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Engineering Biopolymers

Markets, Manufacturing, Properties and Applications

Sample Chapter 6:
End-of-Life Options for Biopolymers

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6 End-of-Life Options for Biopolymers

Biopolymers come with a wide variety of disposal options. In principle, any of the following methods can be used for their disposal:

- Landfill
- Thermo-mechanical recycling
- Chemical recycling
- Industrial and domestic composting
- Dissolving in water/seawater
- Decomposition/degradation in soil
- Anaerobic digestion, i. e. conversion to biogas
- CO₂-neutral incineration (with energy recovery)
- Degradation through various organisms (consumption, biodegradation)
- Littering

These individual options for disposing of biopolymers will be briefly detailed in the following.

6.1 Landfill

Although disposing of biopolymers and/or products made from biopolymers in a landfill is an option, it is generally known that the generation and uncontrolled release of landfill gas (~

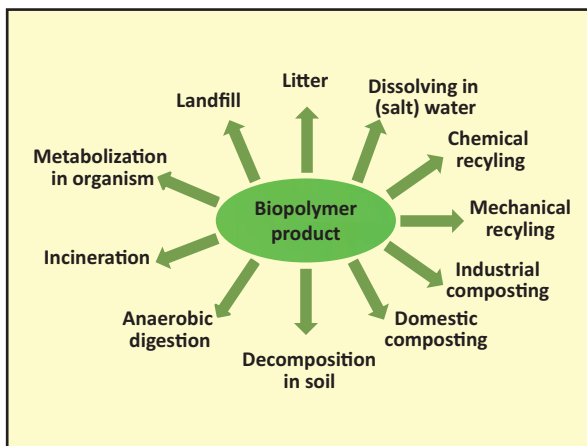


Figure 6.1 End-of-life options for biopolymers

Table 6.1 Comparison of Methane Producers

Methane producers [Mio t/a]	
• Ruminants (mainly bovines)	70 – 100
• Wet-field rice cultivation	70 – 100
• Tundra	40 – 110
• Incineration of biomass	20 – 110
• Swamps, lakes, wetlands	20 – 70
• Landfills	30 – 60
• Insects (mainly termites): (estimated, because termite population unknown)	20 – 80
• Natural-gas losses:	20 – 50
• Coal mining:	12 – 40

55% methane, ~ 45% CO₂ and possibly other elements) increases with increasing biological activity and/or organic content in landfilled waste (cf. Table 6.1).

If suitable technological measures are taken, landfill gas can, for the most part, be collected as it develops. The methane can be collected and converted to energy by incinerating it. However, methane content in landfill gas usually decreases over time, so that incineration is economical only early on. Also, as the methane content decreases, technically incineration becomes more and more difficult. Inert substances, such as the classical plastics are therefore preferred in landfills, because they do not contribute to any uncontrolled production or release of the greenhouse gases.

Landfill of biopolymers is therefore considered the least desirable disposal option: it does not generate any benefit, yet causes an additional release of greenhouse gases.

6.2 Recycling

6.2.1 Thermo-Mechanical Recycling

Within the scope of classic thermo-mechanical recycling (also known as mechanical recycling, material recycling, or material recovery), pre-consumer, i. e., post-industrial mono-material processing scrap and post-consumer material in mixed waste streams have to be distinguished. Other than for PET, PVC or foamed PS, there is currently no record regarding recycling the various thermoplastic biopolymers of either waste stream. In principle, however, it is safe to assume that recycling of biopolymers encounters the same challenges as recycling of conventional synthetic thermoplastics. This includes a downcycling effect and the preference for mono-material,

un-mingled waste streams. The downcycling effect is a function of molecular degradation; thus it is more strongly pronounced in biopolymers because their thermo-mechanical and chemical resistance are generally lower. For instance, biopolymers, which often are polyesters (cf. Section 4.2.4), can depolymerize under repeated thermal load, in particular in the presence of moisture, due to their sensitivity to hydrolysis, much like conventional polyesters.

Moreover, biopolymers may also cause “contamination” in established recycling processes, exemplified by the recent problems with PLA bottles in PET recycling streams. Even when this waste stream contains only a few PLA bottles, they cause a significant loss of quality in the PET recycle and therefore have to be removed. Determining the effects of the mechanical recycling process on the resulting properties of certain biopolymers (or on given mixtures of biopolymers) under real life conditions (e. g., post consumer material) requires more research and will be answered by practical experience. Also, the question whether the biobased equivalents of conventional polymers, such as Bio-PE, Bio-PA, Bio-PUR can be included in the existing and established mechanical recycling schemes for conventional polymers has to be investigated. At this time, there is still very little information on how larger amounts of biopolymers will affect waste streams.

However, post-consumer biopolymers as well as other waste materials have to pass extensive manual and/or automated mechanical sorting processes in specialized facilities, designed to separate the different material streams. As shown in Fig. 6.3, biopolymers in the waste stream can be identified by their characteristic NIR spectrum. NIR systems can be programmed to identify biopolymers, thus ensuring unmixed recycle streams. Mono-material mechanical recycling of post-consumer bioplastics has the potential to become a viable sustainable disposal option, especially when sufficient volumes of homogenous waste material streams are available. First experiments showed that existing sorting systems can be adapted to effectively identify and separate PLA, in particular in PET-waste streams [110].



