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Upgrading glycerol for **high-value-added** applications

Franck Dumeignil

Since the biodiesel boom began in about 2005, the glycerol supply has increased considerably, from about 0.5 million cubic meters (Mm^3) in 2005 to about 2.5 Mm^3 in 2013, due to glycerol being a byproduct of biodiesel production through the transesterification of triglycerides.

- **The smart and efficient conversion of glycerol to high-value-added chemicals is key to ensuring the sustainability of biodiesel production.**

- **In a true biorefinery approach that maximizes profitability, using cheap crude glycerin in a chemical process is not necessarily less costly than using more expensive refined glycerol; using intermediate qualities can be a profitable trade-off.**

- **The deactivation of catalysts during coking can be tackled from different angles, by fine-tuning the chemical properties of the catalysts and/ or by designing a smart adapted process.**

More than 2,000 possible applications of glycerol are reported in the literature. As a pure refined compound, glycerol tastes like sugar, which makes it, for example, a good sweetening agent in toothpastes. It can also be chemically upgraded to yield large-volume compounds such as acrolein and its derivatives. However, although several advanced glycerol processes have been developed on a laboratory/demonstration scale, few have reached commercial-scale production. One exception is the epicerol® process Solvay developed to produce epichlorohydrin from glycerol. This process is actually an inversion of an initial process that was developed for producing glycerol from epichlorohydrin when glycerol was in short supply (http://tinyurl.com/nlahny2).

The commercialization of other advanced glycerol processes is hampered by several factors. One is uncertainty regarding the glycerol supply caused by unpredictable fluctuations in regulations. The revised incorporation rate for biofuels in Europe, which was reduced from an initial target value of 10% by 2020 to 7%, has had repercussions throughout the biodiesel sector. Several existing units in France have closed, and some newly built units in Germany have postponed or discontinued operations. Such fluctuations are a threat to future investments in such projects.

Other hurdles to commercialization include the high cost of purifying the "dirty" glycerol obtained from the transesterification process and the stability of the heterogeneous catalysts used for gas-phase glycerol upgrading. Such catalysts are quickly deactivated by coking (the formation and deposition of undesirable carbonaceous compounds on the catalyst's surface), making their industrial applicability questionable.

The following is a global perspective of these factors and possible solutions, based on work done by our research group.

BETTER ECONOMICS THROUGH DIVERSIFICATION AND INTEGRATION

The commercial challenges described above arise from the historical singular function of biodiesel units, which were exclusively dedicated to biofuels production. The downside of this approach is that biofuels must be cheap to be acceptable to the market, and competitive cost pressures result in low margins and an overall economy that is largely dependent on government incentives and subsidies. In contrast, about 90% of the raw materials used in the
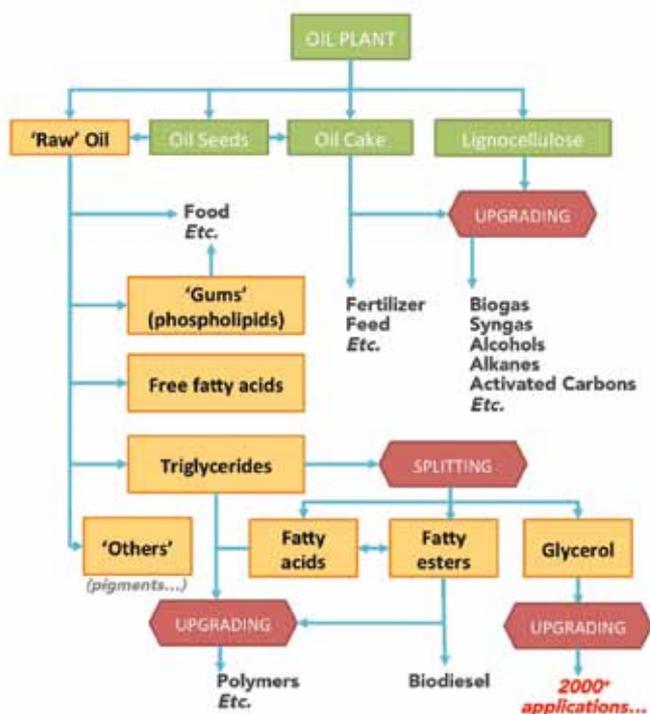
FIG. 1. Schematics of a plant-oil-biorefinery value chain that integrates fuel and chemicals production

petroleum industry (namely oil) is used to produce fuels and the remaining 10% or so to produce high-value chemicals that account for approximately 90% of the industry's overall profits. Believing that an industrial unit will survive only on biofuels production is thus an illusion that will undoubtedly sooner or later fade away.

