

# High catalytic performances of Aquivion® PFSA, a reusable solid perfluorosulfonic acid polymer, in the biphasic glycosylation of glucose with fatty alcohols

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ACS Catal., Just Accepted Manuscript • Publication Date (Web): 15 Mar 2017

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ABSTRACT: The catalytic performances of Aquivion PFSA, a solid super acid, were investigated in the catalytic glycosylation of glucose with fatty alcohols. Four main criteria were considered to evaluate the catalytic performances of Aquivion PFSA (1) the selectivity of the reaction, (2) the Turn Over Frequency, (3) the reactor productivity and (4) the catalyst stability/recycling. To shed light on the catalytic performances of Aquivion PFSA, it was systematically compare to H<sub>2</sub>SO<sub>4</sub> which is industrially employed in such reaction. We discovered that Aquivion PFSA surpassed the catalytic performances of H<sub>2</sub>SO<sub>4</sub> in terms of activity, selectivity and reactor productivity. Particularly, Aquivion PFSA selectively converted glucose to alkyl polyglucosides (DP = 1.2) with 85% yield which corresponded to a reactor productivity as high as 477 kg/m<sup>3</sup>/h. Conversely to H<sub>2</sub>SO<sub>4</sub>, Aquivion PFSA was also capable of selectively producing alkyl polyglucosides directly from glucose syrup, a cheap source of glucose. This result was ascribed to the amphiphilic nature of Aquivion PFSA which facilitated the Pickering-like emulsification of the biphasic reaction medium. Finally, owing to its high chemical and mechanical properties, Aquivion PFSA was highly stable under our working conditions and was recycled at least 10 times without obvious loss of its catalytic performances.

KEYWORDS: Biphasic catalysis, Acid catalysis, Carbohydrates, Glycosides, Aquivion<sup>®</sup> PFSA, Alkyl polyglycosides

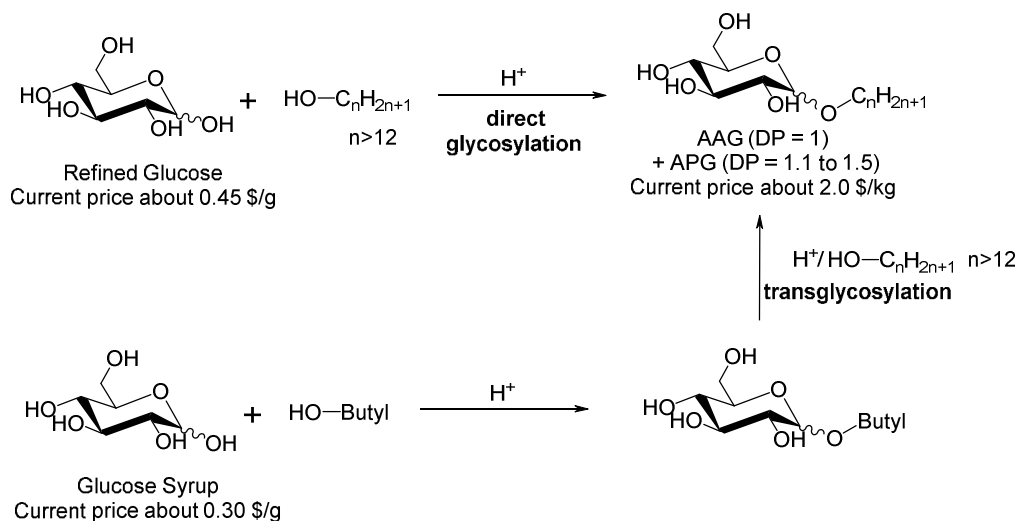
## Introduction

Acids are widely employed in industry to catalyze diverse reactions from carbohydrates such as dehydration, esterification, glycosylation, poly- or depolymerization among many other examples.<sup>1</sup> In most cases, these reactions imply water either as a solvent, reactant or co-product. Industrially, H<sub>2</sub>SO<sub>4</sub> is often a preferred catalyst for carbohydrate processing because it is cheap (0.15 \$/kg), highly active and it also leads to high reactor productivities. From a sustainable point of view, solid acid catalysts are obviously more desirable owing to their possible recycling, the absence of neutralization step at the end of the reaction and also due to their lowest corrosiveness.<sup>1g-h</sup> Solid acid catalysts however often suffer from a low productivity and/or deactivation caused by the presence of water or thermal instability.<sup>2</sup> All these aspects currently hamper the industrial deployment of solid acid catalysts for carbohydrate processing.

The catalytic glycosylation of glucose with alkyl alcohols is a typical example.<sup>3</sup> This reaction is of prime importance in industry. In particular, the glycosylation of glucose with long chain alkyl alcohols affords Amphiphilic Alkyl monoGlycosides (AAG) that are valuable non-ionic bio-based surfactants.<sup>3a</sup> Thanks to their low toxicity, biodegradability and stability (even in alkaline conditions), these non-ionic surfactants are receiving many interests in food, detergence, cosmetic and pharmaceutical industries. For instance, AAG are the main constituents of GlucoPON 600<sup>®</sup> and Milcoside 200<sup>®</sup> produced by BASF and LG, respectively.

The production of AAG is industrially achieved by glycosylation of glucose with an excess of fatty alcohols (10 eq.) in the presence of 1 wt% of H<sub>2</sub>SO<sub>4</sub>.<sup>4</sup> This reaction releases a stoichiometric amount of water. The reaction is conducted under vacuum (100 mbar) to distill water out of the reactor and to shift the process towards the formation of AAG. At the end of the reaction, H<sub>2</sub>SO<sub>4</sub> is neutralized by NaOH leading to the production of Na<sub>2</sub>SO<sub>4</sub>. This salt being

non-toxic and present in a low quantity, it is not separated at the end of the reaction and thus remains with AAG. Industrial processes generally afford AAG with 70% yield. Other products are mostly alkyl polyglycosides (APG). In average, the final product contains 1.1 to 1.5 glucose unit per fatty chains. According to the experimental conditions, glucose may also partly polymerize leading to the formation of unwanted polydextroses.



