Special Feature

Understanding the glycerol market

Rosaria Ciriminna[1], Cristina Della Pina[2], Michele Rossi[2]* and Mario Pagliaro[1]

[1] Istituto per lo Studio dei Materiali Nanostrutturati, Palermo, Italy
[2] Dipartimento di Chimica, Università degli Studi di Milano, Milano, Italy

As a result of the booming biodiesel and oleochemicals manufacturing taking place worldwide since more than a decade, 2 million tonnes of glycerol consistently reach the market every year, even though after a decade of growth the total glycerol supply is expected to slightly decrease in 2014. Today the supply of glycerol is entirely independent of its demand, as there is as much glycerol as the amount of vegetable oils and animal fats are hydrolyzed to make oleochemicals, or transesterified to produce biodiesel. This unique situation has led to consistently low glycerol prices, which initiated both the market penetration of glycerol in countries where it was not used due to traditional high price, as well as new uses of glycerol as raw material for the production of value added chemicals. This article sheds light on the market of this uniquely versatile chemical whose number of applications is unique amid all existing chemicals.

Keywords: Biodiesel market / Glycerol / Glycerol-derived products / Glycerol market / Glycerin / Oleochemicals market

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1 Glycerol, the eminent oleochemical

Glycerol (1,2,3-propanetriol) is the oldest organic molecule isolated by man having being obtained by heating fats in the presence of ash to produce soap since as early as 2800 BC [1]. Providing the molecular skeleton of all animal and vegetable fatty oils, the triol is liberated at slightly more than 10% by weight of tryglicerides level either in the hydrolytic synthesis of fatty acids (soap), and in the transesterification of oils and fats with methanol to make biodiesel (Fig. 1).

Along with FAME, fatty alcohols and fatty acids, glycerol is thus an eminent oleochemical.

With the price of one barrel of oil consistently above 100$, the oleochemicals industry in the last decade has been growing steadily meeting the increasing demand of cheaper (and greener) alternatives to petrochemicals of ever increasing cost [2]. For example, in mid 2012 the Malaysian palm and rubber plantation firm Felda Global Ventures Holdings raised up $3.1 billion at the Malaysia's stock exchange, in the second largest 2012 initial public offering in the world [3].

To understand today's glycerol market it is relevant to look back at its historic development. Glycerol is the raw material for manufacturing leading explosive nitroglycerin, i.e., the base for dynamite and cordite, the smokeless gunpowder for all types of munitions. Invented by Sobrero in 1846, nitroglycerin in its natural liquid state is very volatile and extremely hazardous to handle. In 1866 Nobel discovered that mixing nitroglycerin with siliceous sedimentary rock "kieselguhr" (a form of silica mined in Germany) could turn the liquid into a malleable paste, known as "dynamite," which could be kneaded and shaped into rods for blasting rock through a detonator activated by means of a strong shock.

Glycerol shortly became a strategic military resource. Hence, when glycerol demand due to the 1st World War exceeded the supply from the soap industry, reasons of military security led to the first synthetic plants for glycerol manufacture both in Europe and in the United States, where glycerol for weaponry was produced through microbial sugar fermentation [4]. For example, when World War I began in 1914, DuPont was the only company in the US which manufactured smokeless powder and was the nation's leading producer of dynamite (in 2 years DuPont' sales increased from $25 million to $318 million) [5].

In 1943 the German chemical cartel I. G. Farben started glycerol production from petroleum feedstock, using the new high-temperature chlorination of propene to allyl chloride process. Similar plants were built after the 2nd World War in Europe, in Japan, in Russia and in the United States. In general, for more than 60 years about 25% of the global

Correspondence: Dr. Mario Pagliaro, Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy
E-mail: mario.pagliaro@cnr.it
Fax: +39 091 680 92 47

Abbreviations: EU, European Union; **FFA,** free fatty acid

*Additional Corresponding author: Prof. Michele Rossi
E-mail: michele.rossi@unimi.it

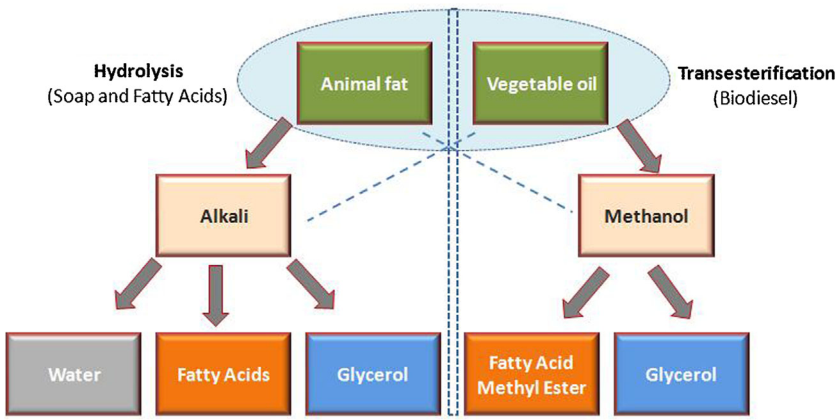


Figure 1. Both saponification and transesterification reactions yield 10 wt% glycerol as main by-product.

glycerol demand was met by the petrochemical synthesis from propylene; and the other fraction was obtained from soap manufacturing, where glycerol by-product has been a source of revenues and profits for 60 years. Since 2003, however, the synthetic glycerol market has been disrupted due to the biodiesel and oleochemicals glycerol surplus.