Diversifying outputs could open the door to many business opportunities. Such a biorefinery approach could, in its most evolved configuration, simultaneously accept multiple types of biomass, treated by multiple processes, to generate multiple products. Specifically concerning the topic of the present article, this approach, as outlined within the framework of the EuroBioRef PCRD7 European program (www.eurobioref.org), seeks to

optimize the value of glycerol by streamlining an additional chemical production unit with a biodiesel unit. This can be further extended to vegetable oil (and also animal and used oils) biorefineries that could produce high-value-added products from fatty compounds, glycerol, and any other coproducts along the value chain (Fig. 1).

My research team is currently involved in the large-scale PIVERT (Institute for Energetic Transition) project, which aims to design a plant-oil biorefinery through such an integrated and diversified concept (http://www.institut-pivert.com/?lang=en). Note that plant-oil-derived fatty compounds are already used to make polymers. For example, both Arkema and Solvay use ricinoleic acid from castor oil as a raw material to produce RILSAN® (http://www.rilsan.com/en/) and Technyl® eXten (http://www.technyl.com/en/solutions/featured-product/technyl-exten/index.html), respectively, as commercial products with superior technical properties. Extending this concept to a variety of chemicals and other value-added products, such as activated carbons (as exemplified in the EuroBioRef project), would provide the basis for a product line that, together with conventional fuel applications, would make the whole integrated process more economical.

GLYCEROL VS. GLYCERINE

As mentioned previously, the biodiesel industry is the main source of glycerol today. However, the glycerol produced in a biodiesel unit is a dirty, complex mixture containing methanol, organic compounds, salts, base residues, and other impurities. Known as "crude glycerol," or "glycerin," this mixture is often subjected to a downstream multiple-step purification process in which the impurities are sequentially eliminated to yield "pure," or "refined,"
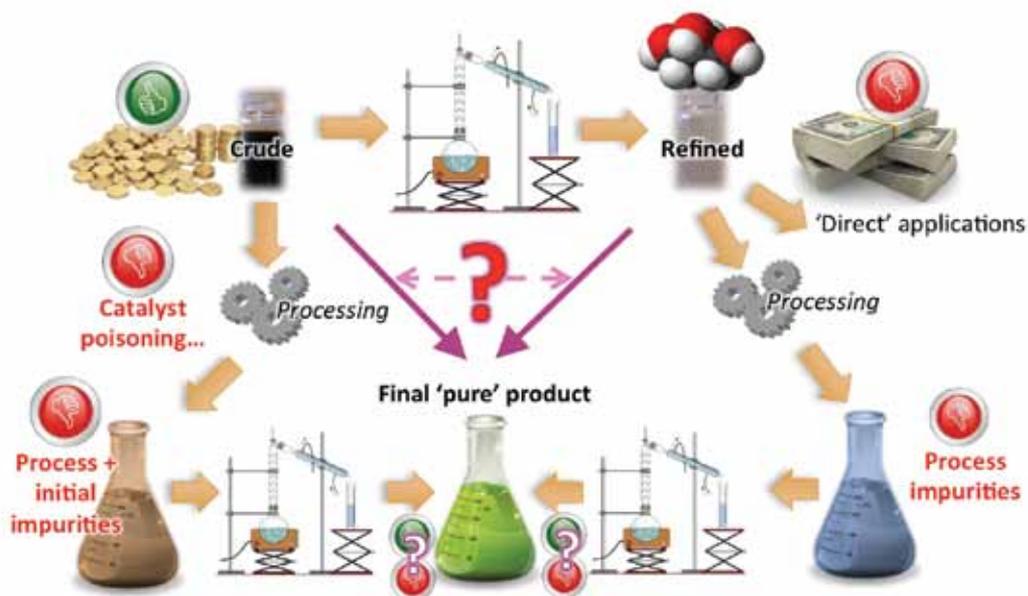

FIG. 2. Should I use crude or refined glycerol in my process to make it more profitable? The answer is not straightforward: The best option will most probably consist on a trade-off between an acceptable degradation in chemical catalytic performances in the presence of impurities and the easiness of separation of the desired final product(s) to get the required final quality at reasonable costs.

commercial glycerol. Unfortunately, this extensive purification process has a significant cost that affects the cost of the final product obtained through subsequent chemical conversion. It is worth mentioning that some research efforts are currently exploring alternative biodiesel production processes that would directly generate "pure" glycerol as a co-product, but such technologies are not likely to be implemented soon, and meanwhile we must cope with substantial amounts of crude glycerol.

The advantageous price of crude glycerol compared to that of pure glycerol (which costs three- to five times as much) raises the question of whether it is possible to design chemical conversion processes that are tolerant to the impurities present in crude glycerol streams. The answer to this question is not straightforward for the reasons illustrated in Fig. 2 (page 625).

