

WHITE PAPER No. 78

Consumables Made of Bioplastics Enter the Lab

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Plastic has entered our daily life. But as versatile and necessary as it is, it also has a major ecologic impact since it is made from fossil fuels. Bioplastics produced from plants like sugar cane seem to be an alternative, but this approach also has its drawbacks. Intending to build a circular economy, waste streams are coming into focus as a source for the production of plastics. This whitepaper explains how used cooking oil can be used to produce polypropylene products that finally find their way into everyday lab work.



Can we solve the plastic problem?

Plastic is present in our daily work – at home and also in the lab. Consumables made of plastic facilitate daily life and ensure sterility and for some products, such as pipette tips, there is no real alternative. But plastic also poses a major problem as it is made from crude oil and contributes to climate change due to the high CO_{2e} emissions during production, processing and disposal [1].

Furthermore, most of the plastic which we put into the waste bin is not recycled but is burned, ends up in landfills or finds its way into the environment. It is important to mention here that the disposal of lab plastic waste underlies strict regulations that make it mandatory to be sent for thermal recycling [BK1].

Since 1950, only 9% of all plastic waste has been recycled, 12% was incinerated and 79% found its way into landfills or in the environment [2]. According to an estimation from 2014, all life sciences labs globally have produced 5.5 million tons of plastic waste. At the same time, it is difficult to replace plastic items in the lab, even though there are many efforts to minimize its use or to find alternatives. Therefore, it is necessary to also focus on the product itself and to look

for alternatives to get away from fossil-fuel-based products. One solution could lie in the use of bioplastic, which is made of renewable resources. As initially appealing as the approach may seem, there are also points of criticism upon closer inspection.

The aim – building a truly circular economy

Today, most bioplastics are made of feedstocks derived from carbohydrate-rich plants like sugar cane, corn, potatoes or wheat. At a first glance, these so-called first-generation bioplastics seem to be a good alternative to petrochemical plastics as they minimize greenhouse gas emissions but a closer look at the life cycle reveals a mixed picture.

The cultivation of sugar cane, corn or all the other plants needed as a source can have a negative environmental impact on land use, the loss of biodiversity as well as on the eutrophication and acidification of soils (due to the use of fertilizers) and water use [3,4]. Furthermore, the competition for agricultural land has been criticized, [5] even if the total



land use with an estimated 0.007% of the global agricultural land for 2023 is still marginal [6]. But if we want to replace all the current EU plastic packaging with bio-based alternatives, we would need 20.4 Mt of bioplastic. The necessary plants would have to be grown on 7.4 million hectares of land - an area larger than Ireland. [5]. These numbers clearly show that the production of bioplastics from feedstock is not necessarily an alternative to replacing all plastics.

In the last years, research focused therefore on other sources for raw materials, e.g., waste streams from agriculture waste, like wheat straw, food waste, like sugarcane bagasse which is a by-product of the production of sugar, or waste oils, like used cooking oil [7, 8]. All these initiatives have a common goal: closing the loop and building a truly circular economy based on so-called cascaded recycling where waste streams are used as a resource for new materials.

One of the most promising resources is used every day in the kitchens of restaurants, canteens or even at your home – used cooking oil (UCO). UCO is a mixture of triglycerides and free fatty acids and is, therefore, a good source of raw materials for many products, mostly used today to synthesize biodiesel, aviation fuel or lubricants, but it is also a useful source for other chemicals and products.



Figure 1: Polypropylene granulate

The way from used cooking oil to polypropylene

Used cooking oil is not only a promising resource but it is also available in sufficient quantities. The potential amount of used cooking oil from commercial users in the European Union is estimated to be 4 million tons per year [9] and more than 200 million metric tons worldwide [10]. Great potential

also lies in the collection of used cooking oil from private households but there are still open questions on how to organise such a diverse collection. Some EU countries already have a collection system installed for private households [11].