Figure 6.2 PET recycling quotas in Europe [111]

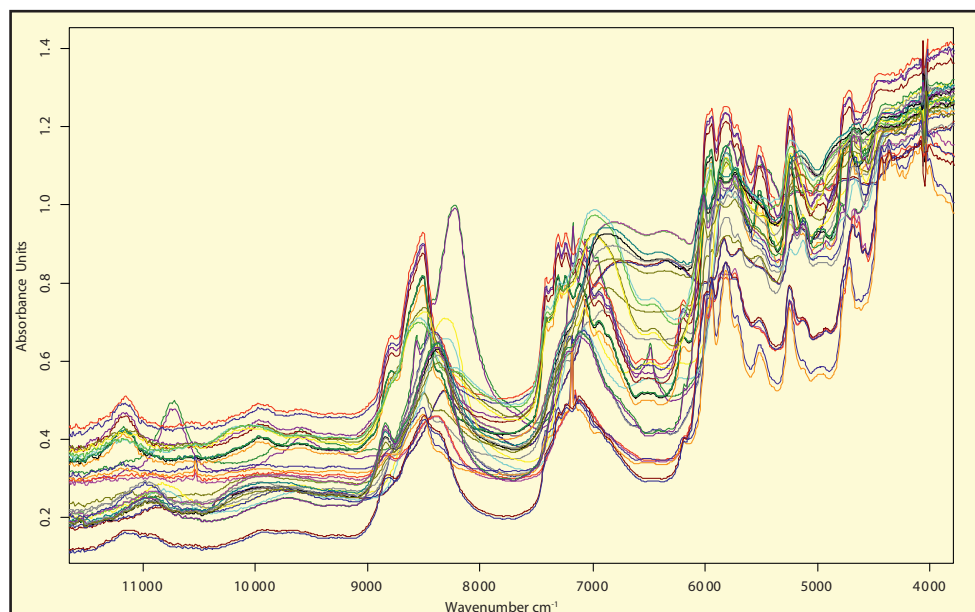


Figure 6.3 Different NIR spectra for characterizing biopolymers

6.2.2 Chemical Recycling

Because most biopolymers are less chemically resistant than conventional plastics (e.g., more hydrolysis-prone), less energy is required for chemical or thermo-chemical methods to convert biopolymers back to their corresponding oligomers and their monomer basic compounds (also known as feedstock recovery). With biopolymers produced via polycondensation, the reverse reaction can be exploited to recover the valuable monomers. The investigation of chemical recycling behavior in biopolymers is the subject of current research. Currently feedstock recovery is investigated for PLA, which can be hydrolyzed into its monomer lactic acid at a rate of almost 99% [110]. In general, it is possible to incorporate the hydrolysis process into existing lactic acid or PLA plants. Although first plants have been built to hydrolyze PLA, sufficient volumes of post-industrial and post-consumer PLA waste streams are a necessary precondition for economically viable recovery plants for PLA as well as for other biopolymer feedstock.

6.3 Composting

Biodegradable biopolymer waste can be treated by aerobic degradation, i.e., composting, or anaerobic digestion (see Fig. 6.4). When biopolymers are composted or digested, their individual elements are recycled naturally, in particular their carbon and hydrogen content.

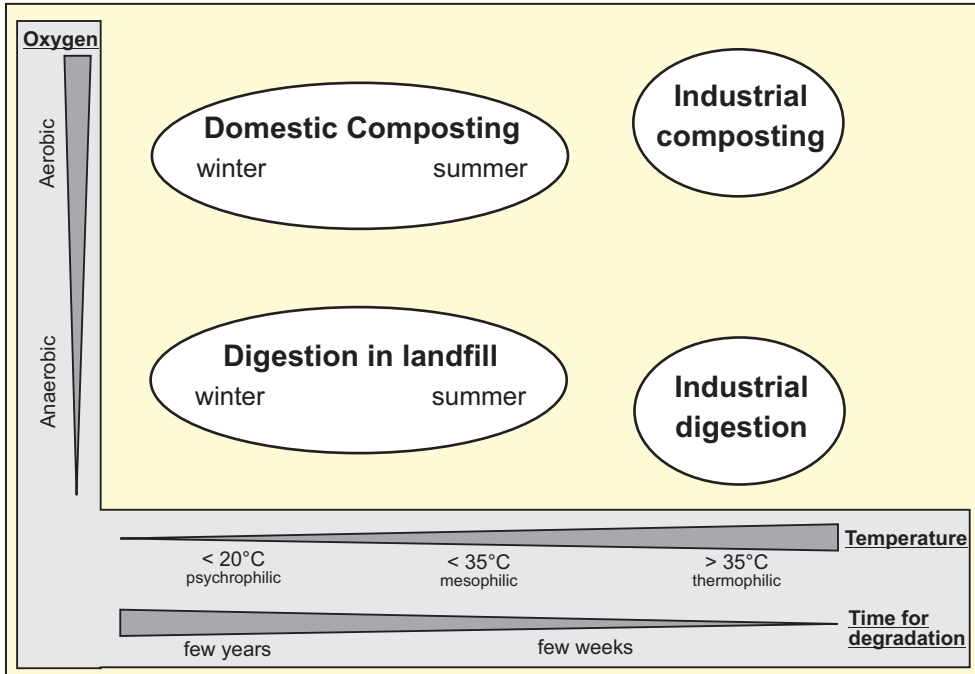


Figure 6.4 Biodegradable polymers offer two types of biological waste treatment (anaerobic and aerobic technologies)

Composting, i. e., final degradation of biopolymers, generates carbon dioxide and water as the main degradation by-products other than compost. However, over time, these compounds represent the raw materials essential for photosynthesis of biomass and/or renewable resources for renewed generation of biopolymers – in other words, this is a closed-loop cycle.

Considering that every year nature “quietly and unobtrusively” creates and degrades some 100 billion tons of cellulose and the same amount of hemicellulose and lignin, composting seems to be a potential option for disposing of the global amount of only approx. 1 billion tons of man-made waste. The framework of statutory requirements and normative rules for composting are presented in great detail in Section 3.2.