2 Biodiesel glycerol

The global production of bioglycerol from biodiesel has climbed from 200 000 tonnes in 2003 to 600 000 tonnes in 2006, progressing to >2 million tonnes in 2011. In 2012, it exceeded again 2 million tonnes including also the fraction due to oleochemicals manufacturing. Traditional market usages for refined glycerol in the United States, Asia, Latin America and Europe suddenly were not capable anymore to absorb this surplus, and most key players pulled out of the market.

In Japan, the main glycerol production factories ceased operations in October 2005. In the US, Dow Chemical closed its 60 000 tonnes/year glycerol plant (the world's largest) in Texas in early 2006 when also Procter & Gamble shut down its 12 500 tonnes/year plant near London. Few months later Solvay closed (and later retrofitted) its glycerol plant in Tavaux, France.

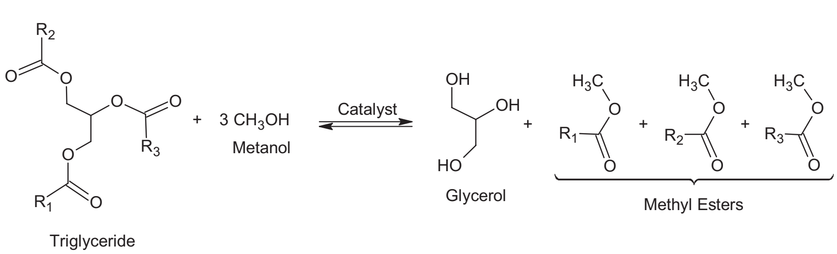
Today, Dow operates in Germany the only chemical plant where glycerol is synthesized according to current Good Manufacturing Practices, affording glycerol aimed to pharmaceutical companies to a purity level of more than 99.7%. Synthetic glycerol, though, is now a negligible fraction of the yearly glycerol output (<5000 tonnes out of 2 million tonnes).

In 2003 the Directive 2003/30/EC on the Promotion of the use of biofuels and other renewable fuels for transport was enforced in the European Union (EU). This new regulation requiring minimum volumes of biofuels (5.75% by 2010) in all transport fossil fuels (petrol and diesel), originated the fiscal incentives that led to the biodiesel boom. In detail, subsidies to biodiesel manufacturers were enforced as tax exemption in main EU countries (Germany, France, Italy, and Spain). The US soon enforced similar regulation with a $1-per-gallon biodiesel tax incentive first implemented in 2005 [6].

The technology to make biodiesel is simple. In the traditional manufacturing process, biodiesel is produced by the homogeneous transesterification reaction between vegetable oil and methanol, catalyzed by strong base. It is an equilibrium reaction with the stoichiometry shown in Scheme 1.

Like many homogeneous chemical processes carried out in batch, the traditional route to this important biofuel is obsolete affording plenty of waste made of spent catalyst, raw glycerol (80 wt%), unreacted methanol, soaps and salts. Several alternative heterogeneously catalyzed processes have been introduced in the last decade [7], among which the

100 kg of oil + 10.5 kg MeOH = 100 kg methyl esters (biodiesel) + 10.5 kg glycerol



Scheme 1. Transesterification of a triglyceride with methanol.

Esterfip continuous process is used since 2006 by the Sofiprotéol group to produce 200 000 tonnes/year of biodiesel at a plant in the south of France over a solid basic catalyst [8]. The heterogeneous process affords much purer glycerol (90–95%) and avoids the expensive distillation step to isolate pure glycerol.

Very soon countries with large availability of land such as Argentina and Brazil or where palm or coconut oil plantations were in place, such as Malaysia, the Philippines, Indonesia, Colombia, and Thailand started to manufacture and sell vegetable oils to biodiesel manufacturers in Europe and in the US, and to and oleochemicals producers in Asia.

The outcome was a flood of glycerol that disrupted a chemical market that in the above mentioned petrochemical/oleochemical split existed since the early 1940s; even though production of soap-derived glycerol (glycerine, or glycerin) started as early as the late 1850s with the commercialization of the first personal care "consumer" products in Europe and in the US.

In brief, until 1999 the main glycerol supplier was the oleochemicals industry. Ten years later the biodiesel industry had become the main overall supplier (Fig. 2).

