of the six production routes is being described, using the conceptual engineering experiences on biobased processes within RHDHV and from literature (a.o. NREL, 2004, De Jong et al, 2012).

In the second step, two substances listed in Annex 2 of the RIVM report on Biobased alternatives for priority substances (van Helmond et al. 2012) have been selected for further detailing of environmental aspects. Both the production process for the biobased route and the process based on fossil oil have been described. The environmental aspects are determined based on extensive expertise in the field of environmental technologies and risks, and literature sources in this field, like Integrated Pollution Prevention and Control – Best Available Techniques Reference documents, handbook of emission factors and other handbooks describing emissions from various processes.

The environmental aspects have been categorised based on:
1.   the environmental classification of the substances involved in the production;

2. the potential emissions during the production using the Environmental Release Categories approach as defined under REACH.

REACH Exposure scenarios
All manufacturer and importers of chemicals must identify and manage the risks linked to the substances they manufacture and place on the market. This is specified under REACH, the Regulation on Registration, Evaluation and Authorisation and restriction of Chemicals (Regulation (EC) no 1907/2006). For hazardous substances, a chemical safety assessment is to be made where the exposure of man and the environment is compared to threshold limits for the toxicity of the substances. To this end, standard procedures were developed including guidance to assess the environmental exposure during various processes in the life cycle of a substance (ECHA Guidance document R.16).
The environmental release category (ERC) describes the broad conditions of use from the environmental perspective. The ERC characterises the use of a substance in order to analyse the mass flow along the life cycle of a substance. The purpose of a substance in a process determines to what extent the substance is consumed on use, produced to enter into a next life cycle stage or released into the environment. In general, there are three possibilities:
1. the substance is intended to become part of a product, either because it has a function in the product or it is a residue from manufacturing;
2. the substance is meant to react on use;
3. the substance is meant to act as a processing aid, so it is released from a process (e.g. surfactant in textile finishing, solvent from spray painting or from cleaners) to waste water, air emission and/or waste.

Within the context of this project we only consider the biobased (or fossil-based) production of a specified chemical, so the life cycle stage is 'manufacturing'. This includes the pretreatment of the biological material and further processing for purification. Within REACH this step is described under ERC 1: Manufacture of substances under industrial conditions.
In REACH, for each Environmental Release Category a so-called default emission scenario was developed to estimate the emission and exposure of the environment. The scenario defines default emission factors to the air, water and soil to allow a conservative estimation ([1]) of the environmental exposure.

In Chapter 3, a semi-quantitative description of the environmental risks of biobased processes has been made for two selected processes, and these have been compared with the conventional process route. In this comparison, the environmental risks have been expressed in three levels to express the relative emission or risk:

X   = relatively small emission/risk
XX   = medium emission/risk
XXX   = relatively large emission/risk

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[1] Conservative: These factors are deliberately chosen to overestimate the emissions. Actual data (measurements, specific process information) can be used to reduce the default release factors.

It appeared that in the framework of this study, it was not possible to enter the level of detail needed to achieve quantitative emission information. Therefore the Reach ERC-1 approach has been followed, without using the related default values for releases (5% to air, 6% to water (before treatment in a sewage treatment plant) and 0.01% to air), and only indicating the relative potential environmental risk.

It should be emphasized, that the regular emissions and safety regulations and permitting requirements are also applicable for biobased production processes. This means that in the end, emissions and risks for the environment are controlled.

1.5 Reader

Biobased production processes can be divided in six main basic production routes. These routes and their potential environmental risks are described in chapter 3. In the next step, for two selected substances (see section 4.1) the biobased production route and the conventional on fossil oil based production processes are described more in detail. For each process the environmental impacts are determined in a semi-quantitative way. In this way the potential environmental risks of the two "raw material – production processes" combinations can be compared. Chapter 5 reflects on the outcomes of this initial exploratory study on the environmental risks of biobased processes.

2 BIOBASED PRODUCTION PROCESSES AND ENVIRONMENTAL IMPACT

2.1 Overview of Production Routes and Processes

In this section a brief overview of the biomass conversion technologies are given. Figure 2.1 is included to show the large number of combinations of bio-feedstocks and process routes that can be followed to produce intermediates and products from various biomass feedstocks. Currently, only a few processes are operational on an industrial scale.

In order to produce the products that are shown in the Figure 2.1, different conversion routes can be used. Figure 2.2 illustrates the simplified diagram for the potential biomass conversion routes. These routes include direct conversion processes such as extraction of vegetable oils followed by esterification (e.g. biodiesel), fermentation of sugar-rich crops (e.g. ethanol), and pyrolysis of wood (e.g. pyrolysis oil derived diesel equivalent). Another possibility is to produce bioproducts from synthesis gas, which results from gasification or anaerobic digestion of biomass. In addition, algae cultivation, the third generation feedstock, is added to the chart in order to examine its specific environmental aspects.
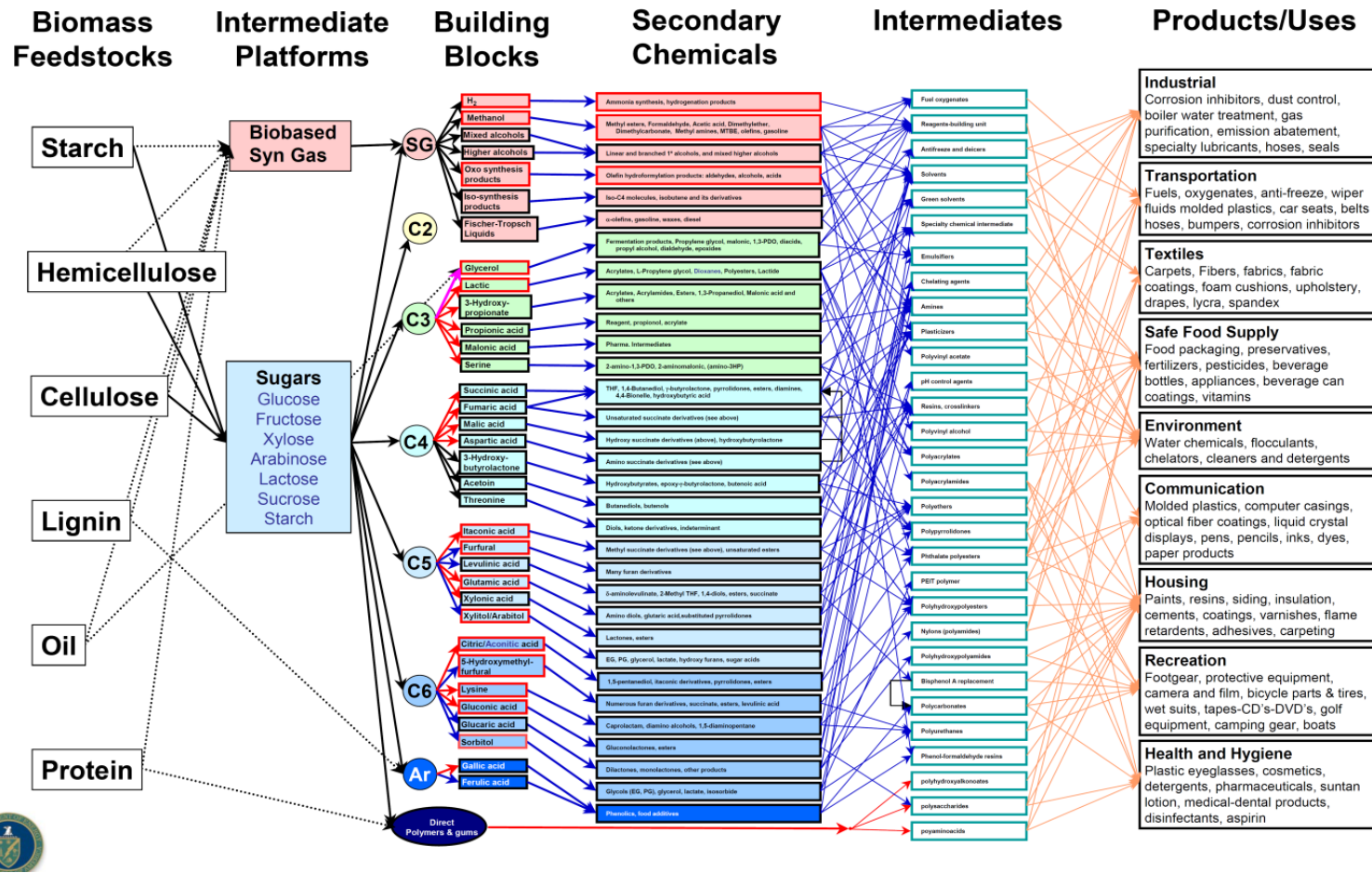
Figure 2.1: **Biobased Product Flow-chart for Biomass Feedstocks (SG = syngas, Ar = aromatics) (Taken from NREL report: Top Value Added Chemicals from Biomass Volume I, August 2004).**

Therefore, the main conversion routes can be summarized as:
1. Hydrolysis/Fermentation,
2. Transesterification/Hydrogenation,
3. Anaerobic digestion,
4. Algae[2]
5. Gasification,
6. Pyrolysis.

In figure 2.2 these basic conversion routes as these are evaluated more in detail in this report to define the environmental aspects are schematically presented.
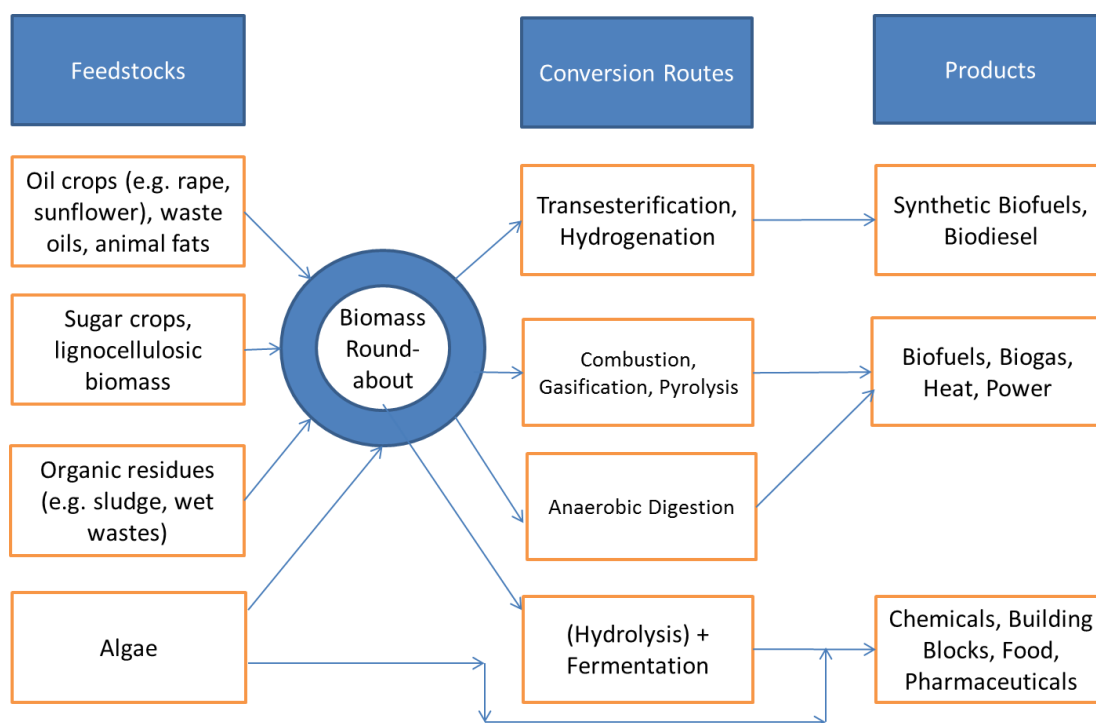
Figure 2.2:   Simplified Biomass Conversion Routes [ref. Erdag, 2012]

2.2   Route 1: Hydrolysis/fermentation

2.2.1   Process description

Currently, many bioproducts are produced from agricultural crops. Suitable raw materials are sugar-containing agricultural products such as sugar beet, sugar cane, molasses and sweet sorghum. Crops that contain starch can also be used, but they have to be converted to sugars first. These include potatoes and various types of grains such as barley, corn, and wheat.

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[2] algae can be seen both as a "bioproduction route" as well as a product/feedstock for other processes

At present, research and development activities are mainly focused on using lignocellulosic or woody materials as a feedstock. These include short rotation crops (e.g. willow, poplar, miscanthus and eucalyptus), agricultural residues (e.g. straw and sugar cane bagasse), forest residues, waste woods, and municipal solid wastes.

There are several reasons for shifting to lignocellulosic biomass. Lignocellulosic biomass is more abundant and less expensive than food crops, especially when it concerns a waste stream with very little or even negative economic value. Furthermore, it has a higher net energy balance, which makes it more attractive from an environmental point of view. However, these kinds of biomass are more difficult to convert to sugars due to their relatively inaccessible molecular structure. Lignocellulosic biomass contains carbohydrate polymers called cellulose (40-60% of dry weight) and hemicellulose (20-40% of dry weight) that can be converted to sugars. Cellulose is composed of glucose molecules bonded together in long chains that form a crystalline structure. Hemicellulose consists of a mixture of polymers made up from xylose, mannose, galactose, or arabinose. It is much less stable than cellulose. Both materials are not soluble in water. The remaining fraction, a complex aromatic polymer called lignin (10-25% of dry weight) cannot be fermented because it is resistant to biological degradation. This material can be utilised for the production of electricity and/or heat or for other potential applications.

Other types of biomass, such as grain, contain larger and more complex carbohydrate molecules that have to be broken down first to simpler sugars by hydrolysis. Then this mixture is cooked to dissolve all the water-soluble starches. The starch is converted to sugars simultaneously. This can be done by enzymes or acid hydrolysis. The short carbohydrates resulting from these processing steps can be fermented by microorganisms.

The conversion process of lignocellulosic biomass only differs from the process described above with respect to the break down (hydrolysis) of the raw material to fermentable sugar. This hydrolysis process is more difficult than the hydrolysis of starch. Therefore a pretreatment step is required before enzyme hydrolysis for lignocellulosic biomass. Pretreatment aims to maximize conversion towards C5 and C6 sugars and minimize the production of inhibitors for enzymatic hydrolysis and fermentation. After the pretreatment section, cellulose can be converted into glucose by using cellulase enzymes that are able to break down the cellulose. This is called separate hydrolysis and fermentation (SHF process). With this, the glucose yield from cellulose is increased. Later, simultaneous saccharification and fermentation (SSF process) was introduced. Here, the enzymatic hydrolysis and sugar fermentation processes take place at the same time in one vessel.

This reduces the number of reactors needed for the conversion process. Furthermore, cellulase enzymes and fermenting microbes are combined. This process was later improved to include the co-fermentation of the sugars glucose and xylose (SSCF technology). An advantage of this process is that sugars produced during hydrolysis are immediately fermented into ethanol, which avoids problems such as sugar accumulation and enzyme inhibition.