6.3.1 Industrial Composting

Industrial composting can be defined as “the controlled biological decomposition of organic waste under managed conditions that are predominantly aerobic and that allow the development of thermophilic conditions as a result of biologically produced exothermic heat [112]. In the course of industrial composting operations, biomass is mixed more frequently and moisture and oxygen content and temperatures are higher (50–70 °C) than during domestic composting. When the temperature of the composting pile increases, the microbes adapted to ambient temperature (mesophiles) stop activity and are replaced by microbes adapted to high temperatures (thermophiles) (cf. Fig. 6.4). The rate of activity of microbes is higher at

thermophilic temperatures. Due to this shift in microbial populations and the additional treatment of the composting pile, a faster and better degradation of the biopolymers can be ensured. Under these conditions composting is a controlled biotechnological process and therefore the term “industrial” (or municipal) composting is used to distinguish it from “home composting” [113]. Experience has shown that biopolymers certified as compostable under industrial composting conditions are degraded and metabolized well. However, not all biopolymers certified as compostable under industrial composting conditions also degrade under home composting conditions.

However, in our opinion composting makes sense only when degradability simultaneously offers an additional functional advantage. For example, votive candle holders on graves that can be cleared away with flowers/wreaths etc., films for agriculture that don't have to be collected and disposed of following use, but can be plowed under, laundry bags that dissolve in the washing machine, grocery bags that can be used to collect organic material for composting, or resorbable implants that are metabolized according to the regenerative loop in the human body, etc. In all these applications, compostability results in additional benefit. By contrast, enforced “composting by decree” requiring separation, collection, and transport to an industrial composting plant represents only additional expense and with it an entropy production lacking additional benefits. The amount of CO₂ generated by composting equals the amount of CO₂ released by incineration, but composting does not provide the additional energetic benefit.

6.3.2 Domestic Composting

Municipal composting and home composting share the same designation; however, the conditions for these technologies are quite different [113]. Certified industrial compostability states that products consisting of a certain material and with specified wall thicknesses degrade biologically during a certain time under industrial composting conditions (sufficient oxygen and moisture, regular turning of the pile, temperature development, presence of corresponding microorganisms, pH, carbon/nitrogen ratio, material structure and size of particles). Industrial compostability of biopolymer materials certified according to legal standards must never be equated with total degradability in domestic compost, also defined as cold composting, i. e., degradation through aerobic biodegradation at ambient temperature (between 21 °C and 28 °C). In particular degradation of PLA (with its high glass transition temperature) or biodegradation of PBS is difficult. Certification according to the standards for municipal composting (e. g., EN 13432 or EN 14995) does not imply good in-home composting properties.

Neither ISO nor ASTM define home composting rules. The Belgian certification organization AIB Vinçotte issues a specific “home compostability” certification program and an “OK Compost Home” label. Materials degrading to a sufficient level in private composting systems, i. e., home compost, can be labeled additionally or exclusively with this symbol. The certification program for home composting is based only on DIN EN 13432 (see Section 3.1.2). In home composting, 90 % biological degradability at ambient temperatures of 20–30 °C (in contrast, composting temperatures in industrial plants run approx. 50–70 °C) and/or in aquatic surroundings is required (test method according to DIN EN ISO 14851; cf. Section 3.2.3.2).

Particularly in Asia, where there is a lack of room and logistics for disposing and industrial composting of biowaste, efforts are being made to support composting in domestic surroundings with heated waste containers to enable domestic composting [114].

6.4 Incineration

In general, incineration (or burning) refers to the reaction of a substance to elevated temperatures in the presence of oxygen. It is a catalytic, exothermic reaction whose progress is maintained by the free radicals and heat radiation that it emits [115]. Pyrolysis, on the other hand, is an irreversible chemical breakdown resulting from increased temperature without the presence of oxygen and without any oxidation process [115, 116]. The incineration of municipal solid waste (also called thermal recovery or energy recovery) is a technology to treat waste while exploiting the energy content of the material and reducing the amount and volume of solid material to be landfilled. It is a widespread technology in Europe.

Especially for biopolymers incineration is a disposal solution favored by the authors, not only because of its high recycling quality, but also because the energy recovery generates maximum benefit at a justifiable amount of effort and expense. With a high content of biobased materials in the biopolymer, incineration provides additional CO₂-neutral energy. Additional energy recovery is suitable for all types of bioplastics and their composites, regardless of their raw material basis, biodegradability or compostability. On the other hand, currently there are few facts available about incineration of biopolymers and there are no material specific standards in place. With this in mind, we present the first results

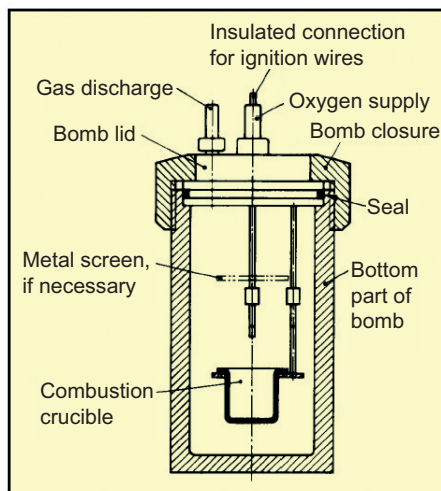


Figure 6.5 Schematic illustration of a calorimetric bomb for determining heat value analogous to DIN 51900-1 [118]

of our own investigations to characterize the incineration behavior of biopolymers in the following.

6.4.1 Calorific Value of Biopolymers

Typically, calorific value is determined with the aid of a bomb calorimeter according to DIN 51900-1 [8]. The essential elements of the test setup can be seen in Fig. 6.5. The calorimetric bomb consists of a corrosion-resistant material with self-sealing closure. An oxygen line leads into the calorimeter, another line draws off the gases present in the bomb following incineration, and there is an insulated connection for the ignition wire. There are also a bracket for the crucible and a lead out for the ignition current. A metal screen can be attached above the incineration pot in order to reflect radiant heat [115, 117].

