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TiO₂/UV based photocatalytic pretreatment of wheat straw for biogas production

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Abstract

The present study deals with the application of an advanced oxidation process combining UV irradiation in the presence of the photocatalyst titanium dioxide (TiO₂), as an effective pretreatment method of wheat straw as means for increasing its biodegradability for increased biogas production by anaerobic digestion (AD). Especially attention was paid in oxidation of the lignin in straw, besides release the sugars from the lignocellulosic structure of straw. Specifically, four different TiO₂ concentrations (0.0, 0.5, 1.0, 1.5, and 2.0% (w/w) TiO₂) were tested at three different irradiation times (0, 1, 2, and 3 h). Products of lignin-fraction oxidation, namely, vanillic acid, ferullic acid and acetic acid were quantified for each set of pretreatment conditions. Subsequently, biochemical methane potentials (BMPs) assays were conducted under thermophilic conditions from differentially pretreated samples and the pretreatment with the best performance was further tested in continuous mode operation. From BMP assays, 1.5% (w/w) TiO₂/straw at 3 hours of UV light exposure pretreatment resulted in 37% ($p < 0.05$) increase in methane yield and 25% in CSTRs. It was concluded that the presence of TiO₂ and the products of lignin oxidation did not inhibit the AD process. Finally, a simplified energy assessment showed that all pretreatment conditions become feasible when amounts of substrate to be treated are greater than the threshold value of 1.15 g.

Key words

Photocatalytic oxidation, Wheat straw, Biogas, Lignin, Vanillic acid, Ferullic acid

1 Introduction

There has been a lot of debate on replacing fossil fuels with renewable energy sources and maintaining a carbon neutral environment. The production of biofuels from lignocellulosic biomasses has the potential to contribute to fossil fuels replacement. However, an important hurdle associated with the use of these abundant biomasses is the complexity of its structure where cellulose, hemicellulose and lignin are compactly packed. Therefore, to efficiently use this resource, a pretreatment step is required to disrupt the complex structure of polymeric matrix. To this respect different pretreatment methods have been developed including chemical, physical, biological, and combinations of them. The goal of most of these pretreatments is to unpack the lignocellulosic structure and to make the sugars in it available for degradation. They achieve this by altering or removing the lignin and/or hemicellulose, decreasing the cellulose crystallinity and increasing the surface area for the hydrolases [1]. Very few methods mainly based on oxidation, are targeting also to solubilize the lignin and make this recalcitrant organic fraction available for biodegradation. Most of the above mentioned pretreatments are associated with various obstacles; for example, high temperature and pressure requirements, or use of chemicals that may introduce toxicity to the fermentation process [2]. In order to develop a pretreatment method with the desired results, oxidation of biomass in the presence of a catalyst can be an alternative choice. Additionally, from a sustainability point of view a process operated under mild conditions without producing toxic compounds is more preferable. Moreover, this method as oxidative would decompose also lignin a fraction which is often unutilized. Several studies focused on lignin oxidation, in order to transform the highly complex polymer into valuable aromatic chemicals and/or provide a source of low molecular mass feedstocks suitable for downstream processing [3].

Photocatalytic oxidation process can be an alternative solution to perform depolymerization of lignin under mild conditions. The catalyst used most frequently is titanium dioxide (TiO_2) due to its

high activity, chemical stability, commercial availability, and low cost [5]. Other semiconductor materials, such as ZnO_2 and CdS , have also been tested. Basically, the photooxidative degradation of lignin is initiated when TiO_2 absorbs ultraviolet (UV) light. The short wavelength and high energy of UV light trigger reactions of two different pathways, namely, electron hole reaction and OH radical oxidation, to complete the photolysis process [4]. Aromatic aldehydes and carboxylic acids are formed as the main products from the oxidative degradation of lignin. Vanillin has been obtained as a major valuable product in the oxidative deconstruction of lignin, with yields in the range 5–15 wt% with respect to the lignin source [3]. The application of the TiO_2 /UV system has been focused on treating effluents such as olive mill waste water, paper mill effluent, black liquor, wheat straw kraft digestion. Although the direct photocatalytic oxidation of the complicated structure of natural lignin without pretreatment is difficult, some attempts have been made to depolymerize some natural and synthetic lignin sources with simpler structures such as rice husk, alkaline lignin, wood flour, into valuable products (acetic acid, malonic acid, succinic acid, vanillin, aldehydes, etc.) [3-5].

