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Bioenergy production from cotton straws using different pretreatment methods

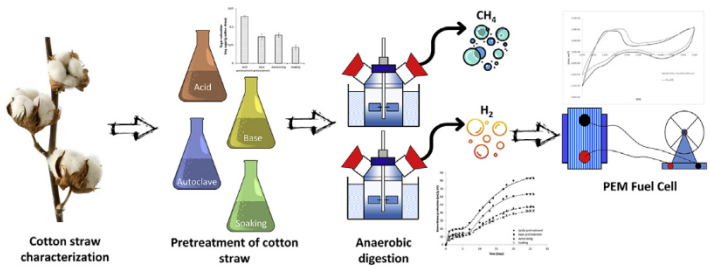
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HIGHLIGHTS

- Cotton straws were extracted by using three different pretreatment methods.
- Acid pretreatment was ~2 times effective than other methods in sugar extraction.
- The highest bioH_2 and bioCH_4 production was 33 and 83 mL/g VS, respectively.
- The biohydrogen was used as fuel in PEM fuel cells for clean energy generation.
- The maximum power and current density in PEMFC were 23 W/cm^2 and 0.522 A/cm^2.

GRAPHICAL ABSTRACT



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ABSTRACT

Cotton straws are one of the most produced agricultural wastes in Turkey and getting attention by not being consumed as animal feed or an industrial stock and having a huge potential in clean energy production. In this study, different pretreatment methods for the conversion of cotton straw to sugar then biohydrogen and biomethane production from cotton straw were examined. The energy potential of cotton straw in case of an evaluation of these biomass residues was also determined using fuel cell technology. Acid pretreatment provided the highest yield in biogas formation as well as sugar extraction from the raw sample. The highest biohydrogen and biomethane production were obtained as 33 mL H_2/g VS and 83 mL CH_4/g VS, respectively. Concomitantly, the maximum power peaks in PEM fuel cell studies were observed as 0.45 W/cm^2 and 0.23 W/cm^2 with current densities of 1.086 A/cm^2 and 0.522 A/cm^2 when the fuel cell was fed with pure H_2 and biogas, respectively. This suggested that acid pretreatment is more suitable for cotton straw

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Biomethane
PEM fuel cell

management in sustainable and renewable ways and the results demonstrated that PEM fuel cell is a promising clean technology for energy generation from cotton straw.

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Introduction

The energy demand is predicted to increase worldwide due to population and technological growth. A huge amount of this energy demand is met by fossil fuels like coal, petroleum and natural gas as a primary energy source. But due to the fossil reserve depletion and the linked greenhouse gas (GHG) emissions increment, energy production via fossil fuels became an important issue for climate change mitigation and energy security at global, national and local scales [1,2]. In order to reduce GHG emissions and promote renewable energy sources, developing sustainable energy sources became one of the most important worth-stressing points. At that point, the improvement of gaseous biofuel plays an important role due to its main environmental advantages, including no sulfur content and harmful gas emissions, abundance and renewability and clean energy [3]. Among all biofuels, biohydrogen, and biomethane attracts attention when being developed a world-wide bioenergy production policy due to its easy-to-use [4].

Anaerobic digestion (AD) is one of the easiest and promising technologies used to convert organic material into energy [5,6]. It also has many advantages compared to other biological processes such as presenting a simple operation, being able to produce an organic by-product that can be used in agriculture and providing a suitable treatment process [7,8]. Biohydrogen is also one of the most studied research areas due to being a potential solution for sustainable energy generation. Because of its advantages, such as only water vapor is released after its combustion and having low density with the highest energy to mass ratio among all the existing fuels, world-wide progress has been carrying out with the hydrogen-based economy [9,10]. But the main obstacle of bio-based fuel production is the unavailability of cheap feedstock sources. Even if there are many sources of valuable feedstock for bio-based fuel production in municipal, agricultural and industrial origin, increasing feedstock and transportation prices makes this aim impractical [11–13].

Biomass is a renewable bioenergy production feedstock that having tons of production potential all over the world which covers agricultural products, agricultural wastes, plants, plant residues, forest resources, and algae species. Agricultural biomass residue is one of the most produced, cheap and easy to handle among these resources [14]. Although most agricultural wastes can be used as animal feed, some of them are non-edible due to their bulky and strong texture, such as cotton and sunflower stalk. The cotton straw is one of the agricultural waste which cannot only be converted to any useful product such as raw material in pharmaceutical industry, animal feed, mulch; but also it is one of the most suitable raw materials for use in bioenergy production due to its high carbon content. Moreover, since cotton straw is considered as waste, it does not cost except transporting and presents a sustainable solution for waste disposal when it is used in bioenergy production. Cotton straw, which has one of the highest production ranks among all agricultural wastes in Turkey, has a significant potential for bioenergy production. Turkey is the seventh-highest cotton producer around the world with around 800 million tons of cotton production [15]. This market causes 2050 kilotons of cotton straw waste production annually [16]. Even if cotton straw contains a high amount of carbon [17,18] which can be converted into a variety of useable forms of energy, studies on bioenergy production potential of cotton straws are rarely available at the global and local scale [19–21].