The way from used cooking oil to polypropylene includes four main steps [12]:

The first step is a pre-treatment of the used cooking oil to remove impurities and water. Main impurities include free fatty acids, heterocycles, Maillard reaction products or metal traces from pads and food leaching. This step starts with an initial gross filtration to remove solid materials dispersed in the oil, followed by a washing step with water to remove water-soluble chemicals. In the so-called "degumming process", the solution is stirred to remove phospholipids and waxes. Subsequent membrane filtration removes smaller particles down to the nanometre range, followed by a distillation that withdraws water and volatile compounds. The refined vegetable oil can now be further processed. [13]

The second step consists of hydrodeoxygenation to remove the oxygen with hydrogen atoms. This chemical reaction results in a mixture of saturated straight and branched-chain hydrocarbons. Part of this mixture, the so-called bio-naphtha, is used for the further production process. Water and propane are typical by-products of this process.

Here's an example of a typical reaction in the hydrodeoxygenation process, where triolein, a component of olive oil, is converted to octadecane:

$$C_{57}H_{104}O_6 + 15 H_2 \longrightarrow 3 C_{18}H_{38} + C_3H_8 + 6 H_2O_6$$

The third step is identical to the production process of the naphtha-fraction from crude oil: Bio-naphtha is cracked into smaller units in a steam cracking process. Here, the same production plants which are used to crack naphtha from crude oil can be used which makes this process economically favourable. During the steam cracking process, short-chain hydrocarbons are produced, one of which is propene. It has the same properties as propene obtained from crude oil.

In the last step, propene is polymerized in the standard polymerization process to polypropylene granulates which can then be further used for the production of different products.

Polypropylene produced in this way has the same properties as polypropylene produced from crude oil and can not be distinguished.



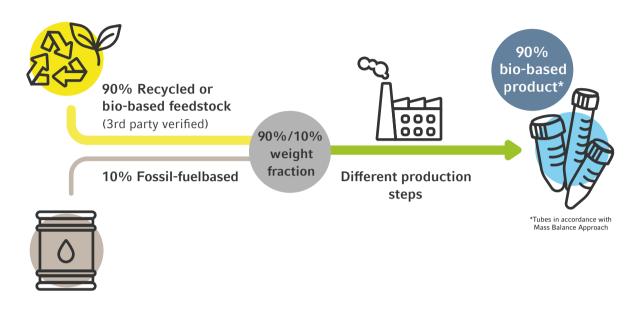


Figure 2: The Mass Balance Approach

The mass balance approach – a way to certify complex product chains in the circular economy

How can you measure the number of renewable building blocks in your end-product, when polypropylene or any other plastic made of building blocks from bio-naphtha has the same properties as polymers made of crude oil?

The Mass Balance approach is a proven and well-established way to measure and track building blocks made of renewable resources [14]. The idea behind is quite simple: renewable feedstock (here the bio-naphtha) replaces an equivalent amount of virgin feedstock from crude oil (here conventional naphtha) at the beginning of the value chain. As a prerequisite, the exact quantity of fossil feedstock which is needed for the production of a certain amount of product has to be determined: how many tons of feedstock is necessary to get one ton of output. In a second step, it has to be determined what quantity of petrochemical feedstock can be replaced by

renewable feedstock. The production process in between is not considered. The amount of replaced feedstock is then allocated to the product so that the input amount matches the output (normally measured in tons).

By using this approach, renewable building blocks are allocated to the product. 50% bio-based indicates that only half of the building blocks are derived from renewable resources while 50% are still fossil-fuel-based. In physical units, this means that 0.5 tons of renewable feedstock are mixed with 0.5 tons of fossil-fuel-based feedstock to give 1 ton of product.

The mass balance approach allows labelling products with a total or certain amount of building blocks made of renewable resources.