In 2005 the top three global glycerol suppliers were Procter & Gamble, Cognis and Uniqema (now Croda) that, combined, had more than one third of the market share [10]. Five years later, the main glycerol suppliers had become biodiesel and oleochemical companies mostly based in the Asia Pacific region (Malaysia, India, Indonesia, and Philippines, Table 1) [11].

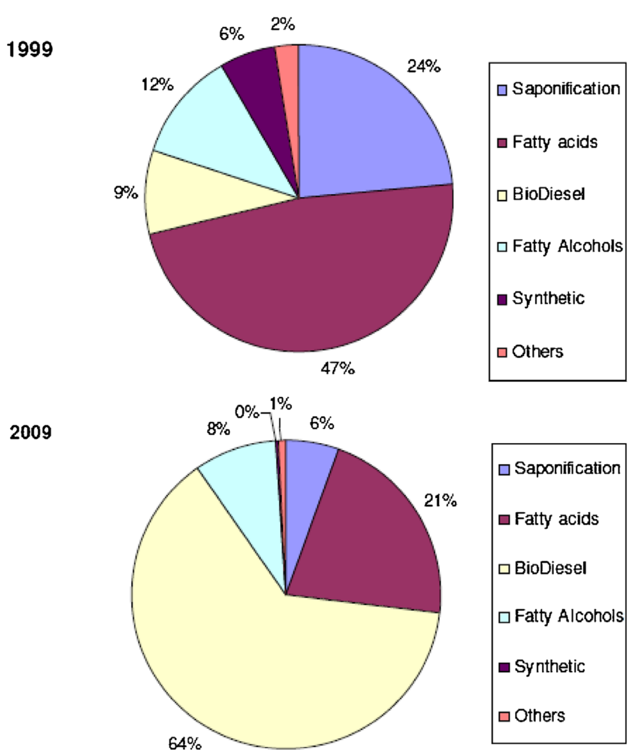


Figure 2. Main drivers affording glycerol before (*top*) and after (*bottom*) the biodiesel boom (reproduced from Ref. [9], with kind permission).

To absorb this surplus, developing new chemical uses of glycerol as platform chemical suddenly became urgent [12]. The number of research papers dealing with new usages for glycerol published annually between 2000 and 2007 doubled to more than 7000, and a number of new catalytic routes to high added value products were discovered or re-discovered, improved, and applied such as in the case of the acetic acid catalyzed route to epichlorohydrin now successfully produced by Solvay and by several other chemical companies in Asia and in Europe [13].

Recent estimates on the new usages of the 2 million tonnes of the 2015 refined glycerol market were projected to equal the traditional usages of this versatile molecule finding broad application in the pharmaceutical, personal care and tobacco industries (Fig. 3) [14].

In 2008 some of us wrote the first edition of a book [12] on the emerging usages of glycerol as a platform chemical, as chemical ingenuity was rapidly opening the route to glycerol derivatives for use in fields as diverse as fuels, chemicals, pharmaceuticals, detergents, and the automotive and building industries. In the book's preface, we were writing that: "*In three to five years glycerol will be seen as an environmentally friendly way of replacing competing petroleum products*."

This forecast turned out to be true. Many of the glycerol derivatives mentioned therein are now commercially manufactured. Examples include epichlorohydrin, propylene glycol (1,2-propanediol), and methanol; and many others

Table 1. Top glycerol producers in 2010

Cognis Corporation (USA)
Emery Oleochemicals (Malaysia)
Croda InternationalPlc (UK)
Dial Corporation (USA)
Dow Chemical Company (USA)
Godrej Industries Ltd. (India)
Sofiproteol Group (France)
IOI Oleochemical Industries Berhad (Malaysia)
Acidchem International Sdn Bhd (Malaysia)
Kao Corporation (Japan)
Pacific Oleochemicals Sdn Bhd (Malaysia)
Palm-Oleo Sdn Bhd (Malaysia)
Procter & Gamble Chemicals (USA)
PT Cisadane Raya Chemicals (Indonesia)
PT Sinar Oleochemical International (Indonesia)
PT Sumi Asih Oleochemical Industry (Indonesia)
Setuza A. S. (Czech Republic)
Unilever (Malaysia) Holdings Sdn Bhd (Malaysia)
United Coconut Chemicals, Inc. (Philippines)

Source: Glycerol: Global Industry Analysts, *A Global Strategic Business Report*, 2011.