**Scheme. 1.** Synthesis of amphiphilic alkyl glycosides

According to the grade of glucose, there are two different pathways to produce AAG in large scale (Scheme 1). From refined glucose (anhydrous or monohydrate crystalline powder, 0.45 \$/kg), AAG are produced by a direct glycosylation of glucose with fatty alcohols in the presence of H<sub>2</sub>SO<sub>4</sub>. From glucose syrup (0.30 \$/kg), the direct glycosylation with a fatty alcohol is not efficient due to the very low solubility of the fatty alcohol in the syrup leading to uncontrolled and dominant polymerization of glucose to polydextroses. In this case, transglycosylation reactions are thus generally preferred. Typically, the syrup is first glycosylated with *n*-butanol followed by a transglycosylation with a fatty alcohol, both reactions taking place subsequently in the same reactor generally with H<sub>2</sub>SO<sub>4</sub> as a homogeneous catalyst.

Nowadays, the price of AAG is a critical issue (about 2.0 \$/kg) and it is too high as compared to fossil-derived surfactants (<1\$ /kg) to deeply penetrate the market. The reactant price accounts for about 60% of the full manufacturing cost of AAG. Hence, there are two options to lower the price of AAG.

The first strategy consists in optimizing the current processes by searching novel and recyclable heterogeneous catalytic systems capable of producing AAG with a high selectivity and productivity, particularly from glucose syrup. Obviously, solid acid catalysts should also lower equipment and process costs in a significant way.

The second strategy consists in starting from a cheapest source of raw material such as waste biomass (< 0.1 \$/kg) instead of edible glucose as it is nowadays the case. If amphiphilic alkyl xylosides can be produced in large scale from the hemicellulosic fraction of biomass,<sup>5</sup> the production of AAG from the cellulosic part is however scientifically more relevant. In 2010, D. E. de Vos and A. Corma independently reported the acid-catalyzed conversion of cellulose to AAG in ionic liquids at 110°C.<sup>6</sup> In 2015, our group has reported the glycosylation of cellulose assisted by ball-milling.<sup>7</sup> Although good yields (60-80%) were claimed starting from C<sub>4</sub> to C<sub>8</sub> alkyl alcohols, these processes remain at the moment too costly for implementation at a larger scale.

In this work, we focused on the first strategy *i.e.* the search of a solid acid catalyst. Despite many studies on the catalytic glycosylation of glucose in the presence of a heterogeneous catalyst, examples of heterogeneously-catalyzed glycosylation of glucose with fatty alcohols (C<sub>8</sub> to C<sub>24</sub>) are very scarce due to the biphasic nature of the reaction medium inducing mass transfer problem and, thus poor selectivity. N. S. Chaubal *et al.* reported the heterogeneously-catalyzed glycosylation of glucose with myristyl alcohol in the presence of spinels of the type ZnFe<sub>2</sub>O<sub>4</sub>

supported on  $\text{ZrO}_2$ .<sup>8</sup> The reaction was carried out in toluene and myristyl glycosides were obtained with 87% yield. Y. Wu *et al.* reported the synthesis of octyl glycosides over  $\text{H}_2\text{SO}_4/\text{SiO}_2$  affording APGs with an average degree of polymerization of 1.37.<sup>9</sup> Same catalyst was employed by I. A. Amin *et al.* for the glycosylation of dextrose with *n*-octanol.<sup>10</sup> In another example, H. Kim *et al.* investigated the glycosylation of glucose with *n*-octanol in the presence of polyvinyl bound trisulfonate ethylamine chloride and polyvinyl bound disulfonate ethylamine as Brønsted solid acid catalysts.<sup>11</sup> Under optimized conditions, APGs were obtained with excellent yields. Although excellent selectivity to APGs was claimed in all these examples, the deactivation/leaching of solid catalysts and the low reactor productivity remain important obstacles for implementation at a larger scale. To date, there is no commercialized heterogeneously-catalyzed process for the glycosylation of carbohydrates and, in this field,  $\text{H}_2\text{SO}_4$  remains the reference in terms of activity, selectivity, productivity and cost-efficiency.

Aquivion<sup>®</sup> PFSA PW98 is a perfluorosulfonic acid ionomer which is synthesized by the free-radical copolymerization of tetrafluoroethylene and sulfonyl fluoride vinyl ether  $\text{CF}_2=\text{CF}-\text{O}-(\text{CF}_2)_2-\text{SO}_2\text{F}$ . The  $-\text{SO}_2\text{F}$  moieties are then converted to  $-\text{SO}_3\text{H}$  groups by a treatment with a mineral base (NaOH or KOH) followed by a cation exchange in acid conditions.<sup>12</sup> Thanks to the presence of perfluorinated chains, Aquivion<sup>®</sup> PFSA is considered as a solid superacid with a Hammett acidity function of -12 which is similar to that of  $\text{H}_2\text{SO}_4$  and higher than that of classical sulfonated polystyrenes such as Amberlyst-15 for instance ( $H_0 = -2$ ).<sup>13</sup> The structure of Aquivion<sup>®</sup> PFSA PW98 is provided in the supporting information (Figure S1). The proton exchange capacity of Aquivion<sup>®</sup> PFSA PW98 used in this study is 1.0 mmol/g. In contrast to Nafion NR-50, the mechanical and chemical integrity of Aquivion<sup>®</sup> PFSA PW98 are preserved

at high temperature (up to 150-160°C).<sup>14</sup> This large operating temperature window is an important aspect with respect to the long term recycling.

In this work, we report that Aquivion<sup>®</sup> PFSA PW98 is not only a highly robust and recyclable heterogeneous catalyst under our working conditions but it is also markedly more selective and more productive than H<sub>2</sub>SO<sub>4</sub>. Importantly, in contrast to H<sub>2</sub>SO<sub>4</sub>, Aquivion<sup>®</sup> PFSA PW98 is also capable of producing amphiphilic AAG by a direct glycosylation of glucose syrup with fatty alcohols. To the best of our knowledge, this work is one of the rare examples where a solid acid catalyst surpasses the industrial performances of H<sub>2</sub>SO<sub>4</sub> in terms of selectivity, productivity and that, whatever the grade of glucose.

