Perspective

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Bioglycerol: a multifunctional aid for the construction industry

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Abstract: Crude bioglycerol from biodiesel and oleochemicals manufacturing is a multifunctional grinding aid and quality improver for the production of cement, capable of largely greening the concrete construction industry. This low-cost renewable by-product is now used by industry as a cement grinding aid as well as a curing and form-release agent, replacing oil-derived ingredients traditionally employed by the industry for over 50 years. Reviewing and providing new data on the usage and applications that have emerged in the last decade, we provide a unified picture answering most aspects required for a wider and fuller utilization of this versatile oleochemical in the ubiquitous concrete building industry. © 2015 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: cement; raw glycerol; concrete; cement aid

Introduction

With annual production exceeding 4 billion tons in 2013 and growing at 4% yearly rate,[1] cement manufacturing by heating limestone ($CaCO_3$), clay or shale (aluminosilicate), sand (silica), and miscellaneous iron oxides to about 1600 °C to form the 'clinker' mixture accounts for 5–7% of global CO_2 emissions. For at least two decades, therefore, major industrial and academic research efforts have aimed to improve the sustainability of cement production.[2] The resulting cement is a mixture of various minerals whose predominant (50–70%) mineral phase is tricalcium silicate (abbreviated as C_3S: Ca_3SiO_5) followed by dicalcium silicate (C_2S, 15–30%), tricalcium aluminate (C_3A, 5–10%), and ferrite (C_4AF, 10–15%).[3]

This energy-intensive process, if followed by a grinding process in which the cement clinker is mixed with gypsum and ground in a ball mill to a finely divided state, gives a particularly high surface area to the resulting 'Portland' hydraulic cement whose comprising particles are 90% (by mass) finer than 44 μm.

Typically a low-cost fuel, used to generate the large amount of thermal energy needed, is employed to heat the calcination furnace, whereas electrical energy is used to grind the resulting clinker in a rotating mill, and to cool the final cement product. The calcination and grinding processes account for 80% of energy consumption, while power for the cooler accounts for the remaining 20%.

In industrially developed countries, where the cost of energy accounts for 40% of the overall cost of production,

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thermal energy consumption has been reduced almost to the theoretical minimum of 3500 MJ per tonne of clinker. On the other hand, the consumption of power, in the 90–130 KWh per tonne of cement range, is increasing due to increasing demand for higher grade cements (increased fineness and reduced packset time).

To save energy, reduce cracking, and reduce corrosion, the concrete construction industry uses cement containing functional aids that are usually present as blends in finished cement particles, or topically applied products after cement application. Used in more than 60% of world cement production, additives are composed primarily of organic ingredients derived from crude oil.

Cement grinding additives (CGAs) are mostly organic compounds that are added to the clinker in the cement mill. Their main purposes are to reduce the energy required to grind the clinker into a given fineness (increasing the efficiency of the cement mill), improve flowability after grinding, and ease storage by reducing packset time and preventing hang-up on the silo's inner surface.

Raw glycerol by-product of biodiesel manufacturing is a performance-enhancer of cement increasingly employed by the concrete construction industry. Crude bioglycerol is a great anti-cracking, waterproofing, and grinding aid as well as a quality enhancer for the building industry.[4]

Following a 2008 patent application,[5] Rossi *et al.* in Italy reported that the addition of crude bioglycerol to clinker eases the clinker grinding process while considerably enhancing the strength of the resulting concrete, improving its resistance to compression. The discovery led to vigorous research efforts in many countries worldwide, and shortly afterwards these results were confirmed and extended. For instance, Johnson *et al.* in Panama confirmed the original results and found that crude biodiesel glycerol added to cement, not only affords stronger concrete structures but it is an effective form releasing agent allowing easier removal of mold structures used during construction.[6]

Similar results were reported from several laboratories including academic researchers in Indonesia,[7] and industrial scientists in the USA.[8] Almost concomitantly, Jerzykiewicz *et al.* in Poland reported in 2009 that glycerol fractions from biodiesel production show excellent lubricant and anticorrosive properties,[9] opening the route to new applications of crude glycerol in lubricant manufacturing.