The objective of the study was to evaluate an integrated technology for cotton straw management in sustainable and renewable ways. In this way, biomethane and biohydrogen production potential from cotton straw were discussed after using different sugar extraction (pretreatment) methods for efficient biogas formation. The biomethane and biohydrogen potential and the effect of pretreatment on biogas formation were discussed using the Modified Gompertz equation. Concomitantly, biohydrogen was evaluated in PEM fuel cells for clean energy generation and electrochemical methods were used to investigate performance loss and power generation considering biogas impurities such as CO_2.

Materials and methods

Sample collection and characterization

Cotton straws were obtained from Sanliurfa-Turkey, in plastic bags and dried at 60 °C overnight. Samples were milled to <0.3 cm with a grinder. Table 1 shows the main characteristics of raw cotton straw samples. The chemical structure of samples was found as 46.0% C, 0.8439% N, and 6.11% H. The VS/TS ratio and total carbon content of the sample was 94% and 46%,

Table 1 – The physicochemical properties of cotton straw.

Parameter	Unit	Value
Humidity	%	7.47
Calorific value	kcal/kg	4053
Total carbon	%	46.0
Total nitrogen	%	0.84
Total hydrogen	%	6.11
Total sulfur	%	0.27
VS/TS	%	94
C/N ratio	–	54.8

respectively, indicating a high organic matter, which was preferred for anaerobic processes [22].

Inoculum

Biohydrogen production from cotton straws was run by *Clostridium* sp. which was isolated previously from an anaerobic digester of domestic wastewater treatment plant [23]. Isolated microorganism culture was cultivated with Reinforced Clostridial Medium (RCM) in a serum bottle under anaerobic conditions. Enriched *Clostridium* sp. was centrifuged at 4000 rpm for 10 min and concentrated culture was fed to the fermenter as inoculum.

Anaerobic granular sludge obtained from a mesophilic digester treating gum industry wastewater was used as inoculum in the anaerobic digester (for biomethane production). The total solid (TS) content of granular anaerobic sludge was 870 mg/g when volatile solid (VS) was 89% of dry weight.

Pretreatment of cotton straw

Three different pretreatment methods were applied to cotton straw samples to examine their effects on sugar production and the biodegradability.

The first method was the acidic pretreatment. In this method, ground and dried samples were pre-treated with 1% (v:v) hydrochloric acid [24] at 120 °C for 20 min. Basic pretreatment was the second pretreatment method and in this method, samples were conducted with 1% (w:v) $Ca(OH)_2$ [24] for 20 min at 120 °C. The third and the last method was autoclaving the samples into distilled water at 120 °C for 20 min to examine the effect of chemical addition to the process. All sets were conducted with a 5% solid content [25].

To compare the effect of chemical and physical pretreatment on hydrolysate production, one set experiment was conducted as control by soaking the grounded cotton straw samples for 20 min in distilled water. The solid content of the control set was also adjusted as 5%.

All samples were centrifuged after pretreatment application to separate the solid and liquid phases. Liquid phases were stored at 4 °C. Solid phases were dried at 60 °C overnight and stored in plastic bags at room temperature.

Total sugar measurement and kinetic modeling

The acid-phenol spectrometric method was used for the total sugar analysis of hydrolysate [26]. Total sugar measurement for raw cotton straw measurement was carried out according to Chow and Landhausser [27]. All sugar measurements were conducted in triplicate.

Experimental data for biohydrogen production were used to fit the Modified Gompertz equation using the least-squares regression technique via the Solver tool of MS Excel 2010.

$$P = P_0 * \exp\left(-\exp\left(\frac{R_m * e}{P_0}(\lambda - t) + 1\right)\right) \quad (1)$$

where P is the cumulative biogas yield at a digestion time of t days (mL/g VS); P_0 is the biogas production potential (mL/g VS); R_m is the maximum biogas production rate (mL/g VS.day); e is the mathematical constant (2.718282); λ is lag phase period or minimum time to produce biogas (days); t is the cumulative time for biogas production (days). For mathematical modeling P_0 and t were used as constants and P, R_m and λ were calculated as variables.