## Results and Discussion

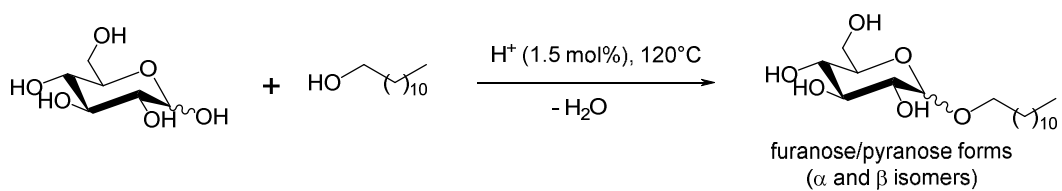
In a first set of experiments, the glycosylation of anhydrous glucose with *n*-dodecanol was investigated in the presence of Aquivion<sup>®</sup> PFSA PW98. Three main criteria were considered to evaluate the catalytic performances of Aquivion<sup>®</sup> PFSA PW98 (1) the selectivity of the reaction, (2) the Turn Over Frequency (TOF) ( $\text{mol}_{\text{converted glucose}} / \text{mol}_{\text{H}^+} / \text{h}$  expressed hereafter in h<sup>-1</sup>) and (3) the reactor productivity expressed in kg/m<sup>3</sup>/h. To shed light on the contribution of Aquivion<sup>®</sup> PFSA PW98, it was systematically compared to H<sub>2</sub>SO<sub>4</sub> but also to heterogeneous acid catalysts such as sulfonated SBA-15 mesoporous silica (SBA-SO<sub>3</sub>H), Amberlyst-15 and a zeolite H-BEA-25. For the sake of clarity, we first focused the discussion on AAG. The formation of alkyl polyglucoside (APG) is discussed later.

In a typical procedure, anhydrous glucose was mixed with 3 eq. of *n*-dodecanol and the resulting mixture was heated at 120°C in the presence of 1.5 mol% of H<sup>+</sup>. The reaction was carried out under vacuum (50 mmHg) to distill water out of the reaction vessel and to enhance



the formation of AAG. As usual for this kind of reaction, the yield of AAG reached a maximum and then decreased due to the formation of APGs. A detailed identification of the different reaction products formed is provided later. Results are summarized in Table 1. A typical kinetic profile and gas chromatogram are provided in the supporting information (Figure S2, S3).

**Table 1.** Catalytic glycosylation of glucose with *n*-dodecanol in the presence of acid catalysts<sup>a</sup>



furanose/pyranose forms  
( $\alpha$  and  $\beta$  isomers)

Entry	Catalyst	Time (min) <sup>b</sup>	Conv. (%)	TOF (h <sup>-1</sup> ) <sup>c</sup>	Yield (%) <sup>d</sup>	Sel. (%)	Productivity (kg/m <sup>3</sup> /h)
1	H <sub>2</sub> SO <sub>4</sub>	60	70	145	50	71	290
2	SBA-SO <sub>3</sub> H	300	94	102	35	37	41
3	Amberlyst-15	240	17	-	9	53	13
4	H-BEA-25	600	38	-	10	26	6
5	Aquivion <sup>®</sup> PFSA PW98	70	85	46	70	82	350
6 <sup>e</sup>	H <sub>2</sub> SO <sub>4</sub>	90	90	86	74	75	86
7 <sup>f</sup>	Aquivion <sup>®</sup> PFSA PW98	30	100	456	47	47	546
8 <sup>g</sup>	Aquivion <sup>®</sup> PFSA PW98	1080	98	<1	52	53	17
9 <sup>h</sup>	Aquivion <sup>®</sup> PFSA PW98	100	96	40	36	38	125

<sup>a</sup> 120°C, 1.5 mol% of H<sup>+</sup>, *n*-dodecanol/glucose molar ratio = 3, <sup>b</sup> time of the reaction to reach the maximum yield to AAG; <sup>c</sup> measured at the initial stage of the reaction (conv. Glucose < 20 %); <sup>d</sup> maximum yield to AAG; <sup>e</sup> *n*-dodecanol/glucose molar ratio = 10; <sup>f</sup> at 150°C; <sup>g</sup> at 90°C; <sup>h</sup> under closed vessel

Under our working conditions, H<sub>2</sub>SO<sub>4</sub> exhibited a TOF of 145 h<sup>-1</sup> and afforded AAG with a maximum yield of 50 % at a conversion of glucose of 70% (*i.e.* AAG selectivity of 71%) (Table 1, entry 1). As expected, the reactor productivity was high with H<sub>2</sub>SO<sub>4</sub> and it reached 290 kg/m<sup>3</sup>/h. Among tested heterogeneous catalysts, SBA-SO<sub>3</sub>H exhibited a TOF of 102 h<sup>-1</sup> but unfortunately it was deactivated during the reaction due to the partial hydrolysis of the siliceous surface at 120°C (Table 1, entry 2, see also kinetic profile in the Figure S4). A maximum yield of AAG of 35% was however obtained at a conversion of glucose of 94% (after 300 min of reaction) which corresponded to an AAG selectivity and a reactor productivity of 37% and 41 kg/m<sup>3</sup>/h, respectively (*i.e.* selectivity and productivity were 1.9 times and 7 times lower than that of H<sub>2</sub>SO<sub>4</sub>). Other products are mostly polydextroses in this case. Their formation is indeed strongly favored over hydrophilic catalytic surface. As expected, due to its low thermal stability, Amberlyst-15 was poorly active under our working conditions (Table 1, entry 3). In contrast to what was previously observed with *n*-butanol,<sup>15</sup> H-BEA (Si/Al = 25) was poorly active from fatty alcohols at 120°C presumably due to the biphasic nature of the medium that induced mass transfer problems (Table 1, entry 4). These selected examples illustrate well the difficulty facing by heterogeneous catalyst to compete with H<sub>2</sub>SO<sub>4</sub> in such reaction.

To our delight, Aquivion® PFSA PW98 afforded the highest yield of AAG (*i.e.* 70%) (Table 1, entry 5). This yield was obtained at a conversion of glucose as high as 85% indicating that Aquivion® PFSA PW98 was markedly more selective than H<sub>2</sub>SO<sub>4</sub> (82% *vs* 71%). A kinetic effect can be ruled out to explain this greatest selectivity since Aquivion® PFSA PW98 has a TOF of 46 h<sup>-1</sup> which is 2 to 4 times lower than those of H<sub>2</sub>SO<sub>4</sub> or SBA-SO<sub>3</sub>H. From the state of the art, the amphiphilic nature of Aquivion® PFSA PW98 was presumably responsible for this high selectivity by favoring a better contact between glucose (hydrophilic) and *n*-dodecanol

(hydrophobic), thus contributing to limit the side oligomerization of glucose. This aspect is discussed later. The reactor productivity was also higher with of Aquivion® PFSA PW98 than with H<sub>2</sub>SO<sub>4</sub> since it reached 348 kg/m<sup>3</sup>/h (Table 1, entry 5).

