# Glycerol, from ingredient to platform chemical

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Called "man's most versatile chemical servant", by Lesser in 1949, (1) glycerol has lately become the main platform biochemical of the chemical industry (2). Lesser was mentioning 1583 commercal direct uses for glycerol due to its unique chemical, phisical and biological properties: humectant or hygroscopic agent, vehicle, solvent, sweetening agent, emollient, lubricant, softening and demulcent agent, antifreeze, refrigerant, preservative and many other.

"Less than a year ago", proudly continued the chemist of the Glycerine's Producers Association based in New York City, "the production of synthetic glycerin from petroleum gases was begun on a commercial scale, thereby yielding additional supplies of this widely demanded material" (1).

The "petroleum gases" was propene, and the production started in 1948 in Houston, Texas, was the high-temperature chlorination of propene to allyl chloride followed by hydrolysis commercialized in Germany by I.G. Farben at two production sites (Oppau and Heydebreck) in 1943.

Seventy years later, all synthetic glycerol production plants but one have been closed, as a large and ever increasing surplus of biodiesel-derived glycerol has flooded the chemical market. Certain plants, such as one in France and another in Czech, were even retrofitted: rather than producing glycerol from epichlorohydrin (ECH), they now produce ECH from glycerol.

Today's large bioglycerol refineries have replaced the former synthetic plants, but at a much larger scale. The old, volatile and highly profitable glycerol market comprised of a few 100,000 tonnes of glycerol from soap and oleochemicals (fatty acids and fatty alcohols) making, plus an additional amount of synthetic glycerol, has been replaced by a much larger and truly global market fed by ever increasing biodiesel and oleochemical productions.

For comparison, the glycerol global output was 2.47 million tons in 2014, and 3.551 million metric tons in 2016. Glycerol today being entirely obtained as a by-product of biodiesel and oleochemical productions, its supply is entirely independent of its demand (3). There is as much glycerol on the market as much biodiesel, fatty alcohols and fatty acids are produced. The only impact higher demand for glycerine can have is on price.

Large supply and low prices created the perfect conditions to start using glycerol as platform chemical to produce commodity and fine chemicals, each time competing with an oil-derived platform chemical (4).

For example, the glycerol-based route to ECH competes with the propene route, and now that ECH prices are increasing again, the glycerol-based plants started to operate again at full capacity (5).

Indeed, as mentioned above, the first chemical manufactured on large scale was ECH, the valued precursor of numerous epoxy resins.

Numerous other chemical and biochemical catalytic routes to high value chemicals have been developed in the last decade, and some successfully commercialized. Examples span from 1,3-propanediol and 1,2-propanediol through bioplastics; and certainly new glycerol-based productions will see the light in the near term.

What is relevant to understand, here, is the key sustainability concept at the origin of the glycerol booming production as by-product. in the last five years, the biodiesel and oleochemical industries have shown an high degree of resilience regardless of prolonged low prices of oil which led to record losses for numerous oil companies. Now that the oil price has started to climb again, the production of biodiesel and oleochemicals will only increase, and so will the glycerol supply, eventually establishing glycerol as the largest platform chemical of the emerging bioeconomy before lignocellulosic sugars of low cost reach out the marketplace.

## REFERENCES

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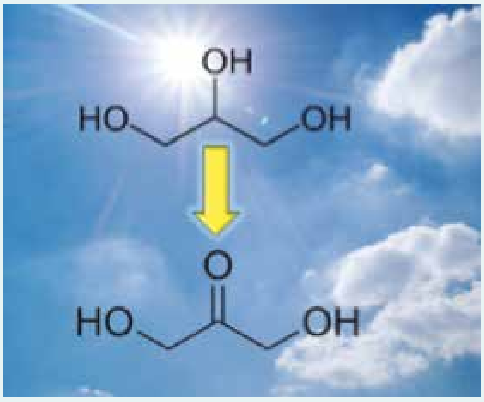
**Fine chemicals from glycerol: DHA**

Plentiful opportunities exist to renew and expand fine chemical productions starting from glycerol. One eminent example is 1,3-dihydroxyacetone (DHA) currently obtained via microbial fermentation of the triol. Driven by concomitantly increasing consumer passion for a tan and awareness of UV photodamage to the skin caused by prolonged exposure to the sun, the demand of DHA has significantly grown during the course of the last decade (6).

The latter valued bioproduct, indeed, is the main ingredient of all self-tan lotions and sprays, rapidly forming a tan via the Maillard reaction between the ketone and the skin proteins.




**Scheme 1.** At least two new solar-driven photocatalytic processes have been developed for converting glycerol dissolved in water directly to DHA with oxygen only at room temperature and pressure. [Reproduced from Ref.6, with kind permission].

Production of DHA based on conventional microbial manufacturing has more than doubled from  2,000 tonnes of  2010. High and increasing demand, coupled to high price, open the route to the introduction of industrial DHA catalytic syntheses, and in particular to the aerobic photooxidation driven by solar light (Scheme 1) (7). A company in Germany, for example, already offers a similar photocatalytic technology using a $Bi_2O_3$/Pt visible-light photocatalyst capable to afford high yields of DHA from a concentrated aqueous solution of glycerol (1:1 glycerol/water) (8).