The polymer specimen to be tested is weighed in a gelatin capsule (the capsule functions as a combustion aid) and placed in close contact with an ignition wire. Inside the calorimetric bomb, the specimens are incinerated in the combustion crucible in pure oxygen at 30 bar pressure. Combustion is introduced by an ignition wire. The temperature in the calorimeter rises above its initial temperature due to the heat created by combustion. The measured temperature increase determines the specific calorimetric value (gross calorific value or higher heating value) H_0 . The calorimetric value of the samples is calculated using the following equation [118, 119]:

$$H_0 = \frac{C \cdot \Delta T - Q_{GZ}}{m_p}$$

where: m_p = initial weight of material specimen [g]

Q_{GZ} = heat quantity generated by the gelatin capsule and the ignition wire [J]

ΔT = temperature increase in the calorimeter [K]

C = calorimeter heat capacity from calibration measurements [J/K]

Here, the heat generated by incineration of the ignition wire and gelatin capsule has to be subtracted from the heat developed by incinerating the biopolymer [118, 119].

The calorific values presented here are the first such values determined for biopolymers. For the sake of verification, they were compared with the theoretically expected calorific values. To this end, the theoretically calorific values were determined from the known stoichiometric compositions of the biopolymers and the individual formation enthalpies of the resulting reaction products CO_2 and water.

The portions of water contained in the biopolymers as well as possible additives were neglected in the determination of the stoichiometric composition. Because the precise quantitative composition of materials is not always known, the various material components sometimes had to be estimated. Given these circumstances, following are the results for theoretical calorific values to be used as guidelines for comparison with the calorific values actually measured:

Table 6.2 Calorific Values of Various Biopolymers Calculated Theoretically and Actually Measured

Biopolymer	Theoretically calculated calorific value [MJ/kg]	Measured calorific value [MJ/kg]
Bio-PE	43	45.1
PCL blend	27	23.3
Bio-polyester	24	25.6
PVAL	23	24.2
PLA blend	20	21.2
Starch blend	18	21.1
PLA	18	19.2
Cellulose ester	18	18.3
PHAs	23	23.9

This comparison of theoretically calculated and actually determined heat values shows good agreement. The slight deviations are mainly due to lack of exact determination of composition as well as the neglected water content in the biopolymers.

The essential conclusion that can be drawn from these measurements performed is that much as with degradability, the heat or calorific value of biopolymers depends exclusively on their stoichiometric composition and not on the source of the raw materials. When carbon exothermically reacts to CO₂, the energy released is independent of whether a biobased or a petrochemical carbon is involved. Therefore, the heat value of biobased polyethylene is equal to that of conventional petrochemical polyethylene, because both materials have the same elementary composition.

Thanks to the presence of heteroatoms, in particular oxygen instead of carbon, the heat value of biopolymers lies more in the calorific value range of PA, PET, or ABS and thereby below the calorific value of plastics consisting of only carbon and hydrogen, e. g., PE or PP. Due to the high density of biopolymers, however, it can be assumed that the calorific value of a kilogram of biopolymer material corresponds to that of one liter of crude oil. Moreover, its incorporated oxygen promotes the oxidation process and prevents local temperature peaks during combustion.

In summary, this especially means that, when biopolymers are incinerated, less CO₂ is generated and more crude oil can be saved as an energy source for other uses. The authors of this study would go so far as to say that the currently mainly energetic “wasting” of crude oil by direct combustion (cf. Fig. 1.16) should be shifted in favor of a much more valuable, multiple use of substances in polymers to be incinerated downstream together with a maximum content of biobased materials in the polymers.

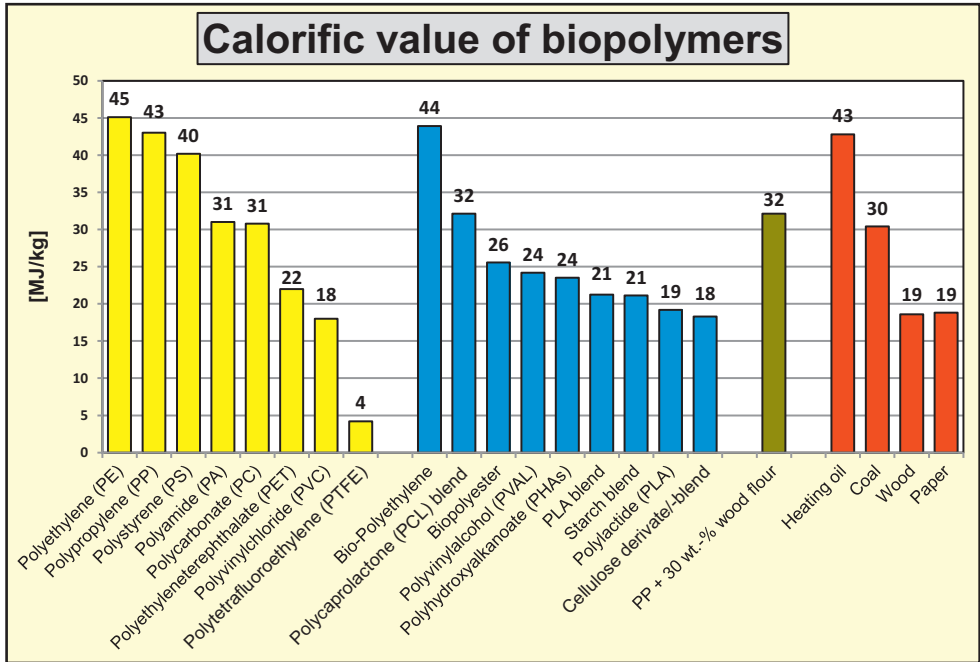


Figure 6.6 Calorific values of biopolymers compared with conventional plastics and petrochemical energy sources

6.4.2 Emissions Created by the Incineration of Biopolymers

The “biobased composition” of biopolymers is the reason why most studies assume a theoretically low pollutant potential from possibly arising combustion gases. More critical attention is given to the usually unknown additives often contained in the biopolymers that will play an even more significant role among third generation biopolymers. Nor has there been any such practical experience with biopolymers as yet, but compostable bioplastics certified, e. g., according to EN 13432, potentially should have advantages due to controlled low levels of heavy metals and other ecologically harmful components. Therefore, a first orienting investigation into the combustion behavior of various currently commercially available biopolymers was performed in the course of writing this book.

