Bio-based drop-in, smart drop-in and dedicated chemicals

(Version 2017-12)

Authors: Michael Carus, Lara Dammer, Dr. Ángel Puente, Achim Raschka, Dr. Oliver Arendt, nova-Institut GmbH

This paper was created in the context of the RoadToBio-project. RoadToBio aims to pave the way for the European chemical industry towards a larger bio-based portfolio and competitive success. The roadmap developed in RoadToBio will specify the benefits for the chemical industry along the path from fossil-based industry towards a bioeconomy to meet the societal needs in 2030 (for more information see www.roadtobio.eu)

The following briefing text provides definitions and explanations of three different kinds of bio-based chemicals, namely drop-in, smart drop-in and dedicated/novel chemicals, as depicted in Figure 1. The text does not aim to provide finite exact definitions in a strict scientific sense. Rather, it intends to outline a structure in which different kinds of bio-based chemicals, which require different market strategies, can be classified. As such, the classification will be used as a basis for the roadmap work carried out in RoadToBio. The paper is meant as food for thought and we would welcome feedback from stakeholders. If you would like to send us your reaction to this paper, please contact us at christopher.vomberg@nova-institut.de

Figure 1 gives a first overview of the different pathways from feedstock to chemicals for fossil-based and different kinds of bio-based chemicals: Drop-ins, smart drop-ins and dedicated. Drop-ins enter the conventional pathway at an early stage, whereas smart drop-ins start with a biomass-related process before they enter the conventional pathway at a late stage. Bio-based dedicated chemicals have their own dedicated pathways with no petrochemical equivalent.

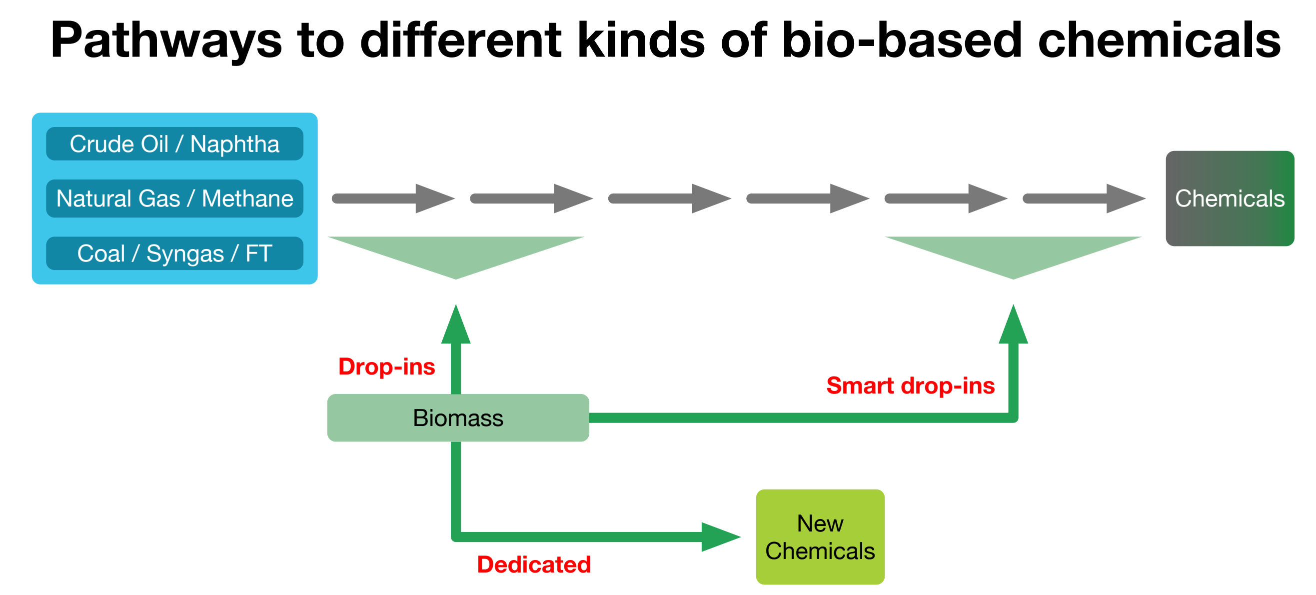

Figure 1: Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals

This project has received funding from the Bio-based Industries Joint Undertaking and the European Union's Horizon 2020 research and innovation programme under the Grant Agreement No. 745623.

Bio-based drop-in chemicals

Definition

Bio-based **drop-in chemicals** are bio-based versions of existing petrochemicals which have established markets. They are chemically identical to existing fossil-based chemicals (BIO-TIC 2014).

