Heliyon 6 (2020) e04717

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Research article

Enhanced hydrogen generation efficiency of methanol using dielectric barrier discharge plasma methodology and conducting sea water as an electrode

Nihar Ranjan Panda [a], Dojalisa Sahu [b,*]

[a] School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Odisha, India
[b] School of Applied Sciences, Centurion University of Technology and Management, Odisha, India

ARTICLE INFO

Keywords:
Energy engineering
Chemical engineering
Plasma physics
Renewable energy
Dielectric barrier discharge
Hydrogen energy
Methanol
Plasma
Water electrode

ABSTRACT

In this work, methanol decomposition method has been discussed for the production of hydrogen gas with the application of plasma. A simple dielectric barrier discharge (DBD) plasma reactor was designed for this purpose with two types of electrode. The DBD plasma reactor was experimented by substituting one of the metal electrodes with feebly conducting sea water which yielded better efficiency in producing hydrogen gas. Experimental parameters such as; discharge voltage and time were varied by maintaining a discharge gap of 1.5 mm and the plasma discharge characteristics were studied. Filamentary type micro-discharges were found to be formed which was observed as numerous streamer clusters in the current waveform. Gas chromatographic study confirmed the production of hydrogen gas with residence time around 3.6 min. Although, the concentration (%) of H_2 was high (98.1 %) and consistent with copper electrode assembly, the rate of formation and concentration was found to be the highest (98.7 %) for water electrode for specific discharge voltage. The energy efficiency was found to be 0.5 mol H_2/kWh and 1.2 mol H_2/kWh for metal (Cu) and water electrodes respectively. The electrode material significantly affects the plasma condition and hence the rate of hydrogen production. Compositional analysis of the water used as electrode showed a minimal change in the composition even after the completion of the experiment as compared to the untreated water. Methanol degradation study shows the presence of untreated methanol in the residue of the plasma reactor which has been confirmed from the absorption spectra.

1. Introduction

Conventional energy generated from fossil fuels is limited and subsidiary to several environmental issues [1, 2, 3, 4, 5]. So, search for an alternative and renewable energy sources has been instigated for a long-term solution to this problem. Amongst the sources of inexhaustible and sustainable energy, solar, wind and biomass energy sources are mainly site specific, intermittent and lack stability [6, 7]. Hydrogen is a promising option for energy supply and termed as clean fuel having high energy per unit mass [8, 9, 10]. On combustion, it can produce high thermal energy which is three times higher than that of petrol [11]. In the present day, this is an ideal energy carrier to be used in the petrochemical, automobile and chemical industry sectors [12]. Future fuel cell market will also be dependent fully on hydrogen as a primary fuel source [3, 4, 5]. It can be formed from various sources of raw materials such as higher hydrocarbons, green house gases, refinery gases and renewable materials such as wood, organic solid waste, sewages and alcohols derived from biomasses [1, 2, 3, 4, 5, 6, 7, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. Out of these, methanol has been widely used as a liquid fuel for production of hydrogen by different conversion technologies because of its high H_2 content, low-cost, easy storage and convenient transportation [16, 25, 26, 27, 28, 29, 30]. Recently, many methods have been introduced for the production of hydrogen such as stream reforming of methanol and natural gas [20, 21, 27], partial oxidation of methanol [31, 32, 33, 34], gasification of coal [22], and electrolysis of methanol-water [23]. Hydrogen yield of 20 mol % was achieved by Gondal et al. by laser exposure of methanol in 90 min [25]. Similarly, Take et al. [24] reported hydrogen production (95–97 mol %) by the electrolysis of methanol-water solution.

Plasma technologies have been employed for a number of applications such as plasma spectra-chemistry, cutting, spraying, welding, etching or deposition of thin layers, catalysis, ozone production, fuel gas

* Corresponding author.
E-mail address: dojalisa.sahu@cutm.ac.in (D. Sahu).

https://doi.org/10.1016/j.heliyon.2020.e04717
Received 28 March 2019; Received in revised form 30 August 2019; Accepted 11 August 2020

cleaning and destruction of volatile organic compounds etc. [35, 36, 37, 38, 39, 40, 41]. Among different nonthermal plasma processes such as dielectric barrier discharge (DBD), corona discharge, glow discharge and gliding arc, DBD plasma process is more stable and uniform having numerous potential industry applications [42, 43, 44]. Several efforts have been made by researchers in this direction for conversion of methane, ethanol and methanol with the help of the DBD plasma technique for the effective production of hydrogen gas. Using a similar method, Wang et al. [27] reported the production of hydrogen and discussed that using stainless steel inner electrode; longer discharge zone and bigger discharge gap would be beneficial for the reaction. Methanol degradation study by Sarmient et al. [45] revealed the effect of parameters like voltage, frequency (1–6 kHz), roughness of electrode and flow rate etc. and found enhanced methanol degradation with a flow rate less than 50 cm^3/s. There are some reports on DBD assisted decomposition of methanol into hydrogen [20, 46, 47]. Such DBD plasma setups for the conversion of methanol are easier to be operated in comparison to other catalytic processes and widely used.

