Biobased Feedstock in Integrated Chemical Production

Mass Balance Approach for Renewable Resources Saves Oil

Thanks to its certified mass balance approach, BASF can adjust the content of biobased feedstock in its integrated raw material production system to customer demand using drop-in solutions. The more customers demand mass balanced products from BASF, the higher the content of biobased materials in BASF’s integrated chemical production system (BASF Verbund). The production of fossil fuel-saving products can thus be managed on the basis of consumption. In this way, virtually all BASF products can be manufactured by using the equivalent amount of renewable instead of fossil raw materials.

With the development of the mass balance approach for the use of biobased (renewable) raw materials in the chemical industry, BASF SE, Ludwigshafen, Germany, has broken new ground. This approach allows fossil raw materials to be replaced by renewable feedstock in the production of virtually all BASF products, including plastics, without changing the established product properties. The special features of this approach are the use of both types of raw material together at the beginning of the value chain, i.e. in the production of the basic chemicals, and the subsequent calculated allocation of the required biobased raw material share to an end product according to an independently certified mass balance system. By purchasing this drop-in solution, customers help conserve fossil raw materials, and reduce greenhouse gas emissions, without having to change their production processes or licenses. The new mass balance approach from BASF will enable many companies to further develop their sustainability and marketing strategies. For the first time, it is now possible to supply products that previously could not be derived from biomass.

The use of biomass in the production of plastics reduces the consumption of fossil raw materials and – depending on the material and process – also cuts greenhouse gas emissions. For this reason and because of the growing environmental awareness of producers and consumers, the demand for biomass-based products is on the rise, not least in the automotive, construction, packaging, and consumer goods industries [1 to 3].

Raw material producers worldwide are already supplying various biobased plastics. However, many of the molecules used for synthesis in the chemical industry cannot be produced from renewable feedstock. As a result of different production methods (e.g. fermentation), the properties of biobased chemical products often differ from their petroleum-based counterparts.

Traceability in the Supply Chain

An important criterion for the acceptance of biobased products is the verifiable use of defined starting materials and their
traceability through to the end user. This can be ensured either by spot checks using quantitative test methods or by a certified documentation system along the value chain. There are three different methods for tracing biobased raw materials (Fig. 1) [4].

**Dedicated production:** In this production approach, fossil (petroleum-based) and biobased (renewable) raw materials are processed in completely separate (dedicated) production plants. Some examples of this approach in the area of biobased plastics include polyethylene based on sugar cane [5] or polylactic acid (polylactide, PLA) derived from corn [6]. Examples in the BASF portfolio are the Ultramid Balance polyamides based on sebacic acid, Lupranol Balance, a polyol component for the production of polyurethanes or bio-butanol (BDO), an intermediate used in polymer manufacture.

**Mass balance approach:** In this approach, two different raw materials may be processed together within defined system limits but must then be allocated proportionately to an end product (mass balance) [7]. For example, BASF uses petroleum-based and certified biobased raw materials together at the beginning of the value chain – in the form of naphtha and bio-naphtha or methane and biogas. The mixture is distributed throughout BASF’s integrated production system. With the aid of the mass balance calculation, it is possible to ensure that exactly as much biomass is fed into the start of the production process as is required to manufacture a specific end product. This amount is allotted via a certificate [8]. The mass balance is checked by an independent accredited body, which also issues a certificate for the sales product. This has the advantage of a very direct link between the purchasing decision of the customer and the use of renewable resources in chemical synthesis. Application examples of mass balance outside the chemical industry include biofuels, sustainable forestry (Forest Stewardship Council, FSC) and Fair Trade-certified chocolate [9]. Now the mass balance approach is also available for products such as plastics.

**Certificate trading:** In this approach, producers can completely separate the use of biomass from their own product manufacturing process. They must, however, prove that the amount of certified biomass they purchase corresponds to the use of such biomass for product manufacture somewhere else in the world. An example of this is the Clean Development Mechanism (CDM) for the reduction of greenhouse gas emissions, under which emission reduction projects can be undertaken in emerging nations and the savings certified [10]. These certificates (Certified Emission Reductions, CERs) can then be credited towards reduction targets in industrialized countries [11]. In the plastics sector, a corresponding system has not so far been used. Because of the physical separation of product and biomass, this approach is particularly difficult to explain to end customers.

