CHEMISTRY & SUSTAINABILITY
CHEMSUSCHEM
ENERGY & MATERIALS

Accepted Article

Title: Aquivion PFSA as an Efficient Pickering Interfacial Catalyst for the Hydrolysis of Triglycerides

Authors: Marc Pera-Titus, Hui Shi, Bing Hong, and Flora Fan

To be cited as: *ChemSusChem* 10.1002/cssc.201700663

Link to VoR: http://dx.doi.org/10.1002/cssc.201700663

A Journal of ChemPubSoc Europe

WILEY-VCH

www.chemsuschem.org

10.1002/cssc.201700663

Aquivion® PFSA as an Efficient Pickering Interfacial Catalyst for the Hydrolysis of Triglycerides

Hui Shi,[a] Zhaoyu Fan,[a]* Bing Hong[a] and Marc Pera-Titus[a]*

Abstract: Aquivion® Perfluorosulfonic Superacid catalyzed efficiently the solvent-free hydrolysis of glyceryl trilaurate at 100 °C and ambient pressure *via* the genesis of stable Pickering emulsions.

Free fatty acids (FFAs) are major components in the synthesis of a great variety of products such as soaps, detergents, lubricants, paints, cosmetics, pharmaceuticals and food additives.[1] Biodiesel can also be produced from fatty acids by esterification with methanol.[2] FFAs are produced industrially by fat splitting (i.e. hydrolysis of triglycerides, TGs) either under superheated steam to promote the water solubility (*e.g.*, Colgate-Emery,3 Twitchell,[3c-3d,4] Eisenlohr[3c-3e,5] processes), or by saponification with a strong base.[3d] TGs can also be hydrolyzed under subcritical water enhancing water solubility in the oil phase.[6] However, all these processes suffer from harsh reaction conditions (i.e. high temperature and pressure, strong acidity/basicity, use of phase-transfer reagents and surfactants[7]), leading to thermal decomposition and corrosion, as well as to multiple steps for purification.

As a greener alternative, solid acid catalysts operating at milder conditions have been advocated for the hydrolysis of vegetable oils and fats. Nonetheless, as a rule, acid catalysts exhibit poor activity even at high temperature (150-350 °C) due to resilient mass transfer limitations.[8] The catalytic activity for TG hydrolysis could be certainly enhanced by designing catalysts affording simultaneous emulsification. Indeed, it is well known that preferential location of lipases at the W/O interface is a key driver for physiological lipid digestion,[9] as well as for the industrial hydrolysis of TGs over naked and immobilized lipases.[10] The sitting of lipases at the W/O interface can be fostered in the presence of µ-emulsions generated using either surfactants (*e.g.*, Aerosol®OT) or surface-active molecules, conditioning in turn their interfacial activation.[11]

Recently, we among other authors have shown how a rational design of the surface properties of heterogeneous catalysts can boost the interfacial activity in biphasic reactions *via* the generation of Pickering emulsions.[12] This concept that we have termed as *Pickering Interfacial Catalysis* (PIC) has shown promising credentials in acid-catalyzed transesterification,[13] ester hydrolysis,[14] acetalization,[15] etherification,[16] and alkylation reactions.[17] In such examples, the particle assembly at the L/L interface can promote not only the interfacial area between the reagents, but also alleviate external mass transfer limitations. Furthermore, this concept might also offer the possibility of large energy saving and easy particle recycling.[18] Despite such benefits, developing PIC systems with tailored surface properties for target reactions remains still a great challenge. Here we report a series of interfacial acid catalysts relying on Aquivion® Perfluorosulfonic Superacid (PFSA) resin affording the acid-catalyzed biphasic hydrolysis of TGs into FFAs at mild temperature (100 °C) and ambient pressure in the presence of Pickering emulsions (Figure 1).

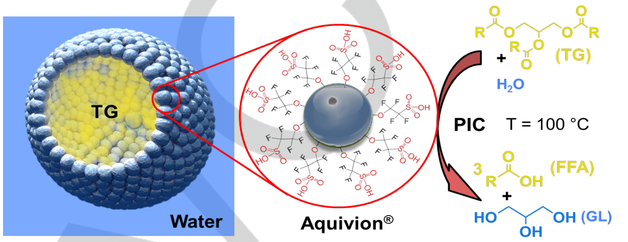
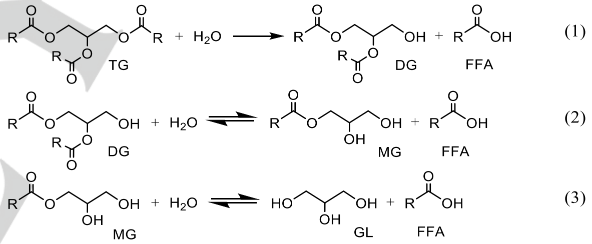


Figure 1. Principle of PIC system for the low-temperature acid-catalyzed biphasic hydrolysis of TGs into FFAs by amphiphilic Aquivion®.