The 2008 discovery created a considerable outlet for glycerol liberated at slightly more than 10% by weight of tryglicerides level in the transesterification of oils and fats with methanol to make biodiesel, namely a 2 million ton per year output which has disrupted and reshaped a market that had existed unchanged for more than a century.[10]

In general, the benefits of using bioglycerol instead of oil-derived glycols or alkanolamines that are the major components of cement additives conventionally used by industry, are significant for both environment and industry. The advantages for industry derive from having a single, readily available material that offers all three major technical improvements required of cement additives, namely (i) enhanced concrete strength, (ii) grinding, and (iii) handling aids for cement.

In other words, in addition to increasing the efficiency of the mill, bioglycerol also provides important positive effects on the final cement, such as rheology of the fresh cement paste and improved strength development. In this study, we summarize achievements in a single account and identify opportunities for increasing utilization of this eminent green biochemical in the ubiquitous building industry.

Cement grinding additives

Cement grindings additives (CGAs) considerably decrease electrical energy consumption due to increased grindability to the required particle size (typically, 32 μm) relative to reference cement (Fig. 1).[11] Accordingly, for more than 50 years the cement industry has added small amounts of grinding additives traditionally consisting of triethanolamine (TEA) or diethylene glycol (DEG) during the milling process.[12]

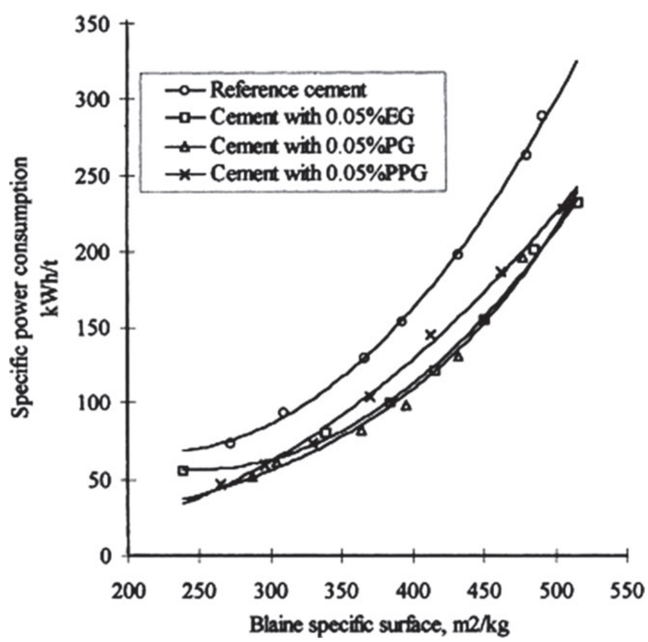

Figure 1. Specific power consumption *vs*. specific surface for cement alone, or with various additives (EG = ethylene glycol, PG = propylene glycol, PPG = polypropylene glycol)

The optimum dosage is achieved when a continuous monolayer is formed on the particle surfaces affording monomolecular coverage,[13] which typically requires a 0.01 to 0.2% by weight of organic compound, usually added as aqueous solution.

Higher amounts lead to lubrication effects with a consequent decrease in the rupture of the particles and reduction in efficiency of the mill (Table 1).

Recently, Heinz and Mishra have conducted a detailed theoretical study[14] aimed to understand the role of CGAs based and the role of molecules (including glycerol) adsorbed at the surface of the clinker/cement particles on the nanometer scale. The team employed four atomic species for C_3S to model the behavior of clinker surfaces, namely Ca^{2+} ions, SiO_4^{4-}, O^{2-} and OH^- ions formed upon hydration of the C_3S surface. In the ball mill fine cement particles (upper left corner in Fig. 2) are collected, whereas larger particles undergo further grinding until reaching the desired particle size.

Table 1. Required grinding aid dosage (g bioglycerol per 100 g cement) for covering the cement surface. (Reproduced from Weibel and Mishra[13] with kind permission.)

Cement fineness (Blaine, $cm^2\ g^{-1}$)	Grinding aid dosage for half covering monolayer between particles (wt %)	Grinding aid dosage for complete covering double layer between particles (wt %)
3000	0.015	0.03
4000	0.020	0.04
5000	0.025	0.05

The work showed that the main mode of action of grinding aids lies in the reduction of agglomeration energy. In other words, the organic additive molecules behave as surfactants by reducing the energy needed to break down the particles.

