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1 Perspectives of surface plasmonic resonance optical fibre sensors for anaerobic
2 digestion

3

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37 **1 Abstract**

38 Biogas production is becoming significantly viable as an energy source for replacing fossil-
39 based fuels. The further development of the biogas production process could lead to
40 significant improvements in its potential. The improvement of anaerobic digestion detection
41 technologies is the cornerstone to reach higher methane productivities and develop fully
42 automatized processes to decrease operational costs. New sensors are requested to automatic
43 obtain a better interpretation of the complex and dynamical internal reactor environment. This
44 will require detailed systematic detection in order to realise a near-optimal production
45 process. There is currently a disparity between the complexity of anaerobic digestion, and on-
46 line detection. By improving the durability, sensitivity and cost of dissolved H₂ sensor
47 technology, further understanding of the anaerobic digestion process may allow the
48 prevention of process failure. Furthermore, the detection of dissolved H₂ directly in the liquid
49 phase would drastically reduce the time for distinguishing an imbalance in the microbial
50 community. The emergence of surface plasmonic resonance (SPR) sensing with optical fibres
51 coupled with the H₂-sensitive metal palladium, allows detection of dissolved hydrogen in
52 liquid. By implementing these SPR sensors into anaerobic digestion, improvements to the
53 biogas production process, even at small scales, may be achieved by guided the process in the
54 optimum direction, avoiding the collapse of the biological process. This review intends to
55 assess the feasibility of on-line, cost-effective, rapid, and efficient detection of dissolved H₂ in
56 anaerobic digestion by SPR.

57

58 **2 Introduction**

59 One route to production of renewable, clean energy is through biogas production, where
60 biogas is derived from organic waste materials. The production of biogas is achieved through
61 the anaerobic digestion (AD) of the organic waste materials by various microorganisms (1).
62 Another route to renewable, clean energy is the so-called Power-to-Gas route, where surplus
63 renewable electrical energy is used to produce H_2 by electrolysis. However, H_2 utilisation is
64 facing unsolved bottlenecks related to H_2 transport and storage. An attractive alternative to H_2
65 distribution is to convert H_2 to methane in a biological methanation process (2,3). Methane
66 has a much higher volumetric energy content than H_2 and thus a lower storage transport cost,
67 and can be distributed in existing natural gas infrastructure (4). By utilising the methanation
68 process, H_2 can be used to reduce the CO_2 in the biogas produced (2,3). A promising
69 approach is to input H_2 to the biogas reactor such that the methanation takes place within the
70 reactor (2). However, increasing the concentration of dissolved H_2 in the reactor can inhibit
71 the production of biogas and accumulate VFAs, and in the worst case cause the whole
72 biological process to collapse (5).

73 Due to the complexity of the biogas production process, it is not always straight-forward to
74 determine the state of the AD process from measuring the chemical variables within the
75 digester (1). Despite this, the hydrogen content of produced biogas is a very sensitive
76 indication of imbalance between microbial groups within the digester (6–8). Although
77 hydrogen is straightforward to measure in the gas-phase, dissolved hydrogen in the liquid
78 phase is considered more appropriate as the liquid to gas mass transfer of hydrogen introduces
79 a significant delay in detection (9). Therefore, dissolved H_2 is recognised as a better approach
80 to an early warning indicator and an excellent complement to VFA monitoring (5). Dissolved
81 H_2 concentrations are, therefore, required control parameters for biogas production
82 monitoring and utilising H_2 for further methanation of CO_2 (2,3). It is essential that dissolved
83 H_2 be monitored closely to gain an understanding of the current biological process within the
84 digester.

85 Cost-effective sensor technologies for monitoring and analysis of H_2 within the reactor are
86 crucial for improving efficiency, productivity and cost of biogas production in many plants.
87 There are many methods for achieving monitoring of a variety of parameters within
88 bioreactors. These may rely on sample extraction, but in some cases, the sensor can be

89 interfaced directly with the internal environment of the bioreactor. Despite this, there are still
90 improvements required to make ideal sensors for the measurement of dissolved H₂ within the
91 biogas production process. Ideally, a monitoring system must have cost-effective, accurate,
92 specific, stable and sensitive sensors, which can send data to software programs for analysis.
93 This data can then be computationally analysed, allowing the correlation of the sensor data to
94 a specific parameter or process model. Furthermore, with the increase in small-scale plants,
95 there is a significant demand for sensor technologies that do not have an associated high cost.