The acid hydrolysis of TGs is a reversible reaction in equilibrium with esterification that proceeds *via* three sequential steps encompassing the formation of the partially hydrolyzed diglyceride (DG) and monoglyceride (MG) as intermediates:3d



In a first step, we assessed the potentials of PIC technology for conducting the biphasic hydrolysis of MGs (Eq. 3 in Figure 1) To this aim, two families of modified silicas with surface acid groups and balanced hydrophilic/hydrophobic properties were prepared (Table S1): (1) Aerosil®200 grafted with propylsulfonic acid centers (16-18%) and alkyl chains with variable length (i.e. A-CX, X = 3, 8 and 18 for propyl, octyl and octadecyl, respectively, 82-84%); and (2) Aerosil®200 grafted with polystyrene brushes (A-PSS-Y) with a molecular weight and sulfonation degree in the range 2100-2700 g/mol and Y=25-62%, respectively. The silicas assembled in small aggregates with a mean radius in the range 41-61 nm for A-CX and 45-79 nm for A-PSS-Y. The acidity of A-CX and A-PSS-Y fell in the range 0.11-0.16 and 0.21-0.60 mmolH^+/g, respectively. The density of alkyl moieties was 0.90, 1.21 and 1.94 groups/nm^2 for A-C3, A-C8 and A-C18, respectively, whereas the corresponding density of SiOH groups was 1.30, 1.24 and 0.96 groups/nm^2 according to combined TGA and ^{29}Si-NMR-MAS. In the case of A-PSS-Y, the density of PSS moieties ranged from 1.1 to 2.1 groups/nm^2 with a density of SiOH groups about 2.8 groups/nm^2.

The interfacial properties of the modified silicas were assessed in the hydrolysis of glycerol monolaurate (GML) at 100 °C for 10 h at 1:19 GML/water molar ratio (1:3 w/w). The silicas displayed much higher activity than homogeneous acids such as H_2SO_4 and p-toluenesulfonic acid (PTSA) (Figure 2A, Figure S1). A-C18 and A-PSS-25 exhibited the highest productivity (P) with

---

[a] Ms. H. Shi, Dr. Z.Y. Fan, Dr. B. Hong and Dr. M. Pera-Titus
Eco-Efficient Products and Processes Laboratory (E2P2L), UMI 3464 CNRS-Solvay,
Shanghai, 201108 (China)
E-mail: flora.fan@solvay.com, marc.pera-titus-ext@solvay.com

Supporting information for this article is given via a link at the end of the document.

a value of 80 mmolGML/mmolH$^+$ at *ca.* 0.10 eq%H$^+$ with respect to GML. This productivity is comparable to the value achieved with dodecylbenzene sulfonic acid (DBSA, 87 mmolGML/mmolH$^+$) at a similar acid concentration. The reaction evolved faster for A-C18, whereas a plateau was observed after 9 h for A-C3 (Figure 2B). The activity increased with the acid loading in the range 0.10-0.44 eq%H$^+$ (2-10 wt.%) for A-C3, but declined after 0.30 eq%H$^+$ (10 wt.%) for A-C8 and after 0.18 eq%H$^+$ (4 wt.%) for A-C18 (Figure 2C, Figure S2). A GML conversion of *ca.* 50% at a productivity of 100 mmolGML/mmolH$^+$ could be attained for A-C3 and A-C18 at 0.44 eq%H$^+$ (10 wt.%) (Figure S3). In contrast, the highest conversion attained with A-PSS-X was 20% (X=62) at a productivity of 80 mmolGML/mmolH$^+$ (Figure S4). In all cases the reaction proceeded far from equilibrium with a maximum conversion of 87% for DBSA at 0.44 eq%H$^+$ (Figure S5).