Experimental procedure

The batch experiments were conducted to observe biohydrogen and biomethane potential of cotton straw samples. 100 mL serum bottle with a working volume of 50 mL consisted of 45 mL of cotton straw hydrolysate, 2.5 g of pre-treated cotton straw, 2 mL inoculum and 3 mL of nutrient solution. The nutrient solution was prepared according to Pattra et al. [28] for biohydrogen production and Yoruklu et al. [29] for biomethane production. All reactors were operated in triplicate. For the biogas characterization, a gas chromatograph (Shimadzu GC2014, Tokyo, Japan) equipped with a thermal conductivity detector (TCD) and a 2 m length, 1 mm inner diameter packed column (Restek, USA) was used for determining methane (CH_4), carbon dioxide (CO_2) and hydrogen contents of biogas.

PEM fuel cell operation and electrochemical analysis

A single test cell with a 5 cm^2 area was used for fuel cell experiments and membrane electrode assembly (MEA) was fabricated as previously described by Koroglu et al. [23]. Pt/Vulcan XC (Tanaka) catalyst (38 wt%) was used in fuel cell and Pt loading rates were 140 $\mu gPt.cm^{-2}$ for anode and cathode. H_2 (99.9%) and biogas (a mixture of H_2 and CO_2) were used as an oxidant in anode compartment and O_2 (99.9%) was used in the cathode. WonATech Smart 2 fuel cell test system was used to monitor performance and constitute polarization curves.

Electrochemical impedance spectroscopy (EIS) and Cyclic Voltammetry (CV) analysis were performed using Gamry Interface 1000-E potentiostat. The EIS and CV measurements were carried out with a frequency range of 37,000 Hz–0.1 Hz at 0.8 V with a 5 mV amplitude and with a potential scan for a range of 0-1.2 V (SHE) at 500 mV/s scan rate, respectively. To estimate the quantity of active surface in the PEM fuel cell, ECSA was calculated as previously described by Koroglu et al. [23] and Ozdemir [30].

Results & discussion

Effects of different pretreatment methods on sugar extraction

As an example of pretreatment, different methods for sugar extraction from cotton straw is discussed here. Fig. 1 shows the effect of different pretreatment methods on sugar extraction from cotton straw. Even all pretreatment methods were effective on sugar extraction from cotton straw, the most efficient one was acidic pretreatment considering sugar extraction. The sugar content of acidic pretreatment hydrolysate was almost 3 times higher than the raw sample and almost 2 times higher than other hydrolysates.

It was also seen that pretreatment with base addition and autoclaving was almost the same in terms of sugar extraction

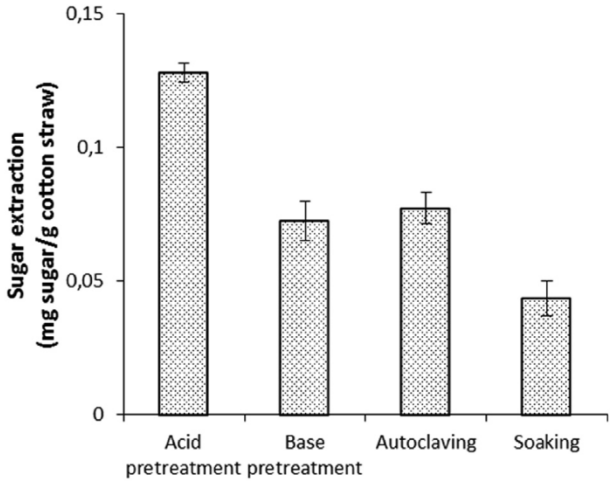


Fig. 1 – Sugar extraction from cotton straw using different pretreatment methods.

ability. The results show that acid pretreatment was the most effective method for the highest sugar concentration in the hydrolysate. In the literature, it was noted that solubilized lignin will quickly condensate and precipitate in acidic environments [31]. It makes the sugar dissolve in the liquid more easily. Otherwise, alkali extraction can also cause condensation of lignin and disruption in the crystal form of the cellulose. These effects can affect lignin removal adversely [32]. Due to this negative effect of alkali pre-treatment, no positive effect observed during alkali pretreatment compared to autoclaving.

Effect of different pretreatment methods on cumulative hydrogen yield

Hydrogen as a product synthesized from cotton straw via anaerobic fermentation is discussed further here. Biohydrogen production experiments were carried out under controlled conditions for 20 days. The bioreactors were incubated in an orbital shaker which operated under 120 rpm and 35 °C. The composition of biogas was measured with a gas chromatograph after reactors reached steady-state conditions. Biogas consisted of 55% H_2 and 45% CO_2. Cumulative biohydrogen produced per gram volatile solids of cotton straw for different pretreatment methods, and, kinetic modeling fitting lines obtained by using the Modified-Gompertz model, is shown in Fig. 2. As can be seen from Fig. 2, the highest biohydrogen production was obtained as 33 mL H_2/g VS on acid pretreatment. The second and third highest biohydrogen production was observed in pretreated-with-base and autoclaved samples, respectively. Acid pretreatment provided the highest yield in biohydrogen formation as well as sugar extraction from the raw sample. Likewise, the soaked sample showed the lowest biohydrogen production yield as expected.