Based on the aforementioned premises, the present study was mainly focused in exploiting the photocatalytic activity of TiO_2 for pretreatment of wheat straw for biogas production in batch and continuous mode experiments. Therefore, different concentrations of TiO_2 were tested together with different UV light irradiation times, for elucidating whether photocatalytic treatment was increasing the biodegradability of lignocellulosic biomass and determine optimal pretreatment conditions. Finally, the energy demand to perform the pretreatment was calculated to determine the overall energy efficiency of the AD process.

2 Materials and methods

All chemicals used in this study were of analytical grade and were purchased from Sigma Aldrich ApS (Brøndby, Denmark) and gases were supplied by AGA A/S (Copenhagen, Denmark).

2.1 Characteristics of inoculum and substrates

Inoculum was collected from Snertinge centralized Biogas plant in Denmark, operated under thermophilic conditions. The pH, total solids (TS), volatile solids (VS) and total volatile fatty acids (TVFAs) of inoculum were found to be 8.31, 27.5 ± 0.2 g/L, 17.1 ± 1.2 g/L and 0.2 ± 0.0 g/L, respectively. Regarding the VFAs composition, the acetate was measured to be 0.1 ± 0.0 g/L while the rest of the compounds were found in negligible fractions (*i.e.*, isobutyrate, butyrate and isovalerate). Additionally, the total Kjeldahl nitrogen (TKN) and ammonium nitrogen ($\text{NH}_4\text{-N}$) were measured to be 3.6 ± 0.1 and 3.2 ± 0.1 g/L, respectively.

Cattle manure was obtained from an animal farm in Zealand, Denmark. Before used, the livestock manure was sieved to discard the remaining lignocellulosic residues and then, was stored at -20 °C. The pH, TS, VS and TVFAs of manure were 7.69, 28.6 ± 0.4 g/L, 19.9 ± 0.3 g/L and 3.6 ± 0.1 g/L, respectively. Moreover, TKN and $\text{NH}_4\text{-N}$ were 2.6 ± 0.1 g/L and 1.7 ± 0.1 g/L, respectively.

Wheat straw was harvested from Zealand, Denmark. After its arrival to the lab it was cut into 2-3 cm length by a cutting mill (Retsch SM 2000) and then, stored at room temperature (21 °C) prior to use. The TS and VS of wheat straw were determined to be $92.8 \pm 0.4\%$ and $86.7 \pm 0.1\%$, of fresh matter (FM) respectively. Furthermore, the wheat straw consisted of $42.0 \pm 0.7\%$ TS, $30.8 \pm 0.5\%$ TS and $26.7 \pm 2.7\%$ TS of cellulose, hemicellulose and Klason lignin, respectively.

2.2 Photocatalytic oxidation experiments

Sample preparation consisted of soaking 0.92 g of wheat straw in 240 mL distilled water. The resulting preparation was transferred into a 500 mL beaker and this exposed to UV irradiation in a

quasi-collimated beam apparatus at ambient temperature (21 °C). This device consisted of a doped medium pressure lamp (SR HUV700) with enhanced emission in the irradiation wavelength of interest (200-400 nm). UV radiations from the lamp were collimated using a hollow tube to maintain a uniform distribution of UV light during the pretreatment and to use the light energy efficiently. The distance from the lamp to the center of the bottom of the beaker was 30 cm and the treated volume of sample was 240 mL. During the irradiation, the samples were gently stirred with the use of a magnetic stirrer (200 rpm). Detailed description of the quasi-collimated beam apparatus can be found in Hansen et al. [6]. UV light irradiation times were varied from 0 to 3 h (i.e. 0, 1, 2, and 3 h) at different TiO₂ concentrations (0, 1.0, 1.5, 2.0% (w/w)). Experimental set up is summarized in Table 1. After completion of pretreatment trials, three parts of the pretreated mixture were used for BMP assays whilst the leftover part was used for further quantification of products of lignin oxidation, VFA's, pH and to perform scanning electron microscopy (SEM). Electrical energy consumption of the device was retrieved from Hansen et al. [6] in order to estimate the energy consumption of the pretreatment.