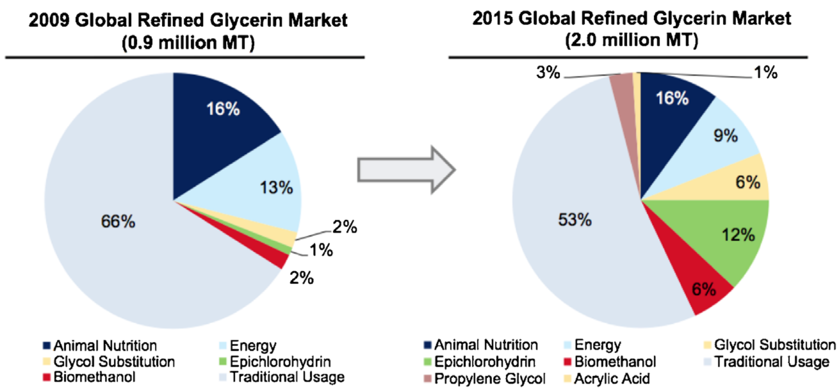


Figure 3. Current and future glycerol applications (image reproduced from Ref. [14], with kind permission).

will emerge in the near term including the manufacture of acrylic acid via glycerol dehydration to acrolein.

In this highly dynamic and somehow uncertain context, one might wonder whether bioglycerol as platform chemical will remain economically sustainable. Or if ceasing of biodiesel fiscal incentives will lead to a rapid fall of the glycerol output and to unsustainable price increases. The answer to these questions requires a better understanding of the glycerol market in today's global economic and energy contexts.

3 The problem with biodiesel glycerol

The problem with crude glycerol from biodiesel production is that it has heavy contamination from toxic methanol and has a high salt and free fatty acids (FFAs) content and a substantial color (yellow to dark brown) [15].

This makes crude glycerol unsuitable for most traditional glycerol markets. The conventional biodiesel manufacturing process utilizes a 6:1 molar ratio of methanol to oil in order to drive the reaction to completion. Most of the excess alcohol ends up in the bioglycerol layer from which costly methanol is recovered via relatively inexpensive flashing or distillation. Purifying high boiling point glycerol via distillation, however, is much more expensive. Hence, perhaps not surprisingly, a number of bioglycerol leakages from biodiesel plant were soon reported, such as in the case of the Alabama Black Warrior river contaminated in 2007 [16].

Still today, a large portion (16%, Fig. 3) of the overall production of glycerol goes into animal feed stock. Cattle, indeed, can tolerate poisonous methanol contaminating raw glycerol, and still efficiently absorb the energy content of the molecule. Adding 7.5 wt% crude glycerol to cattle rations improves the animal's feed to weight-gain ratio, as ruminants can handle toxic methanol and its breakdown product, formaldehyde [17]. Discovered by us in 2008 [18], the only other major use of crude biodiesel glycerol is as superior additive for manufacturing cement of enhanced performance (enhanced concrete strength, and grinding and handling aid for cement) replacing petrochemical amines and glycols.

Bioglycerol streams normally contain 65–85% (w/w) glycerol and >20% methanol. The rest is a mixture of water, methyl esters and lipids, inorganic salts (catalyst residues), FFAs, unreacted mono-, di-, and triglycerides, and a variety of other "many organics non-glycerol" (MONG) in varying amounts (Table 2).

Biodiesel manufacturing started in Austria in 1985 [20]. Out of the 31 biodiesel plants an Austria's leading company (BDI-BioEnergy) has built globally, 26 of them use a proven homogenous potassium-based catalyst. Potassium-based catalysts are better than NaOH, particularly for feedstocks with high FFA content (up to 20%), as they ease separation and recovery of soaps and FFA from glycerol, with further yield increase.

Methyl alkoxides are the current industry standard as they allow almost quantitative biodiesel yields [21]. Hence, plants using hydroxide catalysts are switching to methylate catalysts (the industry has now moved to >30% sodium methylate). Companies such as BASF and Evonik, for instance, recently built sodium methylate manufacturing plants in Brazil and Argentina to reduce catalyst transportation and storage costs.

Rapeseed, soybean and palmitic oils have the most suitable physico-chemical charateristics for transformation into biodiesel. The raw oil is refined by degumming

Table 2. A typical range of bioglycerol composition (adapted from Ref. [19], with kind permission)

Material	wt%
Glycerol	65–85%
Ash	4–6%
Methanol	23.4–37.5%
Water	1–3%
Sodium	0.1–4%
Potassium	0.1–5%
Iron	7–11 mg/kg
Phosphorous	60–110 mg/kg

(elimination of lecithins and phosphorus) and deacidification (elimination and recovery of FFAs which comprise some 2% of the original product).

The refined oil is thus charged into large batch reactors and heated at 55–60°C with an excess mixture of methanol and sodium or potassium methylate, using a methanol: oil = 6:1 molar ratio. After reaction for 2 h, the mixture is left to stand. The glycerol–methanol solution is heavier than methanol and the esters, and is run off from the bottom of the reactor.