The performance of the DBD reactor significantly depends upon the electrode materials (inner & outer). The choice of the inner electrode affects the methanol conversion and product selectivity [27]. It has been reported that methanol conversion is highest for stainless steel electrode and decreases for brass and aluminium gradually [27]. The conversion of methane as per the selectivity of electrode material has been studied by Xu et al. [48]. It shows the variation in the order; stainless steel > red copper > brass > aluminium. These reports suggest the significance of catalytic effect of inner electrodes to convert methanol/methane to generate H_2. The inner electrode remains in the direct contact of the reactive material whose temperature reaches up to 200 °C triggering the decomposition reaction. The outer electrode material also contributes to the production of H_2 as per the available report [48]. The above study shows that the use of aluminium foil as an electrode shows superiority in H_2 selectivity (%) over iron net [48].

This paper presents a study on the generation of high pure hydrogen gas using simple and indigenously developed DBD plasma setup based on both solid and liquid form of electrodes. An attempt has been made to make a cost-effective, laboratory scale DBD plasma reactor and study the discharge characteristics in generating hydrogen from methanol. In a major effort, sea water has been used as the outer electrode replacing the metal electrode in the plasma reactor to study its effectiveness in producing of hydrogen.

2. Experimental

In the present work, a coaxial DBD plasma reactor was designed by using different electrode materials giving two different configurations. In the first configuration, the plasma reactor was made up of a copper rod of 2 mm diameter as the high-voltage electrode (inner electrode) which was covered by a quartz tube of 1 mm thickness. Another hollow glass tube was placed outside the quartz tube with a discharge gap of 1.5 mm. This outer tube was coiled by some copper metallic mesh as grounded electrode (outer electrode). In the second configuration, feebly conducting salt water with conductivity 730 μS/cm was put in the glass tube as the outer electrode along with the same copper rod as inner electrode. In this case, the copper metallic mess was been replaced by conducting water collected from the Bay of Bengal near Puri sea beach, Odisha, India. Here, the outer vertical glass tube was attached to the reactor for placing conducting water in the setup. The schematic diagram of the above reactor is shown in Figure 1. The salty sea water acts as a transparent grounded electrode with an immersed metal ring to provide the electrical connection to it. Ghomi et al. reported plasma reactor of similar configuration based on dielectric barrier discharge [49]. The experimental parameters maintained for the above experiment have been summarized in Table 1.

A high voltage power source (Model-CTP2000K) capable of supplying bipolar sine wave output with 0–30 kV (peak-to-peak) and AC frequency maximum up to 20 kHz was used. In this case, voltage was varied from 1.9 kV to 2.9 kV maintaining the frequency at 9 kHz. Current–voltage waveforms of the plasma discharge were obtained with varying the discharge power. A digital oscilloscope (Tektronix make) was used for this purpose with a high voltage probe. The reactor had a provision to pass both liquids and gases to the discharge zone. Analytical grade methanol (M/s Merck- 67-56-1) was used for this purpose. Methanol was put in the reactor first and then voltage was applied. Provision was there to collect the gases and liquids after the discharge.