Investigation method (Fig. 6.7):

A so-called VCI apparatus (VCI = Verband der chemischen Industrie = Chemical Industry Association) was used for simulating the combustion of the polymer specimens to be investigated. The setup is shown in Fig. 6.7.

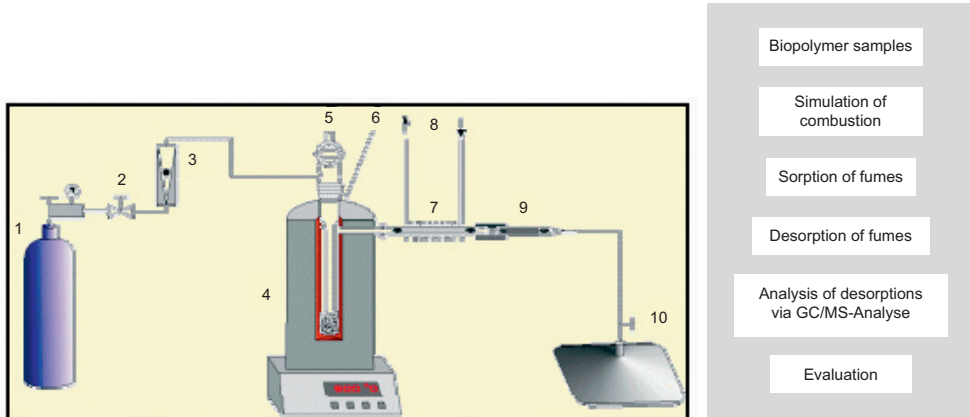


Figure 6.7 Illustration of the measurement apparatus for investigating emission behavior during the incineration of biopolymers (left) with: 1 synthetic air, 2 control valve, 3 fluid flow meter, 4 VCI apparatus with control unit, 5 sample port, 6 fire tube with quartz wool plug and deflection unit, 7 XAD-2 adsorber tubes, 8 water cooling, 9 tube with activated carbon, 10 gas bag with valve and septum and investigation scheme (right) [117]

Combustion of biopolymer specimens

The material sample was burned under controlled conditions regarding specimen mass, ventilation, and temperature by self-combustion in the pre-heated oven of the apparatus.

In order to simulate two different burning conditions, each sample was burned under continuously maintained ventilation and sampling periods at two different temperatures. The following individual parameters were set during the burn simulation:

- Temperatures during specimen combustion: 400 and 800°C, respectively
- Ventilation: 280ml synthetic air/min
- Specimen initial weight: approx. 5mg
- Sampling period: 4 min

Fume sorption

The fumes were sampled by means of a universal adsorbent composition consisting of purified XAD-2 resin (a polystyrene-divinylbenzene copolymer) and downstream serial activated carbon in the area of the VCI apparatus's gas exhaust (see also Fig. 6.7). The XAD-2 adsorption tube was cooled by water to enhance adsorption efficiency.

Fume desorption and regeneration

The loaded adsorbents were desorbed by solvent desorption. For this, the materials (XAD-2 resin and activated carbon) were transferred to sample vials flooded with the corresponding desorption solution. Then the closed vials were allowed to rest 24 hours for desorption equilibrium to set in. The solvent used for XAD-2 was dichloromethane, an efficient solvent

for polycyclic aromatic hydrocarbons (PAK), whereas the universal solvent carbon disulfide was used for the activated carbon.

Fume analysis

Subsequently, the desorbate was subjected to a qualitative gas chromatographic and mass spectrometric investigation (GC/MS analysis). Highly volatile, mainly inorganic combustion products such as CO₂, CO and H₂O were not included in the chosen method of analysis. Blank readings of the apparatus as well as the solvent and adsorbents used were detected analogously.

Results

The composition of the combustion emissions was mainly influenced by the chemical composition of the bio-polymers and the combustion temperature. At the lower combustion temperature (400 °C), the gases exhibit structural compositions similar to those of the incinerated polymers. They consist of the relevant monomers, oligomers, and chain fragments which are partially oxidized to form aldehydes and ketones. Therefore, combustion of biopolymers creates corresponding carbonic acid esters, caprolactone in the case of polycaprolactone and dilactide and lactide oligomers in the case of polylactides.

With increasing temperature of combustion and the increased atomization of the fuel fragments, the structural relationship between polymers and their associated combustion products is reduced [120, 121].

Certain substances in the combustion gases classified as (eco) toxicologically critical. Most common among them were the aromatics benzene, toluene, and naphthalene. The formation of these substances is observed principally at the combustion temperature of 800 °C, but to a reduced extent also at 400 °C. It is important to note that the formation of these critical substances is not limited to the purely hydrocarbon-based plastics, such as PP, but that the substances were detected in the combustion gases of almost all tested polymers, i. e., also in those containing oxygen. At higher combustion temperatures the composition of a polymer's combustion gases is determined above all by the elementary structure of the polymer. In order to guarantee complete waste combustion, the European Directive 2007/76/EC requires all plants to keep the incineration or co-incineration gases at a temperature of at least 850 °C for at least two seconds.