Table 1 Pretreatment experimental set up and conditions. All experiments were performed at temperature of 21 °C and 200 rpm.

2.3 Biomethane potential (BMP) assay

Biomethane potential (BMP) was determined according to Angelidaki et al. [7] in 320 mL glass vessels (batch reactors) with a working volume of 100 mL. A volume of 60 mL of the wheat straw suspension (from the pretreatment trials) was mixed with 40 mL of a thermophilic (53 ± 1 °C) methanogenic inoculum in the batch reactors so that the organic load was diluted from 3.32 to 2

gVS/L. The inoculum was allowed to degas for seven days in an incubator prior to use. The basic characteristics of the inoculum are described in section 2.1. Avicel[®] PH-101 cellulose (Sigma Aldrich) was used (2 gVS/L) to validate the accuracy of the BMP assay experiments. Batch reactors only with inoculum and water (blanks) were included to determine the residual methane production from the inoculum. Finally, the batch reactors were flushed with a N₂/CO₂ (80/20% (v/v)) gas mixture, closed with rubber stoppers and aluminum caps, and incubated for a minimum of 30 days. During incubation period, the reactors were shaken once a day to avoid the development of dead zones. All BMP experiments were performed in triplicates.

2.4 Continuous mode experiments

A lab-scale CSTR with a total and working volume of 5.0 and 3.0 L respectively was used to perform the continuous mode experiment. The reactor was operated at thermophilic conditions (± 1 °C) with heated water jackets. The hydraulic retention time (HRT) was set at 15 days throughout the experiment by supplying 100 mL of feedstock twice per day with a peristaltic feeding pump. The organic loading rate was set at 0.7 gVS/L/d. The feedstock consisted of 85% VS of cattle manure and 15% VS of wheat straw. The experimental period was divided in two distinct operation phases. During first operation phase (OP-I) the reactor was fed with untreated wheat straw and cattle manure until steady-state conditions were established [8]. Subsequently, second operation phase (OP-II) started by feeding the reactor with pretreated wheat straw (1.5% (w/w) TiO₂ and 3 h UV-light irradiation) and cattle manure. Gas and effluent samples were taken twice a week to measure methane content, pH and VFA's respectively. The biogas volume was measured daily using the liquid displacement method [9].

2.5 Analytical methods

Total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN) and ammonium nitrogen ($\text{NH}_4\text{-N}$) were determined as described in Standard Methods [10]. Determination of structural carbohydrates and Klason lignin was performed according to NREL protocol [11]. The pH of inoculum and pretreatments was measured with a PHM 92 LAB pH-meter. VFA's composition of inoculum, cattle manure and pretreatments was measured as described in Kougias et al [12]. Methane concentration in the headspace of batch reactors was determined using a gas chromatograph (GC Shimadzu 14A, Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) [13]. Biogas composition in the headspace of CSTR was measured using a gas chromatograph (Mikrolab, Aarhus A/S, Denmark) equipped with a thermal conductivity detector. For both AD experiments, the methane yields are reported at STP conditions [7]. VFA's were analyzed by gas chromatography on a Shimadzu GC-2010 with a Shimadzu AOI-20i auto injector [14]. Products of lignin oxidation were quantified with a Thermo Scientific Dionex Ultimate 3000 UHPLC system with Multiple Wavelength Detector (MWD-3000 RS). Products were separated on a c18 reversed phase column (BDS HYPERSIL C18, 4.6×100 mm, $5 \mu\text{m}$ - Thermo Scientific) equipped with a guard column (BDS-HYPERSIL-C18, 4×10 mm, $5 \mu\text{m}$ - Thermo Scientific). Separation was achieved with a gradient of acetonitrile and 0.3% (v/v) acetic acid. Flow rate was kept constant at 1 mL/min. The injection volume was 20 μL and the column compartment temperature was set at 30 °C. The total time for analysis was 22 min per sample including equilibration time. Scanning electron microscope (SEM-FEI Inspect S) equipped with thermionic tungsten filament electron gun was used for the qualitative study of morphology changes in wheat straw due to the pretreatment. All the imaging was done under the high vacuum modes with large field detectors.