To more accurately compare the reactor productivity between Aquivion® PFSA PW98 and H<sub>2</sub>SO<sub>4</sub>, the H<sub>2</sub>SO<sub>4</sub>-catalyzed process was optimized in order to find the suitable experimental conditions to compare both catalysts at a similar selectivity and conversion. To this end, it was necessary to increase the *n*-dodecanol/glucose ratio from 3 to 10 with H<sub>2</sub>SO<sub>4</sub>. Under these more diluted conditions, the TOF of H<sub>2</sub>SO<sub>4</sub> was logically reduced from 145 h<sup>-1</sup> to 86 h<sup>-1</sup> but the AAG yield was increased to 74% for a conversion of glucose of 90% (Table 1, entry 6). These conditions are actually very close to the industrial ones. At 82% of selectivity and 85-90% conversion, we were pleased to see that the reactor productivity was much higher with Aquivion® PFSA PW98 than with H<sub>2</sub>SO<sub>4</sub> (350 vs 85 kg/m<sup>3</sup>/h) highlighting the efficiency of Aquivion® PFSA PW98 in glycosylation of glucose.

Next, the impact of the temperature on the Aquivion® PFSA PW98 performances was checked. In accordance with the Arrhenius law, when the temperature was increased from 120°C to 150°C, the TOF of Aquivion® PFSA PW98 was concomitantly increased from 46 h<sup>-1</sup> to 456 h<sup>-1</sup> (Table 1, entries 1 and 7). At 150°C, the maximum yield of AAG (47%) was however markedly lower than at 120°C (70%) due to dominant acid-catalyzed degradation of glucose and glycosides as supported in this case by the formation of unidentified black materials. Conversely, a decrease of the reaction temperature from 120°C to 90°C decreased the reaction rate to an unacceptable level (Table 1, entry 8). Hence, 120°C was selected in the following experiments.

Continuous removal of water was also mandatory to shift the reaction (equilibrium) to the formation of AAG. For instance, when the same reaction was conducted in a closed reactor, the yield of AAG reached a maximum of only 36% (Table 1, entry 9).

Next, Aquivion<sup>®</sup> PFSA catalyst with different sulfonic loadings were checked to evaluate the impact on the TOF, the selectivity and the reactor productivity. To this end, Aquivion<sup>®</sup> PFSA with a proton exchange capacity of 1.0, 1.15, 1.26 and 1.45 mmol/g were tested. Results are summarized in Table 2.

**Table 2.** Influence of the proton exchange capacity on the Aquivion<sup>®</sup> PFSA catalytic performances<sup>a</sup>

Catalyst	H <sup>+</sup> exchange capacity (mmol/g)	Conv. (%)	TOF (h <sup>-1</sup> )	AAG yield (%)	AAG selectivity (%)	Productivity (kg/m <sup>3</sup> /h)
Aquivion <sup>®</sup> PW98	1.0	85	46	70	82	350
Aquivion <sup>®</sup> PW87	1.15	80	42	65	81	378
Aquivion <sup>®</sup> PW79	1.26	80	55	75	87	433
Aquivion <sup>®</sup> PW66	1.45	85	83	75	88	523

<sup>a</sup> 120°C, n-dodecanol/glucose molar ratio = 3, 1.5 mol% of H<sup>+</sup>

Whatever the H<sup>+</sup> loading, the selectivity to AAG remained similar (81-88%). The H<sup>+</sup> loading has however a significant effect on the TOF of Aquivion<sup>®</sup>. The TOF of Aquivion<sup>®</sup> was indeed increased from 46 to 83 h<sup>-1</sup> when the H<sup>+</sup> loading was concomitantly increased from 1.0 to 1.45 mmol/g. Considering that the selectivity was not changed, this result may reflect a possible