Results of the computational study suggest that the grinding aid molecules turn their polar functional groups toward the clinker surface. In detail, the polar hydroxyl groups (–OH) of the grinding aid reduce the surface polarity already partially offset by the water molecules dissociated into protons and hydroxide ions at the surface of the clinker. In their turn, the nonpolar hydrocarbon groups, smaller in the glycerol molecules than in diethylene glycol, further shield the polarity. We remind the reader here that during grinding of clinker particles, very little water is available through the dehydration of gypsum or

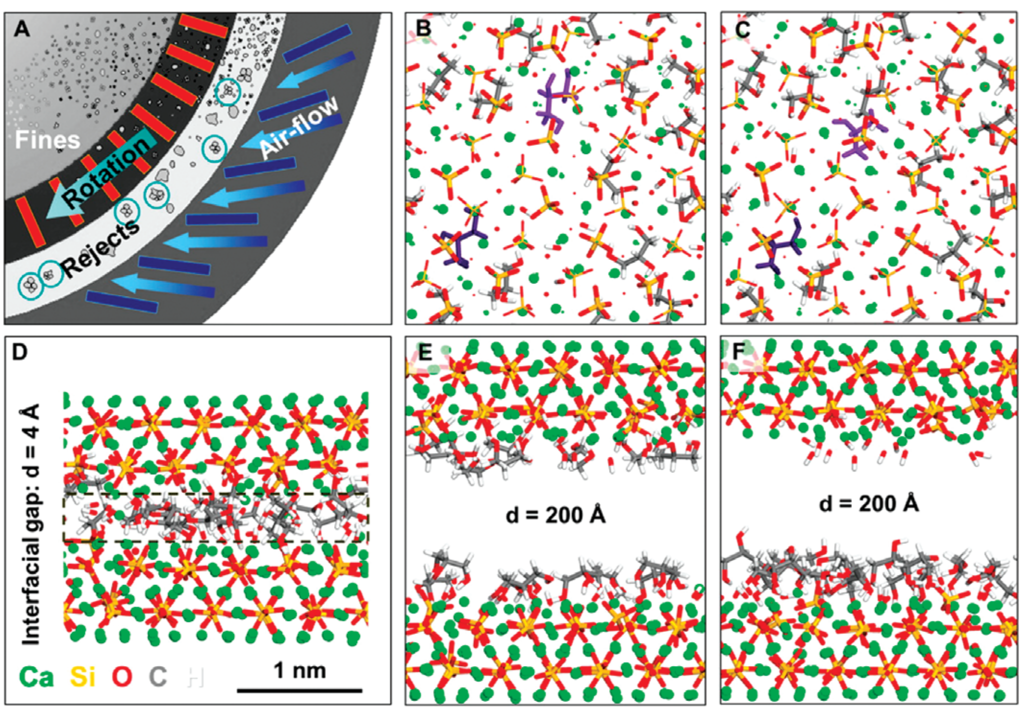

Figure 2. Simulated structure of glycerol molecules confined between cleaved clinker particle surfaces. Snapshots B and C below monolayer coverage in the top view indicate residual mobility during tens of nanoseconds (movement of molecules highlighted in purple and blue from B to C). The distribution of adsorbed molecules on cleaved surfaces can vary between equal and one-sided (E and F). (Reproduced from Mishra *et al.*[14] with kind permission.)

the deliberate addition of additional water in the ball mill. Such water rapidly hydroxylates the CaO surface with formation of less polar $Ca(OH)_2$. Glycerol in that case reacts with hydroxylated surface of clinker phases such as C_3S, C_2S, C_3A, and C_4AF.

The surface-bound glycerol molecules act as a spacer to reduce agglomeration of the highly polar surfaces by creating an organic interlayer that effectively mitigates the attraction between the charged surfaces (Fig. 2(d)). This is the main reason agglomeration is reduced, as the timescale of the 'cleavage-agglomeration' process of nanoseconds is shorter than that of lateral molecular diffusion on the surface (microseconds).

In detail, calculations based on simulation of the cleavage process, show that interfacial gap between tricalcium silicate surfaces at monolayer coverage or above lowers agglomeration energies up to 95% in comparison to cleavage energies.

As a result, clinker surfaces coated with a glycerol monolayer attract each other moderately, enabling the formation of smaller agglomerates and enhancing the grinding efficiency; whereas, in comparison to tertiary amino alcohols, the distance of glycerol to superficial ions is shorter, resulting in stronger binding.