176 2.6 Statistical analysis

177 A one way analysis of variance (ANOVA) followed by Fisher's Least Significant Difference test
178 (LSD, $p < 0.05$) was used to evaluate if any significant differences were observed in experimental
179 measurements. All statistical analyses were performed using OriginPro 9.0.0 SR2 software
180 (OriginLab Corporation, USA).

181

182 3 Results and discussions

183

184 3.1 Photocatalytic oxidation of wheat straw

185 The effectiveness of the pretreatment on wheat straw was evaluated through the quantification of
186 main lignin oxidation products. In this study, the main products quantified from the photocatalytic
187 oxidation of wheat straw were vanillic acid and ferulic acid, for the pretreatments at irradiation
188 times of 0, 2, and 3 h at different concentration of catalyst (0, 1.0, 1.5, and 2.0% (w/w) TiO_2). As
189 shown in Fig. 1, the effect of the pretreatments is directly correlated to the formation of vanillic acid
190 and ferulic acid and was observed to be significant ($p < 0.05$) compared to the untreated wheat straw
191 (0% (w/w) $\text{TiO}_2/0$ h), thereby confirming the effectiveness of the pretreatment. Increasing the
192 irradiation time had a positive effect on the oxidative degradation of the lignin fraction in wheat
193 straw. When the irradiation time was increased from 2 to 3 h for the same catalyst concentration
194 (1.5% (w/w) TiO_2), the concentration of vanillic acid at the end of the reaction was increased by
195 57.7% whilst the ferulic acid concentration followed the opposite trend. This could be an indication
196 that longer irradiation duration favors further oxidation of vanillin and formation of vanillic acid.
197 Ferulic acid underwent a first oxidation pathway to yield vanillin as intermediate compound and
198 then, a further oxidation of vanillin to yield vanillic acid. Recent studies have proposed this

199 mechanism where the most important intermediates from the photocatalytic degradation of ferulic
200 acid were identified as homovanillic acid, vanillyl mandelic acid, trans-caffeic acid, vanillic acid
201 and vanillin and also organic acids such as formic acid, acetic acid and oxalic acid [15,16].

202 Quantification of total VFA's for the pretreatments with an irradiation time of 3 h and a catalyst
203 dose of 1.0 and 3.0% (w/w) TiO_2 , showed that acetic acid concentrations increased from 7.1 ± 1.7
204 mg/L (untreated wheat straw) to 26.82 ± 2.62 and 12.40 ± 8.20 mg/L, respectively.

205 Furthermore, a positive effect was also observed when the dose of catalyst was increased (from 1.5
206 to 2.0% (w/w) TiO_2) for an irradiation time of 3 h. This resulted in 21.6% increase in vanillic acid
207 concentration at the end of the reaction, in comparison to the pretreatment with only 1.5% (w/w)
208 TiO_2 . This effect was also observed by Ksibi et al. [15] when they pretreated the lignin present in
209 alfalfa black liquor using a UV/ TiO_2 system. In the absence of TiO_2 , solely UV-irradiation resulted
210 in negligible degradation of the lignin fraction (approximately 3.3% in 420 min); whilst in the
211 presence of TiO_2 the amount of degraded lignin increased to reach 56% in 420 min. In addition to
212 vanillin, they also identified vanillic acid among the different intermediates as a result of the
213 photocatalytic oxidation treatment of the lignin black liquor.

214 As was expected, a slightly decrease in pH was observed after completion of the pretreatments. This
215 decrease in the pH was attributed to the formation of carboxylic acid groups during the
216 photocatalytic oxidation pretreatments.