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3 cooperativity between -SO<sub>3</sub>H sites at high loading. It was indeed previously shown that the  
4 mobility of H<sup>+</sup> on Aquivion<sup>®</sup> was significantly affected by an increase in the -SO<sub>3</sub>H loading  
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6 owing to the formation of well-connected water clusters.<sup>16</sup> Furthermore, the formation of these  
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8 water clusters may also impacts the swelling of Aquivion<sup>®</sup> and thus the accessibility of -SO<sub>3</sub>H.  
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10 Among the different tested Aquivion<sup>®</sup> PFSA, Aquivion<sup>®</sup> PFSA PW66 was the most performant  
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12 one affording AAG with 75% yield (*i.e.* 88% selectivity) after only 50 min of reaction which  
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14 corresponds to unprecedented reactor productivity as high as 523 kg/m<sup>3</sup>/h.  
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20 The reaction mixture was next carefully analyzed by means of different characterization  
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22 methods in order to determine the nature of other products formed. At the end of the reaction,  
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24 Aquivion<sup>®</sup> PFSA PW98 was filtered off and, as industrially performed, the excess of *n*-  
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26 dodecanol was removed by vacuum distillation. The crude product was next analyzed by GC  
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28 analyses and revealed that the APG sample contained 14% of glucose which is in line with a  
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30 determined conversion of 85%. It also means that less than 1% of glucose was converted to  
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32 polydextrose. This result was also confirmed by titrating the reducing sugar present in the sample  
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34 by 2,6-dinitrosalicylic acid (DNS method).<sup>17</sup> AAG were then analyzed by mass spectrometry  
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36 (electrospray) and the formation of alkyl polyglucosides (APG) was clearly observed.  
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38 Particularly, APGs with a degree of polymerization (DP) going from 1 to 4 were formed.  
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40 Determination of the average DP was achieved by <sup>1</sup>H NMR (in *d*6-DMSO) and revealed a DP of  
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42 1.2 which is a similar value with industrial products (Figure S5, S6). One should note that such  
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44 DP also indicated that glucose was exclusively converted to APG which agrees well with the  
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46 absence of side oligomerization of glucose. Note that all these results were double-checked by  
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48 separating *n*-dodecanol, glucose and APGs by filtration over a plug of silica using consecutively  
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50 ethyl acetate/heptane (1/1) and methanol/H<sub>2</sub>O (1/1) as eluents. This separation also confirmed  
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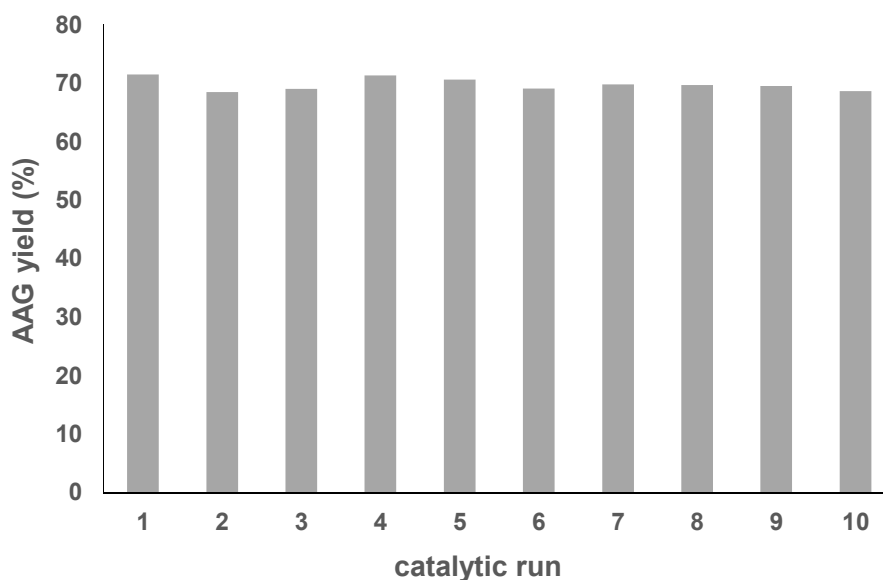
the exclusive conversion of glucose to APG with a DP of 1.2. Finally, GC analyses showed that AAG was formed as a mixture of furanoside and pyranoside forms, both forms co-existed as  $\alpha$  and  $\beta$  isomers which agrees well with a classical reaction mechanism *i.e. in situ* formation of an oxocarbenium cation.<sup>18</sup> The pyranoside form was dominant and the pyranoside/furanoside ratio was 2.5. The  $\alpha/\beta$  ratios for the pyranoside and furanoside forms were 4.72 and 3.38, respectively which is consistent with previous works of the field.<sup>4,19</sup> It is worth mentioning that during the monitoring of the catalytic reaction by GC, we observed that 7% of *n*-dodecanol was also converted to didodecylether during the reaction but this later was not found in APG samples. It was presumably distilled out at the same time with *n*-dodecanol (or hydrolyzed back to *n*-dodecanol during the distillation process).

When *n*-dodecanol was replaced by *n*-hexadecanol or *n*-octadecanol which are both available in larger scale from biomass, the reaction also proceeded well. After purification by filtration over a plug of silica, the corresponding APGs were obtained with 50% and 60% isolated yield, respectively (not optimized results, product was lost during the purification process) showing the attractiveness of Aquivion<sup>®</sup> PFSA PW98 for the synthesis of APG from biomass.

Considering both the selectivity and the reactor productivity, Aquivion<sup>®</sup> PFSA PW98 appeared as a more performant catalyst than H<sub>2</sub>SO<sub>4</sub>. Aquivion<sup>®</sup> PFSA PW98 was also more performant than beta-zeolite previously reported in the literature.<sup>15</sup> While the yields and selectivity were in this case in a similar range between both solid catalysts, the reactor productivity was however nearly 10 times higher with Aquivion<sup>®</sup> PFSA PW98 than with beta zeolite. The best conditions found for Aquivion<sup>®</sup> PFSA PW98 are 120°C, a *n*-dodecanol/glucose molar ratio of 3 and a reaction time of 70 min. Applying these conditions led to the synthesis of AAG with 70% yield (*i.e.* APG with 85% yield, 100% selectivity to APG) and a reactor productivity to AAG of 350

kg/m<sup>3</sup>/h (*i.e.* 477 kg/m<sup>3</sup>/h based on APG) which is in line with industrial specifications. Transposition of these results to a batch reactor of 10 m<sup>3</sup> running for 8000 h per year (typical reactor size in fine chemistry) suggests a production capacity of 38 kT per reactor which is also in accordance with industrial specifications of the field. Note that an even higher productivity may be expected using Aquivion<sup>®</sup> PFSA PW66 as a solid acid catalyst (Table 2).

Although Aquivion<sup>®</sup> PFSA PW98 surpasses the performances of H<sub>2</sub>SO<sub>4</sub>, its recycling is mandatory since solid acid catalysts are generally more expensive than H<sub>2</sub>SO<sub>4</sub>. In this context, recycling experiments were undertaken. At the end of the first cycle, Aquivion<sup>®</sup> PFSA PW98 was filtered off and reused for another run after washing with water and ethanol to remove most of adsorbed glucose and APGs. As expected, owing to its high chemical stability, Aquivion<sup>®</sup> PFSA PW98 was successfully recycled at least 10 times without noticeable decrease in selectivity, activity and productivity (Fig. 1).