Remarkably, the team was able to disprove the role of electrostatic repulsion as no evidence of significant quantities of charges on clinker surfaces was found (e.g. ionic grinding aids do not have advantages over neutral ones).

Crude glycerol from biodiesel streams employed as CGA is not only superior to traditionally employed grinding aids such as TEA or DEG, it also outperforms pure glycerol as a CGA, affording cement with improved mechanical and textural properties, with lower energy consumption during the grinding of different clinker samples originating from widely different cement plants (two in Italy and another in Greece).[4]

In order to understand the excellent CGA properties of biodiesel-derived glycerol, Parvulescu *et al.* studied the interaction of glycerol with cement clinkers.[15] Again, the results of these investigations point to surface tension modification of the clinker particles as the main effect of bioglycerol during the grinding process. No significant change in the composition of the clinker in the presence of the additive was observed, even if high loadings of additive were used.

The formation of polyglycerols or dehydrated/oligomeric species, which in principle can take place due to local overheating in ball mills as calcium hydroxide is an excellent known catalyst for linear polyglycerol formation,[16] was *not* significant and therefore it is not responsible for the significant enhancement of the milling process due to bioglycerol.

We remind here that the crude glycerol stream from biodiesel normally contains a widely varying glycerol amount (25–80 wt%, depending on the plant, catalytic process and oil source), 6–12% methanol (expensive methanol is usually recovered via distillation) and 20–30% soap (free fatty acid salts) formed via undesired saponification reaction during the biodiesel production process, and a substantial color (yellow to dark brown).[17] Moreover, depending on the oil used to produce biodiesel, crude glycerol has a remarkably high α-tocopherol content (0.04–6 mmol/L), which leads to the excellent anticorrosive and antioxidant properties discovered by Jerzykiewicz.[9]

The high content of residual soap explains the enhanced action of crude glycerol as a CGA. The two other effects significantly impacting the performance of the grinding aid molecules are the reduction of surface polarity and the reduction of surface energy that goes along with the reduction of the surface polarity.[14]

The anticorrosion properties of crude glycerol explain why the addition of crude glycerol enhances the resistance to corrosion of finished concrete structures, despite the presence of chloride, which incidentally opened new possibilities of crude glycerol use as a washing agent, degreaser, antifreeze, and anticorrosive agent.[18]

In detail, the antioxidants present in the glycerol fractions from biodiesel production have an α-tocopherol-like structure, and their antioxidant activity is not only due to the phenolic group alone, as the adducts formed from carbon-centered radicals of α-tocopherol (following radical attack at several α-tocopherol positions) are energetically favored in relation to the phenolic ones (Fig. 3).[19]

Compression strength enhancer

Usually added at the clinker milling step, a variety of additives are used in industry as curing agents to improve the resistance to fracture of the finished cement. The high compression strength of cement structures is obviously important. Curing agents prevent fast hardening of wet cement paste which decreases its resistance to

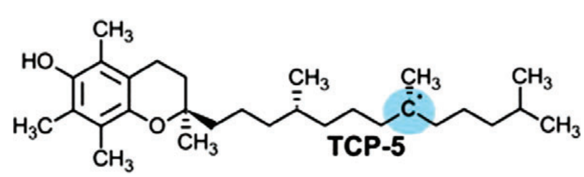

Figure 3. Carbon-centered radical formed upon radical attack of a radical on a non-phenolic position. (Reproduced from Jerzykiewicz *et al.*[19] with kind permission.)

compression. They work by preventing fast evaporation of water, and are usually comprised of polyols and other hydrophilic molecules.

The high cost of refined glycerol, a well-known effective agent capable of improving compression strength,[20] has traditionally limited its use in the cement industry for decades. Low-cost crude glycerol is a better curing agent, when compared to pure glycerol,[4] with optimal addition of 400 ppm of crude glycerol affording between 5 and 7% in the resistance to compression of the concrete object.

The results originally reported[4] in 2008 were confirmed and extended recently in Panama.[6] Concrete cylinders and joists were prepared by filling metal cylinders or joists with wet concrete. After 45 min of pouring the cement paste, a thin layer of crude bioglycerol was spread out on the surface of the set concrete mixtures by repeating at regular intervals three times during the solar day (in the morning, at midday, and in the afternoon) the addition of crude glycerol from a Panama biodiesel plant. The cylinders made of bioglycerol-added cement were slightly darker compared to analogous cylinders made with no added bioglycerol (Fig. 4).