217 It is important to point out that the conversion and selectivity to the intermediate compounds
218 aforementioned highly depend on the structure of lignin. The lignin structure varies between
219 materials, with softwoods and hardwoods having distinctive proportions of the monomer. For
220 instance, grass lignin has additional phenolic acids bound to the polymer by ester groups. In
221 addition, reaction and parameter conditions (catalyst characteristics, catalyst dose, irradiation time,

etc.) determine the conversion and selectivity of the intermediates. Therefore, an accurate understanding of different types of lignin and their chemical structure is fundamental to optimize its use and target cost-effective pretreatments [3].

Fig. 1. Performance comparison of different pretreatments conditions based on vanillic acid and ferullic acid concentrations.

3.2 Scanning Electron Microscopy (SEM)

SEM was performed in order to obtain an insight on the structural changes induced by the pretreatment and visually to evaluate the structural differences between untreated and pretreated wheat straw. SEM images showed that longer irradiation time along with higher concentration of TiO_2 resulted in disruption of the smooth surface of wheat straw with increased porosity. Specifically, the surface of untreated sample has no pits and furrows (Fig. 2a) compared to Fig. 2c and 2d, in which furrows with larger pits can be observed. The furrows are certainly the spaces from where the lignin polymers were disrupted during the pretreatment. The SEM observations provide a qualitative confirmation of the quantitative measurements (i.e. vanillic acid and ferulic acid). Specifically, wheat straw with the most disrupted surface (Fig. 2d) was associated with the highest amount of vanillic acid released after undergoing pretreatment (Fig. 2d). Conversely, an irradiation time of 1 h (Fig. 2b) did not show any noticeable difference compared to untreated samples.

Fig. 2. SEM images of untreated and pretreated wheat straw: a) Untreated; b) 2.0% (w/w) TiO₂/1 h; c) 2.0% (w/w) TiO₂/2 h; d) 2.0% (w/w) TiO₂/3 h.

3.3 BMP assays

A set of BMP experiments was conducted in order to thoroughly examine the effect of the photocatalytic oxidation pretreatment on the biodegradability of wheat straw and the results are shown in Fig. 3. Firstly, both the solely application of UV-irradiation in the absence of TiO₂ as the application of different catalyst doses in absence of UV-light had no significant effect on the biomethanation process. This was also observed by Kang and Kim [16], when they pretreated rice straw with only UV-light in absence of TiO₂. On the other hand, regardless the catalyst dose, irradiation for 1 h did not result in any significant boost in methane yield, probably due to the limited exposure time to induce a significant change in the biomass structure.

The effect of irradiation time on ultimate methane yield increase became significant starting from 1.0 to 2.0% (w/w) TiO₂ catalyst concentrations as observed in Fig. 3. For 1.0% (w/w) TiO₂ and 3 h irradiation time, an increase ($p < 0.05$) in methane yield of 24% (311.96 ± 16.77 NmLCH₄/gVS_{added}) was observed compared to no irradiation time conditions (251.96 ± 12.72 NmLCH₄/gVS_{added}). Similarly, for 1.5 and 2.0 % (w/w) TiO₂ at the same exposure time (3 h), this increased ($p < 0.05$) corresponded to 33% (333.25 ± 10.02 NmLCH₄/gVS_{added}) and 24% (316.65 ± 12.47 NmLCH₄/gVS_{added}) with respect to no irradiation (251.19 ± 14.91 and 255.11 ± 4.16 NmLCH₄/gVS_{added}, respectively) conditions.

Contrary to aforementioned, increasing the catalyst dose did not result in a significant effect on methane yield for the same irradiation treatment. For catalyst dose 1% to 2% (w/w) TiO₂ for all irradiation durations (1, 2, and 3 h), non-statistically differences ($p > 0.05$) were observed in the

ultimate methane yield as shown in Fig. 3. One exception was when the catalyst concentration was increased from 0.5 to 1.0% (w/w) TiO_2 specifically for 3 h irradiation time, where a significant increase in methane yield was observed. Then, as explained by increasing the concentration above the threshold of 1.0% (w/w) TiO_2 , increase on methane yield was no significant ($p > 0.05$).

Actually, it was previously found that the increased concentration of TiO_2 in the solution can potentially level off the efficiency of photocatalysis, as the increased concentration of catalyst can partially prevent the UV transmittance [17]. Thus, the augmented concentration of catalyst is not always associated with increased effectiveness of photocatalysis.