96 In this review, contemporary sensor technologies that can combine AD with on-line sensor
97 technologies focusing on dissolved H₂ are discussed and compared to current industry
98 methods. The contemporary technologies presented have the potential for improving the
99 efficiency, economic costs and productivity of biogas plants, as well as allowing on-line
100 dissolved H₂ monitoring to facilitate H₂ injection for methane upgradation.

101 **3 Sensors Requirements for State of an Anaerobic Digester** 102 **Determination**

103 There are distinctive ways that sensors can be fused into the AD plant to satisfy the on-line
104 observing prerequisite. The sensors utilized for estimations of factors inside an AD plant can
105 require the extraction of digestate from the bioreactor, filtration and external sampling (at-line
106 sensor), the sensor to be located inside the digester (in-line sensor), or to be removed from the
107 digester and sampled in a lab (disconnected sensor) (10).

108 The in-line sensors must be impervious to pressure (somewhat above atmospheric pressure)
109 and temperature (somewhere in the range of 35°C and 55°C), as well as having the capacity to
110 be cleaned. Also, they must be significantly impervious to obstruction by fouling. Ideal
111 sensors must provide proper detection quality, having high precision, specificity and
112 sensitivity. The collected information must then automatically be processed and used in the
113 supervision system. The figured estimations should deliver consistency and be steadiness
114 despite changes in medium changes in biological or chemical contents. In practice, the
115 benefits of the sensor in terms of increasing process reliability and efficiency must be
116 compared to its price, including manpower requirement for human intervention (setup,
117 calibration, cleaning).

118 For live, on-line detection of an AD plant to be valuable, the reaction time of the sensors is a
119 critical trademark (10). Even though the delay of measurements is explicit to every sensor and
120 application, the time required to acquire an outcome must be small (< 10 minutes) concerning
121 the biological dynamics within the digester. All the more explicitly, the time required to
122 acquire a sensor outcome will depend altogether on the retention time of the AD reactor,
123 duration of analysis and the dead volume of the filtration framework utilised. Also, it must be
124 a lot quicker than the time required for the gathering of H₂ to happen to distinguish and avoid
125 a stress event. With this in mind, the sensor framework must be tailored to the procedure with
126 satisfactory sampling locations. Otherwise, the low effectiveness of the process control will
127 occur (11).

128 The location of the sensor inside the digester is fundamental, as the digester can be
129 homogeneous or inhomogeneous. This depends mainly on the feedstock type, process size
130 and AD technologies. Also, there are AD methods that have intended inhomogeneous
131 chemical gradients inside the reactor (e.g., up-flow anaerobic sludge blanket (UASB) &
132 fluidised bed reactors), and this is exacerbated with the expansion of reactor size. Despite this,
133 if the digestate is homogeneous, the sensor can be set anywhere inside the bioreactor, and the
134 signal from the sensor will represent the real state; however, if it is significantly
135 inhomogeneous, several sensors might be required to decipher the state of the digester
136 completely.

137 There are three primary phases (solid, liquid and gas), inside an AD plant. These phases have
138 diverse properties, factors and prerequisites when considering in-line sensors. The liquid
139 phase of the anaerobic digester is an intricate blend of different microorganisms, substrates,
140 nutrients, products, metabolites and dissolved gases. Because of the diffusion rate of
141 components from liquid to gas, it is attractive to make estimations specifically from the liquid
142 phase of the digester. This can decrease the lag time between changes in the AD biological
143 dynamics and identification of these changes.