For both sugar-containing and starch crops and lignocellulosic biomass, the fermentation and are basically identical. Based on the desired product and type of the broth a downstream processing method shall be applied for the separation and purification of the bioproducts.

The main process steps are described in the block diagram below.

Biomass

↓

Storage

↓

Size reduction

↓

Pretreatment

↓

Hydrolysis

↓

Fermentation

↓

Downstream
Processing

↓
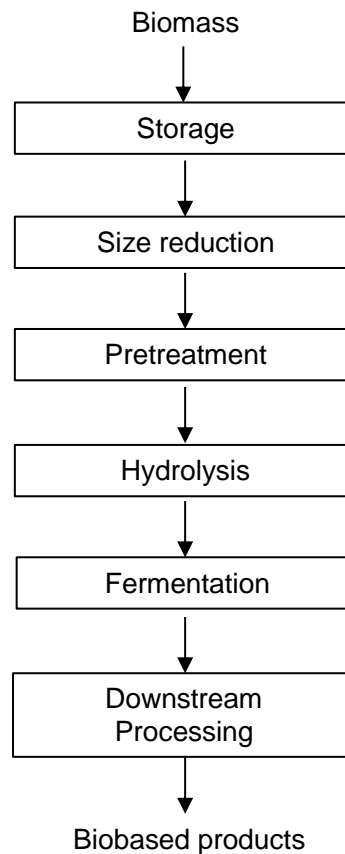
Biobased products

Figure 2.3:   Block diagram for the hydrolysis/fermentation process route

2.2.2   Environmental impacts

The environmental aspects are specified per process block in the sections below.

Storage
The aim of the unit is to receive the feedstock, to store it prior to processing.
The environmental risks are illustrated in the table below.

Table 2.1: **Environmental impacts of storage bio-feedstock**

Environmental aspects	Remarks
Feedstock resource impact	■ Unwanted exotic materials/organisms can be transported in the feedstock from exotic countries; ■ In the feedstock hazardous waste can be present in case of insufficient quality control feedstock (like heavy metals in the case of sludge as a feedstock). Off-spec material will be waste.
Fire	Fire can occur during storage due to excessive heat production by biological reactions
Emissions to air	Odour emissions can occur because of rotten feedstock
Soil contamination risk	Risk for soil contamination occurs due to substances that are produced by biological degradation during storage (like acidic solutions, furfural)

Size Reduction

The aim of the unit is to process the feedstocks to be fed into the pretreatment Unit. This section includes mainly the cleaning equipment such as picking belts and magnetic separators and size reduction equipment such as milling machines and shredders. The environmental risks are illustrated in the table below.

Table 2.2: **Environmental aspects of size reduction**

Environmental aspects	Remarks
Feedstock resource impact	Dust explosion can occur in the size reduction equipment
Emissions to air	Odour emissions can occur because of rotten feedstock
Noise	Feedstock handling and size reduction equipment can create high noise levels
Waste	The biomass will be cleaned during size reduction. The strange materials, metals, stones and non-fermentables can create solid waste

Pretreatment

Cellulosic plant material represents an as-of-yet untapped source of fermentable sugars for significant industrial use. Many physico-chemical structural and compositional factors hinder the enzymatic digestibility of cellulose present in lignocellulosic biomass.

The goal of any pretreatment technology is to alter or remove structural and compositional impediments to hydrolysis in order to improve the rate of enzyme hydrolysis and increase yields of fermentable sugars from cellulose or hemicellulose. Several technologies and process configurations have been developed for the conversion of the fermentable fractions cellulose and hemicellulose. The oldest method is to convert the fermentable materials by diluted acid. Here, low concentration acids break the hydrogen bonding between cellulose chains and decrystallise the material at a temperature of about 200ºC.

This results in the conversion of hemicellulose into soluble C5 sugars, which can directly be fermented. However, C5- sugars cannot be fermented by the typical organisms; therefore genetically modified organisms (GMO) may be applied in the fermentation process. On the other hand, GMO application may also be necessary due to the production of toxic byproducts from lignocellulose (like furfural), as the GMO may have a higher resistance against such toxic by-products. The hydrolysis of hemicellulose can take place under relatively mild process conditions.

The cellulose fraction is more resistant and requires more rigorous treatment. In the pretreatment step, cellulose is exposed by reducing its size and opening up its structure. The different pretreatment methods including the chemicals that are used are shown in the table below.

Table 2.3 Overview of pretreatment methods and chemicals used	
Explosion	Steam explosion
	Ammonia fiber explosion (AFEX)
	Supercritical CO2-explosion
	SO2-explosion
Alkali	Sodium hydroxide
	Ammonia solution
	Ammonium sulphite
	Lime
Acid	Sulphuric acid
	Hydrochloric acid
	Phosphoric acid
Gas	Chlorine dioxide
	Nitrogen dioxide
	Sulphur dioxide
Hot water wash	LiquidHotWater wash under pressurised conditions (ca. 200ºC)
Oxidizing agents	Hydrogen peroxide
	Wet oxidation
	Ozone
Solvent extraction	Ethanol
	Ethylene glycol
	Butanol
	Methanol
	Acetone
	Organic acids

The environmental impacts are illustrated in the table below.

Table 2.4: **Environmental aspects of pretreatment**

Environmental aspects	Remarks
Noise	Pretreatment equipment can create high noise levels
Fire/Explosion	■ Dust explosion can occur in the pretreatment equipment in case of dry processing; ■ Organic solvents can create explosive mixtures.
Emissions to air	■ Gas emissions can be produced during pretreatment, depending on technology applied (like furfural, SO2, NH3); ■ Odour emissions can occur during processing; ■ Solvent emissions can occur during processing using solvent extraction.
Soil contamination risk	Soil contamination can occur due to the chemical spills

Enzymatic Hydrolysis

Pretreatment typically consists of either a physical, thermal or chemical treatment or combination thereof. The pretreatment opens the biomass structure to enable the enzymes to reach the sugar polymers in the biomass.

In enzymatic hydrolysis solid cellulosic fractions of lignocellulosic material are treated and enzymatically hydrolysed to develop conditions for an optimum conversion towards fermentable components.
The environmental risks are illustrated in the table below.

Table 2.5: **Environmental impacts of enzymatic hydrolysis**

Environmental aspects	Remarks
Waste water	There can be enzymes and chemicals in the waste water
Emissions to air	Odour emissions can occur in case of rotten feedstock

Fermentation

In the fermentation section fermentable components are converted by means of enzymes and micro-organisms into chemicals, bioplastics, biofuels and food additives, (colorants, flavoring agents, vitamins). These micro-organisms can be yeasts, fungi or bacteria. Sometimes they are genetically modified to enhance the efficiency of fermentation. The fermentation can either be aerobic or anaerobic. Sometimes the fermentation broth as a whole is the product, sometimes the dried material is the product.

The environmental risks are illustrated in the table below.

Table 2.6: **Environmental impacts of fermentation**

Environmental aspects	Remarks
Fire/Explosion	Organic solvents can create explosive mixtures
Emissions to air	■ Gas emissions can be produced during fermentation (e.g. VOC, CO_2); ■ Odour emissions can occur during processing.
Waste water	There can be enzymes, chemicals and microorganisms in the waste water Bio-waste from fermenter (depending on process)
Genetically Modified Microorganisms	In case of GMO: Containment issue of microorganisms

Downstream Processing (DSP)

In the downstream processing section the bioproducts are separated from the fermentation broth and purified to desired conditions.
The DSP consists of the following main processes:
■ Cell Disruption;
■ Solid liquid separation;
■ Concentration;
■ Purification;
■ Formulation;
■ The environmental risks are illustrated in the table below.

Table 2.7: **Environmental impacts of Down Stream Processing (DSP)**

Environmental aspects	Remarks
Waste water	There can be enzymes, chemicals and microorganisms in the waste water
Fire/Explosion	Organic solvents can create explosive mixtures
Emissions to air	■ Gas emissions can be produced during processing of fermentation broth, extraction, distillation (e.g. VOC, CO_2); ■ Odour emissions can occur depending on type of fermentation and DSP technology.
Genetically Modified Microorganisms	In case of GMO: Containment issue of microorganisms

2.3.1 Summary of Environmental aspects

The environmental risks are summarized per category in the table below.

Table 2.8: **Overview of environmental impacts of the hydrolysis/fermentation process route**

Step	Fire/ Explosion	Noise	Air	Water	Soil	Waste	GMO
Biomass storage	✔		✔		✔	✔	
Size reduction	✔	✔	✔			✔	
Pretreatment	✔	✔	✔		✔		
Hydrolysis			✔	✔			
Fermentation	✔		✔	✔			✔
DSP	✔		✔	✔			✔

2.4 Route 2: Transesterification and hydrogenation

2.4.1 Process description

Biodiesel and glycerol
Due to gradual depletion of world petroleum reserves, there is an urgent need for suitable alternative fuels for use in diesel engines. Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification.

Production of biodiesel involves creation of significant amounts of byproduct glycerol. Since its disposal is very costly, it is being currently recovered and sold to glycerol refiners. This approach has its negative consequences since it leads to over-supply, and resulted in dramatic decrease in prices for glycerol and destabilization of the market. This over-supply of glycerol stimulated research on this compound as starting material for different chemicals, and recently it has been officially categorized as one of the "building block" chemicals [de Jong et al., 2011; Tuck et al., 2012; Mülhaupth, 2013].

In the following paragraphs process for production of biodiesel, which is alike with the process for obtaining glycerol, is described.

Chemically, biodiesel is a mixture of methyl esters with long-chain fatty acids and is typically made from non-toxic biological resources such as vegetable oils, animal fats or even used cooking oils (UFO).

Common vegetable oils or animal fats are esters of saturated and unsaturated monocarboxylic acids with the trihydric alcohol glyceride. These esters are called triglycerides, which can react with alcohol in the presence of a catalyst, a process known as transesterification. The simplified form of its chemical reaction is presented in equation:

$$
\begin{array}{lllll}
CH_2\text{-}O\text{-}CO\text{-}R_1 & & & CH_2\text{-}OH & R\text{-}O\text{-}CO\text{-}R_1 \\
| & & (Catalyst) & | & \\
CH\text{-}O\text{-}CO\text{-}R_2 & +\ 3ROH & \longrightarrow & CH\text{-}OH & R\text{-}O\text{-}CO\text{-}R_2 \\
| & & & | & \\
CH_2\text{-}O\text{-}CO\text{-}R_3 & & & CH_2\text{-}OH & R\text{-}O\text{-}CO\text{-}R_3 \\
(Triglyceride) & (Alcohol) & & (Glycerol) & (Mixture\ of\ fatty\ acid\ esters)
\end{array}
$$
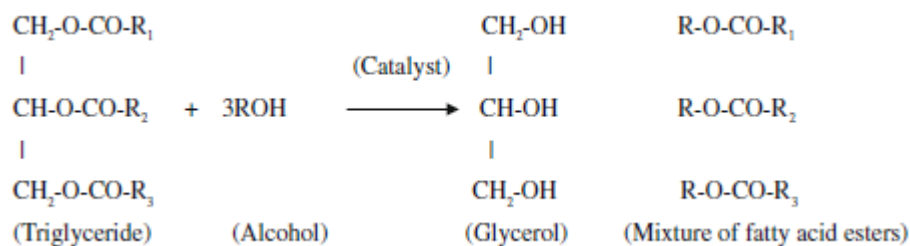
where R1, R2, R3 are long-chain hydrocarbons, sometimes called fatty acid chains. Normally, there are five main types of chains in vegetable oils and animal oils: palmitic, stearic, oleic, linoleic, and linolenic. When the triglyceride is converted stepwise to diglyceride, monoglyceride, and finally to glycerol, 1 mol of fatty acid ester is liberated at each step. Usually, methanol is the preferred alcohol for producing biodiesel because of its low cost.

Waste streams of vegetable oils and fats, may contain small amounts of water and free fatty acids (FFA). For an alkali-catalyzed transesterification, the alkali catalyst that is used will react with the FFA to form soap. Eq. (2.2.2) shows the saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water.

$$
\underset{(FFA)}{R_1\text{—}COOH} + \underset{sodium\ hydroxide}{NaOH} \rightarrow \underset{(soap)}{R_1COONa} + \underset{(water)}{H_2O}
$$
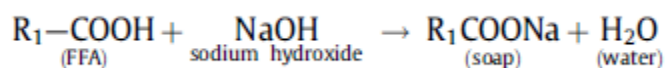
This reaction is undesirable because the soap lowers the yield of the biodiesel and inhibits the separation of the esters from the glycerol. In addition, it binds with the catalyst meaning that more catalyst will be needed and hence the process will involve higher costs. Water, originated either from the oils and fats or formed during the saponification reaction, retards the transesterification reaction through the hydrolysis reaction. It can hydrolyze the triglycerides to diglycerides and forms more FFA. The typical hydrolysis reaction is shown in Eq. 2.2.3

$$
\begin{array}{lllll}
CH_2\text{-}O\text{-}CO\text{-}R_1 & & & CH_2\text{-}OH & \\
| & & & | & \\
CH\text{-}O\text{-}CO\text{-}R_2 & +\ H_2O & \longrightarrow & CH\text{-}O\text{-}CO\text{-}R_2 & +\ R_1\text{-}COOH \\
| & & & | & \\
CH_2\text{-}O\text{-}CO\text{-}R_3 & & & CH_2\text{-}O\text{-}CO\text{-}R_3 & \\
(Triglyceride) & (Water) & & (Diglyceride) & (FFA)
\end{array}
$$
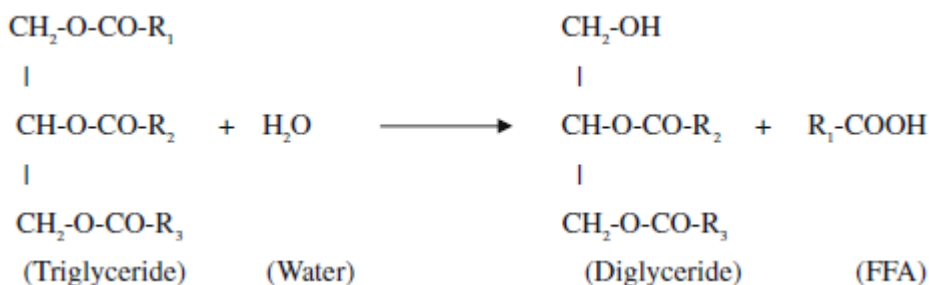
However, the FFA can react with alcohol to form ester (biodiesel) by an acid catalyzed esterification reaction. This reaction is very useful for handling oils or fats with high FFA, as shown in the equation below:

$$R_1-COOH + \underset{(alcohol)}{ROH} \xrightarrow{H^+} \underset{(fatty\ acid\ ester)}{R-O-CO-R_1} + \underset{(water)}{H_2O}$$
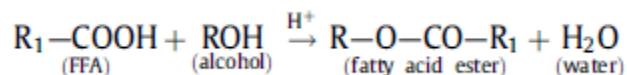
Normally, the catalyst for this reaction is concentrated sulphuric acid. However, due to slow reaction rate and the high methanol to oil molar ratio required, acid-catalyzed esterification has not gained as much attention as the alkali-catalyzed transesterification. Today, most of the biodiesel is produced by the alkali-catalyzed process.