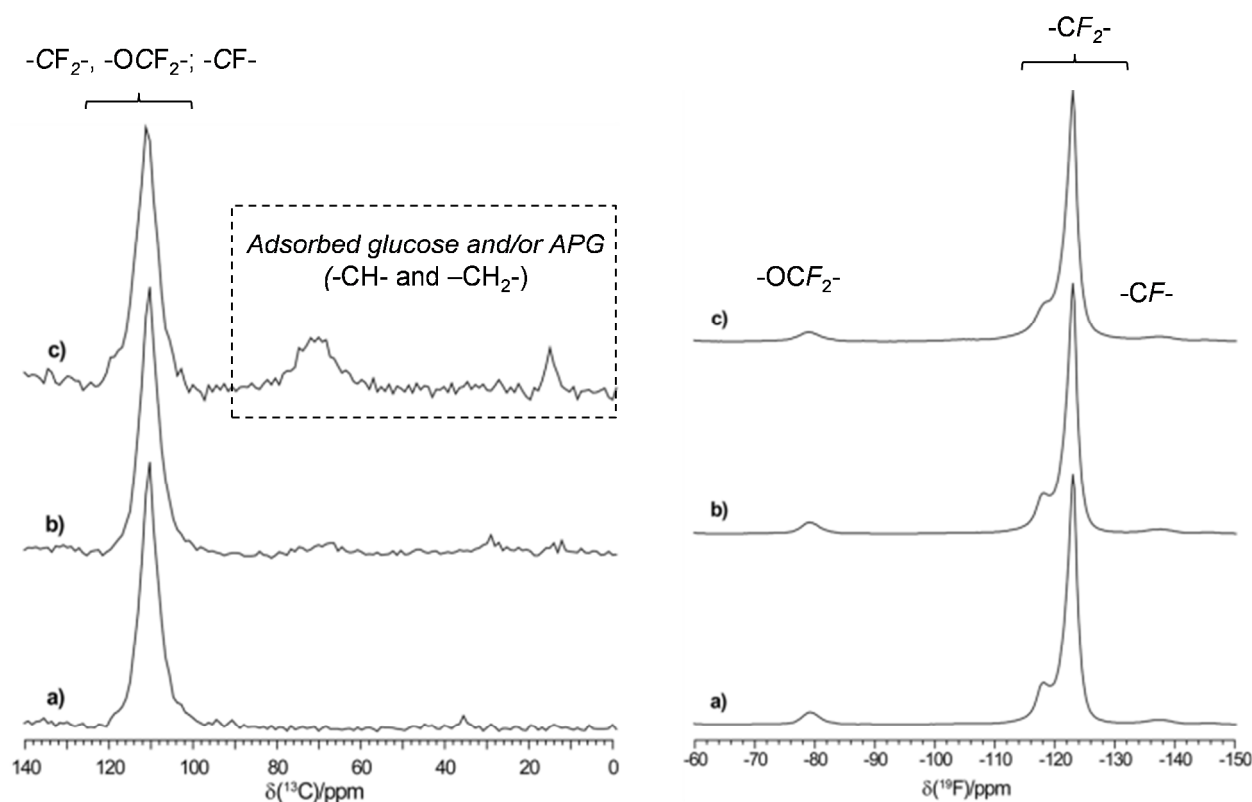
**Figure 1.** Recycling of Aquivion<sup>®</sup> PFSA PW98

After filtration of Aquivion<sup>®</sup> PFSA PW98, the reaction medium was carefully analyzed by ICP and <sup>19</sup>F NMR. No trace of fluorine or sulfur was observed in the sample of AAG which agree well with the high stability of Aquivion<sup>®</sup> PFSA PW98 under our working conditions.

To further support the integrity of Aquivion<sup>®</sup> PFSA PW98 after 10 consecutive runs, this later was analyzed by FT-IR and CP/MAS NMR. In Figure S7 are reported the FT-IR spectrum of the fresh Aquivion<sup>®</sup> PFSA PW98 and the overlapped spectra of the spent Aquivion<sup>®</sup> PFSA PW98 after one and 10 catalytic cycles. The FT-IR spectra show that the characteristic bands of Aquivion<sup>®</sup> PFSA (namely the S-O stretching at about 1000 cm<sup>-1</sup> and the C-C and C-F stretching at 1100-1300 cm<sup>-1</sup>) were conserved over the catalytic runs. Besides, bands associated to compounds adsorbed onto the catalyst surface were also evident at 2800-3000 cm<sup>-1</sup> (C-H stretching) and at 1380-1480 cm<sup>-1</sup> (C-H bending) in the spent Aquivion<sup>®</sup> PFSA PW98 samples. As expected, the intensity of such bands increased with the number of catalytic runs and is presumably related to the increase amount of AAG or APG material deposited onto the catalyst surface over the runs.

Next, the spent Aquivion<sup>®</sup> PFSA PW98 was analyzed by <sup>13</sup>C MAS NMR (Figure 2). Fresh Aquivion<sup>®</sup> PFSA is characterized by an intense signal at 111 ppm, ascribed to the -CF<sub>2</sub>- groups, and by two very small signals blurred in the feet of the main signal at 117 and 108 ppm and ascribed to -OCF<sub>2</sub>- and -CF- groups respectively. The <sup>13</sup>C MAS NMR spectrum recorded for the spent Aquivion<sup>®</sup> PFSA PW98 (after ten catalytic runs) showed additional signals and particularly a broad signal centered at 70 ppm, which could be assigned to adsorbed glucose. This claim is supported by the presence of very weak signals in the 15-30 ppm range, which could be ascribed to aliphatic -CH<sub>2</sub>- groups. A trace of the signal at 70 ppm was already present after one catalytic run (Figure 2).





**Figure 2.**  $^{13}\text{C}\{^1\text{H}\}$  one pulse MAS NMR spectra (left side) and  $^{19}\text{F}$  one pulse MAS NMR spectra (right side) of (a) fresh Aquivion® PFSA PW98 (b) Aquivion® PFSA PW98 after one catalytic run and (c) Aquivion® PFSA PW98 after ten catalytic runs

The  $^{19}\text{F}$  one pulse MAS NMR spectra of the fresh and spent Aquivion® PFSA PW98 samples are also reported in Figure 2. Fresh Aquivion® PFSA PW98 shows signals that can be ascribed to  $-\text{OCF}_2-$  (-79 ppm) and  $-\text{CF}-$  (-138 ppm) groups, whereas the signals in the range between -105 and -123 ppm are assigned to  $-\text{CF}_2-$  groups. Spent Aquivion® PFSA PW98 collected after one or ten catalytic runs did not show additional signals, corroborating the chemical stability of Aquivion® PFSA PW98 already observed with other techniques. Finally, TGA analysis of the fresh and spent Aquivion® PFSA PW98 was carried out (Figure S8). This analysis confirmed that 9 wt% of materials were absorbed on the recycled Aquivion® PFSA PW98 which agrees

well with CP/MAS NMR and FT-IR investigations. The decomposition temperature of the fresh and recycled Aquivion<sup>®</sup> PFSA PW98 was the same (starts at 300°C) which further supported the integrity of the polymer structure during catalysis.