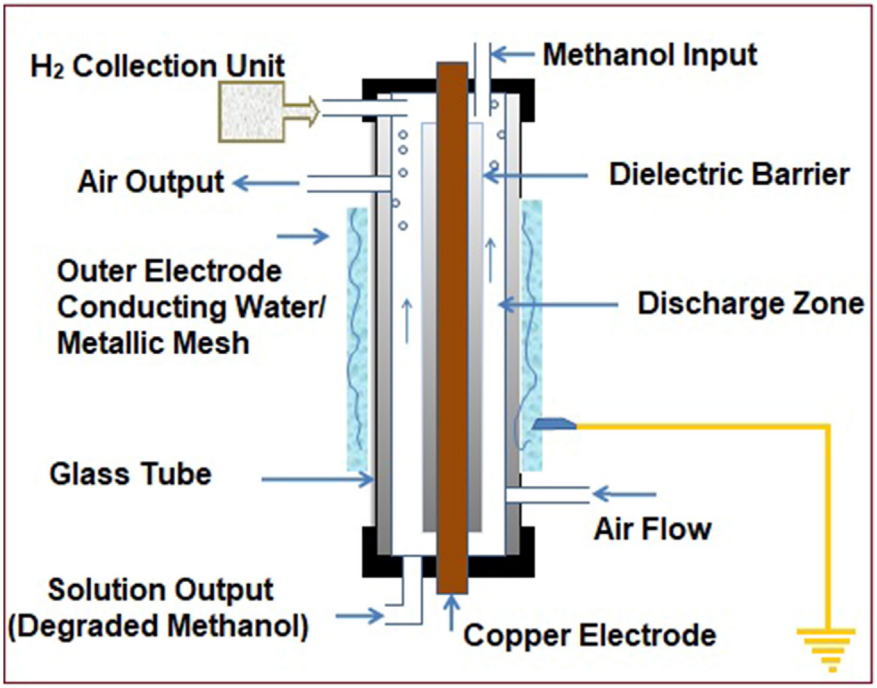

Figure 1. Schematic diagram showing the experimental setup of the DBD plasma reactor.

Table 1. Experimental parameters of the DBD reactor.

Voltage (kV)	1.9 to 2.4
Power (W)	0.4 to 0.61
Frequency (kHz)	9
Discharge Volume (mm^3)	0.744
Volume of methanol (ml)	8
Time (min)	5
Volume of methanol used	15 ml
Treatment Time	5–35 min

The product gas generated in the process was collected using downward displacement of water. The collected hydrogen gas was analyzed by gas chromatography (GC-17A, Shimadzu) using a 5 Å molecular sieve column and a thermal conductivity detector (TCD) to detect hydrogen, carbon monoxide etc. Argon was used as the carrier gas. High pure (99.9% purity) hydrogen, carbon monoxide, methanol vapour were used to check the purity of the product by doing the area mapping in GC analysis. The decomposition study of methanol was carried out at different voltages keeping the residence time constant and both yield and purity of hydrogen were determined. The discharge characteristics obtained for both the electrode configurations were also compared. Compositional analysis of the sea water used as the outer electrode was also carried out before and after the experiment. A UV-visible spectrometer (Shimadzu UV-1700) was used to record the UV absorbance spectra of methanol before plasma treatment. The same experiment was also carried out to record the spectra for the residue obtained from the reactor.

3. Results and discussion

Generally, a DBD reactor operates in homogenous and filamentary modes at atmospheric pressure [50, 51]. In the filamentary mode, a large number of micro-discharges are randomly formed between the two electrodes, whereas in the homogenous discharge, uniform plasma covers the electrode surface. DBD plasma discharge takes place in three phases namely; (1) breakdown stage (2) quasi-equilibrium stage and (3) non-equilibrium stage [43]. The latter one is the most effective for the initiation of chemical reaction due to the presence of high energy electrons which can produce excited molecules and radicals. When non-thermal electric discharge takes place between electrodes in air or oxygen medium, UV light, shock waves and many reactive species such as ions, free radicals, highly reactive molecules and electrons are produced by dissociation, excitation and ionization of gas molecules and molecules at the liquid surface [53]. The strong oxidizers from these species such as hydroxyl ions and ozone produced at the gas–liquid interface can easily diffuse into this interface leading to the dissociation of the working gas/liquid [52, 53, 54, 55].

The decomposition of an organic compound like methanol is also a complex physical and chemical process under plasma treatment. Discharge parameters and chemical reactions with the reactive species generated in the discharge largely influence this decomposition process [55]. In air plasma, three possible ways of decomposition of methanol are possible as given below (Eqs. (1), (2), and (3)) [55].

$$CH_3OH \rightarrow \cdot CH_3 + \cdot OH \quad (1)$$

$$CH_3OH \rightarrow \cdot CH_2OH + \cdot H \quad (2)$$

$$CH_3OH \rightarrow \cdot CH_3O + \cdot H \quad (3)$$

As reported, the dissociation energies of C–O, C–H, and O–H are about 351 kJ/mol, 414 kJ/mol, and 460 kJ/mol respectively [55]. So, the C–O bond will dissociate first by the reactive species produced by the plasma jets. Then, the above intermediates are converted into H_2, HCHO, HCOOH, and $HCOOCH_3$ along with other species by the plasma jets as per the following reactions (Eqs. (4), (5), (6), (7), (8), (9), (10), (11), (12), (13), and (14)) [56, 57, 58, 59]. But, we have not detected any such species like HCHO, HCOOH and CO_2 in our experiment.