In Figure 2.4. the simplified flow chart of this process is displayed:
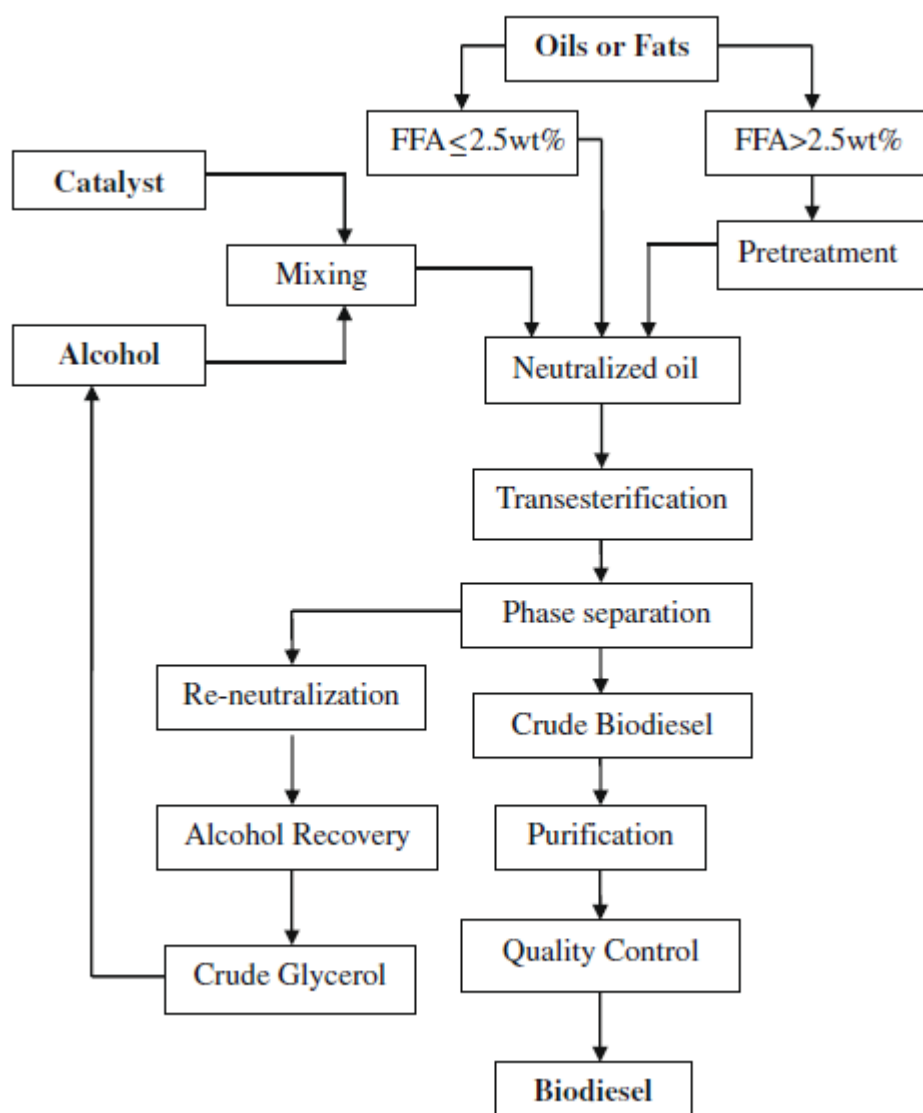
Figure 2.4: **Simplified flow chart of biodiesel and glycerol production**

2.4.2 Environmental impacts

The environmental risks are specified per process block in the sections below.

Transesterification type

Transesterification can be performed with the application of different types of catalysts (acidic, alkali, enzymatic). In Table 2.9 the summary of the main characteristics of the different type of process are presented.

Table 2.9: **Comparison of different technologies of biodiesel production (based on Enweremadu and Mbarawa, 2009)**

Variable	Alkali catalysis	Acid catalysis	Enzyme catalysis	Supercritical alcohol
Reaction temperature (°C)	60-70	55-80	30-40	239-385
Free fatty acid in raw materials	Saponified products	Esters	Methyl esters	Esters
Water in raw materials	Interference with reaction	Interference with reaction	No influence	
Yields of methyl esters	Normal	Normal	Higher	Good
Recovery of glycerol	Difficult	Difficult	Easy	
Purification of methyl esters	Repeated washing	Repeated washing	None	
Production cost of catalyst	Cheap	Cheap	Relatively expensive	Medium

Since currently mainly the alkali route is being applied, below the risks for this type of process are described.

Raw materials treatment (pretreatment)

Usually pretreatment of used cooking oil can be limited to heating and removal of solid particles by filtration. However, in some cases the products of oil decomposition cause deterioration in oil quality, which can lead to reduced yield during biodiesel production and the formation of unwanted by-products. These unwanted effects can be avoided by treatment of the used cooking oil. The following pretreatment methods have been developed:
- Steam injection;
- Column chromatography;
- Neutralization;
- Film vacuum evaporation;
- Vacuum filtration.

The environmental risks associated with these methods are described below:

Table 2.10:   Environmental impacts of pretreatment

Environmental aspect	Alkali transesterification
Solid waste	In column chromatography aluminium oxide is used as filling of the column. In chromatography periodic exchange of column is required, and thus recovery or disposal of used elements need to be arranged.
Waste water	Neutralized by application of KOH or NaOH solutions.

Catalyst and alcohols

In the case of alkali transesterification catalysts applied include potassium hydroxide and sodium hydroxide. The alcohol materials that can be used in transesterification include methanol (mostly used), ethanol, propanol, butanol and amyl alcohol. Among these alcohols, methanol and ethanol are used most frequently.

Table 2.11:   Environmental impacts of use of catalyst and alcohols

Environmental aspect	Alkali transesterification
Application of auxiliary substances (catalysts)	KOH and NaOH are very hygroscopic and absorb water from air during storage.
Creation of waste streams	Application of alkali catalyst result in creation of increased waste water stream that needs to be treated.
Emission of auxiliary substances	Methanol and, to a lesser extent, methoxide cause a potential environmental risk. It should be ensured that no personnel is exposed to these substances during biodiesel production and emissions to the atmosphere and water should be controlled.
Explosion risks	Application of methanol results in creation of colourless and odourless vapours which are highly explosive.
Emissions to air	Methanol or ethanol vapours release

Mixing and neutralization

The purpose of mixing methanol with the catalyst is to produce methoxide which reacts with the base oils.

Table 2.12:   Environmental impacts of mixing and neutralization

Environmental aspect	Alkali transesterification
Emissions to air	In the first steps of biodiesel production catalyst need to be mixed with alcohol and only then created mixture is added to oil. Some releases of volatile compounds to air can occur

Transesterification and separation

When the catalyst, alcohol and oil are mixed and agitated in a reaction vessel, a transesterification reaction will start (at 60 C). A stirred reactor is usually used as the reaction vessel for continuous alkali-catalyzed biodiesel production.

Table 2.13: Environmental impacts of transesterification and separation

Environmental aspect	Alkali transesterification
Emissions to air	Catalyst, alcohol and oil are mixed together in stirred reactor. Some releases can occur from vents (pressure relief).

Refining crude glycerol

Once the transesterification reaction is completed, two major products exist: esters (biodiesel) and glycerol. Both the biodiesel and glycerol are contaminated with an unreacted catalyst, alcohol, and oil during the transesterification steps.
Although biodiesel is the desired product from the reactions, the refining of glycerol is also important due to its numerous applications in different industrial products.
The unused alkali catalyst is usually neutralized by an acid. Water and alcohol are removed to produce 80-88% pure glycerol that can be sold as crude glycerol. In more sophisticated operations, the glycerol is distilled to 99% or higher purity. After the re-neutralization step, the alcohol in the glycerol phase can be removed through a vacuum flash process or by other types of evaporators. Usually, the alcohol vapor is condensed back into liquid and reused in the process.

Table 2.14: Environmental impacts of refining crude glycerol

Environmental aspect	Alkali transesterification
Waste water	The unused alkali catalyst is usually neutralized by an acid, leading to waste water stream
Emissions to air	Alcohol vapour releases

Purification of crude biodiesel

After separation from the glycerol phase, crude biodiesel is mainly contaminated with residual catalyst, water, unreacted alcohol, free glycerol and soaps generated during the transesterification reaction. Normally, before the washing step, biodiesel enters the neutralization step, and then passes through alcohol stripper.
Three main approaches are adopted for purifying biodiesel:
- Water washing;
- Dry washing;
- Membrane extraction.

Table 2.15: Environmental impacts of purification crude diesel

Environmental aspect	Alkali transesterification
Waste water	Both alcohol and glycerol are highly soluble in water, thus washing with water creates a waste water stream enriched with these two compounds
Solid waste	In order to remove water from the biodiesel, silica gels or Na_2SO_4 are applied, to be recovered or disposed as solid waste.

2.4.3 Summary of Environmental impacts

The environmental risks are summarized per category in the table below.

Table 2.16: Overview environmental impacts of transesterification/hydrogenation process route

Step	Fire / Explosion	Noise	Air	Water	Soil	Waste	GMO*
Raw materials treatment (pretreatment)				✓		✓	
Catalyst and alcohol	✓		✓	✓		✓	
Mixing and neutralization	✓		✓			✓	
Transesterification and separation	✓					✓	
Refining crude glycerol	✓		✓	✓		✓	
Purification of crude biodiesel	✓		✓	✓		✓	

* application of GMO in this process is being described in literature, but as it is in stage of R&D and not being
applied on industrial scale, it is not being considered (yet) as an environmental aspect

2.5 Route 3: Anaerobic digestion

2.5.1 Process description

Anaerobic digestion is a series of biological processes in which microorganisms break down biodegradable material in the absence of oxygen. One of the end products is biogas, which is combusted to generate electricity and heat, or can be processed into renewable natural gas and transportation fuels. A range of anaerobic digestion technologies are converting livestock manure, municipal wastewater solids, food waste, industrial wastewater and residuals, fats, oils and grease (FOG), and various other organic waste streams into biogas. Separated digested solids can be composted, utilized for dairy bedding, directly applied to cropland or converted into other products. Nutrients in the liquid stream are used in agriculture as fertilizer. The schematic flow chart is displayed in Figure 2.5 [based on Appels et al., 2008].

```
                    Biomass
                       │
                       ▼
         Proteins, Fats, Carbohydrates
                       │
                       ▼
              ┌─────────────────┐
              │    Hydrolysis   │
              └─────────────────┘
                       │
                       ▼
         Fatty acids, Amino acids, Sugars
                       │
                       ▼
              ┌─────────────────┐
              │   Acidogenesis  │
              └─────────────────┘
                       │
                       ▼
            Carbonic acid, Alcohol,
          Hydrogen, Carbon dioxide,
                   Ammonia
                       │
                       ▼
              ┌─────────────────┐
              │   Acetogenesis  │
              └─────────────────┘
                       │
                       ▼
            Hydrogen, Acetic acid,
               Carbon dioxide
                       │
                       ▼
              ┌─────────────────┐
              │  Methanogenesis │
              └─────────────────┘
                       │
                       ▼
          Methane, Carbon dioxide,
                  Digestate
```
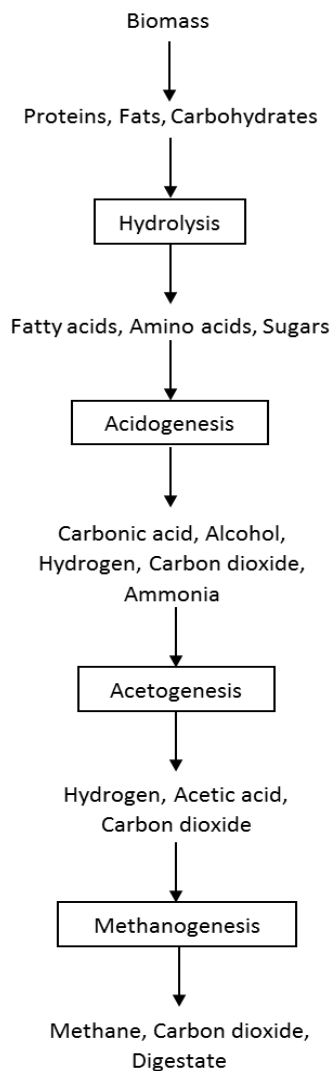
Figure 2.5.   Schematic flow chart for anaerobic digestion (based on Appels et al.)

The digestion process begins with bacterial hydrolysis of the input materials in order to break down in soluble organic polymers such as carbohydrates and make them available for other bacteria. Acidogenic bacteria then convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenic bacteria then convert these resulting organic acids into acetic acid, along with additional ammonia, hydrogen, and carbon dioxide. Finally, methanogens convert these products to methane and carbon dioxide.

In general the digestate is being processed to be used as a fertiliser, so does not create waste.

2.5.2　Environmental impacts

The environmental risks are specified per process block in the sections below.

Biomass storage

The aim of the unit is to receive the feedstock, to store it prior to processing. For anaerobic digestion different types of waste can be used as starting material, including industrial wastewaters, municipal wastewater, municipal solid waste, agricultural waste. The environmental risks are illustrated in the table below.

Table 2.17:　Environmental impacts of storage bio-feedstock

Environmental aspects	Storage
Feedstock resource impact	In the case of wastewaters, the composition of the streams may not be entirely defined. Depending on type of raw material, some toxic compounds can be present, like heavy metals.
Fire	Fire can occur during storage due to biological reactions (especially the case of agricultural waste)
Emissions to air	Odour emissions can occur because of rotten feedstock
Soil contamination risk	Soil contamination can occur due to the chemicals present in the raw material (sludge, manure etc.) and/or being formed, that are produced by biological degradation during storage

Hydrolysis

Large protein macromolecules, fats and carbohydrate polymers (such as cellulose and starch) are broken down through hydrolysis to amino acids, long-chain fatty acids, and sugars.
The environmental risks are illustrated in the table below.

Table 2.18:　Environmental impacts of hydrolysis

Environmental aspects	Enzymatic Hydrolysis
Waste water	There can be residues of enzymes and chemicals (originating from the raw material, or by side reactions (e.g. furfural) in the waste water, depending on hydrolysis conditions. These can have impact on the ecosystem
Emissions to air	Odour emissions can occur because of rotten feedstock

Fermentation: Acidogenesis, Acetogenesis, Methanogenesis

In this step amino acids, sugars and fatty acids obtained in the hydrolysis are fermented to form carbonic acid, alcohol, hydrogen, carbon dioxide, ammonia. For this purpose bacteria are used. These may be genetically modified to either increase the yield or to make them more resistant to additional components present in the applied feed.
The fermentation process consists of 3 steps: acidogenesis, acetogenesis and methanogenesis. Fermentation starts with acidogenesis. In the acidogenesis.

In acetogenesis, the next step in the anaerobic fermentation, bacteria consume the fermentation products formed during acidogenesis and generate acetic acid, carbon dioxide, and hydrogen.