144 **4 Traditional H₂ Detection**

145 **4.1 Dissolved H₂ detection**

146

147 Dissolved H₂ produced in AD has long been recognised as an early warning indicator and an
148 excellent complement to VFA monitoring (5,9). Additionally, the *in situ* hydrogen injection
149 into the anaerobic digester is a promising process aimed at increasing the biogas methane
150 content, at the expense of the CO₂ content. It has been hypothesised that adding hydrogen
151 directly into the anaerobic digester may change microbial community composition promoting
152 hydrogenotrophic methanogenesis pathways (12). This enhances the biological production of
153 methane by 20-40% (2,13), potentially achieving a purity of up to 90% (12,14–16) when
154 combined with *ex situ* upgrading. This allows existing biogas plants to be utilised for H₂,
155 eliminating the need for hydrogen storage (which can be of safety concern) (17). Despite this,
156 dissolved H₂ can potentially inhibit production of methane, and in the worst case cause the
157 whole biological process to collapse (5). Moreover, injection of H₂ to a level exceeding a 4:1
158 stoichiometric ratio between H₂ and CO₂ tends to deplete CO₂ resulting in the rise of pH (13),
159 and inhibiting the autotrophic hydrogenotrophic methanogenesis process (18). Furthermore,
160 the oxidation of acetate towards methane production is only thermodynamically favourable
161 when the partial pressure of H₂ is below 74 Pa (19,20). Therefore, dissolved H₂ must be
162 monitored continually, especially if H₂ is directly injected into the anaerobic digester for
163 methane upgradation.

164 Since the critical concentration of dissolved H₂ is only 74 Pa (19,20) and difficult to measure,
165 the concentration of dissolved H₂ in anaerobic biogas production is currently calculated from
166 a gas fraction of H₂ detected in the gas phase of the digester. However, due to the limited H₂
167 mass-transfer coefficient, there is a significant time delay between an increase in H₂
168 concentration in the liquid and an increase in the gas phase of the digester. Such time delays
169 represent a severe limitation for optimal process control (5,9). Extraction techniques designed
170 for off-line dissolved H₂ monitoring are time-consuming and not an option for the rapid
171 process control desired. Other techniques based on the transfer of H₂ from the liquid through a
172 gas-permeable membrane followed by gas phase quantification (gas chromatography or mass
173 spectrometry), are considered too sophisticated and expensive for on-line monitoring.
174 Therefore, there is a definite need for an effective, reliable, and cost-effective sensor for
175 continuous on-line monitoring of dissolved H₂ in anaerobic bioprocesses.

176 **4.1 Gas-Phase Detection**

177 Detection of H₂ gas in the headspace of the anaerobic digester is straight-forward to measure
178 but is delayed significantly due to the mass-transfer coefficient of H₂. Therefore, the main

179 drawback of the detection in the headspace is that sudden changes in dissolved H₂ levels will
180 not be detected for some time, and, therefore, process failure could occur before any signals
181 of an H₂ increase are detected. Despite this, membrane-covered Clark-type electrodes can be
182 adapted to measure H₂ in the headspace of the reactor, with negligible biofouling of the
183 membrane occurring when in gas-phase. Thermal conductivity sensors like those provided by
184 BlueSens (BlueSens, Germany) can also gauge the concentration of H₂ gas in the headspace.
185 These sensors use a small heated filament to detect thermal conductivity of the gases in
186 simple gas mixtures, allowing the determination of the percentage of specific gases of interest
187 within a mixture.

188 Palladium metal oxide semiconductor (Pd-MOS) sensors have also been studied for their
189 suitability for H₂ detection in the gas phase of AD (21). The palladium can become palladium
190 hydride in the presence of H₂, a rapid and reversible reaction that can alter the conductivity of
191 the metal and used to determine the ppm of H₂. Alternatively, gas chromatography (GC)
192 instruments equipped with thermal conductivity detectors can be used to determine H₂ (8).
193 GC is a very accurate method of H₂ detection in the gas phase and is regularly used as a
194 reference measurement technique for all other H₂ detection methods.