The macroscopic appearance of the reaction system in the presence of the different silicas revealed in all cases the genesis of stable GML/water emulsions, but with variable degree of dispersion (Figure 2D-E, Figure S6). For comparison, emulsions were also generated with DBSA, whereas no emulsion was formed either in the presence of the parent Aerosil®200, or under PTSA, leading in all cases to rapid phase separation after shearing. In light of these results, the generation of emulsions appears to be at the origin of the enhanced catalytic properties of modified silicas for GML hydrolysis.

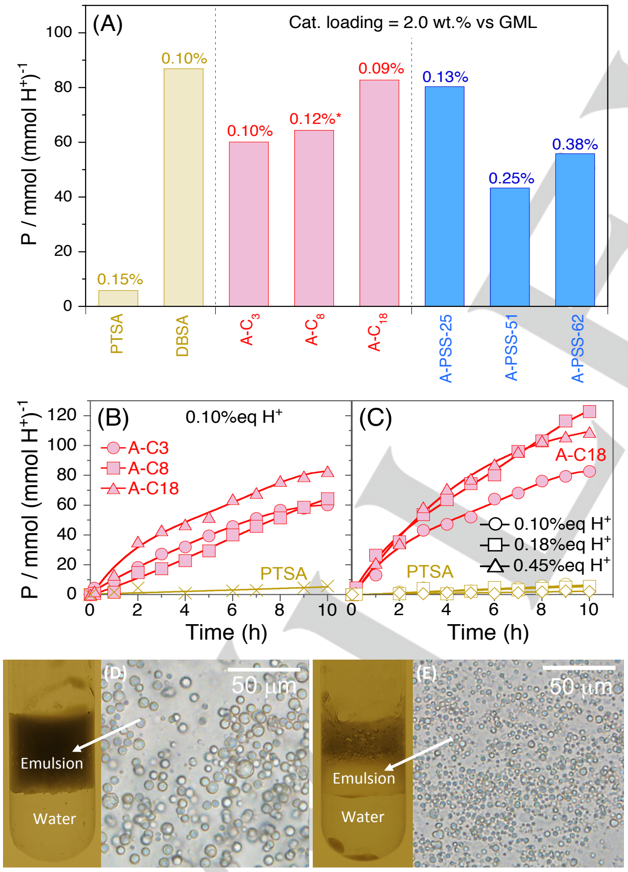


Figure 2. (A) Productivity per unit acid equivalent in GML hydrolysis over alkyl-grafted (A-C3, A-C8, A-C18) and polystyrene-grafted (A-PSS-25, A-PSS-51, A-PSS-62) silicas, as well as benchmark catalysts (PTSA, DBSA); (B, C) macroscopic and microscopic images of GML/water emulsions stabilized by A-C18 and A-PSS-25 (2 wt.%) after 15 h. Reaction conditions: 100 °C, 10 h, GML/water (1:3 w/w), 2 wt.% catalyst (4 wt.% for A-C8), homogenization at 70 °C for 5 min at 20,000 rpm. The values on top of the bars in (A) refer to the %eqH$^+$ with respect to GML in the different catalysts. Additional catalytic results and optical images of emulsions can be found in the SI (Figure S1-S6).

Table 1. Acid density, mean particle size and emulsification properties of PW- and D-type Aquivion® interfacial catalysts for the GTL/water system

Sample[a]	Acidity (mmol/g)[b]	ϕ_p (nm)[c]	Emulsification (GTL/water)[d]			
			Type	V$_d$ (%)	D$_d$ (µm)	S$_{int}$ (m^2)
PW66	1.51	284	O/W (O/W)	41 (42)	100 (-)	0.06 (-)
D66	1.51	414	O/W (O/W)	42 (39)	16.9 (13.8)	0.38 (0.46)
D79	1.26	341	O/W (O/W)	36 (29)	30.6 (27.5)	0.21 (0.23)
D83	1.20	100	O/W (O/W)	50 (49)	30.8 (29.4)	0.21 (0.22)
PW98	1.02	173	O/W (W/O)	60 (55)	12.6 (9.6)	0.49 (0.56)

[a] The number in PW and D-type Aquivion® samples provides an indication of the acid density (*e.g.*, 980 g = 1.0 mmolH$^+$ for PW98). [b] Measured by acid-base titration using NaOH; [c] Supernatant values measured in water on a Malvern Mastersizer 3000. [d] Measured just after homogenization at 70 °C for 5 min at 20,000 rpm (GTL/water 1:3 w/w, 1.0 wt.% cat); in parentheses, values measured after reaction.