Even if the downstream application of the final desired product is unaffected by the presence of impurities, which is highly unlikely, a purification step would still be needed after the chemical conversion—not only to separate the byproducts from the upgrading technology, but also to eliminate any unaltered or converted initial impurity.

In the case of a liquid phase process, even if an operator chose to perform only one global purification at the end of a procedure using crude glycerol as a raw material to eliminate all the impurities in one shot, it is most likely that the catalyst used for the chemical upgrading would not tolerate some of the impurities present in the initial stream. This would degrade chemical performances and yields, burdening the overall efficiency of the approach.

One intermediate solution, if technically possible, would be to define, generate, and use intermediate qualities of glycerol ("semi-refined" glycerol) in which only the impurities harmful to specific catalysts are removed prior to the reaction—or, alternatively, to design catalysts that would be more tolerant to such impurities.

Our research group recently evaluated the effect of various glycerin impurities on the performances of model catalysts used for glycerol liquid phase partial oxidation to high- value-added compounds. The catalysts we examined consisted of monometallic particles of Pt, Au, Pd, and Ag supported on alumina. In all cases, we observed that the matter organic non glycerol (MONG) stuck to the catalyst and blocked the active sites, causing further foaming in the presence of a base. The initial catalytic performances could be recovered by washing the catalyst with inorganic solvents, which sufficiently flushed out the MONG. However, in designing a sustainable process, MONG should obviously be removed from the initial stream.

In contrast, the presence of residual methanol from the transesterification process was observed to be beneficial, as it facilitated the smooth dissolution of the oxidant (molecular oxygen) from the gas phase to the reactive liquid medium, thereby enhancing the oxidation process in the liquid phase. The base residues remaining after transesterification also had a positive effect. This was not surprising given that basic conditions are usually beneficial to the glycerol liquid phase partial oxidation reaction.

The presence of inorganic salts that arise from the neutralization of the homogeneous base used in the transesterification process did not have any significant effect on the reactivity of the catalysts. However, we more recently identified trace amounts of sulfur compounds (the nature and origin if which are still unclear) in the streams that had

a negative effect. Our findings also indicated that some trace metals could also have an effect on the reactivity of the system, but more research is needed to clearly unravel the nature and extent of their action. Finally, among those catalysts we studied, the Pd-based one was the most tolerant to the glycerin impurities. Moving forward, it would be interesting to investigate the effects of impurities on bimetallic systems and/or when using alternative supports (other than alumina), as this might help us identify even more tolerant catalytic formulations.

In designing an optimal operation, such considerations and parameters could ultimately be used to identify the best tradeoff, requiring process designers and reaction developers to work together to choose the best combination of purification options, catalytic activity, and stability to meet required technical specifications (per customers and regulations) and product price point.

Although such considerations are useful for liquid phase processes, they are less relevant for gas phase processes, as vaporizing the impurities together with glycerol to feed a continuous reactor would be impractical due to the heterogeneity of the stream. However, some combined processes that accept crude glycerol as a raw material using specifically designed evaporation/separation devices to selectively bring glycerol vapors to the catalytic conversion reactor have been reported (Dubois, J. –L. (Arkema), WO 200812908, 2008, and Kijenski, J., *et al.*, (Inst. Chemii Przemyslowe), EP 1860090, 2007.)

HETEROGENEOUS CATALYSTS COKING

Heterogeneous catalysts coking is a common issue when addressing gas-phase upgrading of biomass-derived platform molecules. Biomass-derived oxygenated compounds have a high reactivity, which can lead to uncontrolled polymerization reactions between chemical intermediates. Such reactions produce carbonaceous compounds, known as "cokes," that chemically bind to the surface of the catalysts, blocking the active sites and drastically degrading catalytic performances. Another complicating factor to consider is that pure glycerol starts to decompose at about 300 °C, while glycerol atmospheric pressure gas-phase conversion processes typically take place at temperatures between 250 and 350 °C. Nevertheless, glycerol is conventionally introduced as an aqueous solution in the reactor, as it would be too challenging to attempt vaporization of this highly viscous compound under its non-diluted pure form.

Roughly, two strategies for coping with catalyst deactivation issues were proposed in the academic literature and in patents:
1. introducing small quantities of oxygen in the feed, either continuously or in pulses, with optional introduction of an oxygen-splitting functionality to the catalyst to facilitate continuous elimination of the cokes by "burning."
2. using a fluid catalytic cracking-like ("FCC") process in which the catalyst is continuously circulated between too reactors. The reaction takes place in the first reactor, while regeneration by coke burning takes place in the second.

Our research team has developed two additional strategies that can be applied to the conversion of glycerol to acrolein, which is an important intermediate in the chemical industry. The first strategy involves fine-tuning the catalyst's acidity—a critical parameter for the conversion reaction. Indeed, the catalyst must be sufficiently

acidic to enable the glycerol double dehydration reaction to acrolein, but not too acidic, as that would promote the undesired formation of cokes.