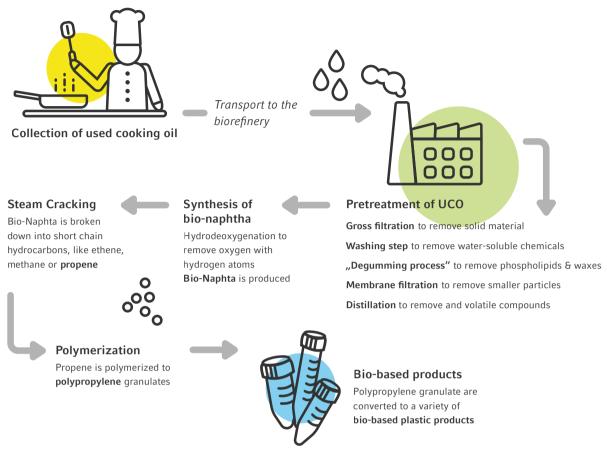


Figure 3: The way from UCO to polypropylene

The use of UCO to produce polypropylene is advantageous – ecologically and economically

From an ecologic point of view, the production of polypropylene from used cooking oil is advantageous. A life cycle analysis compared the conventional way to produce polypropylene made of crude oil and the process with used cooking oil as raw material and showed that the second process has a 62% lower impact on climate change [12].

The mass balance approach gives the possibility to identify the share of renewable resources. Depending on the end product and its desired properties, polypropylene can contain a few per cent of ethene to give a random copolymer [15]. If ethene is made of fossil fuels, the end product is not 100% bio-based. Here, the mass balance approach indicates the correct bio-based proportion in the end product. An independent certification verifies the amount of bio-based and

fossil feedstocks from the start of the value chain to the end product and gives, therefore, credibility across the whole manufacturing chain [16].

The example of polypropylene made of used cooking oil shows how the industry can be transformed into a circular economy. Used cooking oil is a good example as it is a valuable resource that can be broken down into basic chemicals like bio-naphtha, which can be further processed in the same way as naphtha made from fossil fuels.

The use of existing infrastructure is here a huge economical advantage and makes it easier for the industry to adapt to a circular economy.



What comes next?

Plastic will surely not disappear from the lab or our daily life, but a lot more products will be made of renewable resources in the future.

The use of waste streams as a resource will play a vital part in producing more sustainable products – and polypropylene made from used cooking oil is only the beginning. There are still technical challenges that have to be overcome – whether in process development or the quality and properties of the products. After all, the replacement of conventional plastic products with bio-based alternatives has to make sure that these are of the same quality and show the same features as their conventional counterparts. But these challenges surely won't stop the overall development.

If we look into the lab, conventional plastics like polyethylene (PE), polypropylene (PP) or polyethylene terephthalate (PET) have a great potential to be replaced by products made of renewable resources. Besides used cooking oil, there are other waste streams which could be used as well to generate second-generation plastic. Here are some examples showing the potential:

- 1) Forestry wastes like sawdust or bark are typical lignocellulosic residues of sawmills. By pre-treating the lignocellulose contained therein, cellulose is obtained which can be further converted into ethanol, processed into bio ethylene and polymerized to polyethene or further polyolefins. Commercial-scale production is not yet feasible as there are still challenges such as the suitable treatment of the lignocellulosic biomass or the conversion process of cellulose to ethanol [17].
- 2) Food waste and agricultural by-products like pulping residues from bagasse, crop husks or even straw can be converted into glucose and further processed into ethanol. This is then further dehydrated to ethylene, the building block to synthesize polyolefins like PE or PP. Also here, further process optimization is still needed [18].
- 3) Bio-PET is made of terephthalic acid (PTA) and ethylene glycol. Ethylene glycol can be synthesized based on sugar derived e.g., from corn or waste streams. Terephthalic acid however is mostly synthesized from crude oil due to economic reasons, but greener ways are being investigated, like the use of orange peels as raw material [19].

These are just a few examples that show the dynamics in the field of bioplastics and there will certainly be further exciting developments in this area in the coming years.



Literature

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