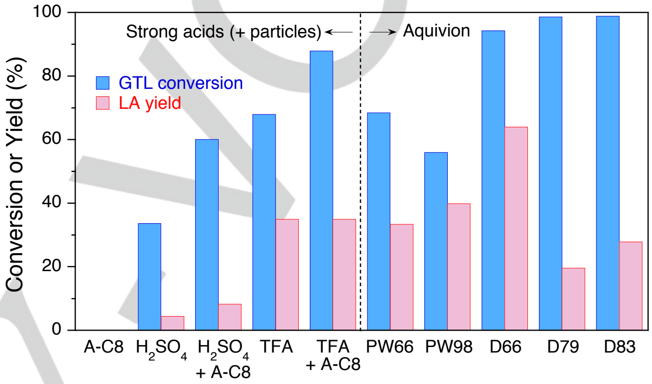


Figure 3. GTL conversion and LA yield in GTL hydrolysis over PW- and D-type Aquivion® catalysts, as well as A-C8 silica bearing sulfonic acid groups and benchmark H_2SO_4 and H_2SO_4 + A-C8. Reaction conditions: 100 °C, 8 h, GTL/water (1:3 w/w), homogenization at 70 °C for 5 min at 20,000 rpm. The catalyst loading was adjusted to provide 1eqH$^+$ for all catalysts. In the case of the experiment combining H_2SO_4 and A-C8, 1eqH$^+$ for H_2SO_4 was used with 1.0 wt.% A-C8. Additional catalytic results can be found in the SI (Figure S7).

With these results in hand, we explored the activity of the modified silicas for glyceryl trilaurate (GTL) hydrolysis at 100 °C for 10 h at 1:106 GTL/water molar ratio (1:3 w/w) and a catalyst loading providing 1 eqH$^+$ with respect to GTL (Figure 3-left). A large water excess was used to favor glycerol extraction during hydrolysis. At such conditions, none of the silicas was active, even if stable emulsions could be formed (Figure S7). For comparison, H_2SO_4 (1 eqH$^+$) only afforded 33% GTL conversion at 4.4% lauric acid (LA) yield. The GTL conversion could be enhanced to 60% at almost constant LA yield when adding A-C8 (1.0 wt.%), entailing the genesis of stable emulsions. A similar effect was observed for triflic acid (TFA, 1eqH$^+$), the GTL conversion evolving from 68% to more than 80% in the presence of Aerosil® 200, A-C3, A-C8 and A-C18 (1.0 wt.%, Figure S8). These observations combined with the catalytic results for GML hydrolysis presented above suggest a lack of acid centers of suitable strength in the grafted silicas for performing the first step of GTL hydrolysis (Eq. 1, Figure 1), which can be regarded as the rate-limiting reaction.[6d]

This *rationale* prompted us to redirect our strategy to catalysts combining hydrophobic surface properties favoring GTL/water emulsification (as for A-C8 and A-C18) and strong acid sites (as in TFA) boosting the first step of GTL hydrolysis. A catalyst meeting these two prerequisites was found to be Aquivion®. Aquivion® represents a new class of Perfluorosulfonic Superacid resin (H_0 ~12) constituted by a tetrafluoroethylene backbone and vinyl ether side chain (Figure S9, ref.[19]). Aquivion® can be either formulated as a powder (PW) or water dispersion (D). Table 1 compiles the acidity and mean particle size (ϕ_p) of the different samples. Aquivion® can be regarded as a supported TFA catalyst with amphiphilic properties due to the combination of apolar $-CF_2-$ groups and polar $-SO_3H$ acid centers. Indeed, the interfacial properties of Aquivion® (PW98) and Aquivion®-carbon hybrids was recently reported in the biphasic acetalization of dodecyl aldehyde with ethylene glycol, exhibiting the formation of Pickering emulsions.[19]

In a first series of experiments, we investigated the catalytic properties of PW66, PW98, D66, D79 and D83 for GTL hydrolysis at 100 °C for 8 h using a particle loading providing 1 eqH$^+$ with respect to GTL (17-27 wt.%) (Figure 3-right). Overall, the different samples displayed a much higher catalytic activity and LA yield than H_2SO_4 (1 eqH$^+$). Interestingly, PW66 and PW98 exhibited a GTL conversion and LA yield in the range 56-68% and 33-40%, respectively, which are comparable to the values measured over TFA (1 eqH$^+$). The largest LA yield was achieved over D66, achieving a value of 64% at almost 94% GTL conversion. In contrast, D79 and D83 exhibited a LA yield lower than 30% at almost full GTL conversion.