195 **4.2 Liquid-Phase Detection**

196 H₂ can be detected using a membrane-covered Clark-type electrode (22) in the liquid phase as
197 well. There are extraction and H₂ permeable membrane methods designed for dissolved H₂
198 monitoring within the digester, but these can be expensive and time-consuming processes.
199 The membrane requiring Clark-type electrodes can be used for on-line monitoring of
200 dissolved H₂ in the liquid-phase, which relies on the oxidation of H₂ at a Pt electrode and
201 dissociation of molecular hydrogen at a Pd electrode (23,24). Unfortunately, these are prone
202 to biofouling on the membrane surface. Once biofouling occurs, the measurements from this
203 type of electrode are mostly unreliable, and, therefore, the membrane must regularly be
204 replaced to avoid this. So far all reported electrochemical sensors for H₂ detection suffer from
205 membrane fouling resulting in a short lifetime, low selectivity and low signal-to-noise ratio
206 (24). Although these Clark-type sensors can operate at room temperature, temperature
207 fluctuations must also be taken into account to maintain correct O₂ and H₂ calculations (25).

208 Measurements of dissolved hydrogen can also be performed using hydrogen microsensors
209 like those provided by Unisense (Unisense A/S, Denmark). Microsensors allow H₂ to diffuse
210 from the internal liquid phase of the anaerobic digester through a silicone membrane to a

211 platinum anode that is polarized against an internal reference. The current between the
212 palladium electrode and the reference is linearly indicative of the dissolved hydrogen at the
213 tip of the sensor. The current change is in the picoamp range and is measured using a
214 picoammeter. An alternative method for dissolved H₂ detection was described by Björnsson et
215 al. (2001). Here, a liquid-to-gas membrane was utilised to extract dissolved H₂ from the liquid
216 phase, through a Teflon membrane placed in the internal environment of the anaerobic
217 digester. The H₂ was then detected using a Pd-MOS sensor (26).

218 **4.3 Remarks**

219 The methods outlined here suffer from disadvantages including sample preparation,
220 contamination and biofouling. GC is a real proven alternative at very high accuracy, but
221 requires advanced systems for auto-sampling, transfer of the sample and filtering, and
222 requires a significant amount of time to obtain a measurement. Forms of ultrafiltration are
223 required for liquid phase detection to produce a clear particle-free sample for GC and
224 electrochemical detection methods. This filtration will result in biofouling in the long term, a
225 property that must be considered when using such methods for detection in the liquid phase.

226 Measurements undertaken in the gas phase of the reactor have limited issues with biofouling
227 of filtration systems; however, the presence of H₂S in the biogas massively reduces the
228 sensitivity of the sensor systems (21). Additionally, the mass-transfer rate of H₂ from the
229 liquid phase to the gas phase is prolonged, resulting in significant delays when detecting H₂
230 spikes in the AD process (9).

231 **5 Software Sensors**

232 Using mathematical approaches, information provided by on-line sensor systems can be
233 extended. The two strategies for achieving this are based on methods of data analysis and the
234 representation of the dynamics of the plant by mathematical models.

235 **5.1 Observers**

236 The incorporation of software sensors with on-line sensor systems allows the prediction of the
237 biological process state by estimating non-measured variables. In the case of dissolved H₂
238 measurements, estimations of the dominating microbial processes within the reactor can be
239 made. Additionally, software sensor systems are a vital supporting component of closed-loop
240 central strategies. These approaches are also known as state observers or state estimators, and

241 have a large amount of theoretical background. Assimilation of the real-time on-line
242 measured variable(s) can be combined with the theoretical knowledge base of the AD process
243 through a mathematical model allowing the prediction of variables that have a low frequency
244 or no sampling. Depending on the desired accuracy, the frequency of sampling, sensor
245 information quality and frequency of sampling, different strategies for the design of an
246 appropriate software sensor can be applied.

247 Linear frameworks, or extensions thereof, are popular approaches to software sensing. The
248 most known algorithms for achieving software sensors are based on extended Kalman filters
249 (EKF) and extended Luenberger observers (ELO) (27). Despite their popularity, the required
250 local linear approximation of the process model reduces the certainties of the stability and
251 convergence properties for wide operating ranges. Furthermore, perfect knowledge of the
252 model and its parameters are assumed by these algorithms, allowing the approach to be
253 sensitive to any inaccuracy within the model parameters.