$$\cdot CH_3 + \cdot H \rightarrow CH_4 \quad (4)$$

$$H\cdot + H\cdot \rightarrow H_2 \quad (5)$$

$$\cdot OH + \cdot H \rightarrow H_2O \quad (6)$$

$$CH_3OH + \cdot OH \rightarrow H_2O + CH_2OH\cdot \quad (7)$$

$$\cdot CH_2OH + \cdot H \rightarrow H_2 + HCHO \quad (8)$$

$$\cdot CH_2OH + \cdot OH \rightarrow H_2O + HCHO \quad (9)$$

$$CH_3OH + \cdot H \rightarrow \cdot CH_2OH + H_2 \quad (10)$$

$$\cdot CH_3O + \cdot H \rightarrow H_2 + HCHO \quad (11)$$

$$2H_2 + O_2 \rightarrow 2H_2O. \quad (12)$$

$$\cdot OH + \cdot H \rightarrow H_2O \quad (13)$$

$$H_2 + \cdot OH \rightarrow H_2O + H\cdot \quad (14)$$

The experiment was carried out by feeding methanol as the working liquid to the DBD plasma reactor connected to a high voltage power supply. The waveforms of discharge voltage and current were recorded for different applied voltages (1.9–2.9 kV) for the two types of electrode configuration. But, the frequency and the discharge gap were fixed at 9 kHz and 1.5 mm respectively. Figure 2a shows the voltage waveforms recorded for an applied voltage of 2.4 kV. When the electric field in the discharge gap is high enough to cause breakdown, a large number of micro-discharges are observed. In this case, the applied air pressure is of the order of 10^5 Pa. This pressure range is ideal for ozone generation, excimer formation as well as for flue gas treatment application. The discharge occurs either by filamentary or homogeneous mode over the dielectric surface. In our case, the filamentary type micro-discharges were observed, which can be seen as numerous streamer clusters in the current waveforms. This has been depicted in Figure 2b, which shows the current waveform recorded for an applied voltage of 2.6 kV for both type of electrodes. A single streamer cluster consists of a number of streamers/spikes whose typical lifetime is 50 ns [60]. These are randomly distributed in time and space over the dielectric surface and extend at the discharge gap [60]. These streamers or pulses are very essential and efficient to induce chemical reaction with improved reaction rate [61]. The Lissajous pattern contains important information about the discharge and accordingly recorded by us [43]. This has been depicted in Figure 3 (a & b) for copper and water electrodes based DBD reactors at an applied voltage of 2.6 kV. For the majority of DBD applications, the figure closely resembles like an ideal parallelogram which can be ascertained from Figure 3 [43]. In this case, the voltage is high enough to cause the breakdown of the gas inside the reactor. As a result, the charge is phase

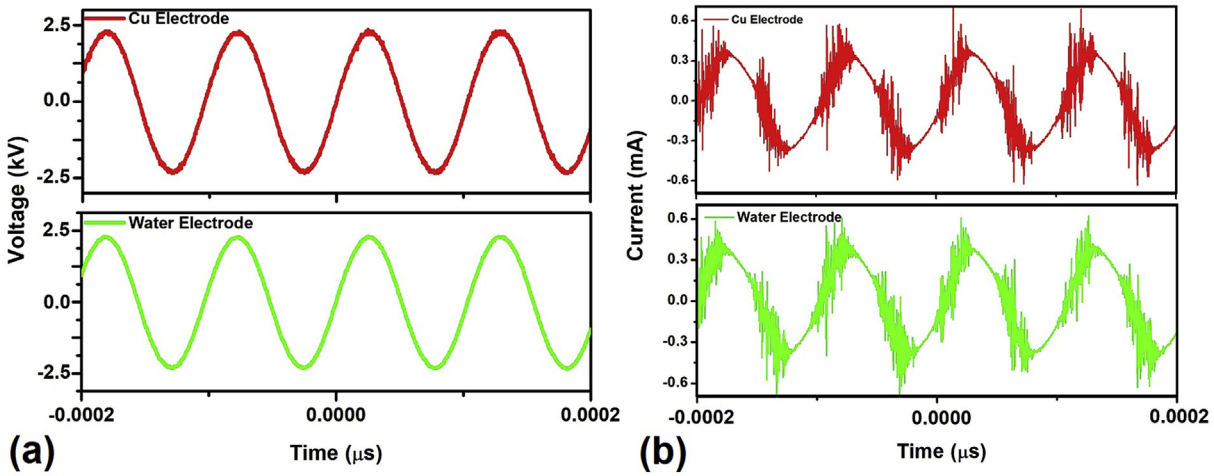

Figure 2. (a) Voltage waveforms and (b) current waveforms showing filamentary type microdischarges, recorded for the DBD plasma reactor using copper and water electrode configurations.