To find use in food grade and pharmaceutical applications, the bioglycerol stream must be purified. We remind here that fatty acid and fatty alcohol producers refine glycerol making a clean glycerol co-product (the "splitter crude") that is not sold into the commercial market, but moves directly into the refining process to become USP certified or kosher/halal certified if the process and feedstocks are free of animal contaminants. Refined glycerol is classified into three main classes:

- **Technical grade** – used as a building block in chemicals, not used for food or drug formulation;
- **USP glycerol** from animal fat or plant oil sources, suitable for food products, pharmaceuticals;
- **Kosher glycerol** from plant oil sources, suitable for use in kosher foods.

Purified glycerol is generally sold as 99.5% or 99.7% pure. Crude biodiesel glycerol, even at 80% purity, cannot be used by traditional oleochemical refiners because it would damage expensive pipe and storage equipment. Prior to use it must be refined to an acceptable purity level in dedicated refineries and then either sold at low price as "technical-grade" refined glycerol or, more conveniently, further refined to USP or kosher/halal grade (Table 3).

A 2011 analysis aimed to estimate the cost of glycerol purification up to 98 wt% (by combination of neutralization, centrifugation, evaporation, and column distillation) concluded that the lowest cost for glycerol purification was 0.15$ per kg [22].

Traditional purification of crude glycerol employs high temperature, vacuum-distillation. Glycerol at atmospheric pressure indeed boils at 290°C. The process is energy-intensive and thus a cost-efficient refinery using distillation requires large-scale operation. Such a refinery can cost upwards of $20 million, which excludes small-to-medium-scale biodiesel plants.

Table 3. Purification quality of glycerol can be identified by its grade

Refined glycerol	Purity
Technical grade	95.5%
USP	96%, vegetable-based
USP	99.5%, tallow-based
USP/FCC-Kosher	99.5%
USP/FCC-Kosher	99.7%

4 A unique chemical market

For decades the glycerol market was mainly devoted to direct usage with only two major chemical end-uses as raw material, namely in the manufacture of nitroglycerine and in alkyd resins production. Highly pure glycerol was sold at high price (2500–4000$/tonne) to pharmaceutical and personal care product manufacturers and, prior to the biodiesel boom, the related revenues were an important part of the profitability of the soap and oleochemicals industries. Since 2003, however, the rapidly increasing glycerol oversupply caused a dramatic fall in the price of both refined and crude glycerol (Fig. 4).

In detail, the price for refined glycerol (99.5% Kosher grade) decreased from about 4000€/tonne in year 2000 to less than €450/tonne in early 2010, when the price of crude glycerol went to €0 per tonne, i.e., bioglycerol had become a waste product of no economic value, whose only use was as low-energy content fuel for incineration or for cattle feeding.

On the other hand, such unprecedented low prices generated new demand in China, India, Russia and Latin America, namely large regions of the world where glycerol in various areas such as oral and personal care, pharmaceuticals, and food and beverage products was historically *not* used due to its high price. The rapidly rising living standards of consumers in these large countries met the offer of low cost of glycerol. Hence, for example, in 2010 the main consumer of EU glycerol was Russia, absorbing 30% of the total Europe's export deliveries [23].

In affluent economies, too, glycerol consumption rose susbstantially (in the EU in 2010 it increased in one year only by 21%, to 319 698 tonnes). Similar double-digit growth was recorded in the United States and in South East Asia ("Asia-Pacific").

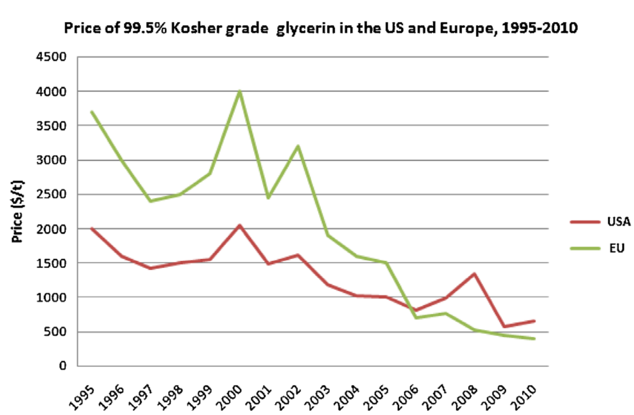


Figure 4. The change of the market price of 99.5% Kosher grade glycerol in the in US and Europe (realized by the Author, 2010).

The latter region surpassed Europe as the largest market in 2009. Today, Asia-Pacific represents the largest as well as fastest growing regional market for glycerol worldwide with increased demand for all applications, including new markets for refined glycerol, such as production of epichlorohydrin. Almost concomitantly, indeed, new industrial processes for the production of epichlorohydrin propylene glycol, that require refined (and not crude) glycerol, were established in China, Thailand and, to a lesser extent, in Europe and in the US [13].