**Less Fossil Raw Materials in Integrated Chemical Production**

To meet the rising demand for products based on renewable resources and offer customers a complete solution for products, BASF and TUV SUD Industrie Service GmbH, Munich, Germany, have developed a mass balance standard for integrated chemical production using biomass [12]. As an independent testing body, TUV SUD regularly confirms the correct use of renewable resources instead of fossil raw materials. That means TUV Sud experts conduct annual audits in selected BASF plants in Ludwigshafen, familiarize themselves with the product formulations and process steps, and check the quantitative allocation of biobased raw materials to an end product.
In 2013, after extensive discussions with customers, trade associations, and other interest groups, BASF introduced the system that can be used for the majority of the company’s products. The mass balance process is now certified for the BASF production sites at Ludwigshafen, Antwerp, Belgium, Schwarzheide, Germany, and soon also Lemförde, Germany (from June 2015).

The certification process for mass balance products includes all the steps for the manufacture of a product and an audit of the quantities of biomass used annually. In this way, all the materials used are taken into account, including those that do not end up in the finished product (e.g., solvents). This happens throughout the production period and not just in the form of spot checks.

In its mass balance concept, BASF uses renewable resources from certified sustainable production together with fossil raw materials (Fig. 2). In this way, the production advantages of BASF’s highly efficient integrated production system, optimized over 150 years, can be exploited for products certificated by the mass balance approach. This, of course, also includes the production of plastics. In BASF’s integrated production system, for example, by-products from one factory can be used as starting products in another. Unlike in a dedicated production system based on biomass feedstock, which usually involves a completely new production process that must then be developed to high efficiency, this has already happened in the BASF mass balance approach thanks to the company’s integrated production system.

To assign the renewable resources and associated savings in fossil raw materials and greenhouse gas emissions to a particular product, it is possible to credit the amount of biobased feedstock used to a specified customer product by means of a certified calculation method similar to that for green electricity – here the balancing method is already a recognized standard. The product’s individual formulation, including all yields and losses, forms the basis for the calculation.

The use of the mass balance concept in the chemical industry makes it possible for the first time to employ biobased raw materials for virtually all chemical products. Customers and consumers can now produce or buy not just selected products or product parts manufactured from renewable feedstock but complete product solutions (including packaging). In this way, a significantly higher contribution to conserving fossil resources and reducing greenhouse gas emissions can be achieved. Customers that purchase mass balanced products from BASF thus ensure that BASF replaces the corresponding amounts of fossil raw materials with renewable resources. The certified content of renewable feedstock can range from 25% to 100%, depending on customer requirements.

This certified approach gives customers and end users reliable data on the replacement of fossil raw materials by renewable resources. Customers obtain end products that verifiably reduce the consumption of fossil raw materials and greenhouse gas emissions. Their composition and performance are identical to those of their conventional counterparts based on fossil raw materials, so that customers’ product formulations remain unchanged. Consequently, users of mass balance products do not have to conduct new tests or make changes to their existing processes, and additional investments in plants or processes are not required.

TÜV SÜD has now issued certificates for products supplied to virtually all BASF customer industries. These can be viewed directly on the TÜV SÜD website (http://www.tuev-sued.de/ER-ID). The certified products include superabsorbers for diapers, dispersions for adhesives, plastics such as polyamides and polyurethanes, and intermediates—all available on the market as 100% drop-in products.

Contrary to the present understanding of “biobased”, which is defined by the content of biomass in the end product, the mass balance concept focuses on the amount of biomass used in production and the saving in fossil raw materials thus enabled. In other words, mass balance products from BASF do not themselves necessarily have to contain biobased material verifiable with the 14C radiocarbon method.