Acid pretreatment has been the most widely used method to breakdown the complex structure of lignocellulosic biomass due to it is a simple process, has low cost, and results in high yield [33]. Besides, in biohydrogen production from raw lignocellulosic biomass which initially had a very low hydrogen potential, massive gains were observed by implementing different pretreatment applications. Among these examples, the greatest enhancement was obtained after acid or alkali pretreatment [34]. There are very few studies on the potential of biohydrogen production from cotton wastes. In a limited number of studies conducted, the effect of different pretreatments on biohydrogen production was not investigated. Ghasemian et al. [35] noted that the hydrogen production efficiency of the cotton stalk as a result of the alkali pretreatment was reached to 15.2 mL H_2/g VS. Chu et al. [36] stated that the hydrogen production yields of cotton stems, which applied acidic pretreatment, were 0.95 mol H_2/mol R-sugar, which corresponds to approximately 910 mL H_2/kg cotton.

Biohydrogen production curves consisted of two steps for all sets. This indicates that waste fed to the system as a substrate is composed of easily biodegradable and slowly biodegradable components. It is known that the primary effect of

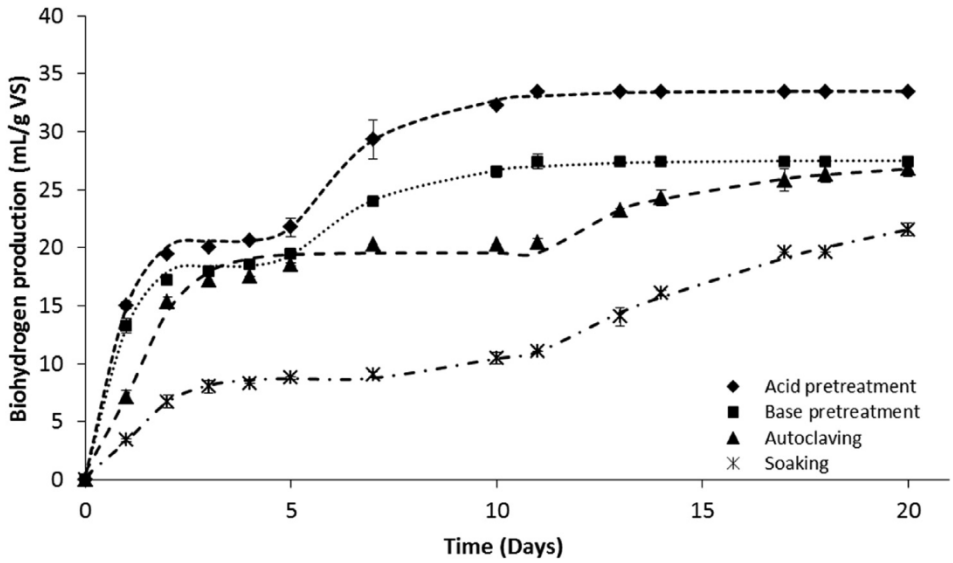


Fig. 2 – The cumulative biohydrogen production profile of different cotton straw samples.

the pretreatment on substrates having complex structures is to shorten the hydrolysis time, which is usually the rate-limiting step in anaerobic digestion [37–39]. Among the different pretreatments, acidic and basic pretreatment is the most effective method in terms of shortening the hydrolysis time. 70% of the biogas production capacity was reached within 7 days after the reactor setup with acid and base pretreatment. But it took almost 17 days for autoclaving and soaking. Even though a large variety of pretreatment methods are available to extract the lignocellulosic sugars, there is not a universal solution to be suggested for all kinds of lignocellulosic biomass [9]. Starting from this point of view, it can be said that the most suitable pretreatment method for the production of biohydrogen from cotton straws is acid pretreatment.

The kinetic coefficients obtained by the application of the Modified Gompertz equation to biohydrogen curves are given in Table 2. The maximum cumulative hydrogen production (P_0) and hydrogen production rate (R_m) were obtained when using acid-pretreated samples. The highest value was 33.5 mL with acid pretreatment, which was almost 20% higher than other pretreatment methods. In contrast to P_0 and R_m, there are no big differences between the lag times (λ) of pretreated samples.

Effects of different pretreatment methods on cumulative methane yield

In addition to hydrogen, methane production from cotton straw via anaerobic digestion was discussed here. Reactors were operated for 26 days under mesophilic conditions to determine the biomethane potential. Biogas was collected periodically during this period and the methane content of biogas was determined as 52% by chromatographic analysis. Cumulative biomethane produced per gram volatile solids of cotton straw for different pretreatment methods, and, kinetic model data are shown in Fig. 3. Similar to biohydrogen production results, the highest biomethane was formed in acid pretreatment with 83 mL CH_4/g VS. Base pretreated, autoclaved and soaked samples followed it as the second, third and fourth, respectively. Although there seems to be a relationship between sugar extraction and biogas formation, autoclaving and basic pretreatment do not confirm this hypothesis.