The methanogenic organisms consume the acetate, hydrogen, and some of the carbon dioxide to produce methane.

The environmental risks are illustrated in the table below.

Table 2.19:   Environmental impacts of fermentation

Environmental aspects	Remarks
Waste water	There can be residues of chemicals and microorganisms in the waste water. This can have impact on the ecosystem
Explosion	Organic components can create explosive mixtures
Emissions to air	▪ Gas emissions can be produced during fermentation (e.g. VOC, CO_2, NH_3/amines, mercaptanes); ▪ Odour emissions can occur during processing.
Genetically Modified Microorganisms	Containment issue of microorganisms

2.5.3   Summary of environmental impacts

The environmental risks are summarized per category in the table below.

Table 2.20:   Overview of environmental aspects of anaerobic digestion route

Step	Fire / Explosion	Noise	Air	Water	Soil	Waste	GMO
Biomass storage	✓		✓		✓	✓	
Hydrolysis			✓	✓			
Fermentation	✓		✓	✓			✓

2.6   Route 4: Algae

2.6.1   Process description

Algae can be considered to be both a biomass that can be used as an end-product (like in pharma and food), or can be seen as a producing unit for intermediate building blocks, like biodiesel, or omega-3.

Photoautotrophic algae use light as an energy source and CO_2 as a carbon source, while heterotrophic (chemo-organic) algae use organic carbon, such as simple sugars, for energy and as a carbon source.

Photoautotrophic microalgae are microscopic photosynthetic organisms that are found in both marine and freshwater environments. Their photosynthetic mechanism is similar to land based plants, but due to a simple cellular structure, and submerged in an aqueous environment where they have efficient access to water, CO_2 and other nutrients, they are generally more efficient than plants in converting solar energy into biomass. Today, the most common procedure for cultivation of microalgae is autotrophic growth. Because all microalgae are photosynthetic, microalgae are cultivated in environments naturally (open ponds) or artificially (e.g. photobioreactors).

A feasible alternative for photo-autotrophic cultures is the use of heterotrophic cultures. These grow in the absence of light, in closed systems, by replacing the fixation of atmospheric CO_2 of autotrophic cultures with organic carbon sources dissolved in the culture media. The basic culture medium composition for heterotrophic cultures is similar to the autotrophic culture with the sole exception of adding an organic carbon feed.

The core of the algae production unit is the cultivation unit. Algae grow in a water environment enriched with carbon dioxide/carbon source and nutrients. The CO_2 for biomass production can be obtained from different sources, like waste gas from industrial (combustion) processes. Water and nutrients are provided to the to the cultivation unit in a controlled way. In general, the limiting growth factor is the incoming light for autotrophic algae. The block diagram in figure 2.6 illustrates the process characteristics.
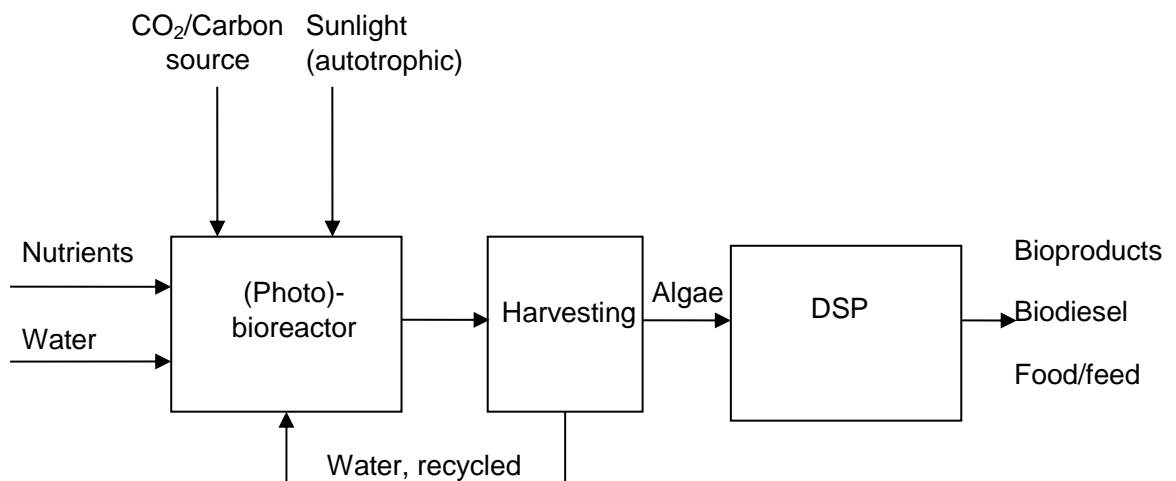

Figure 2.6: **Block diagram for the algae production route**

2.6.2 Environmental impacts

The environmental risks are specified per process block in the sections below.

Cultivation

Two cultivation technologies are used in this study: (1) an autotrophic system with open ponds and closed photobioreactors, and (2) a heterotrophic system with closed bioreactors.

The environmental risks are illustrated in the table below.

Table 2.21: **Environmental impacts of algae cultivation**

Environmental Risks	Autotrophic system	Heterotrophic system
Water Resource Impact	Open ponds cultivation may be water-intensive, requiring freshwater inputs due to evaporation, with possible impacts to ecosystems across the landscape	Less water evaporation and consequently less impact on the ecosystems around the cultivation site.
Genetically Modified Organisms (in some cases)	Open autotrophic systems expose modified algae directly to natural environments. Biological containment may be applicable.	Closed heterotrophic systems reduce risk of release. Depending on the type of GMO, a more or less strict containment level is applicable.

Harvesting

Usually, after the cultivation unit, the algae are separated from the water and the separated water can be recycled. Harvesting of microalgae is a major contributor to the total cost and energy consumption of algal biomass production. The harvesting method must handle large volumes due to dilute culture broths. The small size of microalgae, typically ranging from 3-30 microns in diameter makes the process complex. Many separation processes could be used for the harvesting of microalgae and the choice of method depends on a number of parameters such as algal species, cell density and culture conditions.

The environmental risks are illustrated in the table below.

Table 2.22: **Environmental impacts of algae harvesting**

Environmental Risks	Autotrophic system	Heterotrophic system
Waste water	Large volumes of waste water, containing low concentrations of minerals and organic compounds (BOD)	Compared to autotrophic system smaller amounts of waste water, containing low concentrations of minerals and organic compounds (BOD)
(bio-)waste	Bio-waste material sometimes containing GMO	Bio-waste material sometimes containing GMO

Down Stream Processing

The DSP consists of the following main processes:
- Cell Disruption;
- Solid liquid separation;
- Concentration;
- Purification;
- Formulation.

The environmental risks are illustrated in the table below.

Table 2.23: Environmental impacts of algae Down Stream Processing

Environmental aspects	Remarks
Waste water	There can be microorganisms in the waste water
Fire/Explosion	Solvents used in DSP can create explosive mixtures (like hexane, dodecane, sulphuric acid, methanol)
Emissions to air	Odour emissions can occur depending on type of fermentation and DSP technology.
Genetically Modified Microorganisms	In case of GMO: Containment issue of microorganisms

2.6.3 Summary of environmental impacts

The environmental risks are summarized per category in the table below.

Table 2.24: Overview of environmental impacts of algae production route

Step	Fire/ Explosion	Noise	Air	Water	Soil	Waste	GMO
Cultivation				✓	✓		✓
Harvesting				✓		✓	✓
Downstream Processing	✓		✓	✓			✓

2.7 Route 5 Gasification

2.7.1 Process description

Gasification and pyrolysis are comparable processes, but leading to different products: gasification leads to syngas (synthesis gas, a mixture of CO and H_2), pyrolysis leads mainly to pyrolysis oil. In gasification, the first reaction (unit operation) is always pyrolysis, followed by a gasification chamber.

Biomass gasification is considered as one of the most promising routes for syngas. Syngas is a building block for various chemicals. Another application of gasification is the combined heat and power production.

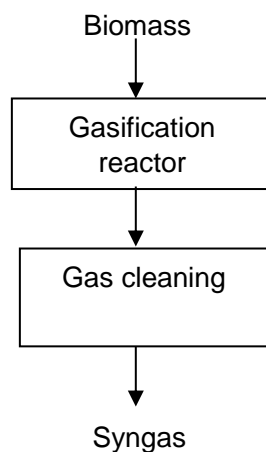A gasification system consists of 2 main stages:

Biomass

↓

```
┌──────────────────┐
│   Gasification   │
│     reactor      │
└──────────────────┘
```

↓

```
┌──────────────────┐
│   Gas cleaning   │
│                  │
└──────────────────┘
```

↓

Syngas

Figure 2.7:   Block diagram for the gasification process route

Gasifiable biomass means that the biomass materials can be converted into gas fuel through thermo-chemistry processing. The list below gives some examples of biomass resources for gasification:

◼ Crops residues: such as rice straw, bean stalks, corn stalks, cotton stalks, maize stalks;
◼ Firewood and wood residues: timber from firewood forest and residues from forestry;
◼ Industrial wastes:
  ◼ Grain processing: corncob, husk and wheat bran;
  ◼ Wood industry: paper mill and timber;
  ◼ Sugar mill: sugarcane and beet root.
◼ Municipal refuses.

Gasifier reactor
Thermochemical gasification is the conversion by partial oxidation at elevated temperature of a carbonaceous feedstock such as biomass or coal into a gaseous energy carrier. This gas contains carbon monoxide, carbon dioxide, hydrogen, methane; trace amounts of higher hydrocarbons such as ethane and ethene, water, nitrogen (if air is used as the oxidizing agent) and various contaminants such as small char particles, ash, tars and oils.

The partial oxidation can be carried out using air, oxygen, steam or a mixture of these. Air gasification produces a low heating value gas suitable for boiler, engine and turbine operation but not for pipeline transportation due to its low energy density. Oxygen gasification produces a medium heating value gas suitable for limited pipeline distribution and as synthesis gas for conversion, for example, to methanol and gasoline.

Such a medium heating value gas can also be produced by pyrolytic or steam gasification. Gasification with air is the more widely used technology since there is not the cost or hazard of oxygen production and usage, nor the complexity and cost of multiple reactors.

Gasification occurs in a number of sequential steps:

- ■ drying to evaporate moisture,
- ■ pyrolysis to give gas, vaporised tars or oils and a solid char residue,
- ■ gasification or partial oxidation of the solid char, pyrolysis tars and pyrolysis gases.

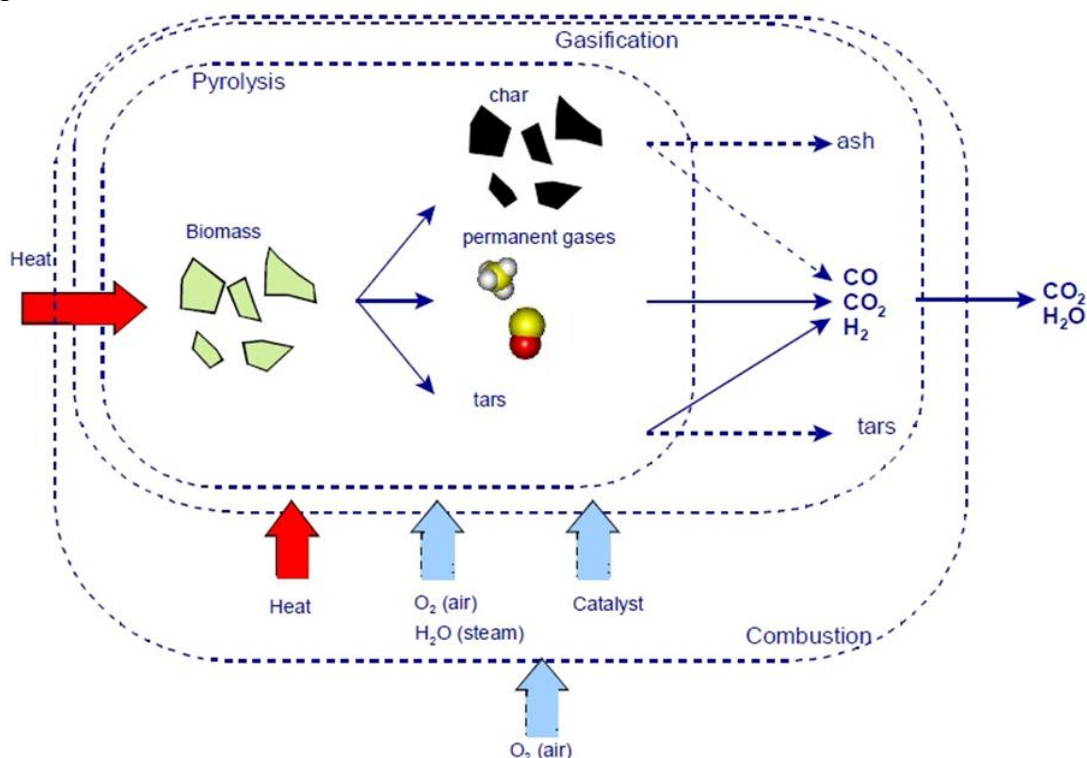The figure 2.8 below shows the presentation of the process involved in biomass gasification.

Figure 2.8:   Schematic overview of the gasification/pyrolysis process route

When a solid fuel is heated to 300-500°C in the absence of an oxidising agent, it pyrolyses to solid char, condensable hydrocarbons or tar, and gases. The relative yields of gas, liquid and char depend mostly on the rate of heating and the final temperature. Generally in gasification, pyrolysis proceeds at a much quicker rate than gasification and the latter is thus the rate controlling step.

The gas, liquid and solid products of pyrolysis then react with the oxidising agent - usually air - to give permanent gases of CO, CO_2, H_2, and lesser quantities of hydrocarbon gases. Char gasification is the interactive combination of several gas-solid and gas-gas reactions in which solid carbon is oxidised to carbon monoxide and carbon dioxide, and hydrogen is generated through the water gas shift reaction. The gas-solid reactions of char oxidation are the slowest and limit the overall rate of the gasification process. Many of the reactions are catalysed by the alkali metals present in wood ash, but still do not reach equilibrium.

The gas composition is influenced by many factors such as feed composition, water content, reaction temperature, and the extent of oxidation of the pyrolysis products.

Not all the liquid products from the pyrolysis step are completely converted due to the physical or geometrical limitations of the reactor and the chemical limitations of the reactions involved, and these give rise to contaminant tars in the final product gas. Due to the higher temperatures involved in gasification compared to pyrolysis, these tars tend to be refractory and are difficult to remove by thermal, catalytic or physical processes. This aspect of tar cracking / removal in gas clean-up is one of the most important technical uncertainties in implementation of gasification technologies.

The environmental risks of the gasification step are summarised in the table below.

Table 2.25:   Environmental impacts of gasification step

Environmental aspects	Gasifier reactor
Explosion	Dust explosion Gas explosion
Noise	Gasification equipment can create high noise levels
Emissions to air	benzene, toluene, and xylenes), inorganic impurities NH_3, HCN, H_2S, COS, and HCl, volatile metals, dust, and soot. Odours may arise because of the degradation of organic matter
Toxic substances	Carbon monoxide is a major constituent of producer gas and is toxic. PAH's?