To further ascertain the interfacial properties of the different Aquivion® samples towards LA formation, a second series of catalytic and emulsification tests was conducted at lower catalyst loading (1.0 wt.%, 2.6-3.9 eqH$^+$%) while keeping the other reaction conditions unchanged (Figure 4A, Table 1). PW66, D66, D79 and D83 exhibited a GTL conversion ranging from 15% to 33% at low LA yield (<11%), comparing well with the value achieved with Nafion® NR50 used here as benchmark catalyst (19%). The GTL productivity evolved from 4.0 mmol/mmolH$^+$ for PW66 to 11 mmol/mmolH$^+$ for D83. The highest GTL conversion and LA yield was obtained over PW98 with values of 46% and 34%, respectively, encompassing an unprecedented GTL and LA productivity of 18 and 40 mmol/ mmolH$^+$, respectively, at 100 °C. The productivity of PW98 kept stable upon recycling in three consecutive catalytic cycles (Figure S10).

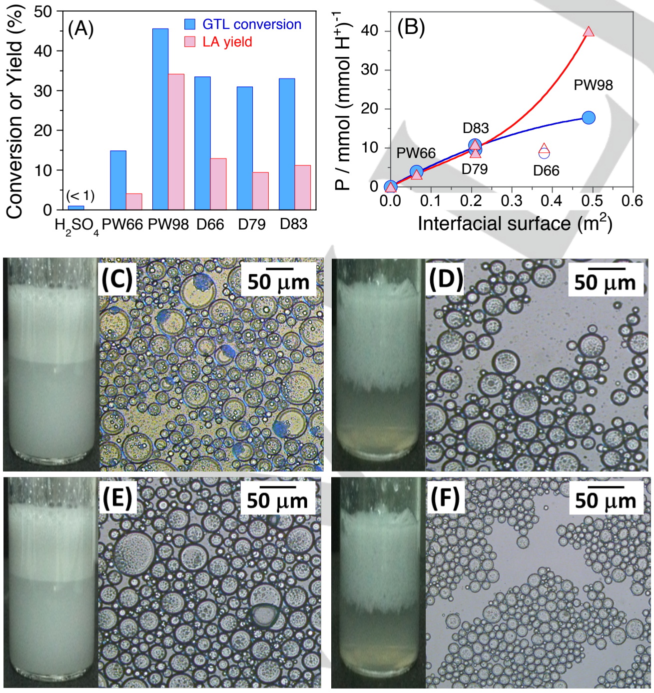


Figure 4. (A) GTL conversion and LA yield in GTL hydrolysis over PW- and D-type Aquivion® interfacial catalysts at low catalyst loading (1.0 wt.%); (B) GTL conversion and LA yield per unit acid equivalent; (C-D) macroscopic and microscopic images of water/GTL emulsions stabilized by D66 and PW98 Aquivion® before reaction, and (D) corresponding images of GTL/water emulsions after reaction. Reaction conditions: 100 °C, 8 h, GTL : water (1:3 w/w), 1.0 wt.% cat (1.7-2.5 eqH$^+$% vs. GTL), homogenization at 70 °C for 5 min and 20,000 rpm. Additional images of emulsions can be found in the SI (Figure S11). The experiment with H_2SO_4 was conducted at 2.3 eqH+% vs. GTL.

The emulsification properties of the different Aquivion® samples were assessed by homogenizing the catalysts (1.0 wt.%) with GTL and water (1:3 w/w) at 70 °C for 5 min at 20,000 rpm and visualized after 5 h stabilization (Table 1). PW66 generated unstable emulsions with very large droplets of *ca.* 100 μm. D-type samples afforded the generation of stable GTL/water emulsions with a dispersion level in the range 36-50% and a mean droplet size in the range 16.9-30.8 μm (Figure 4C, Figure S10A,C). For comparison, similar emulsification results were obtained with Nafion® NR50 (dispersion level, 41%; mean droplet size, 24 μm), even if the emulsions exhibited fast destabilization Finally, PW98 favored the formation of GTL/water emulsions at a much higher dispersion degree (60%) and an average droplet size of 12.6 μm (Figure 4E). Overall, these observations point out the surface-active properties of Aquivion® for the GTL/water system, affording the stabilization of Pickering emulsions.