Explanation

The term drop-in is usually used in relation to commodity chemicals and polymers with large production volumes.

Bio-based drop-in chemicals usually differ from their petrochemical counterparts in price (mostly more expensive) and in environmental footprint (mostly lower).

Regarding the ease of implementation, bio-based drop-in chemicals are easy to implement technically, as existing infrastructure can be used. However, due to their usually higher price compared to their fossil counterparts they are often not competitive.

Examples: Bio-based methane, ethylene/PE/PET, propylene/PP and bio-naphtha (since the compositions of fossil and bio-naphtha differ from each other, the latter may enter value chains at a different stage than fossil-based naphtha).

Bio-based smart drop-in chemicals

Definition

Smart drop-in chemicals are a special sub-group of drop-in chemicals. They are also chemically identical to existing chemicals based on fossil hydrocarbons, but their bio-based pathways provide advantages compared to the conventional pathways. We consider drop-in chemicals to be 'smart drop-ins' if at least two of the following criteria apply:

- The Biomass Utilization Efficiency (BUE, see Iffland et al. 2015) from feedstock to product is significantly higher compared to other drop-ins.
- Their production requires significantly less energy compared to other production alternatives.
- Time-to-product is shorter due to shorter and less complex production pathways compared to the fossil-based counterpart or other drop-ins.
- Less toxic or harsh chemicals are used or occur as by-products during their production process compared to the fossil-based counterpart or other drop-ins.

Explanation

The pathways leading to smart drop-ins are advantageous combinations of novel/dedicated and conventional chemical pathways. This means, for example, that the biomass is processed in a new way up to a certain status, and is then at a later stage fed into the conventional pathway, making the overall process shorter and more efficient.

One example of a smart drop-in is epichlorohydrin, a precursor of epoxy resins. Being produced from glycerol makes it much smarter than its conventional fossil-based manufacture. In this case, almost all mentioned criteria are fulfilled (see Figure 2).

The term drop-in is usually used in relation to large commodity chemicals. In the case of smart drop-ins, this will probably apply to commodities of smaller volume (but still larger than specialty chemicals).

Other examples of smart bio-based drop-in chemicals: Acetic acid, acrylic acid, adipic acid, aniline, butadiene, 1,4-butanediol, isoprene, PA (6,6), polybutylene succinate, 1,3-propanediol, succinic acid.

Example of a smart drop-in chemical

(±)-Epichlorohydrin, a highly reactive building block used in the manufacture of plastics and epoxy resins, is industrially produced from propylene in a three-step process. An alternative two-step process starts from glycerol, a readily available chemical from biodiesel production, which is produced through saponification of triglycerides from plants and animal sources. Glycerol is converted to dichloropropanol with hydrochloric acid in the presence of an acidic catalyst. This smart route avoids the chlorination of propylene using toxic chlorine at 500 °C and yielding many other chlorinated by-products (Hirth et al. 2015).

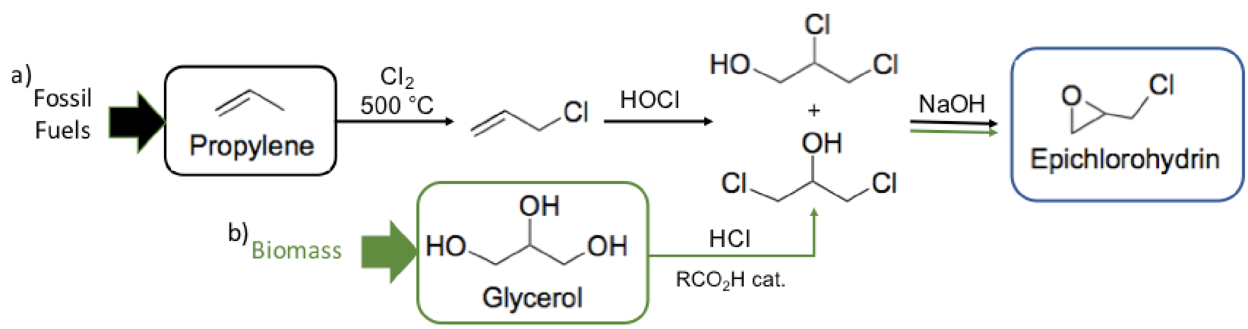

Figure 2: Synthesis of epichlorohydrin following a petrochemical a) or a bio-based b) pathway

This project has received funding from the Bio-based Industries Joint Undertaking and the European Union's Horizon 2020 research and innovation programme under the Grant Agreement No. 745623.