Low cost glycerol is used as low-glycemic sweetener and is replacing previously cheaper polyols in many applications. For example, today glycerol is less expensive than other humectants such as propylene glycol and sorbitol. Hence, glycerol has become an essential component for cereal manufacturers and dried fruit processors due to its capability to enhance shelf life of products (glycerol not only prevents moisture loss but preserves the texture of food products, building humectancy of cereals, raisins, and dried fruits).

Thanks to the combination of new applications, market expansion in traditional markets and replacement of other polyols, the price of glycerol partly recovered since the 2009 historic lows. As of mid 2014, in the US pharmaceutical grade glycerol could be bought for \$900 per tonne, whereas crude glycerol (80% pure) was sold at 240\$/tonne [24]. Yet prices never reached the high levels expected by many analysts.

Showing the price trend for refined glycerol up to 2003, Figure 5 contains the prediction of a researcher that by 2010 the glycerol price could be "as low as \$0.35 per lb" [26]. Subsequent developments have shown that the above prediction was too conservative. The refined glycerol price plunged even more rapidly. In early 2007 it was 29–35 cents/lb; while at the end of 2009 prices were in "the low-to-mid 30s" [27].

In early 2012, the price started to recover with prices of vegetable glycerol in the US recorded at \$838/tonne–1014/tonne [28], and at \$700–780/tonne in Asia [29]; with good global demand across several key end-uses, particularly in food-grade and pharmaceutical applications. Eventually, in late 2013 (tallow) glycerol contract prices in the US were around \$900/tonne [30]; and Asia's (vegetable) refined glycerol prices were reported at an average of \$965/tonne due to higher feedstock (vegetable oil) prices [31].

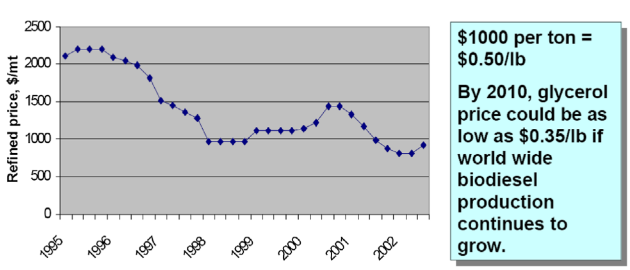


Figure 5. Price trend of industrial glycerol (reproduced from Ref. [25], with kind permission).

5 Conclusions and perspectives

The glycerol's price is historically volatile. Prior to the biodiesel boom, when one fourth of the global (and relatively low) demand was met by synthetic glycerol and the rest from soap and oleochemicals manufacturing, the price was dictated primarily by weather and by the fluctuating demand of soap and fatty alcohols. This volatility, that once was linked to the volatile *demand* of a chemical mainly used by the pharmaceutical and personal care industries, today originates from the volatile nature of the glycerol *supply*; which in its turn is influenced by two main factors: politics (i.e., fiscal incentives to biodiesel in the EU and in the US; and subventions to biodiesel and oleochemicals manufacturing in many countries) and oil.

In other words, as glycerol today originates as a by-product of biodiesel and fatty acids and fatty alcohols manufacturing, its supply is entirely independent of market demand. There is as much glycerol as much vegetable oils are converted into biofuels, and oleochemicals. Said otherwise, this is one of the few examples in economics of a good whose price is *not* affected by the demand for various end-use segments.

This explains the so called glycerol-derived products "pyramid of value." In order to generate profits, a company's product obtained from glycerol needs to be positioned close to the top of the pyramid of value, namely there where price fluctuations of glycerol will not make its product uneconomic.

Otherwise, sitting at the bottom of the pyramid – for example all usages of raw glycerol as such, like in cattle feeding or as concrete additive – customers will simply shift to the less pricey alternatives. Epicholorohydrin, propylene glycol, 1,3-propanediol, methanol, acrolein, glyceric acid, dihydroxyacetone, and similar derivatives obtained by chemoselective catalytic processes sit close to the top of the pyramid, where also highly pure glycerol for pharmaceutical and personal care usages resides.

Recent market analysis projects that demand for glycerine by-product of oleochemicals and biodiesel production will expand at an annualized average rate of 7% during 2007–2021; with a 6 million tonnes overall production in 2025 [6]. Graphs such as the one shown in Figure 6, produced by a reputed analyst company [6], are commonly presented in research papers and market reports.

Yet, after a decade of growth, the total glycerol supply is expected to slightly *decrease* in 2014 due to a 11% reduction in the global biodiesel production following lower output of biodiesel in the US, Argentina and Indonesia [33]. With about 60–65% of total glycerol output being generated as a by-product of biodiesel, this clearly shows the reliance of low-cost glycerol availability on biodiesel global production.