Having all these data in our hands, we then evaluated the possibility to produce AAG from glucose syrup (typically 70 wt% of glucose in water) which is a cheaper source of glucose. As above-mentioned, the H<sub>2</sub>SO<sub>4</sub>-catalyzed glycosylation of glucose syrup with fatty alcohols is not directly feasible at an industrial scale and it requires a two-step process involving (1) a catalytic glycosylation of glucose syrup with *n*-butanol followed by (2) a transglycosylation of butyl glycosides with *n*-dodecanol. Despite acceptable yields of APGs, this industrial process is however more costly than the direct glycosylation with fatty alcohols.

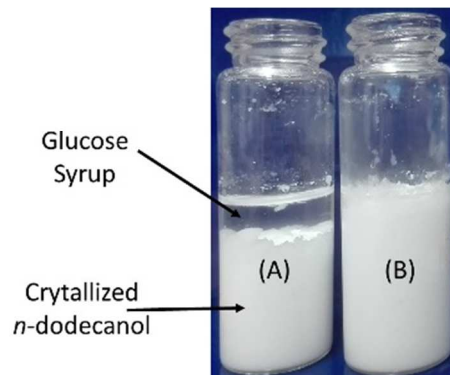
In this context, the direct glycosylation of glucose syrup with *n*-dodecanol was investigated either in the presence of Aquivion<sup>®</sup> PFSA PW98 or H<sub>2</sub>SO<sub>4</sub> (Table 3). Similar conditions than those described above (Table 1, entry 5) were employed. As expected, in the presence of H<sub>2</sub>SO<sub>4</sub>, AAG were produced with only 30% yield at total conversion after 90 min of reaction and the stirring was rapidly hampered by the formation of a sticky gel (polydextrose, Figure S9). To our delight, when Aquivion<sup>®</sup> PFSA PW98 was employed, AAG was produced with 64 % yield (at a glucose conversion of 90%) and no formation of polydextroses was visually observed. Other products were mostly APG. The selectivity to AAG was 71% (vs 30% with H<sub>2</sub>SO<sub>4</sub>) and the reactor productivity to AAG reached 223 kg/m<sup>3</sup>/h (vs 106 kg/m<sup>3</sup>/h for H<sub>2</sub>SO<sub>4</sub>) which represent an important advance in the field. Aquivion<sup>®</sup> PFSA PW66 also afforded similar results (66% yield to AAG, Table 3).

**Table 3.** Catalytic glycosylation of glucose syrup with *n*-dodecanol<sup>a</sup>

Catalyst	Conv. (%)	AAG yield (%)	AAG selectivity (%)	Productivity (kg/m <sup>3</sup> /h)
H <sub>2</sub> SO <sub>4</sub>	99	30	30	106
Aquivion <sup>®</sup> PFSA PW98	90	64	71	223
Aquivion <sup>®</sup> PFSA PW66	96	66	69	300

<sup>a</sup> 120°C, 1.5 mol% of H<sup>+</sup>, *n*-dodecanol/glucose molar ratio = 3, 90 min

Previously, it has been well documented that the concomitant presence of perfluoroalkyl chains and -SO<sub>3</sub>H groups conferred to Aquivion<sup>®</sup> PFSA PW98 amphiphilic properties.<sup>20</sup> One may thus suspect that Aquivion<sup>®</sup> PFSA PW98 facilitated a more intimate contact between glucose syrup and the *n*-dodecanol phases than in the case of H<sub>2</sub>SO<sub>4</sub>. This kind of Pickering-like emulsification of the reaction medium by Aquivion<sup>®</sup> PFSA PW98 is expected to inhibit the side oligomerization of glucose. To support this claim, the glucose syrup was stirred in the presence of *n*-dodecanol (ratio 1:3) at 40°C for 15 min at 24 000 rpm in the presence of 1.5 mol% of H<sup>+</sup> (relative to glucose) either with H<sub>2</sub>SO<sub>4</sub> or Aquivion<sup>®</sup> PFSA PW98. After emulsification of the reaction medium, it was progressively cooled down to room temperature within 30 min. At room temperature, *n*-dodecanol crystallized, thus providing a clear frozen image of the emulsion.



**Figure. 3.** Frozen image of the emulsification of the reaction medium with (A)  $\text{H}_2\text{SO}_4$  and (B) Aquivion<sup>®</sup> PFSA PW98

In the case of  $\text{H}_2\text{SO}_4$ , a clear phase separation was observed between crystallized *n*-dodecanol and the glucose syrup (Figure 3). Conversely, in the case of Aquivion<sup>®</sup> PFSA PW98, the glucose syrup remained fully dispersed in *n*-dodecanol. The sample was even kept overnight without obvious decantation of the syrup. These results strongly support the effect of the Aquivion<sup>®</sup> PFSA PW98 polymeric structure on the emulsification of the reaction medium which may rationalize the better selectivity observed with Aquivion<sup>®</sup> PFSA PW98.

## Conclusion

We report here that Aquivion<sup>®</sup> PFSA, a perfluorosulfonic acid polymer, surpasses the performances of  $\text{H}_2\text{SO}_4$  industrially employed in the glycosylation of glucose with fatty alcohols. Under close conditions with industrial processes, Aquivion<sup>®</sup> PFSA was found markedly more selective than  $\text{H}_2\text{SO}_4$  and led to higher reactor productivities. Furthermore, its high chemical stability allowed its recycling for at least 10 consecutive catalytic cycles. Under optimized conditions, Aquivion<sup>®</sup> PFSA provided selectively APGs (DP of 1.2) with a reactor productivity

of 477 kg/m<sup>3</sup>/h which is in line with the industrial specifications of the yield. Origin of these superior performances of Aquivion<sup>®</sup> PFSA not only stems from its super acid properties but also from its amphiphilic properties leading to an emulsification of the biphasic medium, a pivotal aspect to limit the unwanted oligomerization of glucose to polydextroses. Conversely to H<sub>2</sub>SO<sub>4</sub>, owing to this amphiphilic property, Aquivion<sup>®</sup> PFSA was even capable of catalyzing the direct glycosylation of glucose syrup with *n*-dodecanol, thus opening a straightforward access to APGs from a cheaper source of glucose.