Finally, the most effective pretreatment conditions found in this study corresponded to 1.5% (w/w) TiO_2 and 3 h irradiation time, which resulted in a significant ($p < 0.05$) increase of 37% ($333.25 \pm 15.02 \text{ NmLCH}_4/\text{gVS}_{\text{added}}$) in methane yield compared to the one obtained from untreated wheat straw ($243.23 \pm 8.19 \text{ NmLCH}_4/\text{gVS}_{\text{added}}$).

Similarly, significant increase ($p < 0.05$) in methane yield was also observed for pretreatment conditions with 1.0 and 2.0% (w/w) TiO_2 at 3 h irradiation time resulting in an increment of 28% ($311.96 \pm 16.77 \text{ NmLCH}_4/\text{gVS}_{\text{added}}$) and 30% ($316.65 \pm 12.47 \text{ NmLCH}_4/\text{gVS}_{\text{added}}$), compared to untreated wheat straw, respectively.

This is in agreement and is supported with our previous observation (section 3.1) that longer irradiation times favor the formation of the products (aromatic aldehydes and carboxylic acids) from the oxidative degradation of lignin, thereby having a positive effect on the biomethanation process.

Fig. 3. BMP assay – methane yield for the different pretreatment conditions (means with the same letter are not significantly different from each other $p > 0.05$).

3.4 Continuous mode experiments

The most effective pretreatment identified by BMP tests (i.e. 1.5% (w/w) TiO_2 , 3 h UV irradiation) was further investigated in continuous mode operation. Initially, the CSTR reactor was operated at stable conditions using cattle manure and untreated wheat straw in the feedstock for one HRT. As shown in Fig. 4a and 4b the steady state conditions of reactor can be seen with low VFA accumulation, stable pH and steady methane yield for more than ten days [14]. After this period, the feedstock was changed and specifically, the lignocellulosic biomass was pretreated before feeding into the reactor. The effect of pretreatment was immediately observed, as a rapid increase in methane yield was monitored due to the changed feedstock. This rapid change can be explained on the basis of increased susceptibility of wheat straw – due to the applied pretreatment – to microbial attack and also from the utilization as microbial substrates of the formed lignin oxidation products (i.e., vanillic acid, ferulic acid, acetic acid) to methane. At steady state conditions, the methane yield was increased up to 25% compared to untreated feedstock, without provoking any instability to the reactor, as seen by the stable pH and low VFA accumulation (Fig. 4a and b). On the other hand, the achieved increment was remarkably lower compared to BMP results. Indeed, in continuous trials the substrate is constantly fed to and removed from the reactor so that the reaction time is lower to achieve the maximum biodegradability as in batch reactors.

Moreover, from the stability of reactor with pretreated wheat straw and steady operation throughout the second and third HRT, advocate the benefit of photocatalytic oxidation process to be used at larger scale.

310

311 **Fig. 4.** CSTR reactor performance; a) methane yield; b) VFA accumulation and pH.

312

313 3.5 Energy balance

314 A simplified energy balance analysis was performed to calculate energy efficiency as function of
315 the amount of substrate for the different pretreatment conditions tested in BMP assays. The
316 procedure for evaluating energy efficiency is given by the equation:

$$317 \quad \eta = 1 - \left(E_{\text{Pretreatment}} / E_{\text{CH}_4} \right)$$

318 Where E_{CH_4} is the heating value of the produced methane and $E_{\text{pretreatment}}$ is the energy used in the
319 pretreatment, for each particular set of pretreatment conditions, respectively. The electrical energy
320 consumption by the UV-lamp was considered as solely energy used during the pretreatment and
321 was determined experimentally according to Hansen et al. [6] obtaining a value of 0.061 kWh per
322 unit of volume (m^3) of the suspension treated per unit of time (min). Based on this and the
323 aforementioned assumptions, results are depicted in Fig. 5. Except for untreated wheat straw
324 ($E_{\text{pretreatment}} = 0$) for each specific pretreatment condition a break-even point is defined. As observed
325 for amounts of substrate to be treated lesser than 0.7 g all pretreatments become infeasible.
326 Conversely above this threshold value, the energetic feasibility of the process depends on both
327 amount of substrate as pretreatment conditions; whilst above 1.15 g the energy balance is positive
328 for all pretreatment conditions. For instance, for 1 g of substrate to be treated all pretreatments are
329 feasible except for 0.5% (w/w) $\text{TiO}_2/3\text{h}$ conditions. However, 1.5 and 2.0% (w/w) $\text{TiO}_2/2\text{ h}$ present
330 a higher efficiency compared to other conditions. From an economical point of view, it would be