The required balance was achieved by designing a composite catalyst based on a rather conventional acidic active phase known as silicotungstic acid, which we supported on an original carrier composed of ZrO_2 (zirconia) nanocrystallites dispersed in a nano-designed honeycomb-like structure of silica (called an "SBA-15"). The silica structure was designed to be resistant to the hydrothermal conditions under reaction, and its pore-size diameter was set at an optimal value for avoiding the confinement effects that would lead to undesirable side-coking reactions. The use of an SBA-15 as a host matrix for the ZrO_2 support further enables conferring to the whole catalytic system mechanical properties that ZrO_2 alone, while being a very good support from a chemical point of view for this reaction, could not afford. With this innovative composite catalytic system, we could significantly extend the life of the silicotungstic acid active phase, by substantially limiting its coking.

The second strategy we used was based on continuous regeneration in a specifically designed single reactor. It consists of a two-zone fluidized bed reactor (TZFBR; Fig. 3), in which the catalyst is continuously mixed (fluidization) by an upflow gas stream. A glycerol cane is plunged into the middle of the reactor from above. In the process we designed, the fluidization gas contained oxygen to regenerate the catalyst. To avoid oxidation of the reactants and products as well as creation of explosive atmospheres, the system must be perfectly controlled so that all of the oxygen is consumed just before the place where glycerol is introduced. With an optimized system, we were able to substantially extend the life of a conventional silicotungstic acid catalyst directly supported on a silica (without ZrO_2 modification), thus proving our concept.

There is still work to do, and we are enhancing these technologies in the lab and at demonstration scale with industrial partners. We have also designed an efficient liquid-phase continuous process with Japanese partners; are working with Philip Xiaofei Ye, a professor at the University of Tennessee (Knoxville, Tennessee, USA) to develop an alternative catalysts regeneration technology based on cold plasma; and have designed a new glycerol
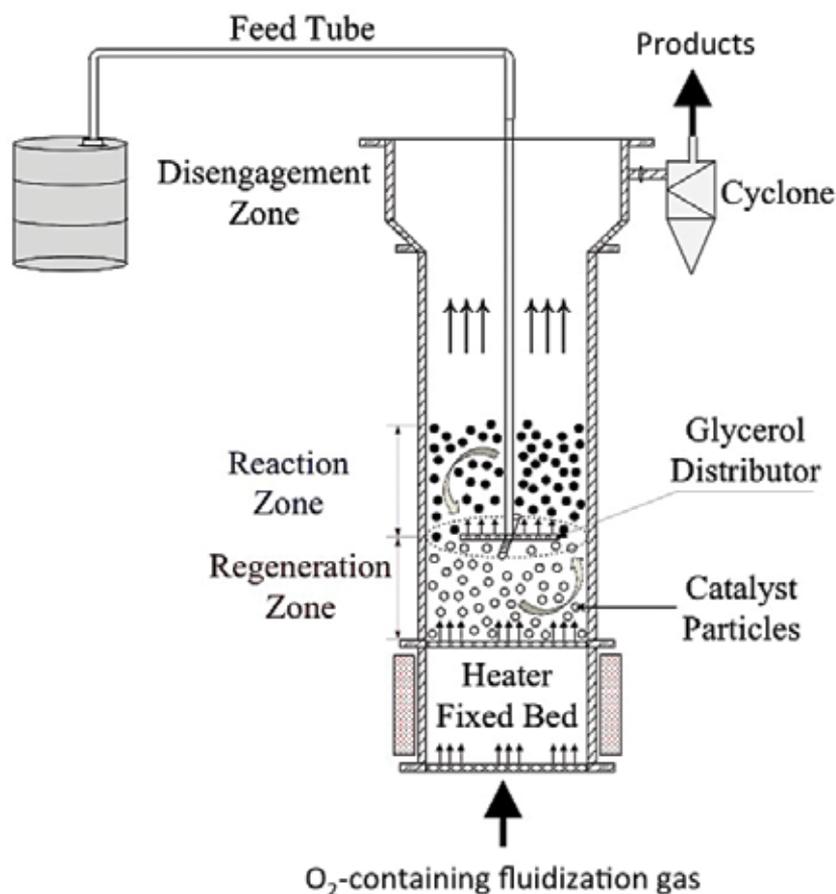

FIG. 3. Schematic principle of the two-zone fluidized bed reactor (TZFR) used for continuous regeneration of the catalyst

value chain based on allyl alcohol from glycerol that presents many advantages compared to the conventional value chain mimicking the petroleum one (patents filed).

Many groups in the World are working on new technological solutions, and it is only a matter of time before novel technologies for increasing the value of glycerol hit the market and generate a new and more profitable value chain interweaved with biodiesel industry.

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