Syngas cleaning

The syngas produced by gasification contains impurities. Typical are the organic impurities tars and BTX (benzene, toluene, and xylenes), the inorganic impurities NH_3, HCN, H_2S, COS, and HCl, and furthermore volatile metals, dust, and soot.
In gasification, larger hydrocarbons are formed, generally categorised as 'tars'. When condensing, they foul downstream equipment, coat surfaces and enter pores in filters and sorbents. On the other hand, they contain a lot of potential CO and H_2. They should thus preferably be cracked into smaller hydrocarbons.
Three methods may be considered for tar removal/cracking: thermal cracking, catalytic cracking, and scrubbing. When the tars and BTX are removed, the other impurities are removed by standard wet gas cleaning technologies.

The table below gives a summary of the contaminants and the methods for the syngas cleaning step.

Table 2.26: Overview of contaminants and treatment methods for syngas cleaning

Contaminants to air and (scrubber) water	Examples	Cleaning method
Particulates	Ash, char	Filtration, Scrubbing
Alkali metals	Sodium, potassium compounds	Cooling, Adsorption, Condensation, Filtration
Fuel-bound nitrogen	Mainly ammonia and HCN	Scrubbing
Tars	Refractive aromatics	Tar cracking, scrubbing
Sulphur, chlorine	HCl, H_2S	Lime or dolomite, Scrubbing, Absorption

2.7.2 Environmental impacts

The environmental risks for the syngas cleaning are presented in the table below.

Table 2.27: Environmental impacts of syngas cleaning

Environmental aspects	Syngas cleaning
Explosion	Gas explosion and gas leaks can occur
Emissions to air	Odours may arise because of the degradation of organic matter VOC, benzene, toluene, and xylenes), inorganic impurities NH_3, HCN, H_2S, COS, and HCl, volatile metals, dust, and soot.
Waste water	Waste water and condensates may be produced during wet gas cleaning, containing to a more or less extent the substances present in the gas phase

2.7.3 Summary of environmental impacts

The environmental risks are summarized per category in the table below.

Table 2.28: Overview of environmental impacts of the gasification process route

Step	Fire/ Explosion	Noise	Air	Water	Soil	Waste	GMO
Gasifier reactor	✓		✓				
Gas cleaning	✓	✓	✓	✓		✓	

2.8 Route 6 Pyrolysis

2.8.1 Process description

Pyrolysis of biomass is the heating of biomass in an inert atmosphere (absence of oxygen) to produce gaseous products (mainly CO_2, H_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, benzene, etc.), liquid products (tars, high molecular hydrocarbons and water) and solid products.
The method of wood conversion to charcoal by slow pyrolysis (slow heating rate) has been practiced for many years. This requires relatively slow reactions at low temperatures to maximize solid char yield.

Liquid fuel production by fast pyrolysis is an alternative process. High yields of liquid products can be obtained under temperatures of around 500°C and rapid cooling of pyrolysis vapours to give bio-oil product. Pyrolysis oil consists of water and a mixture of organic compounds that are condensed after the pyrolysis step. The time and the temperature profile affects the composition and the quality of the liquid product. High temperatures will continue to crack the vapours and the longer the vapours are at high temperatures the greater the extent of cracking. Therefore, vapour residence time shall be up to 1 second for fuel production.

2.8.2 Environmental impacts

Since the pyrolysis process is similar to the gasification process the environmental risks are similar. Please see the previous section for the environmental risks.

3 ENVIRONMENTAL RISK ASSESSMENT FOR SELECTED PROCESSES

3.1 Selection of processes

3.1.1 Selection criteria

In the framework of this project, two processes and/or products were selected for further evaluation of the environmental risks of both the biobased route as well as the conventional route based on petroleum derivatives.

According the previous RIVM study on Biobased alternatives for priority substances, (Van Helmond et al., 2012), priority substances are selected for policy reasons based on their intrinsic hazardous properties. As a result, substitution of priority substances is possible in number of ways:

■ One-to-one (direct) substitution by a substance with the same structural formula. This biobased substance remains a priority substance. There is only a change from petrobased to biobased origin;

■ A subtype of one-to-one substitution by a substance with the same structural formula but produced without the impurities that determined the priority status of the petrobased chemical. In this case the biobased substance should not be qualified as a priority substance;

■ Substitution with another substance that has the same function (functional substitution). This will lead to replacement of the priority substance under the assumption that the biobased substitute does not have characteristics making it another priority substance.

The following criteria were applied to select two biobased production processes:

1. Contributing via one of the three ways mentioned above for substituting priority substances. (However, it should be realized that most of the substances discussed here are not priority substances);

2. Being operational or expected to be operational within a few years on an industrial scale in The Netherlands or surrounding countries.

Bio-ethylene

Ethylene is one of the basic organic chemicals serving as feedstock for a large number of downstream chemical products including many plastics. Today, almost all ethylene is produced from petroleum derivatives, but biomass can also be used as an alternative feedstock for the production of bio-ethylene. Ethylene is the building block for chemicals such as ethylene dichloride, ethylene dioxide and vinyl chloride (see Van Helmond et al., 2012). According the categorization in this report, bio-ethylene is an example of direct substitution, in this case of an identical building block.

Glycerol

Glycerol holds the potential of being an extremely versatile building block within the biorefinery. Since glycerol is a key co-product of biodiesel manufacture, increasing use of biodiesel will lead to much greater glycerol availability and lower costs.
Glycerol can be used as the building block for triacetine that can replace various prioritised petrochemical plasticizers.

As such it is an example of functional substitution. Glycerol is also the building block for epichlorohydrine where it replaces the extremely flammable fossil based propylene, also an example of functional substitution. Besides that, the replacement of conventionally produced glycerol by biobased glycerol is as well an 1-1 substitution.

Therefore the glycerol production routes will be investigated in more detail on environmental risks and compared with the traditional production routes: based on application of animal fats and on propene coming from fossil feedstock.

3.2 Production of Bio-ethylene

3.2.1 Introduction

Ethylene, H2C=CH2, is a colourless, flammable gas. Ethylene is one of the basic organic chemicals serving as feedstock for a number of downstream chemical products. Ethylene is an intermediate petrochemical for direct or indirect production of most important synthetic polymers, including high- and low-density polyethylene (HDPE and LDPE), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET). With a production exceeding 140 million tonnes per year, ethylene is by far the largest bulk chemical (in volume) used for the production of around half of all plastics. The demand for ethylene is expected to continue to rise, particularly in the emerging economies. Today, almost all ethylene is produced from petroleum derivatives, but biomass can also be used as an alternative feedstock for the production of bio-ethylene. Ethylene and bio-ethylene are chemically identical, so existing equipment and production capacity can use both to produce plastics or other downstream products. Currently, increasingly production of bio-ethanol is taking place in The Netherlands, however the next step to produce bio-ethylene from the bio-ethanol is not being done yet.

3.2.2 Ethylene production from biomass (bio-ethylene)

The first step in bio-ethylene production is the creation of bio-ethanol from biomass feedstock. This is a well-known process as bio-ethanol is now used as a transportation fuel. Currently, bio-ethanol is mainly produced from agricultural crops. Bio-ethanol can also be produced from starchy biomass and lignocellulosic biomass by converting the biomass to sugars first.
Bio-ethanol is produced by the fermentation of sugars that are produced from the biomass. Section 2.2 gives the process description of the fermentation process route which is also used to produce bio-ethanol. Therefore, in this part of the report the focus will be the production of bio-ethylene from bio-ethanol.
Once bio-ethanol has been produced and purified to chemical grade, it is converted to bio-ethylene by an alumina or silica-alumina catalyst.

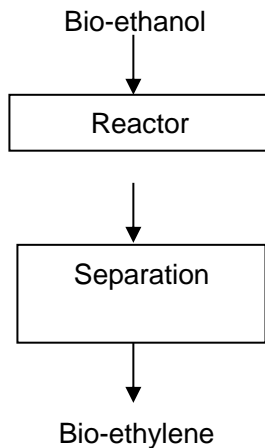The block diagram in figure 3.1 shows the process steps.

Bio-ethanol

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┌─────────────────────┐
│       Reactor       │
└─────────────────────┘
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┌─────────────────────┐
│                     │
│     Separation      │
│                     │
└─────────────────────┘
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↓

Bio-ethylene

Figure3.1:   Block diagram for the bio-ethylene process route

Reactor

Ethanol is catalytically dehydrated to produce ethylene according to the following chemical reaction:

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

One tonne of bio-ethylene requires 1.74 tonnes of (hydrated) bio-ethanol. Conversion yields of 99% with 97% selectivity to ethylene have been achieved. The reaction is endothermic and requires a minimum theoretical energy use of 1.6 gigajoules per tonne of bioethylene. Also the reaction is reversible with the equilibrium being favoured by higher temperatures and hindered by higher pressures and water vapour in the feed.

Separation

The reaction outlet stream primarily consists of unreacted ethanol, ethylene and diethyl ether. The stream is sent to a series of columns for ethylene purification. The separations section brings the ethylene product to 99.96% purity. It can roughly be broken into 4 sections: a flash section that removes the high boiling components, a distillation section that removes most of the water from the process so that the unreacted ethanol can be recycled without causing reactor volume to grow too large, a drying section in which adsorption is used to remove any remaining water and ethanol, and a cryogenic distillation section in which very low temperatures are used to finally achieve the needed purity of ethylene.

3.2.3 Environmental impacts of biobased ethylene production

Environmental impacts

The environmental aspects are summarized in the table below.

Table 3.1: Environmental impacts of biobased ethylene production

Environmental aspects	Ethylene from biomass
Explosion	Ethanol and ethylene are both very flammable, and as such careful attention must be paid to their transport to and from and storage at the facility
Emissions to air	Volatile organic compounds (ethanol and by-product from reaction di-ethylether)
Waste water	Separation section produces waste water stream containing organic components (BOD)

Summary of environmental impacts

The environmental risks are summarized per category in the table below.

Table 3.2: Overview of environmental aspects of bio-ethylene production

Step	Fire/ Explosion	Noise	Air	Water	Soil	Waste	GMO
Ethylene from Biomass	✔		✔	✔		✔	

3.3 Ethylene from petroleum derivatives

3.3.1 Process description

Various feedstocks (liquid and gaseous) are used for the production of ethylene. The principal feedstocks are naphtas, a mixture of hydrocarbons in the boiling range of 30 to 200 °C. In the US and the Middle East preferably light feedstocks (natural gas, ethane, propane, butane) are used. Gas oils (crude oil fractions) are also gaining importance as feedstocks in some areas of the world.

The bulk of the worldwide production is based on thermal cracking with steam. The process can be split in 4 main sections.
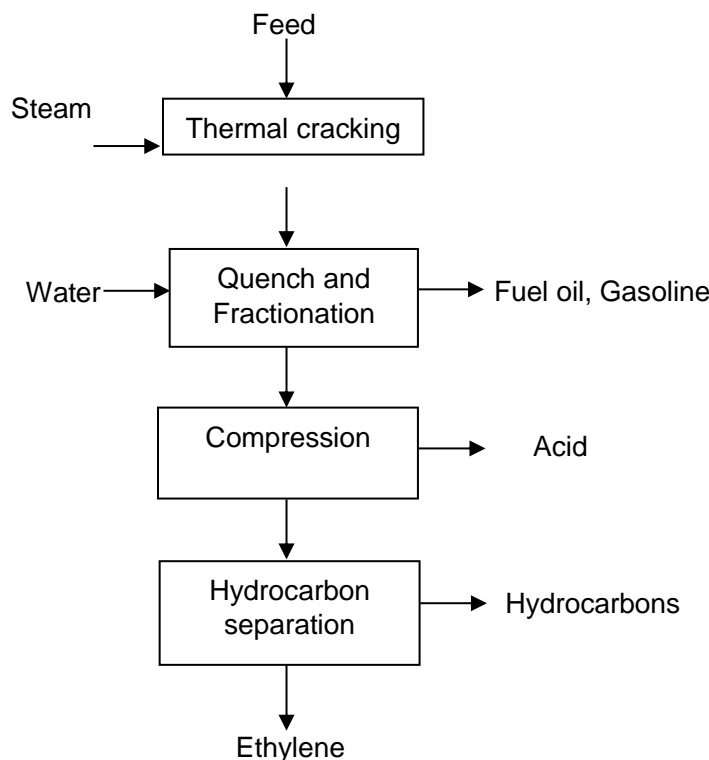
See figure 3.2 below for the block diagram.

Figure 3.2:   Block diagram for the conventional process route for ethylene.

The first 3 sections are more or less identical for all commercial processes. However, a large variety of process routes exist for hydrocarbon separation section.

Thermal cracking
The hydrocarbon molecules of the feedstock are cracked in the furnace in the presence of a catalyst at high temperatures. Cracking is an endothermic reaction with heat supplied by side-wall or floor burners or a combination of both, which use gaseous and/or liquid fuels.
The fundamental parameters of cracking furnaces are temperature and temperature profile, residence time of the gas during cracking, and partial pressure. Hydrocarbon feed stream is preheated, mixed with steam and further heated to 500 to 700°C. The stream enters a fired tubular reactor (known as cracker, cracking heater), where under controlled conditions the feedstock is cracked at 800 to 850°C into smaller molecules within a residence time of 0.1 to 0.5 s.

Quench and Fractionation
The reaction mixture exiting the radiant coil of the furnace contains a large spectrum of hydrocarbons. This stream is instantaneously cooled in quench coolers called transfer line exchangers to preserve the gas composition. Heavy fuel oils cuts are separated from the bulk of the effluent stream in the fractionator. Further cooling is performed in the quench tower.

Compression

The gas from the quench tower is then compressed in a 4 or 5 stage compressor train to an optimum pressure for separating it into various components. Water and hydrocarbons are separated between stages and recycled. Acid gases (CO_2 and H_2S) are removed after the 3rd or 4th compression stage by scrubbing them with a dilute caustic soda solution. In case of higher sulfur content a separate gas removal system is used.

Hydrocarbon separation

Various separation methods are used to separate the hydrocarbons. Mainly different distillation columns are used to separate various hydrocarbons.

3.3.2   Environmental impacts

Ethylene plants require special measures for protection of personnel and the environment. The environmental risks are summarized in the table below.

Table 3.3:   **Environmental impacts of petrochemical production route of ethylene**

Environmental aspects	Ethylene from petroleum derivatives
Explosion	Explosion by highly flammable substances
Emissions to air	NOx emissions from thermal cracking furnace Particulate emissions during decoking Volatile hydrocarbons Acidic and sulphur containing compounds.
Waste water	Liquid emission of the plant mainly results from quench water, dilution steam, caustic-stripping (acid gas removal) liquid and decoking water, Organic compounds
Waste	Sludge and catalysts

Summary of environmental impacts

The environmental risks are summarized per category in the table below.