preferred to select the pretreatment with lower catalyst dose as both present practically the same efficiency.

Finally, it should be remarked that this energy efficiency analysis was based on the ultimate methane yields obtained from BMP assays and it will differ when continuous mode operation is considered.

Fig. 5. Comparison of different pretreatment conditions in terms of energy efficiency analysis.

4 Conclusions

This study defined that photocatalytic pretreatment can boost the lignin disruption and subsequently, improve the anaerobic degradation of recalcitrant wheat straw. Among the products from the oxidative degradation of lignin under TiO_2 /UV catalyst system, vanillic acid and ferulic acid were detected at a maximum value of 91.18 ± 2.00 and 1.67 ± 0.01 , using 2.0% (w/w) TiO_2 and 3 hours UV irradiation in the range of 200-400 nm. Moreover, the most effective pretreatment strategy (1.5% (w/w) TiO_2 and 3 h) was found to increase the biodegradability of wheat straw up to 37% compared to untreated biomass. The positive impact of photocatalytic pretreatment was also observed in continuous trials, as the methane production was increased by 25%. It was concluded that the photocatalytic oxidation of lignin-rich substrates is a promising method to disrupt the non-degradable organic fraction under mild conditions. However, a simplified energy balance was computed and revealed that further investigations are still needed to improve the overall process efficiency and possibly transform lignocellulosic biomass directly into products of economic

interest such as vanillin, vanillic acid and/or ferulic acid, rather than the low economic value biogas as the only product.

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413 Table 1 Pretreatment experimental set up and conditions. All experiments were performed at
 414 temperature of 21 °C and 200 rpm.

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Pretreatment	Organic load gVS/L	Catalyst concentration % (w/w) TiO ₂	Irradiation time h
1	3.32	0.0	0
2	3.32	0.0	1
3	3.32	0.0	2
4	3.32	0.0	3
5	3.32	0.5	0
6	3.32	0.5	1
7	3.32	0.5	2
8	3.32	0.5	3
9	3.32	1.0	0
10	3.32	1.0	1
11	3.32	1.0	2
12	3.32	1.0	3
13	3.32	1.5	0
14	3.32	1.5	1
15	3.32	1.5	2
16	3.32	1.5	3
17	3.32	2.0	0
18	3.32	2.0	1
19	3.32	2.0	2
20	3.32	2.0	3

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Fig. 1. Performance comparison of different pretreatments conditions based on vanillic acid and ferulic acid concentrations.

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425 Fig. 2. SEM images of untreated and pretreated wheat straw: a) Untreated; b) 2.0% (w/w) TiO_2 /1 h;
 426 c) 2.0% (w/w) TiO_2 /2 h; d) 2.0% (w/w) TiO_2 /3 h.

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Fig. 3. BMP assay – methane yield for the different pretreatment conditions (means with the same letter are not significantly different from each other $p > 0.05$).

Fig. 4. CSTR reactor performance; a) methane yield; b) VFA accumulation and pH.

Fig. 5. Comparison of different pretreatment conditions in terms of energy efficiency analysis.

Highlights

- TiO_2 /UV based photocatalytic pretreatment was successfully applied to wheat straw
- Products of economic interest (vanillic acid and ferulic acid) were identified
- Best pretreatment conditions: 1.5% (w/w) TiO_2 /straw at 3 hours of UV light exposure
- Best pretreatment in BMP assays resulted in 37% increase in methane yield
- Best pretreatment in CSTR's resulted in 25% increase in methane yield