The following detailed results were obtained:

- Lower combustion temperature (400 °C):
 - Fumes often exhibit structural similarities with the combusted biopolymers.
 - Emissions in the form of chain fragments, oligomers and monomers (partly oxidized to aldehydes and ketones), e. g.:
 - Polyesters (PBAT) → aromatics
 - (PBS) → carbonic acid ester
 - Polycaprolactone (PCL) → caprolactone
 - Polypropylene (PP) → branched hydrocarbons
 - more diversified product spectrum than at 800 °C → larger number of different groups of substances (e. g., carbonic acid esters, aldehydes, ketones, aromatics)

- Higher combustion temperature (800°C):
 - increasing harmonization of chemically different combinations of fume emissions
 - growing atomization of fuel fragments → disappearing structural relationship between combusted polymer and combustion emission
 - elemental combination mainly determines which combustion products are formed; polymer structure plays a secondary role
 - product spectrum: almost exclusively aromatic compounds
 - conclusion: formation of aromatics is based above all on reactions of smaller chain fragments with each other → recombination to cyclization products
 - smaller number of combustion products than at 400°C
- (Eco) toxicologically known substances:
 - most common representatives: the aromatics benzene (T, K+M), toluol (Xn, R) and naphthalene (Xn, N)
 - created mainly at 800°C, but also at 400°C
 - creation is not limited to purely hydrocarbon-based plastics (bio-PE and PP), but occurs in nearly all biopolymers investigated
 - incineration of biopolymers also creates substances dangerous to health and the environment
 - the type of fumes is determined by the elemental composition of polymers; the raw material base is insignificant, (e.g.: bio-PE with regenerative raw material base → benzene, toluol, naphthalene)

These measurements provide an initial overview. Comprehensive, farther reaching and more thorough investigations of the heat values and emissions is the subject of current research by the authors. Additional combustion properties (ash content, ash softening) of the biopolymers will also be topics of future research.

However, it can be assumed that biopolymer combustion behavior corresponds to that of conventional plastics. That means that as with conventional plastics, heat and calorific values and resulting emissions depend exclusively on materials composition, i.e., the chemical structure of the elements involved, and that the sources of the raw materials have no influence. Furthermore, it means that, from an engineering standpoint, no modifications or adaptations are required for existing incineration technologies to incinerate biopolymers separately or together with conventional plastics. The essential advantage of incinerating biopolymers, however, is that the content of biobased materials determines whether energy generation is CO₂ neutral (cf. Section 2.6).

6.5 Anaerobic Digestion (Biogas Generation)

Anaerobic digestion is also known as biogasification. The metabolization to biogas (mainly methane, carbon dioxide, water), for example biogas production from biopolymer packag-

ing, is an additional option for disposing of biopolymers that has scarcely been considered so far. The available data are mostly limited to organic waste with high moisture contents, such as mixed green biowaste, kitchen waste, or food waste.

The typical scenario is that biogas is generated from organic substrates (manure, energy crops, silage, etc.) in several steps in a biogas plant under anaerobic conditions. It is thus quite logical that biopolymers are efficient raw materials for biogas plants [122].

The conversion of organic compounds into biogas can generally be subdivided into the following four anaerobic process steps:

1. Hydrolysis:

Solid substances (proteins, fats, carbohydrates) are broken down (hydrolyzed) by bacterial enzymes into water soluble monomers (e. g., amino acids, glucose, fatty acids).

2. Bacterial acidification:

The dissolved substances are degraded to organic acids (acetic acid, propionic acid, and butyric acid), low alcohols, aldehydes, hydrogen, carbon dioxide and other gases, such as ammonia and hydrogen sulfide. This process continues until the bacteria are inhibited by their own degradation products (low pH value).

3. Acetogenesis:

In their acetogenetic phase, the substances are converted further to acetic acid by acid-forming bacteria.

4. Methanogenesis:

Methane bacteria form methane by splitting acetic acid or by reduction of CO₂ with hydrogen in a strongly anaerobic milieu (pH 6.7–8.0).

The anaerobic digestion processes can be distinguished as mesophilic and thermophilic processes, 1-phase or 2-phase processes, or as dry and wet processes. In a 2-phase digestion process, hydrolysis and acidification and then subsequently methanogenesis are run in separate tanks. In a 1-phase digestion process, the complete digestion is taking place in one unit. Dry digestion processes run at a moisture contents < 85%, while in wet systems the process is run at a moisture content >85% [122, 123].

In general, all commercial anaerobic digestion systems consist of a first step of anaerobic fermentation in a wet system, followed by an aerobic composting step. This second step is needed to stabilize the anaerobic sludge. For the majority of biogas facilities the digestion step runs on a mesophilic level. Whether the biodegradation occurs during the first anaerobic phase or during the second aerobic phase impacts only the biogas production; however, it does not impact the quality of final the compost. Here again, whether or not bioplastics are based on renewable resources is not relevant. The key element is the fact that the material is biodegradable and compatible with the anaerobic digestion process. Correct recovery is assured as long as it is eventually biodegraded and no residues are left after the process is completed.

In densely populated areas, such as metropolitan areas or countries such as Japan or Korea, anaerobic digestion is often the preferred biological waste treatment option. This is due to good odor control and a reduced need for surface area [124].