Table 3.4:   **Overview of environmental impacts of petrochemical production of ethylene**

Step	Fire/ Explosion	Noise	Air	Water	Soil	Waste	GMO
Ethylene from Petroleum Derivatives	✓	✓	✓	✓	✓	✓	

3.4   Comparison of ethylene from petroleum derivatives and from biomass

In general, bio-ethylene can significantly reduce the environmental impact of the chemical industry. Based on recent estimates, bio-ethylene can reduce Greenhouse gas (GHG) emissions by up to 40% and save fossil energy by up to 60% compared to petrochemical ethylene [IEA-ETSAP, 2013].

Additionally, bio-ethanol dehydration produces far less solid (catalyst) and liquid (sludge) waste and carbon emissions than cracking does.

The environmental aspects are expressed in relative terms as x, xx and xxx, that show which of the two routes, biobased or conventional route, is leading to the higher environmental risk. These are not absolute values.

The efficiency/process yield is expressed with the Environmental Release (ER) factor, telling which percentage of the product is not gained as a product but lost in emissions to air, waste water or waste.

Hazardous /toxic by-products to air, waste water or waste are substance groups like VOCs, acids, organic-by products, etc. As emissions to air, the two types of air pollution that are currently most critical in meeting the EU air quality standards (NO_2 and PM10) are being described, as well as Greenhouse gas emissions (mainly CO_2). Water emissions are expressed in terms of their Biological Oxygen Demand and Chemical Oxygen Demand.

Table 3.5: **Overview of releases to the environment of bio-ethylene production versus the conventional fossil feedstock based production process**

Process route	Environmental Release			Hazardous/toxic by-products			Air emissions			Water	
	Air	Water	Waste	Air	water	Waste	NOx	PM10	GHG	BOD	COD
Bio-based	X	XX	XX	X	XX	XX	-	-	X	X	X
Fossil oil based	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XXX

X = relatively small emission/risk

XX = medium emission/risk

XXX = relatively large emission/risk

3.5 Production of Glycerol

3.5.1 Introduction

Glycerol holds the potential of being an extremely versatile building block within the biorefinery. Glycerol is currently a well-recognized item of commerce with an annual world production of $500 – 750 \times 10^3$ tonnes. Since glycerol is a key co-product of biodiesel manufacture, increasing use of biodiesel will lead to much greater glycerol availability and lower cost. As glycerol is a nontoxic, edible, biodegradable compound, it will provide important environmental benefits to the new platform products.
Therefore the glycerol production route will be investigated further on environmental risks and compared with the traditional production routes:
- using animal fats and/or used cooking oil as feedstock;
- based on propene coming from fossil feedstock. As this route is not being used anymore, this process is not described in this report.

Currently there is a number of industries producing bio-glycerol as a by-product from biodiesel production.

3.5.2 Glycerol production from biomass

Glycerol is a by-product obtained via the production of biodiesel (methyl or ethyl esters of fatty acids) by transesterification of oils and fats – therefore the risks involved in the production of glycerine (=glycerol) are the same as for the production of biodiesel. Due to its potential as building block, it is further refined (see the marked area in Figure 3.3.1) to meet the requirements imposed by its diverse industrial applications, and this part of the process brings the risks that are glycerol-specific. Here we will first describe the steps required for the glycerine upgrade, and next a summary is given of the related environmental risks.

The transesterification reaction produces two major streams: glycerine and biodiesel. The glycerine phase is much denser than the biodiesel phase and the two can be gravity separated with glycerine simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.
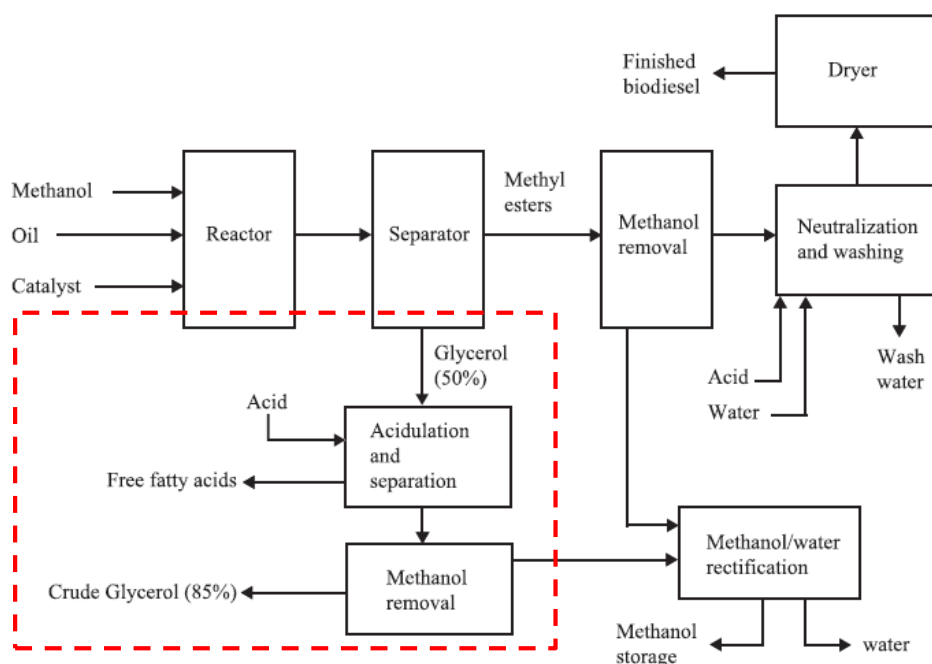
Figure 3.3: **Block diagram for the bio-glycerol process route**

Typically, the glycerine after the separator is usually 50% glycerine, 40% methanol and 10% soap and catalyst. The glycerine by-product contains unused catalyst and soaps that are neutralized with an acid and sent to the storage as crude glycerine. In some cases the salt formed during this phase is recovered for use as fertilizer, however in most of the cases salt is simply left in the glycerine. Removal of water and alcohol results in production of approximately 80% pure glycerine that is ready to be sold as crude neutralized glycerine.

If further refining is required (for pharmaceutical and food applications), water and salts are removed by vacuum distillation or ion exchange, which can upgrade the purity to 99.5%-99.7%.

3.5.3 Environmental impacts of biobased glycerol production

For the first steps of the glycerol production process, the environmental aspects are the same as the aspects identified for the production of biodiesel. Therefore, here only the risks identified for the refining steps of glycerol are included.

Table 3.6:   Environmental aspects of bio-glycerol production

Step	Activity	Risks involved
Acidulation and separation	Application of highly concentrated sulphuric or phosphoric acid	Waste water streams
Methanol removal	Application of vacuum flash evaporator	Creation of methanol vapours to air
Further refining to pharma and food standards	Vacuum distillation application	Emissions to air (methanol)

3.6   Traditional route (saponification)

Traditionally, glycerine (glycerol) was a byproduct of the industrial soap manufacturing process (saponification). The route based on fossil fuels (using propene as the starting point) in the so-called epichlorohydrin process has been mainly used during the World War II, when the demand for glycerol for the production of explosives was tremendous. However, this route is no longer in use.
With the current overflow of the market with glycerine, even more attention is paid to the research diverting it: epichlorohydrin and acrolein can now actually be obtained from glycerol being byproduct of biodiesel route [Tuck et al., 2012; Mulhaupt, 2013].

Modern soap manufacturers use fatty acids and sodium hydroxide as an input. Fatty acids for soap are manufactured through the process of hydrolysis (fat splitting). The process separates the lipid source, either animal fat or vegetable oil, into water, fatty acids and glycerine. The glycerine is then removed from the water and fatty acids (sweet water) and is processed into refined glycerine.

The production of fatty acids and biodiesel is a similar process (as can be seen in Figure 3.4). Both processes can use animal fat or vegetable oil as input, both produce glycerine as by-product.
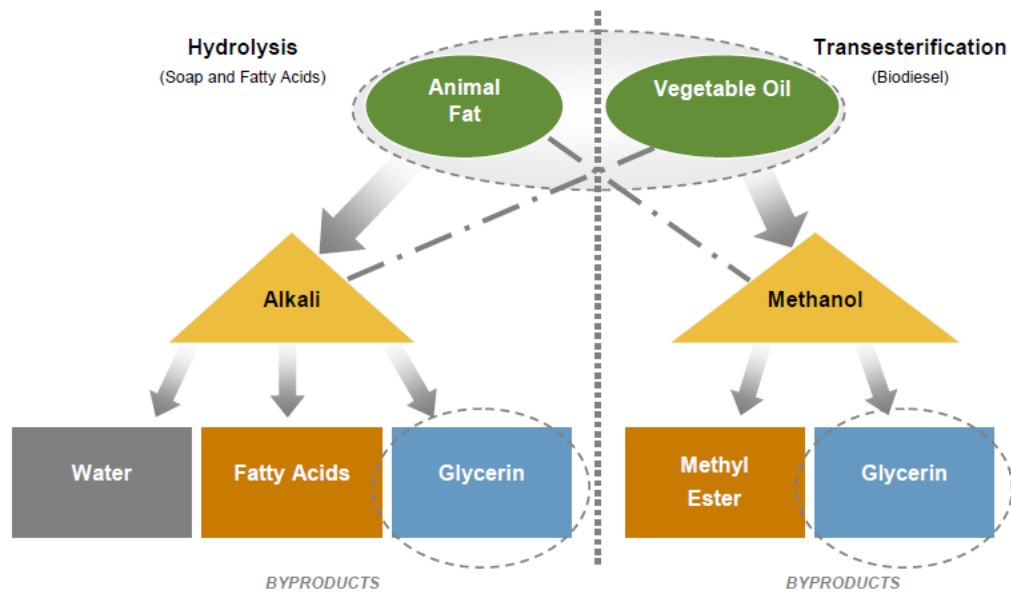
Figure 3.4: Comparison of Saponification and Transesterification (based on the Glycerin Market Analysis by ABG)

The essence of soap production is the saponification reaction, which is exothermic and progresses quickly and efficiently at around 125°C, inside an autoclave type of reactor:
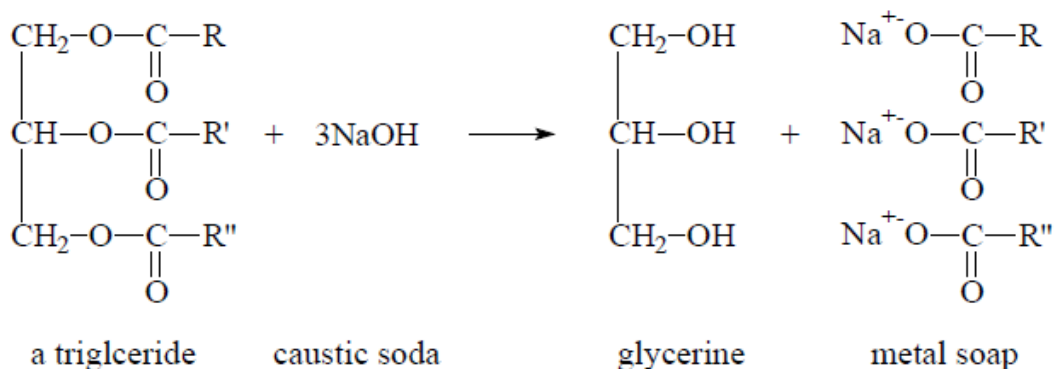
Figure 3.5: Saponification reaction to produce soap and glycerin

The glycerine is extracted from the soap with lye – a brine solution that is added to the soap at the saponification stage.

The general process flow for the production of soap (and glycerine as byproduct) can be presented with the use of scheme describing the Colgate-Palmolive continuous process (see Figure 3.6).

Figure 3.6: **The Colgate Palmolive continuous soap manufacturing process**

Saponification

In the first step raw materials (coconut oil, tallow and 50% NaOH solution) are continuously fed into reactor. Soap needs to be about 30% water to be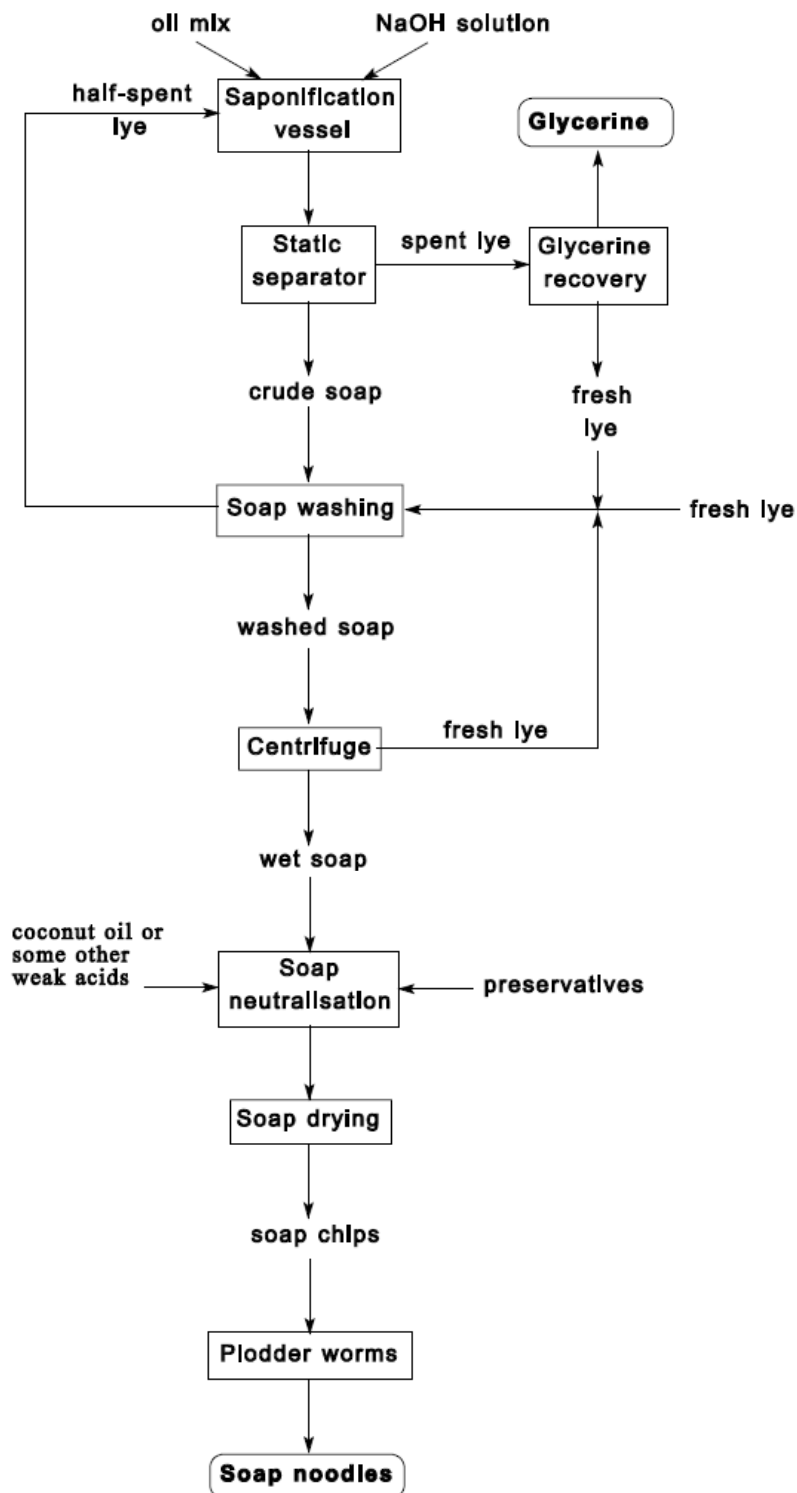 easily pumpable, and even then needs to be held at around 70°C, so excess lye is added to hydrate the soap and dissolve out some of the glycerine.