Considering Figs. 2 and 3, biohydrogen production yield is considerably lower than biomethane production, because of the cell production rate (max. 0.061 g cell/g sucrose) and H_2 production rate (max. 254 mL/h/g cell) of *Clostridium* sp. performing hydrogen production is quite low compared to methanogens (0.82 g cell/g acetate and 0.5 g CH_4/g cell/d,

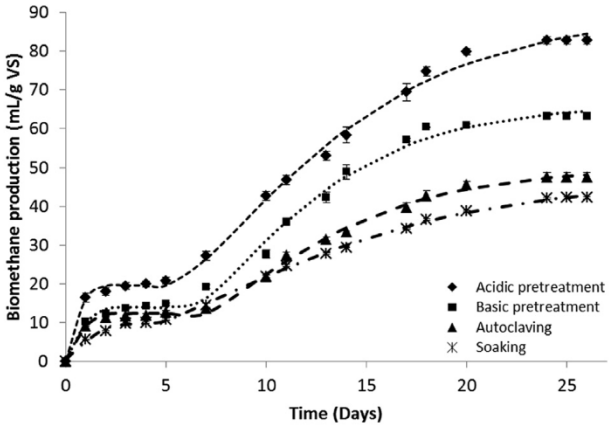


Fig. 3 – The cumulative biomethane production profile of different cotton straw samples.

respectively) [40,41]. It means that one unit of H_2 or two units of CH_4 could be produced by using the same amount of substrate, theoretically. In previous studies conducted to determine the biohydrogen and biomethane potentials of different waste streams, biohydrogen production yield was also found much lower than biomethane production yield [42–47].

Unlike biohydrogen production, biomethane production from cotton straw has been studied in many studies due to its high biomethane production potential (473 mL CH_4/g VS) and high producing rate [48]. Ali et al. [19] fed ground cotton straws to bioreactors and 327 mL/g VS methane was produced. Studies were also conducted by Zhang et al. [22] to determine the most appropriate pretreatment method for effective anaerobic digestion, by application of various pretreatments including base pretreatment, acid pretreatment, and steam explosion. Their results showed that the highest cumulative methane yield of 192.4 mL/g VS was obtained by alkali pretreatment of cotton straw, which is improved by nearly 250% than the untreated sample. In the study which examined the biomethane potential of different lignocellulosic wastes, it was suggested that non-pretreated cotton straw is not a suitable substrate for the AD process. However, the methane potential of the sample was increased from 174 to 271 mL CH_4/g VS after pretreatment [49].

Table 3 gives the kinetic parameters estimated based on the best fit of the modified Gompertz model. The calculated biomethane production potential (P_0, mL/g VS) was very close to the cumulative results obtained during reactor operation (P), which is indicating that the curve is fitted well with the modified Gompertz equation. Correlation coefficients were also kept >0.975. Lag phases of samples stayed very close to each other.

Table 2 – Kinetic coefficients of biohydrogen production from cotton straw.

Methods	P_0 (mL/g VS)	R_m (mL/g VS.day)	λ (days)
Acid pretreatment	33.5	19.4	0.17
Base pretreatment	27.5	16.7	0.16
Autoclaving	27.5	6.7	0.19
Soaking	26.3	4.1	0.20

Table 3 – Kinetic coefficients of biomethane production from cotton straw.

Methods	P_0 (mL/g VS)	R_m (mL/g VS.day)	λ (days)
Acid pretreatment	90.0	22.7	0.16
Base pretreatment	66.3	11.8	0.16
Autoclaving	50.0	11.3	0.14
Soaking	46.8	5.4	0.06

Energy production from biohydrogen using PEM fuel cell

The fuel cells are widely used among the technologies in which hydrogen is evaluated. When the researches with fuel cells that use hydrogen as a fuel are examined, researchers have deeply evaluated many factors such as fuel composition, amount and type of catalyst, operating parameters of the fuel cell to highlight the parameters affecting the efficiency and performance and to improve the performance. Among these parameters, the purity of hydrogen is important for determining the performance of fuel cells. The impurities such as CO, CO_2, H_2S, NH_3, NO_x, SO_x, organic carbon/sulfur, and carbon/hydrogen compounds causing performance deterioration and damage of active surface area of the catalyst [50]. In this study, the feasibility of biogas produced by fermentation of agricultural wastes in energy production using PEM fuel cell was evaluated by determining the composition of biogas. As previously discussed CO_2 affects the performance of fuel cell, therefore the main goal of this study was to determine fuel cell efficiency operating with hydrogen feeds containing CO_2. The reason for determining the effect of CO_2 was because of biogas was primarily a mixture of hydrogen (H_2) and inert carbonic gas (CO_2). Biogas produced from anaerobic fermenter contained 55% H_2 and 45% CO_2, in this study. This high concentration of CO_2 leads to the poisoning of the catalyst by conversion to CO and decreasing the performance of fuel cell due to water-CO_2 gas shift reaction (WGSR) reaction as given below [23,50].