Aquivion PFSA has a clear potential to induce a cut of cost as no catalyst or base are consumed in the process. As a consequence, Aquivion<sup>®</sup> PFSA allows producing APG without any ashes, an important point with respect to their physico-chemical properties. At this stage, the cost of this process is however difficult to be correctly worked out because of the lack of reliable data and the difficulty to weight the different costs (capex, catalyst recycling, purification steps, idle time due to catalyst maintenance, etc..). In our views, as compared to current routes, Aquivion<sup>®</sup> PFSA should not induce supplemental cost as it is conveniently recovered by filtration and reused as collected without any treatment and it does not require any new equipment or investments.

## Experimental section

**Chemical and reagents:** *n*-Dodecanol, *n*-Hexadecanol, *n*-Octadecanol and H<sub>2</sub>SO<sub>4</sub> were purchased to Sigma-Aldrich and used without further purification. Aquivion<sup>®</sup> PFSA PW98, Aquivion<sup>®</sup> PFSA PW66-S, Aquivion<sup>®</sup> PFSA PW79-S and Aquivion<sup>®</sup> PFSA PW87-S were kindly provided by Solvay Specialty Polymers. Amberlyst-15 was purchased to ACROS and SBA-15-SO<sub>3</sub>H was prepared according to a known procedure.<sup>21</sup>

**Gas Chromatography analyses:** AAGs were analyzed on a Varian 3350 equipped with a flame ionization detector. Before analysis, AAGs were silylated. Typically, a sample (0.1 g) was taken from the reactor and diluted in 2 mL of a solution of pyridine containing 1 mg.mL<sup>-1</sup> of sorbitol (internal standard). After solubilization, 1.0 mL of HDMS and 1.0 mL of TMSCl were successively added. The solution was then centrifuged for 10 minutes and 0.5 µL of the solution was injected. A HT 5 column was used (L = 30 m, Ø = 0.32 mm, e = 0.25 µm). The oven was heated from 50°C to 220°C with a heating ramp of 10°C/min and then to 320°C with a heating ramp of 10°C/min.

**Solid State MAS NMR:** experiments were acquired on an Agilent DirectDrive2 400 MHz NB spectrometer operating at 399.81 MHz for <sup>1</sup>H, 376.62 MHz for <sup>19</sup>F and 100.50 MHz for <sup>13</sup>C, using a 1.6 mm T3 MAS special HFX probe. <sup>1</sup>H one pulse MAS experiments were acquired at 25 kHz using a 90° pulse of 4.2 µs, a recycle delay of 4 s and 64 scans. <sup>19</sup>F one pulse MAS experiments were acquired at 25 kHz using a 90° pulse of 3.5 µs, a recycle delay of 8 s and 64 scans. <sup>13</sup>C(<sup>1</sup>H) dipolar decoupled one pulse experiments were acquired at 20 kHz, using a 90° pulse of 4.0 µs, a TPPM <sup>1</sup>H decoupling scheme, a recycle delay of 6 s and 8800 scans. Chemical shifts (δCS) for <sup>1</sup>H and <sup>13</sup>C are reported relative to TMS, using adamantane as secondary standard. <sup>19</sup>F δCS are reported relative to CFCl<sub>3</sub>, using PTFE (δCS= -123 ppm) as secondary standard.

**Catalytic glycosylation of glucose:** Typically, glucose (1.08 g, 6 mmol) was mixed with *n*-dodecanol (3.35 g, 18 mmol) in a 50 mL round bottom flask, equipped with a magnetic stirring bar. Then an acid catalyst (1.5 mol% of H<sup>+</sup> relative to glucose) was added and the solution was heated in an oil bath at 120°C under vacuum (15 mmHg) for the desired reaction time. The reaction was monitored by GC as mentioned above. In the case of Aquivion<sup>®</sup> PFSA, this later

was filtered off at the end of the reaction and the excess of *n*-dodecanol was removed under vacuum using an industrialized standard procedure. Alternatively, APGs can be also purified by filtration on a plug of silica using consecutively ethyl acetate/heptane (1/1) and methanol/H<sub>2</sub>O (1/1) as eluents. The same procedure was used from *n*-hexadecanol and *n*-octadecanol.

Note: filtration of the Aquivion<sup>®</sup> PFSA solid acid catalyst should be performed at 100°C to avoid the solidification of *n*-dodecanol. Alternatively, the reaction medium can be also diluted with ethanol to facilitate the filtration of Aquivion<sup>®</sup> PFSA at room temperature.

**Recycling experiments:** After the catalytic first run, the Aquivion<sup>®</sup> PFSA was filtered off at 100°C. Then, Aquivion<sup>®</sup> PFSA was washed with water and with ethanol to remove most of adsorbed glucose and APGs. The recovered catalyst was then dried for one hour at ambient temperature under vacuum (15 mHg) and directly re-engaged in the next catalytic run without any further purification. Experimental parameters (reaction time, temperature, *n*-dodecanol/glucose ratio, catalyst loading, etc.) remained unchanged between each run.

## ASSOCIATED CONTENT

Supporting Information Available: <http://pubs.acs.org> Selected kinetic profiles, a representative chromatogram, copies of NMR spectra of APGs, copies of FT-IR, <sup>13</sup>C and <sup>19</sup>F MAS NMR spectra of fresh and spent Aquivion<sup>®</sup> PFSA PW98 and a picture of the reaction medium during the H<sub>2</sub>SO<sub>4</sub>-catalyzed glycosylation of glucose syrup with *n*-dodecanol.

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**Author Contributions:** The paper was written through contributions of all authors. All authors have given approval to the final version of the paper. A. Karam, K. De Oliveira Vigier, and F. Jérôme contributed equally to catalytic experiments. S. Marinkovic, B. Estrine contributed equally to the purification and characterization of APG. C. Oldani contributed to the characterization of Aquivion PFSA before and after use.

**Notes:** The authors declare no competing financial interest.

**Acknowledgement:** This work was supported by the CNRS, the French Ministry of Research, ARD and ADEME (project APG-2G). G. Canil (FT-IR analyses), R. Biancardi and A. Cattaneo (MAS NMR spectroscopy) are gratefully acknowledged.

**Abbreviations:** AAG, Amphiphilic Alkyl monoGlycosides; APG, Alkylpolyglycosides, PFSA, perfluoro sulfonic acid; DP, Degree of Polymerization, TOF, Turn Over Frequency; GC, Gas Chromatography, NMR, Nuclear Magnetic Resonance; FT-IR, Fourier Transformation-Infra Red.

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SYNOPSIS