254 To reduce the dependency of the algorithms on parameter uncertainty, different strategies
255 have been developed by using the mass balance information from the reactor as the base of
256 the estimation scheme. Although mass balance only represents the process partially, it can
257 robustly deal with any missing information. Moreover, estimates of kinetics for some
258 processes in the model can be achieved with the support of gaseous flow rates using
259 asymptotic observers (28). These methods can achieve a linear observer by relying on
260 changes of variables cancelling nonlinear terms within the process (29). However, the dilution
261 rate controls the convergence rate when utilising asymptotic observers. Simultaneous
262 estimating of model parameters and the state of the process can be performed with adaptive
263 observers (30). Alternatively, using the process model and its known parameters allows the
264 tailoring of nonlinear observers with the nonlinearity of the process accounted for by the
265 algorithm (31). A significant limitation of the implementation and calibration of such
266 observer algorithms is their inherent complexity.

267 Internal observers offer a flexible method by providing guaranteed estimate intervals where
268 the state of the variable lies, avoiding reconstruction of precise numerical values (32,33). This
269 has been observed successfully for use in AD (34,35). Due to the uncertainty of
270 concentrations in the influent, this parameter is inherently difficult to use to estimate the
271 process accurately. To overcome this, an algorithm that simultaneously estimates the influent
272 concentrations using both input and state observers has been shown to alleviate this drawback

273 (36). Further development of these observers has resulted in their extension to handle spatial
274 distributions within the anaerobic digester (37,38).

275 **6 Emerging SPR Sensor Technologies**

276 More recently, various optical sensor principles have been proposed for H₂ monitoring (39–
277 51). Sensors based on the H₂ uptake in palladium appear particularly promising. The volume
278 expansion of palladium films or nanoparticles caused by metal-hydride formation can be
279 measured very accurately using optical techniques (39,40,44,47,49,50). Additionally, the
280 surface plasmon resonance (SPR) of gold (when coupled to palladium in a layer stack), can be
281 measured accurately, with the plasmon resonance frequency being modulated by the
282 hydrogenation of the palladium layer (43,45,48).

283 SPR sensors exploit the interaction of incident electromagnetic waves with the oscillation of
284 the plasmon wave of a material (e.g., gold). When the momentum of incident electromagnetic
285 waves matches the momentum of the surface plasmon waves in the gold, the electromagnetic
286 waves are coupled to the plasmon wave and are diminished (FIG??). The frequency of the
287 plasmon wave can be altered by changes in the materials used, therefore changing the
288 wavelength of incident electromagnetic waves absorbed. An example of this is the use of a
289 bare, cladding-less optical fibre with a gold and palladium layer-stack (Fig). The incident
290 electromagnetic wave interacts with the plasmon wave on the surface of the gold layer.
291 Furthermore, this plasmon wave can be modulated by changes in the permittivity of the gold.

292 By adding an H₂-sensitive layer of palladium, the formation of palladium hydride effects the
293 electrical field of the gold, changing its permittivity, and changing the momentum of the
294 surface plasmon resonance of the gold. The interaction of the incident electromagnetic waves
295 with the gold will be changed, causing different electromagnetic waves to be diminished.
296 Using spectroscopic methods, this will culminate in a shift in apparent absorption of
297 electromagnetic waves as a consequence of H₂ presence.

298 In order to engineer an SPR-based sensor with palladium as the sensing material for use in the
299 liquid phase of an anaerobic digester, the thicknesses of the gold and palladium layers, and
300 the incident angle of the light to the layers must be considered. Using a straight-forward
301 model accounting for the refractive indexes of the silicon optical fibre, gold, palladium and
302 water, a considerable variation in sensor ability is observed as a function of the incident angle

303 (FIG). This is also apparent with varied thicknesses of the two metal layers (FIG). To achieve
304 a dissolved H₂ sensor with high sensitivity and high signal using only gold and palladium
305 metal layers, an incident angle of XX, with metal thicknesses of XX of gold and XX of
306 palladium is required. Although the thickness of the metal is straight-forward to achieve with
307 sputtering deposition techniques, the angle of incidence requires further design
308 considerations.