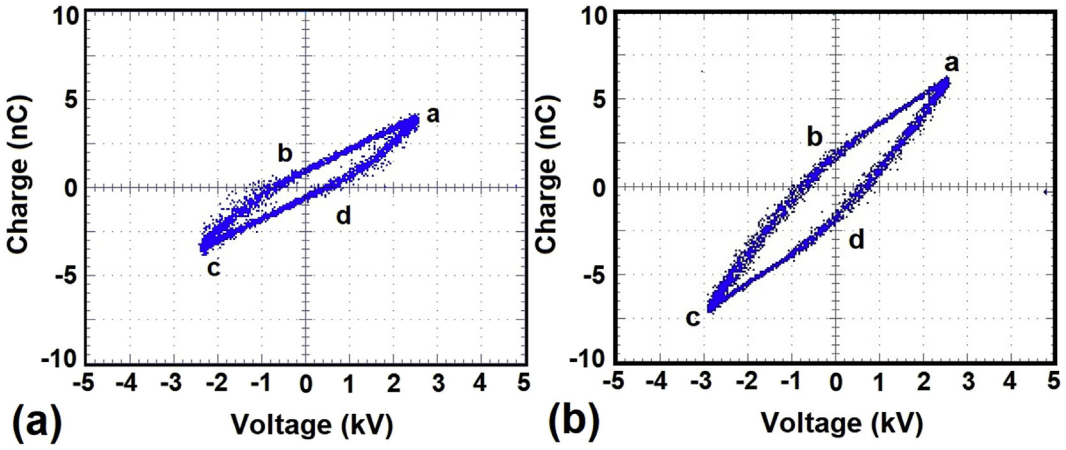

Figure 3. Lissajous patterns (Q–V) obtained for discharge plasma using (a) copper and (b) water electrode configurations.

shifted with respect to the voltage due to resistive losses in the discharge, which results in such type of pattern [62]. From this figure, one can find out the discharge voltage and the effective capacitances of the discharge gap and dielectrics [43]. The lines (a–b) and (c–d) in Figure 3 represent the capacitive transitions and lines (b–c) and (d–a) are the discharge transitions [62]. The slopes of the lines representing capacitive transitions give the total capacitance of the discharge reactor which is denoted as C_{tot}. The slopes of the lines representing discharge transitions are equal to C_{diel} which is the capacitance of the dielectric [62]. The energy dissipated in the discharge during one period of the voltage can be calculated by measuring the area of the Lissajous pattern [43, 62, 63]. If we multiply frequency with this area then the average power (W) dissipated in the discharge can be obtained [63, 64, 65, 66, 67]. The discharge power can also be calculated using the value of discharge current and voltage, which is found to vary from 0.40 to 0.61 W in our case.

The reaction rate for degradation of methanol with varying input power has been studied. Let us take C_0 and C_t as the initial and final concentrations of methanol solution at reaction time t respectively. Now, C_t/C_0 has been calculated and plotted against the treatment time for different input powers. This has been depicted in Figure 4. It shows that the degradation plots follow first order kinetics with the following expression (Eqn.15).

$$\ln C_t/C_0 = -kt \tag{15}$$

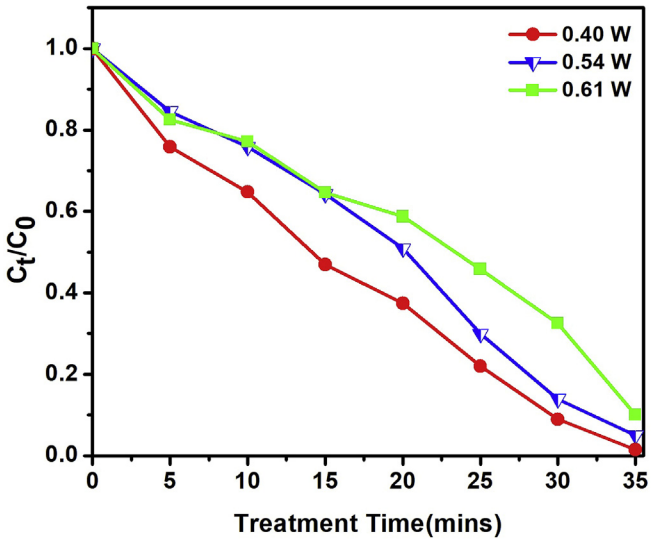

Figure 4. Methanol degradation (Ct/C_0) with time for different input powers showing first order kinetics.