Lye separation

The wet soap is pumped to a "static separator" - a settling vessel which does not use any mechanical action. The soap / lye mix is pumped into the tank where it separates out on the basis of weight. The spent lye settles to the bottom from where it is piped off to the glycerine recovery unit, while the soap rises to the top and is piped away for further processing.

Glycerine recovery takes place in 3 steps:
1. Soap removal;
2. Salt removal;
3. Glycerine purification.

The spent lye contains a small quantity of dissolved soap which must be removed before the evaporation process. This is done by treating the spent lye with ferrous chloride. However, if any hydroxide ions remain present, the ferrous ions react with them instead, so these are first removed with hydrochloric acid:

$$HCl + NaOH \rightarrow NaCl + H_2O$$
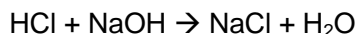
The ferrous chloride is then added. This reacts with the soap to form an insoluble ferrous soap:

$$FeCl_2 + 2RCOONa \rightarrow 2NaCl + (RCOO)_2Fe$$
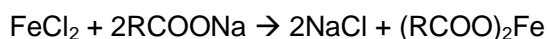
This precipitate is filtered out and then any excess ferrous chloride removed with caustic:
$$2NaOH + FeCl_2 \rightarrow Fe(OH)_2 + 2NaCl$$
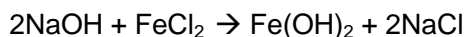
This is filtered out, leaving a soap free lye solution.

Water is removed from the lye in a vacuum evaporator, causing the salt to crystallise out as the solution becomes supersaturated. This is removed in a centrifuge, dissolved in hot water and stored for use as fresh lye. When the glycerine content of the solution reaches 80 - 85% it is pumped to the crude settling tank where more salt separates out.

A small amount of caustic soda is added to the crude glycerine and then the solution is distilled under vacuum in a heated still. Two fractions are taken off - one of pure glycerine and one of glycerine and water. The glycerine thus extracted is bleached with carbon black and then transferred to drums for sale, while the water/glycerine fraction is mixed with the incoming spent lye and repeats the treatment cycle.

3.7 Comparison of saponification and biodiesel production routes

In the table below an overview of the environmental aspects involved in the production of glycerine via traditional saponification route and modern biodiesel route is provided. Since these processes involve different steps, but generally the same production phases (reaction, separation of glycerine, further processing of the main product, refining of the glycerine), the risk analysis will use the more generic description for each process.

Table 3.7: Comparison of environmental impacts of conventional and biobased production of glycerol

Process step	Identified environmental aspect	Saponification	Biodiesel production
Reaction to obtain main product	Application of harmful substances that can be released to environment	✓	✓
	Creation of waste streams	✓	✓
	Air contamination		✓
Separation of glycerine	Possible leakage in the system (low probability)	✓	✓
Further processing of the main product	Creation of waste streams	✓	✓
	Application of hazardous substances	✓	✓
	Application of high temperatures and pressure	✓	✓
Refining of the glycerine	High temperature	✓	✓
	Waste stream of hazardous substances	✓	✓
	Release of hazardous substances to air		✓

As it can be seen from the table above, the saponification and biodiesel production processes are quite similar when it comes to environmental risks. Particular steps in each process are alike, since in both cases first reaction to produce the main product (and glycerol as by-product) needs to take place, then created products need to be separated, and further processing is taking place – with one route for the main product, and another route for glycerine refining.
The main differences between biodiesel route and saponification originate in the fact, that even though starting materials are the same, the core reaction needs to be directed in such a way that different main products are obtained – that is biodiesel or soap. This leads to application of methanol in biodiesel route, which has influence on the refining steps of both obtained products. Due to the characteristic of methanol, an additional burden of air contamination risk is involved in the biodiesel route.

Other than this, both processes are to a big extent comparable, and their level of sustainability can also be described as comparable, since they both use renewable resources as the starting material.

The environmental risks are expressed in relative terms as x, xx and xxx, that show which of the two routes, biobased or conventional route, is leading to the higher environmental risk. These are not absolute values.

The efficiency/process yield is expressed with the Environmental Release (ER) factor, telling which percentage of the product is not gained as a product but lost in emissions to air, waste water or waste.

Hazardous /toxic by-products to air, waste water or waste are substances like VOCs, acids, organic-by products, etc. As emissions to air, the two types of air pollution that are currently most critical in meeting the EU air quality standards (NO_2 and PM10) are being described, as well as Greenhouse gas emissions (mainly CO_2). Water emissions are expressed in terms of their Biological Oxygen Demand and Chemical Oxygen Demand.

Table 3.8 **Overview of releases to the environment of glycerol production by the biodiesel production route versus the saponification route**

Process route	Environmental Release			Hazardous/toxic by-products			Air emissions			Water	
	Air	Water	Waste	Air	water	Waste	NO2	PM10	GHG	BOD	COD
Biobased: Biodiesel byproduct	X	X	X	XX	X	X	-	-	X*	X	X
Conventional: Saponification	-	X	X	-	X	X	-	-	X*	X	X

* depending on the source of energy provided to obtain heat in distillation/evaporation operations

X   = relatively small emission/risk

XX   = medium emission/risk

XXX   = relatively large emission/risk

4 EVALUATION OF FINDINGS AND RECOMMENDATIONS

4.1 Evaluation of results

- The report provides an overview of basic production routes for biobased chemicals and their environmental aspects (qualitatively). Six main biobased process technologies are being distinguished and each one is studied on its environmental impacts. Although environmental impact also covers 'sustainability' aspects like CO_2- emissions, water consumption, etc. the main focus of this study is on the traditional Environment, Health and Safety items and the potential use of GMO's related to biobased processes;

- It shows that also biobased processes are requiring catalysts and auxiliary chemicals in the various process steps. However, generally speaking, the amount of auxiliary chemicals (especially of organic solvents) is considerable less than in conventional processes, and less energy (leading to less CO_2 emissions) will be required in most biobased processes compared to conventional, petro-chemical process routes. Among the six biobased process technologies, three routes are based on the use of micro-organisms (hydrolysis/fermentation, anaerobic digestion, algae), and generally speaking these processes have less environmental releases in terms of release rates of (toxic) compounds and are more energy friendly, due to the moderate process conditions necessary for living organisms to operate. The three other biobased process routes (transesterification/hydrogenation, gasification and pyrolysis) are chemical processes using bio-feedstock instead of fossil feedstock, but are process wise comparable to the conventional route in terms of releases to the environment;

- Biobased production processes are thus not *a priori* more clean processes than the conventional production processes based on fossil feedstock. The catalysts and auxiliary chemicals can be hazardous themselves and, additionally, do in most cases not originate from a non-fossil feedstock. But, based on this first exploration of biobased process routes and its environmental risks, the new formation of priority substances is not expected, except that in the high temperature processes of pyrolysis and gasification hazardous, priority chemicals (e.g. PAHs) may unintentionally occur. The actual biobased production of chemical building blocks is currently very limited in the Netherlands. Examples of the application of GMO in biobased production processes based on second/third generation feedstock at an industrial scale in the Netherlands could not be identified within the framework of this study;

- Many biobased chemicals are currently building blocks to produce the same chemicals that are otherwise produced from fossil-based sources. If the specific chemical is classified as SVHC the biobased alternative still contains this 'label'. So, the main advantage so far, is not the replacement of a priority chemical by a more environmentally friendly alternative with the same functionality, but only the use of a biobased feedstock (renewable source), which means less CO_2-emissions and no other fossil oil related disadvantages in terms of pollution and sustainability.

- Related to REACH there is no difference in approach for the production and application of a chemical that is produced by a biobased process compared to the conventional route, in case it concerns the same chemical compound.

The REACH Environmental Release Category nr. 1 (ERC-1), covers biobased production processes as well as fossil-based production processes calculating the releases of the substance produced to air, water and waste. However, the biobased production route may lead to different emissions (of the produced chemical or of auxiliary chemicals) to the environment compared to the conventional production route. The REACH ERC provides a generic approach, not differentiating between various types of production processes.

For two selected biobased chemicals and process routes, the environmental impacts have been compared in a semi-quantitative way with the conventional process routes:

Ethylene
- Bio-ethylene is an example of one-to-one substitution of fossil-based ethylene. Comparison of the environmental risks show that the environmental emissions of the fossil-based route are relatively large compared to the biobased route.

Glycerol
- Glycerol is produced as a by-product from the production of soap as well as from biodiesel. The conventional production is also from a renewable source.
- Due to the increased availability of glycerol more applications of glycerol as raw material are currently being developed, for example, potentially leading to functional replacement of prioritised petrochemical plasticisers. It may also serve as a one-to-one replacement of propylene for the production of the building block epichlorohydrin (which is a priority substance itself);
- For glycerol the comparison in environmental risks shows that the biodiesel route, due to the use of methanol, leads to a higher emission to air than the production by saponification. Otherwise, the processes are more or less similar and so are the environmental emissions and potential risks. For both biobased and fossil feedstock based processes on an industrial scale, the environmental regulations are applicable: for emissions to the air the Dutch Emission Guidelines (NER) are applicable, for water the Water Law, and more in general the General Provisions Act Environment law is applicable. These regulations limit the resulting releases to the environment to a considerable extent.
One important part of the current environmental legislation is the application of integrated Best Available Techniques, as these are defined in the so called best Available Techniques reference documents (Brefs) for a large number of industrial sectors in the Industrial Emissions Directive (IPPC/IED).So far, there is no specific Bref existing for large scale biobased production of biobased chemicals.
As soon as more biobased chemical production facilities are coming into operation at an industrial scale, it is advisable to draft a specific Bref for such biobased production processes, in order to define and realize the Best Available Techniques in this new developing sector.

4.2 Recommendations

In general, one of the associations with biobased processes is that these are inherently "environmentally friendly". This report shows the results of a first exploration on the environmental risks of biobased processes, showing that also biobased production processes often require catalysts and/or auxiliary chemicals. Therefore, biobased production does not mean by definition a "green production process".

In some cases, it cannot be excluded that although the biobased raw material is an advantage in terms of sustainability over the use of fossil feedstock, the production process itself appears to be less efficient, and/or less environmentally friendly in terms of emissions to air, water and production of waste. In general, biobased production processes take place at more moderate temperatures than fossil based processes, so energy wise usually the biobased process is expected to be more energy efficient. But more detailed analysis is needed, as the fossil based production routes often make part of highly optimised (petro-)chemical production complexes, which might sometimes make that the fossil production route is more energy efficient than the biobased route. However, in this stage, not many biobased productions take place at an industrial scale yet, and over time, when more biobased processes come into operation, also the biobased production can be expected to evolve into more (energy) efficient processes.

In developing policy on biobased processes, it is recommended to take into account the environmental aspects of biobased processes as well, as in some cases the biobased production process might have considerable environmental consequences as well. More in depth studies to determine quantitatively the environmental aspects of biobased production processes and compare these with the conventional routes are advised to support the policy development in this field.

In evaluations of the sustainability of production process and feedstock use, it is advised to include detailed and quantitative comparisons of environmental aspects in order to determine which process and feedstock are overall most sustainable. The results of this study are useful when weighing biobased substitutes for fossil-based SVHC chemicals in a broader way (both on sustainability and EHS). For example, when performing an Life Cycle Analysis or another decision support systems, we have more focus now on the parameters that should be included in such analyses. When knowing the process technology behind the biobased chemical, one knows if certain environmental aspects should be covered or not in the weighing process (e.g. the use of catalysts and their origin).

Elements of this study can be used for the further development of the REACH/SEA guidance. This guidance is used to underpin the (non)authorisations of SVHC chemicals (Annex XV dossiers). When weighing potential less harmful functional alternatives for these SVHC, the sustainability and EHS aspects of these substitutes should be considered as well. The results of this exploratory study provide a focus on the kind of aspects that should be addressed in case of a 'biobased' substitute. Future revisions of the REACH/SEA guidance could implement these points of attention.

As in future more industrial scale biobased production processes are expected to be present, the introduction of Best Available Techniques (IPPC/IED) in biobased processing might be a useful instrument to guarantee that the design and operation of biobased industries is according best available techniques, including both managerial and technical aspects.

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6 LIST OF ABBREVIATIONS

BOD = Biological Oxygen Demand
COD = Chemical Oxygen Demand
DSP = Down Stream Processing
EHS = Environment, Health and Safety
ERC = Environmental Release Category (in REACH)
GHG = Green House Gases
PM10 = Particulate Matter with median diameter of 10 μm, fine dust
REACH = Regulation on Registration, Evaluation and Authorisation and restriction of Chemicals (Regulation (EC) no 1907/2006).
SEA = Social Economic Analysis
SVHC = Substance of Very High Concern (REACH)

7   **RIVM GUIDANCE COMMITTEE**

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Annex A
List of biobased products and priority substances (ref.
Van Helmond – annex 2)

Bijlage 2   Overzicht biobased stoffen en prioritaire stoffen

Tabel a en b bevatten de biobased stoffen waarmee respectievelijk directe en functionele substitutie plaats kan vinden. In tabel b wordt tevens de te vervangen petrochemische stof vermeld. Bij enkele stoffen is de informatie niet volledig, omdat de referentie daarover onvolledig was. Dit heeft geen invloed op de conclusies van het onderzoek.