Resistance to compression of the concrete structures for both joist and cylinder samples obtained after 7 and 14 days of curing was measured according to the ASTM 39/C 39M05 (for the compression of cylinders) and ASTM C78-02 (for the flexion of small joists) standards. Results in Table 2 show that the resistance to compression was between 10 and 15% higher for the joist structures made with bioglycerol-added cement, and 2.7 to 10% higher for the corresponding cylinders, pointing, as expected, to insufficient penetration of crude glycerol in the relatively high cylinder cement body. In commercial cement samples, as mentioned earlier and as done for the cement samples tested in Europe,[5] crude glycerol is added at the clinker milling stage becoming available as curing agent during set of the concrete structures.

Table 2. Resistances of concrete objects with and without crude bioglycerol. For cylinders the resistance towards compression and for small joists the resistance to flexion were measured. (Reproduced from Johnson *et al.*[6] with kind permission.)

Cement object shape	Sample	(kN)	(N mm^{-2})
7 days			
Small joist	Reference	13.89	1.79
Small joist	Reference + crude glycerol	16.11	2.08
Cylinder	Reference	85.30	10.36
Cylinder	Reference + crude glycerol	89.90	10.92
14 days			
Small joist	Reference	17.89	2.31
Small joist	Reference + crude glycerol	19.83	2.56
Cylinder	Reference	92.90	11.46
Cylinder	Reference + crude glycerol	95.50	11.77

Form release agent

In the concrete construction industry, form release agents prevent the adhesion of freshly placed concrete to the forming surface usually made of plywood, steel, or aluminum. A good release agent promotes the clean release of forms and helps to reduce surface imperfections in concrete, minimizing dusting of formed surfaces and

Figure 4. Cylinders of concrete midday (left) and at the end of the same day (right). The slightly coloured cylinders are the samples added with crude glycerol. (Photograph by Prof. S. Vásquez.)

reducing labor costs associated with stripping and cleaning forms and equipment.

Traditionally, form coatings are lubricant oils derived from petroleum, including diesel fuel and used motor oil.[21] Typically, during construction with plywood panels, the panels are treated with the chemical release agent before first use, and between each pour. This will prolong the life of the plywood panel by enhancing its release characteristics.

The use of glycols, including pure glycerol, as release agents was investigated as early as 1984,[22] when it turned out that glycerol was a good additive for traditional form release agents. It is therefore remarkable that crude glycerol alone is also an excellent form release agent.

Figure 5 shows evidence that easy removal of the molds from the concrete structures made from cement modified with crude glycerol leaves the molds clean; no stains are formed on the concrete structures as happens often with mineral oils. In detail, crude bioglycerol was spread out onto the internal surfaces of several molds of cylinders and joists. A recently prepared fluid concrete mixture was then poured in the molds. After 48 h the molds were stripped and the clean, excellent state of the inner surface was evident. The molds were easily washed with water, and left ready for reuse.

To explain this additional excellent property of crude glycerol of interest to the construction industry, it may be noted that in the case of fresh concrete, hydration reaction will dominate partial hydroxylation reaction due to the presence of suffienct amounts of water. Hence, the glycerol molecules in crude bioglycerol react with hydrated C_3S particles in hydrated concrete to form a soapy film which prevents adhesion, leaving no residue on the forming concrete surface. The presence of soap molecules in crude glycerol further enhances such anti-adhesion action, leading to a better form release agent. Furthermore, glycerol in crude bioglycerol is an effective antifreeze[23] agent, which favors its preferential use in cold weather conditions.

Figure 5. Molds and cylinders with cement residues following stripping of the set cement after 48 h. The mold in front, containing cement added with crude glycerol, is clean. (Photograph by Prof. S. Vásquez.)

Conclusions and perspectives

Crude bioglycerol obtained from the production of biodiesel is a multifunctional grinding aid and quality improver for the production and utilization of cement, providing the concrete construction industry with several economic and environmental benefits.

Technical and economic benefits include enhanced concrete strength, easier (and lower cost) grinding and handling with access to higher grade cement, and reduced construction time due to easy removal of plywood and other molding structures when crude bioglycerol is utilized as a form release agent.