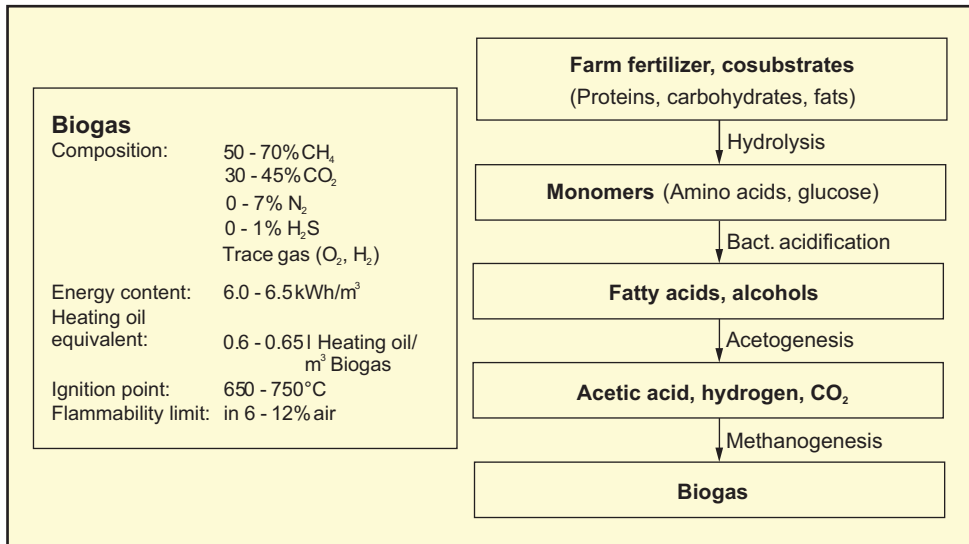


Figure 6.8 Steps of biogas formation

Again, there are little published data regarding the conversion of biopolymers to biogas in a biogas plant, such as temperature, pH value, microorganisms present, anaerobic/aquatic conditions, etc., or regarding the precise optimum parameters, such as materials flow density, dwell time, gas composition, and gas output. Further research will have to assess the potential biogas (energy) production due to the bioplastics. Also, the discussion and standardization of requirements for anaerobic biodegradation or anaerobic treatability is still in an early, initial phase [124].

Initial exploratory analysis of biopolymer degradation behavior under anaerobic conditions was performed jointly with the University of Rostock. These initial investigations resulted in the gas yields shown in Fig. 6.9 (blue bars).

These gas yields were obtained by means of small biogas batch plants with fermenters on a 50 liter scale. Batch investigations are characterized by one-time addition of substrate as well as qualitative and quantitative fermentation product detection during the entire experiment. Performing the experiments in this way provides information

- on potential biogas yield from the substance investigated,
- for qualitative assessment of anaerobic degradation speed in the substance investigated,
- on the qualitative inhibitive effect by the substance investigated in the investigated range of concentration.

The experiments were performed according to VDI guideline 4630.

According to the VDI guideline, specimen initial weight was determined using the quotient of organic dry substance (ODS) of the substrate and the inoculum. The various biopolymers in this experiment are in granular form. Untreated digested sludge from a communal water

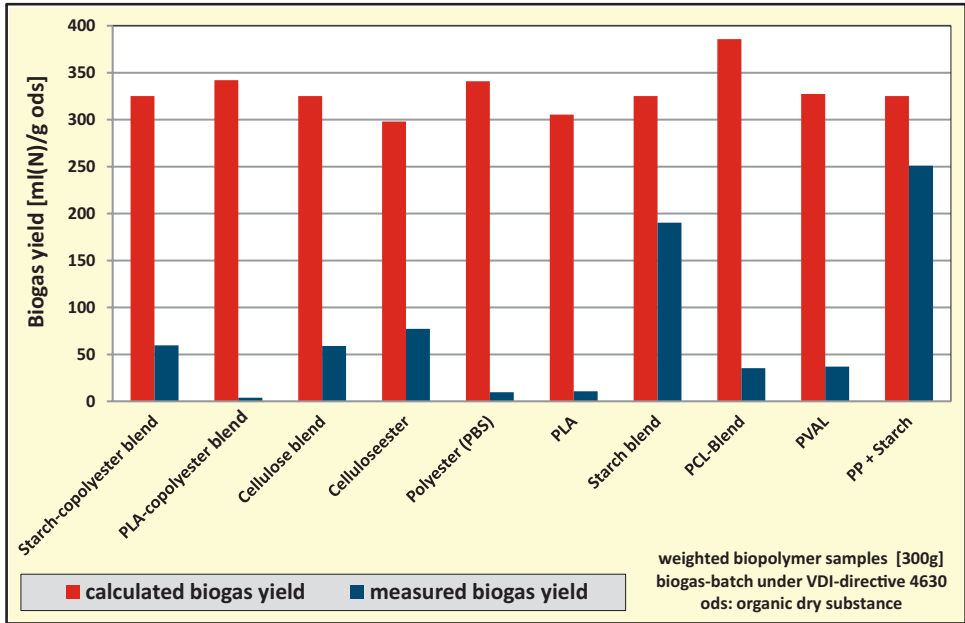


Figure 6.9 Biogas yields for various biopolymers as substrates

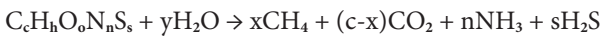
treatment plant was used as the inoculum and mixed daily by magnetic stirrers. Biogas yield was determined at a mesophilic temperature level (37 °C), and the experiment was performed as a 3-fold approach.

Biogas arising during the experiment was collected in gas- and diffusion-tight gas bags and periodically emptied. Gas volume and gas composition (CH₄, CO₂, H₂S) were then determined. Gas volume is presented as standard volume (T = 273 K, 1,013 hPa).

The duration of the investigation depended on the amount of biogas formed each day. The termination criterion was the point at which daily biogas rate equaled 1% of the biogas volume accumulated to date.

In order to assess biogas production from the biopolymer used, the average biogas production in the “null experiment” (inoculum without biopolymer substrate) was subtracted from the individual gas yields from the batch fermenter and the scattering was observed. The natural variation in the inoculum ranges from 4 to 5%.