Tabel a   **Biobased stoffen voor directe substitutie**
Onderstaande biobased stoffen kunnen identieke stoffen van petrochemische oorsprong vervangen (één-op-één vervanging). Prioritaire stoffen zijn **vet gedrukt**, <u>onderstreept</u> *en in* <mark>kleur</mark> *weergegeven.*

Biobased stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Referentie*
aceton	o.a. syngas, koolhydraten	Aceton-Butanol-Ethanol (ABE)-fermentatie	C3	building block, oplosmiddel	onderzoek	1
acroleine	glycerol	transformatie	C3	tussenstap in productie acrylzuur	onderzoek	1
<mark>**<u>acrylamide</u>**</mark>	koolhydraten	transformatie 3-HPA	C3	building block, o.a. harsen	onderzoek	1
<mark>**<u>acrylonitril</u>**</mark>	koolhydraten	transformatie 3-HPA	C3	building block, o.a. textiel, rubber, buizen	onderzoek	1
acrylzuur	koolhydraten (uit mais, suikerriet), glycerol	fermentatie, transformatie, dehydratie 3-HPA	C3	building block (poly)acrylaten, lijmen, coatings, absorbers	onderzoek	1
adipinezuur	glucose, productie door gg-micro-organismen	fermentatie	C6	nylon, conserveermiddel	onderzoek	1,7
6-aminocapronzuur (6-ACA)	productie micro-organismen	fermentatie	C6	nylon	onderzoek	1
appelzuur	glucose, productie door gg-micro-organismen	fermentatie	C4	building block, o.a. voedingsmiddelen, cosmetica	onderzoek	7
arabinose	hemicellulose	o.a. thermomechanise behandeling en hydrolyse	C5	building block	onderzoek	1,4

Biobased stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Referentie*
arabitol	hemicellulose, arabinose	dehydrogenering arabinose	C5	zoetstof	onderzoek	1
ascorbinezuur	sorbitol	biotechnologisch-chemisch proces	C6	o.a. voeding	productie	1
asparaginezuur	glucose	fermentatie	C4	o.a. productie aspartaam (zoetstof)	onderzoek	1,4
azelaïnezuur	oliezuur	ozonolyse	C9	nylon	productie	1
azijnzuur	o.a. ethanol, sucrose	fermentatie	C2	building block, o.a. oplosmiddel, smaakstof, conserveermiddel	productie	1,4
1,4-butaandiamine	barnsteenzuur		C4	building block o.a. nylon	productie	1
1,4-butaandiol (BDO)	barnsteenzuur	reductie	C4	building block o.a. PBT, PBS, THF	onderzoek	1,4
1,3-butadieen	glucose		C4	building block, o.a. rubber	onderzoek	6
butanol (incl. n- en iso-)	koolhydraten, syngas	fermentatie, vergassing, coproduct van aceton en ethanol	C4	productie propyleen, polymeren, plastics, oplosmiddel, verdunner, brandstof	productie	1,4
buteen	butanol	dehydratie butanol	C4	tussenstap in productie propyleen	productie	1
n-butylacrylaat	acrylzuur	verestering	C7	o.a. coatings, lijmen, textiel	onderzoek	1
cadaverine	lysine	decarboxylering	C5	building block, nylon	productie	1
caprolactam	lysine	fermentatie	C5	nylon	productie	1
3-carboxymuconzuur (3CM)	vanilline, productie door gg-micro-organismen	fermentatie	C7	buiding block	onderzoek	7
citroenzuur	glucose, sucrose, zetmeel	fermentatie	C6	o.a. conserveermiddel, levensmiddelen, schoonmaakmiddel	productie	1,4
dichloorethaan	ethaan	chlorering ethaan	C2	o.a. oplosmiddel	onderzoek	1
2,5-dimethylfuran	koolhydraten	pyrolyse	C6	building block, brandstof	onderzoek	1

Biobased stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Referentie*
dimethyl 1,19-nonadecaandionaat	onverzadigde C18-zuren	methoxycarbonylering	C19	plastics	onderzoek	1
ethanol	o.a. syngas, koolhydraten	fermentatie kool-hydraten	C2	building block ethyleen en propyleen, in drank, desinfectant, oplosmiddel, brandstof	productie	1,4
ethyleen	ethanol	dehydratering ethanol, cracking bionafta	C2	building block plastics, polyethyleen (HDPE, LDPE, LLDPE, PVC, PET), monoethyleenglycol, ethyleendichloride	productie	1,4
ethyleendiamine	1,2-dichloorethaan	reactie met ammonia	C2	building block	productie	1
ethyleendichloride	ethyleen	o.a. dehydratering	C2	productie PVC	onderzoek	1,4
ethyleenglycol	ethyleen	o.a. dehydratering	C2	antivriesmiddel	productie	1,4
ethyleenoxide	ethyleen	oxidatie	C2	building block	onderzoek	1,4
2-ethylhexylacrylaat	acrylzuur	verestering	C11	building block, o.a. coatings, lijmen, textiel	onderzoek	1
farneseen (trans-B-)	isopreen	synthetische biologie	C15	dieselbrandstof, specialties	onderzoek	1
formaldehyde	methanol	dehydrogenering	C1	building block	onderzoek	1
furfurylalcohol	furfural	dehydrogenering	C5	oplosmiddel, harsen, coatings, farmaceutica	productie	1,2,4
glutaminezuur	lysine	fermentatie	C5	building block	productie	1
glycerol	vetten en oliën	o.a. splitting, coproduct van vetzuren, alcohol en FAME-biodiesel	C3	building block, productie o.a. propyleenglycol, epichloorhydrine	productie	1,4
glycolzuur	o.a. glucose		C2	o.a. cosmetica, conserveringsmiddel	productie	1
(R)-3-hydroxybutyric zuur	polyhydroxybutyraat (PHB)	hydrolyse / biosynthese	C4	building block	onderzoek	1
5-hydroxymethylfurfural (HMF)	glucose, fructose, zetmeel, cellulose	dehydratering, pyrolyse	C6	building block, polymeren, farmaceutica, brandstof	onderzoek	1,2

Biobased stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Referentie*
3-hydroxypropionaldehyde	glycerol	fermentatie	C3	productie acrylzuur	onderzoek	1
3-hydroxypropionzuur (3-HPA)	koolhydraten, zetmeel	fermentatie	C3	building block o.a. acrylzuur	onderzoek	1,4
isobuteen			C4	building block, o.a. butylrubber	onderzoek	1
isopreen	koolhydraten, productie door gg-micro-organismen	fermentatie	C5	rubber	onderzoek	1,7
isopropanol	glycerol	fermentatie	C3	productie propyleen	onderzoek	1
koolmonoxide	syngas	anaerobe omzetting / fermentatie	C1	building block o.a. Fischer-Tropsch chemie	productie	1
levulinezuur	glucose, zetmeel, lignocellulose, hemicellulose	transformatie	C5	building block	onderzoek	1
limoneen	citrusvruchten		C10	productie tereftaalzuur (PTA)	onderzoek	1
lysine		productie m.b.v. ggo's	C6		onderzoek productie	1
melkzuur	zetmeel, glucose, productie door gg-micro-organismen	fermentatie	C3	o.a. voedsel, drank, cos-metica, farmaceutica, op-losmiddel, productiepoly-meren en lactaatester	onderzoek productie	1,2,7
methaan	biodegradeerbare materialen (o.a. mest, plantenresten	anaerobe omzetting / fermentatie	C1	productie diverse chemicaliën, brandstoffen	productie	1
methanol	syngas, glycerol	o.a. black liquor gasification	C1	building block propylene, schoonmaakmiddel	productie	1
mierenzuur	lignocellulose, hemicellulose	coproduct van levulinezuur	C1	building block	onderzoek	1
muconzuur	glucose	fermentatie en dehydrogenering	C6	productie adipinezuur	onderzoek	1
1,18-octadec-9-enedioiczuur	oliezuur	zelf-metathese	C18	plastics	onderzoek	1
oliezuur	plantaardige olie		C18	building block, o.a. nylon, smeermiddelen	productie	1

Biobased stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Referentie*
polyacrylaat	acrylzuur	polymerisatie	Cn	polyacrylaten	onderzoek	1
polyethyleen (HDPE, LDPE, LLDPE)	ethylene	polymerisatie	Cn	plastics	productie	1
polyethyleentereftalaat (PET)	ethyleen	polymerisatie	Cn	plastic flessen, textielvezels	productie	1
polyhydroxyalkanaat (PHA)	glucose, zetmeel, productie door (gg-) micro-organismen, gg-planten of gg-gisten	fermentatie	Cn	plastics	productie	1,2,7
polyhydroxybutyraat (PHB)	glucose, zetmeel, productie door gg-micro-organismen	fermentatie	Cn	plastics	onderzoek productie	1,2,7
polymelkzuur (PLA)	melkzuur, glucose, productie door gg-micro-organismen	ringopening polymersiatie	Cn	o.a. voedselverpakking, afvalzakken, textielvezels	productie	1,2,7
polypropyleen	ethyleen		Cn	o.a. plastic flessen, tapijt, auto-onderdelen	onderzoek	1,2
poly(trimethyleen)tereftalaat (PTT)	1,3-propaandiol	copolymerisatie met tereftaalzuur	Cn	o.a. textiel, tapijt	productie	1
polyvinylchloride (PVC)	ethyleen	chlorering	Cn	plastics	productie	1
propaan	palm-, raap-, sojaolie	bijproduct van biodieselproductie	C3	propyleen	onderzoek	1
1,3-propaandiol (PDO)	glucose, glycerol	o.a. transformatie 3-HPA, productie door organismen	C3	textiel, coatings, plastics	productie	1,4
n-propanol	glycerol	fermentatie	C3	productie propyleen	onderzoek	1
propionzuur	melkzuur	reductie	C3	building block	onderzoek	1
propyleen	glycerol, ethanol, butanol, propaan, methanol, plantaardige olie	transformatie	C3	productie polypropyleen, propyleenoxide, acryloni-tril, acrylzuur, butanol	onderzoek productie	1
propyleenglycol	glycerol	fermentatie, transfor-matie, hydrogenolyse	C3	o.a. antivries, koel-middel, remvloeistof, verf	productie	1,4

Biobased stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Referentie*
putrescine	glucose, productie door gg-micro-organismen	fermentatie	C4	building block, o.a. nylon	onderzoek	7
ricinolzuur	castorolie		C18	building block, o.a. nylon, verf, coatings, inkten	productie	1,2
sebacinezuur	ricinolzuur	fragmentatie	C10	o.a. nylon	productie	1
sorbitan	sorbitol	dehydratering	C6	o.a. cosmetica, farmaceutica	productie	1
sorbitol	glucose	transformatie	C6	o.a. voedsel, cosmetica	productie	1
tereftaalzuur	glucose, lignine, p-xyleen	o.a. oxidatie p-xyleen	C8	building block voor o.a. PET	onderzoek	1,2
tetrahydrofuraan (THF)	barnsteenzuur		C4	building block, oplosmiddel, lijmen	productie	1
10-undecanoicSzuur	ricinolzuur	fragmentatie	Cn	nylon	productie	1
vetzuurderivaten	plantaardige olie		Cn	o.a. zeep, cosmetica, coatings, inkt, linoleum, smeermiddelen	productie	1
vinylchloride	ethyleen, dichloorethaan	dehydrochlorering	C2	building block PVC	onderzoek	1
p-xyleen	glucose	transformatie	C8	building block	onderzoek	1
xylitol	xylose	hydrogenering, black liquor raffinage	C5	zoetstof	onderzoek productie	1
xylose	hemicellulose	o.a. thermo-mechanische behandeling en hydrolyse, black liquor raffinage	C5	building block	onderzoek productie	1

* Referenties: Zie onder tabel b.

Tabel b   Biobased stoffen voor directe en functionele substitutie
Deze biobased stoffen kunnen, naast één-op-één substitutie, ook de aangeduide petrochemische stoffen vervangen.
*Prioritaire stoffen zijn **vet gedrukt** en in* <mark>kleur</mark> *weergegeven.*

Biobased stof	Te vervangen petrochemische stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Refe-rentie*
acetyltriethylcitraat	<mark>bepaalde petrochemische weekmakers</mark>	citroenzuur			weekmakers	productie	2
1,2,4-butaantriol	nitroglycerine	xylose, arabinose	fermentatie	C5	o.a. drijfgas, farmaceutica	onderzoek	4
2,5-furaandicarbonzuur (FDCA)	tereftaalzuur (PTA), hexamethyleendiamine, p-diaminobenzeen	koolhydraten, D-fructose	o.a. pyrolyse / transformatie, reductie	C6	building block o.a. polyesters, nylon	onderzoek	1,2,4
barnsteenzuur	maleinezuuranhydride, ace-tyleen en <mark>propyleenoxide</mark> bij BDO-productie	koolhydraten, productie door (gg-) organismen	fermentatie m.b.v. E. coli, Coryne, gist	C4	building block, zoetstof	productie onderzoek	1,4,7
diphenolic acid	bisfenol-A	levulinezuur	reactie met fenol	C17	productie polycarbonaten	onderzoek	4
<mark>epichloorhydrine</mark>	voorkomt gebruik propyleen bij petrochemische productie	glycerol	transformatie	C3	(epoxy)harsen, polyme-ren, papierversterkers, waterzuivering	productie	1,3,4
ethylacetaat	bepaalde petrochemische oplosmiddelen	ethyleen, ethanol	verestering	C2	o.a. oplosmiddel	onderzoek	1,4
ethylacrylaat	bepaalde petrochemische oplosmiddelen	acrylzuur, ethanol	o.a. verestering	C5	o.a. oplosmiddel, coatings, lijmen, textiel,	onderzoek	1,4
ethyllactaat	bepaalde petrochemische oplosmiddelen	melkzuur, ethyleen, ethanol	o.a. fermenta-tie, verestering	C3	oplosmiddel	productie	1,4
fumaarzuur	maleïnezuur	o.a. glucose, productie door gg-micro-organismen	fermentatie	C4	voedsel, drank	onderzoek	4,7
furfural	bepaalde nematiciden en fungiciden	hemicellulose	pyrolyse	C5	building block, extractie-middel, pesticide	productie	1,4
glucaarzuur	fosfaten in wasmiddelen	glucose, productie door gg-micro-organismen	transformatie	C6	wasmiddelen, corrosiewering	onderzoek	1,7

Biobased stof	Te vervangen petrochemische stof	Bron	Chemische bewerking	Keten-lengte	Toepassing	Status	Refe-rentie*
gluconzuur	aminocarboxylzouten (o.a. EDTA)	glucose	o.a. oxidatie	C6	o.a. schoonmaakmiddel	productie	4
isosorbide	ethyleenglycol (gedeeltelijke vervanging), bisfenol-A	sorbitol	selectieve dehydratering	C6	building block, tussenstap productie polymeren en plastics	productie	1,2,4
isosorbide diesters	bepaalde weekmakers op basis van ftalaten	sorbitol		C6	weekmakers	onderzoek productie	2,4
itaconzuur	polyacrylzuren	glucose, productie door gg-micro-organismen	fermentatie	C5	polymeren (absorbers) in luiers, femcare-produc-ten, cosmetica e.d.	onderzoek productie	1,5,7
methylmetacrylaat (MMA)	voorkomt gebruik aceton, hydrocyaanzuur en isobutyleen	ethyleen, methanol, koolmonoxide	ALPHA-technologie	C4	plastics, harsen, poly-meren, coatings, lijmen	productie	1
methylmethacry-laat-butadieen-styreen (MBS)	voorkomt gebruik aceton, hydrocyaanzuur en isobutyleen	methyl-metacrylaat	copolymeer bij ALPHA-technologie	Cn	PVC-modificering	productie	1
polybutyleensuc-cinaat (PBS)	o.a. polypropyleen	barnsteenzuur en 1,4-butaandiol	copolymerisatie	Cn	o.a. plastics	productie	2
sebacaat-esters	bepaalde petrochemische weekmakers	natuurlijke zuren			weekmakers	productie	2
triacetine	bepaalde petrochemische weekmakers	glycerol		C9	weekmaker	productie	2
triethylcitraat	bepaalde petrochemische weekmakers	citroenzuur			weekmaker	productie	2

* Referenties:

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