Most of the beneficial properties of crude glycerol as CGAs can be rationalized in light of the reduction of the agglomeration energy of cement particles as cleavage and agglomeration of cement particles play a key role in cement grinding, hardening, and ultimately, in the stability of concrete building structures.[14]

Similar excellent results using crude biodiesel glycerol as a concrete additive are confirmed and reported on a regular basis from many countries, including recent tests in Portugal.[24]

A decade ago, a large construction products company started to commercialize crude glycerol as a cement quality improver, first in Europe and then worldwide.[25] The new additive, and its reliable sourcing from one or more selected biodiesel plants, incidentally proved to be capable of effectively replacing oil-derived additives purchased by a few large oil refineries.

For example, during the devastation brought about by hurricane Katrina in 2005 in the USA, the New Orleans petrochemical refineries were shut down, interrupting the supply of numerous chemicals, including ethylene and propylene glycols. This led said construction products company to replace oil-derived glycols with crude glycerol from biodiesel refineries. In 2010, when the annual market for grinding aids in the EU exceeded 50 000 tonnes, market consumption of crude glycerol as a CGA was estimated to be at least 10 000 tonnes.[24]

Since then, the commercial utilization of crude glycerol by the construction industry has steadily increased, even though figures are generally not published.

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What is remarkable from a scientific and environmental viewpoint is that the use of crude glycerol in construction provides additional environmental benefits that should not be underestimated. In the USA, for example, the use of diesel fuel as a form releasing agent has recently been banned. Diesel oil is combustible, contributes to smog, and presents health and safety risks to workers. Both diesel and used motor oils also contaminate the soil and groundwater where the cement was unloaded and applied. New bioglycerol-based cement release products,* on the other hand, consist of biodegradable crude glycerol thereby fully meeting the new environmental regulation.

Construction companies traditionally using oil-derived cement additives, as well as manufacturers of construction products considering switching to renewable glycerol may worry about the price volatility of glycerol, an oleochemical whose output primarily relies on large biodiesel and fatty alcohols and fatty acids production. However, the price of glycerol remains low, and it will not return to the high levels prior to the biodiesel and oleochemicals boom.[10]

Overall, the combined global production of biodiesel and fatty acids and alcohols is continuing to grow as governments and consumers increase the mandate of biodiesel in diesel fuel and the demand of greener and safer chemicals, respectively.[26] As a consequence, the global glycerol supply (of which 65% is generated as a by-product of biodiesel and the remnant from fatty alcohols) continues to grow, albeit at a lower rate than in the last few years. Accordingly, following ample supply as of December 2014 crude glycerol (80 wt%) was sold at about \$200/tonne in China and Southeast Asia,[27] and at \$130/tonne in Europe (where even refined pure vegetable kosher glycerol was sold at record low prices <€400/tonne).[28]

By reaching long-term agreements with biodiesel and oleochemical companies, as chemical manufacturers did when opting to replace propylene with glycerol in related chemical production of epichlorohydrin,[23] construction products companies will be able to secure nonvolatile prices for their new admixture products based on crude bioglycerol. Construction companies using crude glycerol, in their turn, will benefit from a better, faster construction process with reduced occupational health hazards and a far better environmental footprint† for their products: the buildings in which we all live and work.

*See for example, the *Eco Slide* product developed in 2013 by Extreme Biodiesel in the US.

†A thorough life cycle assessment (LCA) of using crude glycerol in place of oil-derived additives is an interesting task that we leave to LCA professionals.

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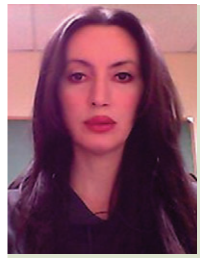

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Sebastián Vásquez Bonilla

Sebastián Vásquez Bonilla, research chemist and lecturer at Panama's University, has worked on catalysts to reduce soot from diesel fuel combustion, catalytic hydrogenation of acetylene, catalytic reduction of NOx, photochemical paint stripping, production of biodiesel, use of Panamanian natural zeolites, and other topics. His team has advanced the use of crude glycerin in the concrete construction industry. Dr Vásquez is also a frequent columnist in leading local newspapers.

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Mario Pagliaro is a chemistry and solar energy scholar based at Italy's CNR where he leads a research Group whose achievements are reflected in over 130 research papers, 20 books, several book chapters and patents. His research Group organizes the SuNEC Sun New Energy Conference and the FineCat Symposium on Heterogeneous Catalysis for Fine Chemicals, held in Sicily every year.