The emulsions were further visualized after reaction to assess their dynamics in the presence of the reaction products (Table 1). GTL/water emulsions were still observed for D-type samples at an almost constant dispersion degree, while the droplet size only exhibited a slight reduction (<10%) (Figure 4D, Figure S10B,D). Opposing this behavior, the initial GTL/water emulsion observed for PW98 inversed along the reaction. The emulsion kept a high dispersion degree (55%) with a shrinking of the droplet size from the initial 12.6 μm to 9.6 μm (Figure 4F).

Finally, we represented the productivity of the Aquivion® samples against the interfacial area generated during emulsification (S_{int}) (Figure 4B). A correlation was observed for all samples except D66, suggesting that emulsification is at the origin of the high catalytic activity observed for Aquivion®, especially for PW98. Opposing this behavior, D66 showed an unexpectedly low activity according to the correlation in Figure 4B. Unlike PW98, D66 exhibited a markedly hydrophilic behavior due to its higher surface acid density (1.51 mmolH$^+$/g for D66 vs. 1.02 mmolH$^+$/g for PW98), resulting most likely in a higher degree of deactivation by water. Overall, this body of results indicates that a low acid loading favors the interfacial catalytic activity of Aquivion® by promoting not only the generation of interfacial area, but also the intrinsic activity of the acid centers.

In summary, Aquivion® PW98 formulated in powder form and showing an acid loading of 1.0 mmolH$^+$/g realized efficiently the solvent-free hydrolysis of glyceryl trilaurate to lauric acid at mild temperature (100 °C) in the presence of water/oil emulsions that kept stable along the reaction. The small droplet sizes attained (<10 μm) afforded the generation of a large interfacial area and in turn the alleviation of external mass transfer resistance towards the acid centers. The emulsification and accordingly the catalytic properties might be adjusted by a fine design of Aquivion® hybrids relying on oxides and carbon. These results, as well as their potential advantages for recycling, will be communicated in due time.

Experimental Section

The details of the experiments are provided in the Supporting Information.

Acknowledgements

This project was financially supported by CNRS and Solvay. Dr. C. Oldani (Solvay Specialty Polymers, Italy) is sincerely acknowledged for providing the Aquivion® samples and for insightful discussion.

Keywords: Interfacial catalysis, Pickering emulsion, hydrolysis, triglyceride, Aquivion®

[1] Ullmann's Encyclopedia, Industrial Organic Chemicals: Starting Materials and Intermediates, Vol. 4, Wiley-VCH, Weinheim, **1999**, pp. 2481-2532; (b) F. D. Gunstone in Oleochemical Manufacture and Applications (Eds.: F. D. Gunstone, R. J. Hamilton), Sheffield Academic Press, Sheffield, **2001**, pp. 1-22.

[2] D. Kusdiana, S. Saka, *Applied Biochem. Biotechnol.* **2004**, *113-116*, 781-791.

[3] a) J. D. Allen, W. A. Kline, E. A. Lawrence, C. J. Arrowsmith, C. Marcel, *Chem. Eng. Progress* **1947**, *43*, 459-466; b) H. L. Barnebey, *J. Am. Oil Chem. Soc.* **1948**, *25*, 95-99; c) M. D. Reinish, *J. Am. Org. Chem. Soc.* **1956**, *33*, 516-520; d) O. J. Ackelsberg, *J. Am. Org. Chem. Soc.* **1958**, *35*, 635-640; e) G. C. Gervajio in Fatty Acids and Derivatives from Coconut Oil, Bailey's Industrial Oil and Fat Products (Ed.: F. Shahidi), Wiley-Interscience, NY, **2005**, pp. 1-56.

[4] a) E. Twitchell, US 601,603, **1898**; b) L. Lascaray, *J. Am. Org. Chem. Soc.* **1952**, *29*, 362-366; c) L. Hartman, *J. Am. Oil Chem. Soc.* **1953**, *30*, 349-350; d) N. O. V. Sonntag, *J. Am. Oil Chem. Soc.* **1979**, *56*, 729A-732A; (e) T. A. Patil, D. N. Butala, T. S. Raghunathan, H. S. Shankar, *Ind. Eng. Chem. Res.* **1988**, *27*, 727-735.