$$2Pt + H_2 \rightarrow 2Pt - H_{ads} \quad (2)$$

$$CO_2 + 2Pt - H_{ads} \rightarrow Pt - CO_{ads} + H_2O + Pt \quad (3)$$

In this study, biogas from fermenter was directly fed to the PEM fuel cell and pure H_2 gas was used as control fuel to compare the effect of CO_2 and evaluate the level of performance deterioration. Their individual effects on PEM fuel cell performance have been discussed extensively. Fig. 4 shows the fuel cell performance profile of biogas and control fuel under similar operating conditions. The maximum power peaks were observed as 0.45 W/cm^2 and 0.23 W/cm^2 with current densities of 1.086 A/cm^2 and 0.522 A/cm^2 when the fuel cell was fed with pure H_2 and biogas, respectively.

The 45% CO_2 content of biogas was decreased the fuel cell efficiency around 48.9% and resulted in a half loss of performance in electricity production. The electrochemical impedance spectroscopy (EIS) analysis was also shown that CO_2 content increased the polarization resistance of the cell from 1.72 Ω to 3.86 Ω compared to pure H_2 as shown in Fig. 5.

Recognized as a well-known, activation losses of catalysts occur at low over-voltages. Therefore, the Linear Sweep Voltammetry (LSV) analyzes of the catalysts at low over-voltages performed and the polarization curves obtained

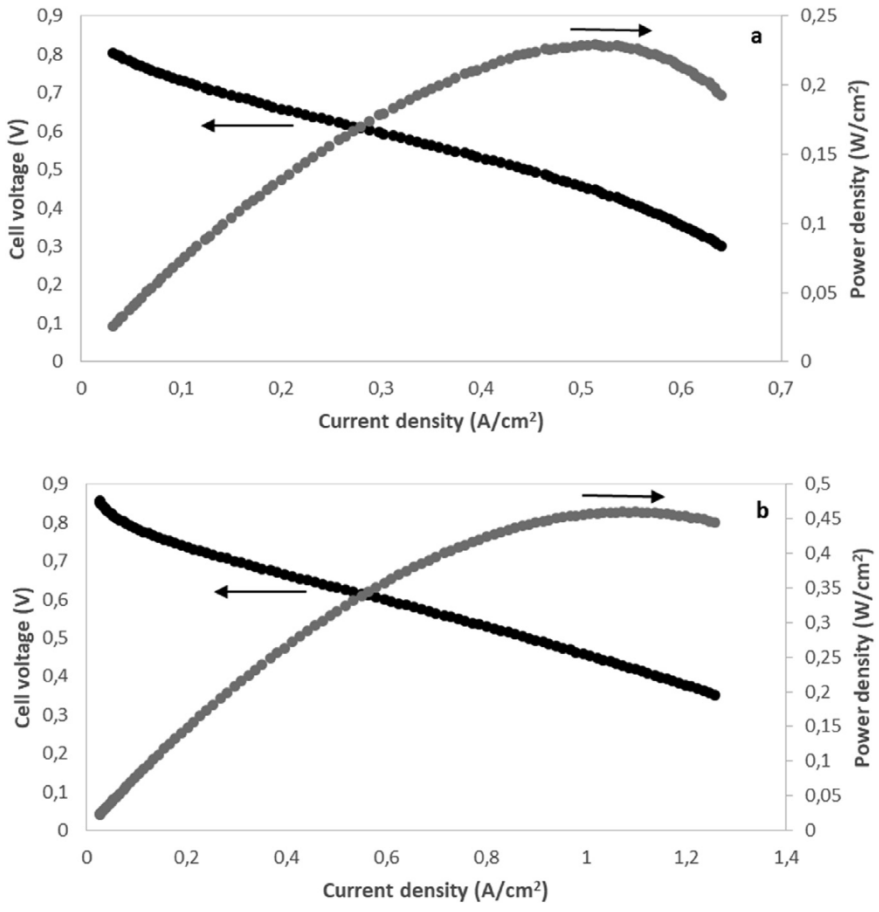


Fig. 4 – Comparison of the power density and polarization curves. (a) H_2 (55% v/v) + CO_2 (45% v/v) and (b) pure H_2.