Dedicated bio-based chemicals

Definition

Dedicated bio-based chemicals are chemicals which are produced via a dedicated pathway and do not have an identical fossil-based counterpart. As such, they "can be used to produce products that cannot be obtained through traditional chemical reactions and products that may offer unique and superior properties that are unattainable with fossil-based alternatives" (BIO-TIC 2014).

Explanation

"Compared to drop-in commodity chemicals, **bio-based dedicated pathways** are more efficient, utilising not only the carbon in the biomass, but the whole biomass – carbon, oxygen, hydrogen and nitrogen. This is reflected in a high biomass utilization efficiency (BUE)." (Carus et al. 2016).

New emerging synthetic strategies based on biomass can take advantage of utilizing higher levels of structure (functionalized building blocks) already provided by nature. Instead of breaking down (defunctionalising) the naturally grown molecules into very simple molecules (e.g. syngas) which are then utilised further, the valuable existing functional groups can be used which results in the mentioned higher efficiency. Against this background, these chemicals are sometimes also called "novel", but many of these bio-based options have been around for quite some time, at least in scientific literature. This group therefore comprises both new and well-known chemicals.

Industrial biotechnology and other novel technologies are becoming important biomass transformation technologies: highly specific transformation processes can be accomplished under mild reaction conditions with often very high yields. One example of a dedicated bio-based chemical is dihydrolevoglucosenone (see Figure 3).

Other examples of dedicated bio-based chemicals:

- Glycerol and derivates, 3-hydroxypropionic acid and 3-hydroxypropanal, itaconic acid, farnesene, furans (HMF, furfural, FDCA), lactic acid, levulinic acid, methylenesuccinic acid, sorbitol, xylitol
- PEF, PHA, PLA, PA (10,10, 10,12 and 12,12)
- Bio-based lubricants and surfactants, e.g. sophoro- and rhamnolipids, alkylpolyglycosides
- Cellulose fibres, nano- and microcellulose

Example of a dedicated chemical

Dihydrolevoglucosenone (Cyrene™), a dipolar aprotic solvent, is an example of a dedicated bio-based chemical. It can be directly derived from waste cellulose in two simple steps, having therefore a high stoichiometric Biomass Utilization Efficiency (BUEs) of 79%. Cyrene™ has demonstrated a similar solvent performance as toxic petrochemically derived solvents such as *N*-2-methyl pyrrolidone (NMP), whose industrial synthesis involves multiple reaction steps starting from acetylene and acetaldehyde (Figure 3) (Clark et al. 2014).

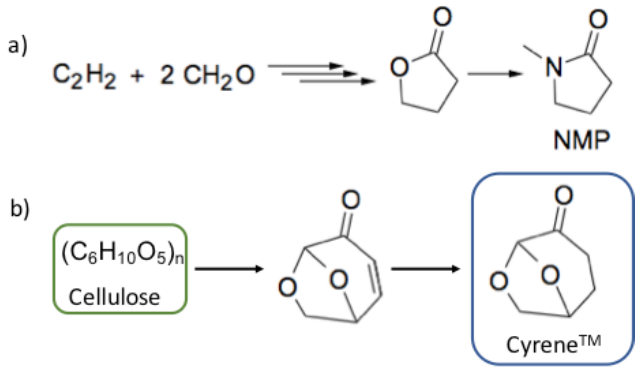

Figure 3: Scheme of the production of a) *N*-2-methyl pyrrolidone (NMP) and b) dihydrolevogluocosenone (Cyrene™)

References

BIO-TIC (2014): Overcoming hurdles for innovation in industrial biotechnology in Europe, Biobased Chemical Building Blocks, Summary; http://mig.www.industrialbiotech-europe.eu/new/wp-content/uploads/2014/08/Summary-of-the-findings-related-to-chemical-building-blocks.pdf

Carus, M. et al. (2016): How to shape the next level of the European Bio-based Economy? (www.bio-based.eu/policy)

Clark, J. H. et al. (2014): Dyhidrolevoglucosenone (Cyrene) as a bio-based alternative for dipolar aprotic solvents. Chem. Commun., 50, 9650-9652

Hirth, T., Iden, J.-M. and Busch, R. (2015): Sustainability and the Chemical Industry. Ullmann's Encyclopedia of Industrial Chemistry. 1–19

Iffland, K. et al. (2015): Definition, Calculation and Comparison of the "Biomass Utilization Efficiencies (BUE)" of Various Bio-based Chemicals, Polymers and Fuels. http://bio-based.eu/nova-papers/#novapaper8en

This project has received funding from the Bio-based Industries Joint Undertaking and the European Union's Horizon 2020 research and innovation programme under the Grant Agreement No. 745623.