[5] G. W. Eisenlohr, US 2,154,885, **1939**.

[6] a) R. L. Holliday, J. W. King, G. R. List. *Ind. Eng. Chem. Res.* **1997**, *36*, 932-935; b) J. W. King, R. L. Holliday, G. R. List, *Green Chem.* **1999**, *1*, 261-264; c) J. S. S. Pinto, F. M. Lancas, *J. Brazilian Chem. Soc.* **2006**, *17*, 85-89; d) R. Alenezi, G. A. Leeke, R. C. D. Santos, A. R. Khan, *Chem. Eng. Res. Design* **2009**, *87*, 867-873; e) F. J. Eller, J. A. Teel, D. E. Palmquist, *J. Am. Oil. Chem. Soc.* **2011**, *88*, 1455-1461.

[7] a) R. Schomäcker, *Progr. Colloid Polym. Sci.* **1990**, *81*, 131-135; b) A. N. Anozie, J. M. Dzobo, *Ind. Eng. Chem. Res.* **2006**, *45*, 1604-1612; c) E. Fernández, L. García-Río, P. Rodríguez-Dafonte, *J. Phys. Chem. B* **2007**, *111*, 11437-11442; d) E. Fernández, L. García-Río, M. Méndez-Pérez, P. Rodríguez-Dafonte, *J. Phys. Chem. B* **2009**, *113*, 8828-8834; e) N. Mazouzi-Sennour, F. Henry, *Int. J. Org. Chem.* **2014**, *4*, 24-28.

[8] (a) C. J. Yow, K. Y. Liew, *J. Am. Oil Chem. Soc.* **1999**, *76*, 529-533; *J. Am. Oil Chem. Soc.* **2002**, *79*, 357-361; b) K. Ngaosuwan, E. Lotero, K. Suwannakaru, J. G. Goodwin Jr., P. Praserthdam, *Ind. Eng. Chem. Res.* **2009**, *48*, 4757-4767; c) K. Ngaosuwan, X. Mo, J. G. Goodwin Jr., P. Praserthdam, *Top. Catal.* **2010**, *53*, 783-794; d) J. K. Satyarthi, D. Srinivas, P. Ratnasamy, *Appl. Catal. A: Gen.* **2011**, *391*, 427-435.

[9] a) O. Hernell, J. E. Staggers, M. C. Carey, *Biochem.* **1990**, *29*, 2041-2056; b) E. Reboul, A. Berton, M. Moussa, C. Kreuzer, I. Crenon P. Borel, *Biochim. Biophys. Acta* **2006**, *1761*, 4-10; c) P. Reis, K. Holmberg, R. Miller, M. E. Leser, T. Raab, H. J. Watzke, *CR Chimie* **2009**, *12*, 163-170.

[10] a) Y. Kimura, A. Tanaka, K. Sonomoto, T. Nihira, S. Fukui, *Eur. J. Appl. Microbiol. Biotechnol.* **1983**, *17*, 107-112; b) M. M. Hoq, T. Yamane, S. Shimizu, T. Funada, S. Ishida, *J. Am. Oil Chem. Soc.* **1985**, *62*, 1016-1021; c) L. Giorno, R. Molinari, M. Natoli, E. Drioli, *J. Membr. Sci.* **1997**, *125*, 177-187; d) A. H-Kittikun, P. Prasertsan, C. Sungpud, *J. Am. Oil Chem. Soc.* **2000**, *77*, 599-603; e) H. Noureddini, X. Gao, S. Joshi, P. R. Wagner, *J. Am. Oil Chem. Soc.* **2002**, *79*, 33-40; f) E. Jurado, F. Camacho, G. Luzón, M. Fernández-Serrano, M. García-Román, *Chem. Eng. Sci.* **2006**, *61*, 5010-5020; *Biochem. Eng. J.* **2008**, *40*, 473-484; g) P. Adlercreutz, *Chem. Soc. Rev.* **2013**, *42*, 6406-6436; h) E. Z. Ramos, R. H. Miotti Jr., P. F. de Castro, P. W. Tardioli. A. A. Mendes, R. Fernández-Lafuente, D. B. Hirata, *J. Mol. Catal. B: Enzymatic* **2015**, *118*, 43-51; i) J. J. Bassi, L. M. Todero, F. A. P. Lage, G. I. Khedy, J. D. Lucas, A. P. Custódio, M. A. Pinto, A. A. Mendes, *Int. J. Biol. Macromol.* **2016**, *92*, 900-909.