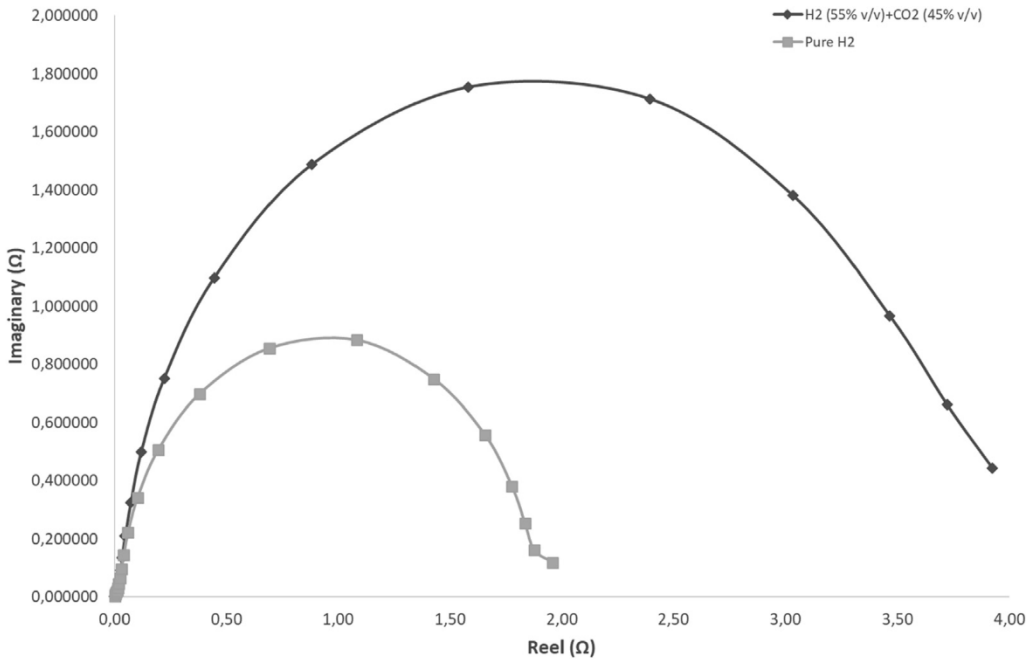


Fig. 5 – Nyquist plots of the fuel cell at different fuel concentration.

are given in Fig. 6. As shown in Fig. 6, when the mixture of hydrogen and carbon dioxide is used instead of pure hydrogen, the open circuit potential of the fuel cell system shows an almost 10 mV decrease due to Pt poisoning. In parallel with the decrease of the open circuit potential, the polarization curve shows a significant decrease in the Tafel slope with the addition of carbon dioxide into the fuel. This decrease in the slope of the Tafel is a result of the platinum surfaces being poisoned with carbon monoxide and a certain reduction in the active surface area.

Catalyst decrement in PEM fuel cells is admitted as a loss of platinum catalyst surface area over time [51–54]. Especially fuel impurities such as CO_2 leads to active catalyst surface area loss in the electrode and results in a loss of fuel cell efficiency [23]. Electrochemically active surface area (ECSA) of the platinum is a key parameter evaluating the efficiency of a