However, the price of crude oil as well as of petrol fuels remains at historic highs despite a global recession that caused a dramatic reduction of the world's industrial output since the global financial crisis started in 2008. Such high cost

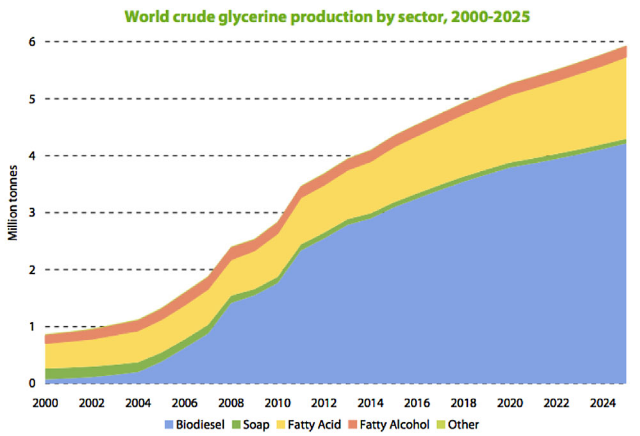


Figure 6. World crude glycerol production NY sector. Actual and projected values, 2000–2025 (reproduced from Ref. [32], with kind permission).

of oil translates directly and immediately into higher prices for petrochemical derived ingredients and into higher demand of biofuels. These poweful economic drivers meet what de Guzman aptly calls the consumer preference for "naturals" [34].

Now, even a 10% biofuel demand threshold is sufficient to create a definite price linkage between agricultural and petroleum prices [35]. At such high levels of linked oil and agricultural prices, the production of vegetable oils to be converted into biodiesel and oleochemicals ensures expanding revenues to farming companies, most of which today owe enormous plantations in many regions of the world including the African continent. These companies will continue to produce seeds and oil, and their yearly output will continue to make glycerol's supply substantially independent of its demand.

The market surplus of glycerol from biodiesel and oleochemicals (the supply) is far from being coped by new demand as platform chemical. Even assuming that all the industrial plants currently producing epichlorohydrin, methanol and propylene glycol will run at full capacity (which is not the case) not even 20% of the >2 million tonnes amount of crude glycerol generated in 2014 will find industrial use as chemical raw material. In these conditions, the price variations of both crude and refined glycerol will not impact the glycerol position as the main platform biochemical employed by the chemical industry as raw material.

The price recovery of the last 2 years already makes glycerol refining convenient. As soon as the first process to make acrolein via glycerol dehydration will be industrialized (likely within the next 2 years), along with many new biotechnology we rather forecast that low value added usages of crude glycerol as animal feedstock or as low energy will end. The highly functionalized triol glycerol molecule has too many extraordinary chemical and physical properties to continue to waste it in such 1st-generation biorefinery practices. Bioglycerol will be an eminent raw material for the 2nd-generation biorefinery [36].

This article is dedicated to University of St Andrew's Professor David Cole-Hamilton, on the occasion of his wonderful lecture at Palermo's FineCat 2014. We thank Doris de Guzman, Green Chemicals Blog, and Dr Thibaud Caulier, Solvay, for helpful discussion. Their contribution towards a research article useful to practitioners of the oleochemicals, biodiesel and glycerol industries is gratefully acknowledged.

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References

[1] Miller, S., *The Soapmaker's Companion: A Comprehensive Guide With Recipes, Techniques & Know-How*, Storey Books, North Adams, MA 1997.

[2] Kee, W. F., *Market and Technology Foresights for the Oleochemical Industry and Market Outlook for the SEA Region*, Frost & Sullivan, Mountain View, California 2010.

[3] Chin, J., Felda Global world's 2nd largest IPO this year, opens at RM5.39, *The Star Online*, June 28, 2012.

[4] Wang, Z. X., Zhuge, J., Fang, H., Prior, B. A., Glycerol production by microbial fermentation: A review. *Biotechnol. Adv.* 2001, *19*, 201–223.

[5] Pont, Du., Innovation Starts Here, http://www2.dupont.com/Phoenix_Heritage/en_US/1804_a_detail.html

[6] The US Congress has allowed the fiscal incentive to lapse three times, in 2010, 2012 and again in 2013. On April 2014, a Senate Committee approved a two-year extension of the $1-per-gallon biodiesel credit through 2015, retroactive back to January 1, 2014. For more information, see, R. Kotrba, Senate Finance Committee passes tax package with biodiesel credit, 3 April 2014, at the URL: http://www.biodieselmagazine.com/articles/41973/senate-finance-committee-passes-tax-package-with-biodiesel-credit

[7] Melero, J. A., Iglesias, J., Morales, G., Heterogeneous acid catalysts for biodiesel production: Current status and future challenges, *Green Chem.* 2009, *11*, 1285–1308.

[8] Bloch, M., Improved glycerin quality via solid catalyst trasnesterification technology: The Esterfip-H process, *Bio-Oil International Conference*, Vigo, Spain, February 2006, Available at: http://www.biodieselspain.com/articulos/axens.pdf (last time accessed: June 10, 2014).