309 The metal layers can be deposited on the side surface of the fibre. Increases in the incident
310 light angle can be performed on such designs by placing the optical fibre in a d-loop (Fig), or
311 by using a Bragg grating fibres (Fig). This will allow the incident light angle to be optimised
312 for coupling of the electromagnetic wave to the SPR wave of the gold layer. Alternatively, the
313 metal layer stack can be deposited on the end-tip of a fibre, acting as a mirror (Fig). With the
314 use of a multimode fibre, this will allow the electromagnetic wave to achieve coupling with
315 the SPR wave of the gold layer. Furthermore, the metal layer stack could be deposited onto a
316 transparent patch and installed on the internal space of the reactor behind a glass window.
317 Probing of the sensor patch would then be achieved using an external optical fibre, reducing
318 complexity and cost.

319 **7 Calibration of SPR Sensors**

320 With using palladium as the sensing material, the selectivity for hydrogen is very high.
321 Therefore, calibration can be achieved straightforwardly by use of GC measurements of
322 hydrogen concentration in the liquid phase.

323 Before a palladium-based SPR sensor can be utilised, the consistency and accuracy of the
324 sensor must be confirmed. Different SPR sensor datasets must be comparable to establish
325 successful data analysis. A variety of pre-processing methods can be applied to the data sets
326 to achieve this. Some examples include deviation (52), filtering (53) normalisation,
327 standardisation, centring, weighing and scaling (54) of the data sets. Pre-processing is a
328 powerful and sensitive component in data analysis (55), where consideration of the chosen
329 method is required depending on the type of data used. The exclusion of irrelevant data is also
330 a pre-processing method that is essential. This can be achieved by normalisation or baseline
331 subtraction/correction. Matching of the data set to known dissolved H₂ concentrations
332 determined by GC can then be performed.

333 **8. Promising Perspectives of SPR Sensors in AD**

334 SPR sensors are advantageous as they can also be applied to other variables revealing the
335 internal state of the complex anaerobic process. Acetic acid is a VFA that can be produced
336 during certain stages within the AD of biomass. At high concentrations, it will inhibit the
337 activity of many microorganisms within the digester (REF NEEDED). Using SPR
338 technologies, measurements can be made of acetic acid with the receptor dye aluminium
339 phthalocyanine chloride deposited on a layer of gold (56). This design has been shown to
340 sense acetic acid in a liquid environment (56), suggesting its adaptation into AD may provide
341 an accurate only measurement of acetic acid.

342 By utilising colloidal copper nanoparticles, detection of ammonia concentrations have been
343 observed utilising SPR (57). By suspending colloidal copper nanoparticles in a solgel on a
344 transparent disk behind an observation window within the digester, direct measurements of
345 ammonia levels would be possible by external probing of the sensor disk with an optical fibre.

346 Methane concentration is usually measured in the gas-phase of the digester; however, it is
347 also possible to measure this variable within the liquid-phase of the digester. By depositing a
348 layer of modified polydimethylsiloxane (PDMS) polymer that contains cryptophane-A
349 molecules as the receptor, on top of a layer of gold, methane may be detected using SPR (58).
350 This detection is due to the selective, yet reversible, affinity of cryptophane-A to methane.

351 The H_2S must be removed from the exhaust gases by bio-filtration methods. It is imperative
352 that the post-filtration gas has no H_2S component, and therefore, this gas must be monitored
353 continuously. Titanium oxide is known to react with H_2S , producing titanium sulphide. This
354 reaction has been observed to cause a change in the resonance frequency of the surface
355 electrons of silver (59). The resonance can then interfere with incident light, as a function of
356 the H_2S concentration in the gas.

357 Although these variables have been detected using developed surface plasmon detection
358 techniques, they are all yet to be adapted for utilisation in an anaerobic digester.