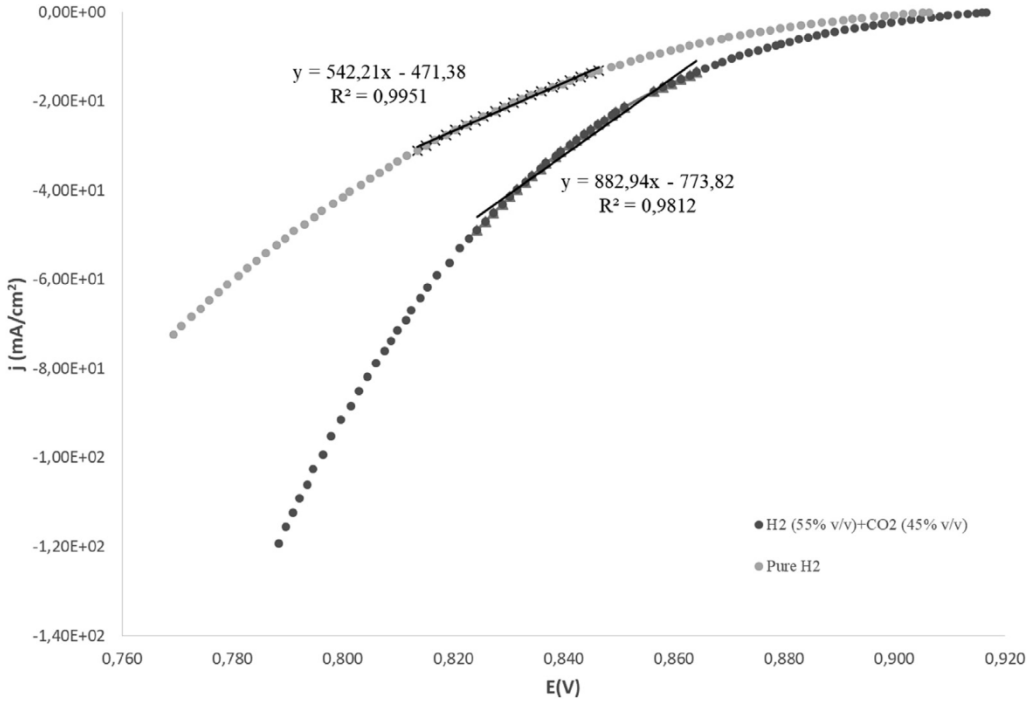


Fig. 6 – Linear Sweep Voltammetry results performed in PEM fuel cell with biogas (H_2 (55%v/v) + CO_2 (45% v/v)) and pure H_2.

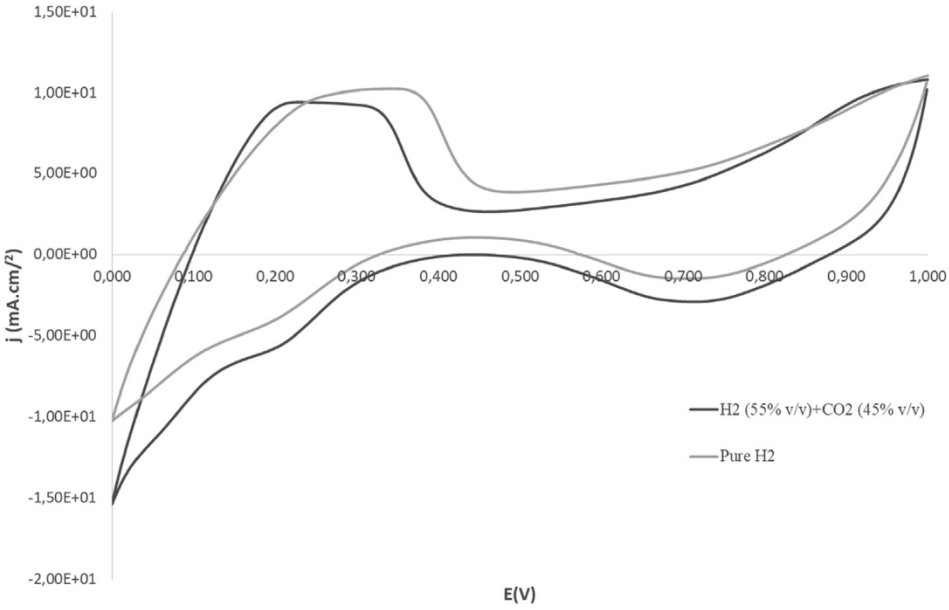


Fig. 7 – Cyclic voltammetry curves of different fuels during PEM fuel cell operation.

PEM fuel cell, especially for electrodes that contain low Pt-catalyst [55]. Designating the ECSA through the hydrogen adsorption/desorption reaction using cyclic voltammetry (CV) is a very common method. Therefore, CV analysis was performed for biogas and pure H_2 fed PEM fuel cell to determine ECSA. To estimate the quantity of active surface in the PEM fuel cell, ECSA was calculated as previously described by Koroglu et al. [23] and Ozdemir [30].

The studies have shown that ECSA tends to decrease with increasing CO_2 concentration in fuel. We observed that the ECSA was 96 m^2/g_{Pt} for pure H_2 fed fuel cell and 83 m^2/g_{Pt} for biogas fed fuel cell (Fig. 7). A CO_2 content of 45% in fuel caused the measured ECSA to decrease by about ~9%. A similar active platinum site decrease was also observed by Koroglu et al. [23], with increasing CO_2 ratio.

Conclusion

This study revealed that the pretreatment of cotton straw effects the yield in biogas formation as well as sugar extraction. The results show that acid pretreatment was the most effective method for the highest sugar concentration in the hydrolysate as well as biohydrogen and biomethane formation. The information provided the important insight of which method must be applied to cotton straw at first in order to provide efficient fuel formation. Another significant finding was the integration of fuel cell technology to evaluate H_2 produced from cotton straw. Methane is currently being evaluated well by different technologies however there were different drawbacks in the evaluation of hydrogen. Therefore this study provided the first insight of how fuel impurities affect the performance of fuel cells when hydrogen is used as fuel. However future research efforts are deemed in this direction most necessary. It is determined that agricultural wastes can be evaluated in hydrogen and methane production and also it is possible to produce zero-carbon energy using the energy produced from agricultural wastes in fuel cells. These findings are important for understanding the fundamentals of agricultural waste management in sustainable ways. It is considered that the results of this research study will provide insights and directions for researchers in the field of waste management.

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