[9] Bogaart, V., (Croda), "Glycerin Market Brief", 2009, http://www.npt.nl/cms/images/stories/Verslagen/Presentatie_Bogaart_Croda_15042010.pdf

[10] Graff, G., Glycerol glut sends prices plummeting. Purchasing, June 15, 2006, The archived article can be accessed at the URL: http://bepi.mpob.gov.my/news/detail.php?id=3395 (last time accessed, May 13, 2014).

[11] Global Industry Analysts, *Glycerol: A Global Strategic Business Report*, Industry Analysts, San Jose, California 2011.

[12] Pagliaro, M., Rossi, M., *The Future of Glycerol*, RSC Publishing, Cambridge 2008.

[13] Pagliaro, M., *Glycerol: The Platform Biochemical of the Chemical Industry*, Simplicissimus Book Farm, Milan 2013.

[14] Han, L. J. (Frost & Sullivan), *ICIS Asia Oleochemicals Conference 2013*, Kuala Lumpur, 30–31 January 2013.

[15] Singhabhandhu, A., Tezuka, T., A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock, *Energy* 2010, *35*, 2493–2504.

[16] Nor Roslam, W., Isahaka, W., Amali Che Ramli, Z., Ismail, M., et al. Recovery and purification of crude glycerol from vegetable oil transesterification: A review, *Sep. Purif. Rev.* 2014, doi: 10.1080/15422119.2013.851696

[17] Crude glycerin improves feed efficiency in finishing heifers, Van Cleef, E. H. C. B., Uwituze, S., Alvarado, C. A., et al. Cattlemen's Day, 2013, Kansas State University, Manhattan, KS, March 1, 2013, pp. 59–62.

[18] Rossi, M., Della Pina, C., Pagliaro, M., Ciriminna, R., Forni, P., Greening the construction industry: Enhancing the performance of cements by adding bioglycerol. *ChemSusChem* 2008, *1*, 809–812.

[19] Thompson, J. C., He, B. B., Characterization of crude glycerol from biodiesel production from multiple feedstocks. *Appl. Eng. Agric.* 2006, *22*, 261–265.

[20] For more information on the history of biodiesel, see History of Biodiesel at eXtension at the URL: http://www.extension.org/pages/27135/history-of-biodiesel#.U3HxS3m_ugg

[21] Sims, B., Catalyzing biodiesel growth, *Biodiesel Mag.* 2012, *9*, 24–28.

[22] Posada, J. A., Higuita, J. C., Cardona, C. A., Optimization on the use of crude glycerol from the biodiesel to obtain poly-3-hydroxybutyrate. *World Renewable Energy Congress*, May 8–13, 2011, Linkoping, Sweden.

[23] The Market Publishers, *Glycerol Other Than Crude (Including Synthetic): European Union Market Outlook 2011 and Forecast till 2017*, BAC Reports, Birmingham, UK 2012.

[24] *OPIS Ethanol & Biodiesel Information Service*, March 24, 2014, Vol. 11.

[25] Shaine Tyson, K., *Biodiesel R&D potential*, Montana Biodiesel Workshop, October 8, 2003.

[26] Taylor, J., US glycerine makers seek to use market changes, *Icis.com*, March 7, 2007.

[27] Graff, G., Glycerin demand climbs, with prices poised to follow, *Purchasing*, September 17, 2009.

[28] Taylor, J., Outlook '12: New uses make refined glycerine oleochem leader, *Icis.com*, January 4, 2012.

[29] Lei Lei, W., High inventory weighs on Asia refined glycerine market, *Icis.com*, January 13, 2012.

[30] Landress, L., Outlook '14: Oleochemical markets eyes US biodiesel sector's fate, *Icis.com*, December 23, 2013.

[31] Gan, A., Asia's refined glycerine prices to stabilise in Q4 2013, *Icis.com*, August 30, 2013.

[32] LMC International, *Feedstocks for Bio-Based Chemicals*, LMC International, Oxford, UK 2013.

[33] Agra Renewable Chemicals, 2014 glycerine supply to drop on lower fame production, April 9, 2014.

[34] de Guzman, D., *Oleochemicals: The Next Generation, Plant Bio-Industrial Oils Workshop*, Saskatoon, Saskatchewan, Canada 2013.

[35] Kaur Sandhu, A., *The outlook for agricultural feedstocks – supply, demand, price & relationship to crude oil*, Biowerkstoff-Kongress Conference, Cologne, March 14, 2012.

[36] Dumeignil, F., Pagliaro, M., Ciriminna, R. (Eds.), For a discussion of 2nd-generarion biorefineries see the Thematic series on *Biorefineries of Sustainable Chemical Processes*: http://www.sustainablechemicalprocesses.com/about/update/biorefinerysustainableworld