359 **9 Perspective and Challenges for the Developments of SPR** 360 **Sensors**

361 The main limitations for palladium-based SPR sensors detecting dissolved H_2 in an AD are
362 palladium poisoning by H_2S , biofouling and the chemical complexity of the digestate.
363 Moreover, the repeatability of the data from the sensor in a specific digester may change as a
364 result of influent changes, and the comparability between different digestors with different
365 feedstocks may also be a challenge. This can be due to a variety of reasons were certain
366 unknowns within a complex mixture affect the dissolved hydrogen detection of the palladium-
367 based SPR sensor.

368 H_2S is produced in small quantities in AD and has a negative effect on the sensitivity of
369 palladium to H_2 . Interferences of H_2S to palladium is partly reversible, but to some extent, it
370 is irreversible (21). This has to be considered when developing a mathematical model for the
371 sensor, as the level of poisoning will have some dynamic trend due to H_2S poisoning being
372 partly reversible. Sample preprocessing is also possible by significantly increasing the pH of
373 the sample to remove H_2S ; however, this is not desirable as it adds another step to the
374 detection of H_2 .

375 As with many sensor systems placed inside the liquid phase of an anaerobic digester,
376 biofouling is a real limitation. There are plenty of methods for filtration of samples available
377 that significantly reduce biofouling on the sensor at the cost of filter biofouling. An
378 alternative is to utilise thin non-stick films of XXX on top of the palladium layer, to limit
379 fouling of the sensor. Additionally, by allowing the sensor patch to be replaceable, the sensor
380 could easily be replaced routinely without replacing any of the other components within the
381 sensor setup.

382 Despite this, the selectivity of palladium for H_2 in such a complex mixture allows many
383 variables within the digestate to be ignored by this sensor. Therefore, the ability for the sensor
384 to detect a rapid rise in dissolved H_2 (irrespective of providing an entirely accurate
385 concentration measurement), would allow rapid altercations to be made to avoid biological
386 inhibition and potential biological process collapse. This will give the controller of the plant
387 valuable time to rectify the biological process, by eliminating the delay in H_2 detection in the
388 gas phase due to the slow mass transfer of H_2 between liquid and gas phases.

389 Optically-based SPR sensors integrated directly into the AD would result in rapid on-line
390 dissolved H_2 detection within the liquid phase. Direct integration of these sensors (whether
391 directly placed within the reactor, or behind an observation window), and negligible time

392 required to achieve sensor-H₂ interactions, will allow instantaneous measurements of the
393 dissolved H₂ within the anaerobic digester. The development of an on-line sensor system
394 based on SPR sensors for detection of dissolved H₂ for use in AD, coupled with automated
395 post-treatment of the sensor data sets is a realistic alternative to traditional H₂ detection
396 methods as.

397 **10 Concluding Remarks**

398 Current AD plants require sensor advances that permit the estimation of dissolved H₂ on-line,
399 not only in large-scale plants but in small scale plants also. These advances will give the
400 operators of AD plants the possibility to acquire not only a higher comprehension of the
401 perplexing dynamics inside the AD plant but additionally foresee the heading of the reactor.
402 Traditional variable estimations required extensive and sophisticated instrumentation.
403 Additionally, with difficult extraction and preparation, experts are required leading to
404 increased expenses. These costly, for the most part, off-line procedures are highly accurate,
405 albeit typically do not depict an altogether precise display of the interior AD plant condition
406 due to the potential time delay in obtaining the information. New sensor frameworks for
407 detecting the internal dissolved H₂ condition of an AD plant must most likely show high
408 sensitivity, specificity and precision while keeping up the practicality of an on-line
409 information stream.

410 New sensor frameworks may expect parts to be disposable (e.g., SPR sensor patches);
411 however, they must be able to achieve comparable detection attributes between disposable
412 parts. The lifetime of such sensor segments like the sensor patches might be short in
413 traditional terms; however, must be low-cost so they can be replaced as required. These
414 sensors must be simple, small and isolated to encourage this. SPR optical-based sensor
415 advances for liquid phase dissolved H₂ detection can fulfil the necessities as future on-line
416 biogas sensors, and will fundamentally avoid the identification delay as seen with traditional
417 gas-phase detection.

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424 **Figures**

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