If the stoichiometric composition is known, the biogas yield can be calculated theoretically. An approximation according to Buswell is:



With: c, h, o, n and s = molar ratios

$$x = 1/8 (4c + h - 2o - 3n - 2s) \text{ and } y = 1/4 (4c - h - 2o + 3n + 2s)$$

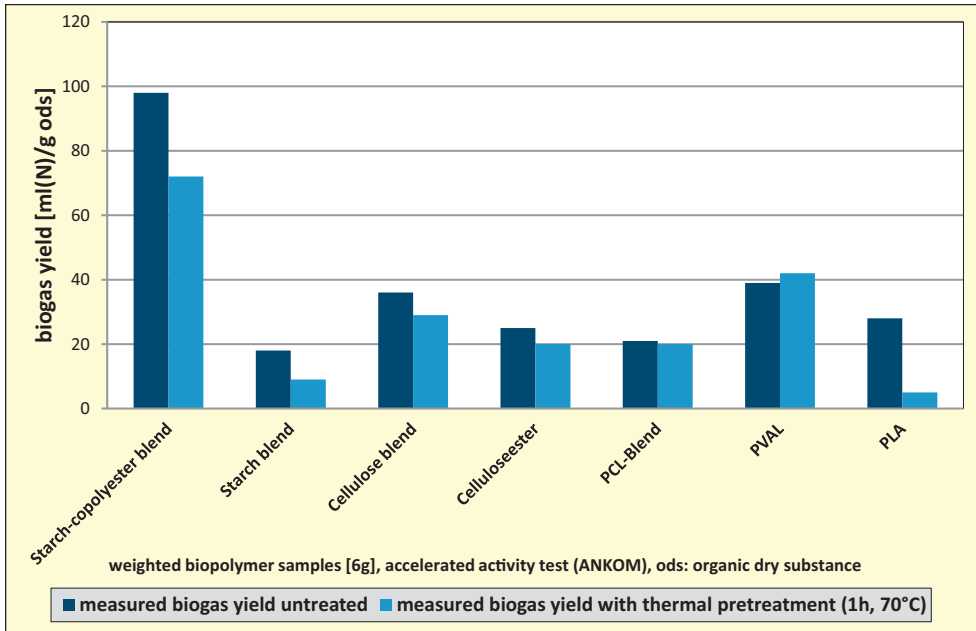
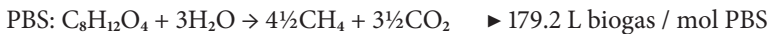


Figure 6.10 Biogas yields for various untreated and thermally treated biopolymers as substrate

Examples:



PVAL:

Hydroxyl groups (88-wt%):



Acetate groups (12-wt%):



Total: 54.9 L biogas / mol PVAL

The comparison of the results shows that the calculated biogas yields (Fig. 6.9, red bars) are clearly higher than the yields measured in the practical investigations (Fig. 6.9, blue bars). One underlying reason for these differences may be due to the influence of fungi. Fungi are abundantly available and very active in aerobic composting, while in anaerobic fermentation no fungi are active. Some polymers are mainly (or even only) degraded by fungi and not by bacteria and will therefore biodegrade by aerobic composting and not, or only much slower, by anaerobic digestion. Another reason for the partly insufficient material degradation is the reduced temperature compared to industrial composting processes. The anaerobic mesophilic

degradation of PCL, PVAL, PBS, and PLA with its high glass transition temperature is particularly difficult.

First experiments were carried out using a thermal pretreatment of biopolymers; however, the digestion rate could not be improved (Fig. 6.10). Only PCL with its low melting temperature showed improved digestion rates. For all other biopolymers investigated the digestion rate and the resulting biogas yield decreased. In particular for PLA and other biopolyesters, the thermal pretreatment led to post-processing re-crystallization, which reduced their anaerobic digestability. A legislative framework regarding the use of biopolymers as a substrate for generating biogas has not been established.

6.6 Product-Specific Disposal

Here we will present disposal options linked directly to the product or the application and/or use of the product. In some cases, corresponding test standards exist for regulating the characterization of individual degradation behavior under special use and/or disposal conditions specific to the application (see also Section 3.2).

6.6.1 Solution/Degradation in Water

Several polymers, such as various polyvinyl alcohols, are water soluble. When these polymers dissolve in water, macroscopic dissociation occurs. Based on this property, water soluble polymers find application, e. g., as laundry bags, secondary packaging for dishwasher tabs or as marine packaging materials. Macroscopic material dissociation is key in these applications.

Here, the various degradation mechanisms lead to primary macroscopic component degradation and to partial microscopic degradation; however, they do not ensure final degradation of the fission products. Complete final degradation of water soluble polymers is essentially determined by the total degradability of the resulting molecular fragments. If the molecular fragments of the oligomer are not entirely degradable, i. e., cannot be metabolized in a short time, the result is an accumulation of fission products in the Earth's water supply.

It is difficult to differentiate between water soluble polymers, and non-, partially or entirely biodegradable and compostable biopolymers.

6.6.2 Decomposition/Degradation in Soil

Degradation in soil is a disposal option in particular for products in agricultural applications, e. g., mulch films or flower pots. Degradation in terrestrial systems eliminates the expense of collecting and cleaning products as well as of disposing of the product itself. Simultaneously, the opportunity arises for controlled release of active substances such as fertilizer or herbicides. The effects from degradation products on soil quality play a decisive role in degradation behavior. Also important is a sufficiently short degradation time. If degradation is incomplete, or if environmental, or rather soil-damaging substances are formed, the result

is a deterioration of soil quality. For some applications test standards for characterizing terrestrial degradation are available (see Section 3.3.4).

6.6.3 Decomposition/Degradation in the Organism (Consumption, Biodegradation)

These are typically medical applications, either for controlled drug release or to support the healing process following surgery. The best known applications in this field are absorbable suture materials made from PLA, which can remain inside the body. For the same reason, various temporary implants, such as bone screws for fixating fractures, etc. were developed in recent years using PLA.

Besides these applications, there have also been various attempts to establish biopolymers as edible packaging. However, these attempts have failed, because, among other things, such edible packaging itself requires secondary packaging in order to meet food hygiene and food safety requirements.

6.7 Littering

By 'littering' we mean throwing away products carelessly, i. e., ambient disposal as is very often found on roadsides and parking lots or also following mass events. Since littering is done without regard to degradability and environmental effects, the use of corresponding biodegradable polymers would ensure decomposition and degradation of the products in the course of time. On the other hand, one could argue that, when biopolymers are used, the throw-away attitude would spread and consumers would no longer differentiate between degradable and non-degradable plastics waste.