[11] a) P. D. I. Fletcher, B. H. Robinson, *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 2667-2679; b) K. Holmberg, *Adv. Colloid Interface Sci.* **1994**, *51*, 137-174; c) Y. Miyake, T. Owari, F. Ishiga, M. Teramoto, *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 979-986; d) H. Stamatis, A. Xenakis, F. N. Kolisis, A. Malliaris, *Progr. Colloid Polym. Sci.* **1994**, *97*, 253-255; e) R. Verger, *Trends Biotechnol.* **1997**, *15*, 32-38; f) P. Skagerlind, B. Folmer, B. K. Jha, M. Svensson, K. Holmberg, *Progr. Colloid Polym. Sci.* **1998**, *108*, 47-57; g) H. Stamatis, A. Xenakis, F. N. Kolisis, *Biotechnol. Adv.* **1999**, *17*, 293-318; h) A. B. Mirgorodskaya, L. A. Kudryavtseva, *Russ. J. Gen. Chem.* **2002**, *72*, 1261-1265; i) A. Dasgupta, D. Das, R. N. Mitra, P. K. Das, *J. Colloid Interface Sci.* **2005**, *289*, 566-573.

[12] M. Pera-Titus, L. Leclercq, J-M. Clacens, F. De Campo, V. Nardello-Rataj, *Angew. Chem. Int. Ed.* **2015**, *54*, 2006-2021.

[13] a) W. Li, F. Ma, F. Su, L. Ma, S. Zhang, Y. Guo, *ChemSusChem*. 2011, **4**, 744; b) A. P. C. Teixeira, A. D. Purceno, A. S. Barros, B. R. S. Lemos, J. D. Ardisson, W. A. A. Macedo, E. C. O. Nassor, C. C. Amorim, F. C. C. Moura, M. G. Hernandez-Terrones, F. S. M. Portela, R. M. Lago, *Catal. Today* **2012**, *190*, 133-143.

[14] I. M. Okhapkin, E. E. Makhaeva, A. R. Khokhlov, *Russ. Chem. Bull. Int. Ed* **2006**, *55*, 2190-2192.

[15] W. Zhou, L. Fang, Z. Y. Fan, B. Albela, L. Bonneviot, F. De Campo, M. Pera-Titus, J-M. Clacens, *J. Am. Chem. Soc.* **2014**, *136*, 4869-4872.

[16] a) Z. Y. Fan, A. Tay, M. Pera-Titus, W-J. Zhou, S. Benhabbari, X. Feng, G. Malcouronne, L. Bonneviot, F. De Campo, L. Wang, J-M. Clacens, *J. Colloid Interface Sci.* **2014**, *427*, 80-90; b) H. Shi, F. Fan, V. Ponsinet, R. Sellier, H. Liu, M. Pera-Titus, J. M. Clacens, *ChemCatChem*. **2015**, *7*, 3229-3233.

[17] P. A. Zapata, J. Faria, M. P. Ruiz, R. E. Jentoft, D. E. Resasco, *J. Am. Chem. Soc.* **2012**, *134*, 8570-8578.

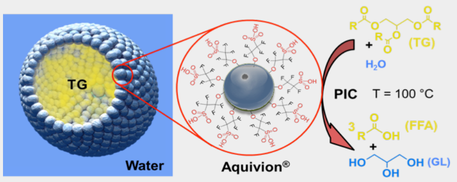
[18] W. Zhang, L. Fu, H. Yang, *ChemSusChem*. **2014**, *7*, 391-396; *ChemSusChem*. **2014**, *7*, 1888-1900.

[19] W. Fang, Z. Y. Fan, H. Shi, S. Wang, W. Shen, H. Shu, J-M. Clacens, F. De Campo, A. Liebens. M. Pera-Titus, *J. Mater. Chem. A* **2016**, *41*, 4380-4385.

10.1002/cssc.201700663

Entry for the Table of Contents

Aquivion® Perfluorosulfonic Superacid catalyzed efficiently the solvent-free hydrolysis of glyceryl trilaurate at 100 °C and ambient pressure *via* the genesis of stable Pickering emulsions.



Hui Shi, Zhaoyu Fan, Bing Hong and Marc Pera-Titus

Page No. – Page No.