One reason for this is that BASF feeds a combination of fossil and renewable resources into its complex integrated production system. The path of the renewable resources cannot therefore be separated or attributed to a specific product because the raw material mix is spread over many thousands of the company’s products. The use of biobased raw materials would only be measurable in the final products when...
they account for a certain proportion in BASF’s integrated production. This pre-condition is not currently met in the initial phase of applying the mass balance approach. But the more customers take this path, the more renewable resources will be used in the integrated production system and also become verifiable in the end product.

**Organic Waste as a Raw Material**

For its mass balance process, BASF uses only biobased raw materials that have been produced sustainably and that enable a reduction in greenhouse gas emissions compared with fossil raw materials. The biobased materials must at least meet the criteria required in Article 17 of the European Renewable Energy Directive (RED), which today already specifies a greenhouse gas reduction of 35% [13]. All certificates recognized in accordance with RED can be used to verify sustainable production of biobased raw materials. In addition, biobased waste streams are also accepted as sustainable raw materials on the basis of a standardized life cycle assessment (LCA) in accordance with ISO 14040.

Biobased raw materials are not necessarily more sustainable than their fossil counterparts. While they contribute to conservation of fossil resources and reduce emissions of greenhouse gases, on account of agricultural activities they often involve higher land use and water pollution or are even in competition with food.

As far as possible, BASF therefore purchases only raw materials consisting of 100% organic waste for its mass balance approach, e.g. kitchen waste, slurry or used frying fat. With the latter material mix, for example, plastics have been produced based on over 60% waste.

Strict sustainability requirements generally apply to biobased raw materials used in the BASF mass balance process, with criteria such as:

- reduction of greenhouse gas emissions,
- sustainable land use,
- protection of the natural habitat,
- fulfilment of social requirements in cultivation.

**First Customer Applications**

**Polyamides**: BASF’s first plastics customer for materials based on the mass balance approach is Kunststoffwerk AG Buchs, Buchs, Switzerland, a subsidiary of Wiha Werkzeuge GmbH, Schonach, Germany. The company uses Ultradim B3EG6MB (a 30 wt.-% glass fiber-reinforced PA6) in serial production of its Longlife meter rule brand (Fig. 3). In launching this product, Kunststoffwerk AG Buchs also obtained certification from TÜV SÜD for use of this material.

The plastic grade used is one of the first BASF mass balance polyamides available in commercial quantities. In the production of this plastic, fossil raw materials are replaced by 100% renewable feedstock. Nevertheless, the plastic is chemically identical to its predecessor, the established polyamide Ultradim B3EG6.

As of now, BASF can also supply Ultradim PA grades based on the mass balance approach for the production of flexible packaging film. This opens up entirely new marketing possibilities for both plastic film producers and manufacturers of film-packed products. The Taiwanese company Italon Fiber Co. Ltd, Erhshui Hsiang, is the first in the textile industry to use a mass balance polyamide from the Ultradim range. Among the reasons for this decision was the realization that end customers of the company are placing increasing importance on the origin of a textile and the materials used in its production.

**Polyurethanes**: The use of biobased feedstock for the production of polyurethanes (PU) has so far proved quite challenging. It is mainly confined to polyols based on sugar and oils, while there is no marketable solution for aromatic isocyanates. Generally speaking the properties of biobased and petroleum-based polyurethanes are very different so that replacement requires considerable time and effort. On the other hand, the mass balance approach at the beginning of the process chain offers the possibility of manufacturing polyurethane products with polyol and isocyanate components produced using biomass and, despite this, properties no different from those of petroleum-based products. In this way, BASF can for the first time supply polyurethanes derived almost 100% from biobased feedstock used at the start of production.

A potential application for these polyurethanes might be in refrigerator insulation, where, for example, the use of the mass balance PU system, Elastocool, could make a significant contribution towards achieving environmental targets, given the considerable quantities of insulation in such appliances. For pillows, cushions (Fig. 4), and mattresses, mass balance products could make it possible to replace up to 95% of the fossil raw materials used. There is also great potential for the use of mass balance products in the production of shoes with soles consisting of Elastollan (TPU) or Elastoplan (PU) systems (Title figure).