In the above equation, k denotes the rate constant (s^{-1}). From the analysis, it has been concluded that with increasing power, methanol degradation will be more effective.

The product obtained from the reactor has been analyzed using gas chromatography (GC) and the data obtained are presented in Table 2 and Table 3 for copper and water electrodes respectively. One set of such chromatograms obtained from the spectrometer for the product gases generated from the plasma reactor with an applied voltage of 2.9 kV and power 0.61 W has been displayed in Figure 5 (a & b) for copper and water electrodes. It can be observed that one major peak with retention time around 3 min has been observed in both the chromatograms. This peak has been ascribed to H_2 gas [68]. For Cu electrode, the concentration of hydrogen gas varied from 79.2 to 98.1 % with variation in discharge power from 0.40 to 0.61 W. But, for conducting water as an electrode, the H_2 concentration is less for initial power up to 0.46 W. The concentration increases thereafter and attains a maximum (98.7 %) with retention time 3.681 min at highest discharge power of 0.61 W. This value is higher than that of the concentration obtained for Cu electrode. So, out of all the observations, highest concentration of H_2 with highest purity is observed for water electrode assembly. But, the concentration is more consistent for the setup with Cu electrode. The change in concentration of hydrogen produced for different input voltages and electrodes has been depicted in Figure 6.

From the above experiment, it has also been observed that the rate of formation (mole %) of hydrogen increases with an increase in discharge power. The mole % of H_2 is directly dependent on the decomposition of methanol [27, 28]. For a fixed volume and concentration of methanol, the decomposition will depend upon the applied energy generated from the plasma which initiates the chemical reaction. This energy is supplied from the electrical generator to the reactor to activate the methanol molecule to higher energy levels and generate more energetic electrons and radicals. Due to this, initiation in the breaking of C–H and O–H bonds in methanol takes place leading to decomposition [27]. This results in the elevation in mole % of hydrogen with increase in discharge power which has been illustrated in Figure 7. Hydrogen yield (%) is calculated by using the values of the product amount (mol %) and the amount (mol %) of methanol [60]. Keeping the discharge power constant at 0.61 W, methanol degradation studies have been carried out for 35 min and the yield (%) of hydrogen has been determined. The change in the value of yield (%) w.r.t. time has been shown in Figure 8. As we feed the measured amount of methanol to the reactor, all the molecules spread over the total volume may not find equal exposure to the major discharge zone to acquire sufficient energy for the decomposition to start. So, a part of the methanol decomposes to give hydrogen leading to lower yield (%) initially. But, with the increase in time more and more methanol molecules get excited leading to the increase in hydrogen yield. The rate of collision of methanol molecules with other ionic species like electrons or radicals increases which results in an increase in the conversion of methanol to hydrogen and other products [27]. This attains a maximum and then decreases as the methanol concentration also decreases with time. In our case, the same has been observed and after 35 min, we observed a decrease in H_2 yield. With the increase in discharge time, the yield of hydrogen increases and reaches a maximum of 12.4 % for copper electrode whereas it is 24.3 % for water electrode. Initially, the rate of formation of hydrogen increases up to 15 min and subsequently the rate decreases. Methanol conversion increases from 67 % to 88 % as the time increases from 5 min to 35 min. Energy efficiency is found to be 0.5 mol H_2/kWh and 1.2 mol H_2/kWh for copper and water electrodes respectively. The discharge zone also plays a major role in methanol conversion and production of hydrogen for the same dielectric material at constant input power [11, 42, 60, 69, 70, 71]. In the present study, discharge is characterized by multiple current and a series of micro-discharges per half-cycle of the applied voltage. Discharge is continuous throughout the zone and continuous production of the gas is observed for 20 min. It is observed that after 20 min the rate of hydrogen production becomes slower and then increases with further increase in the power. However, the yield of hydrogen depends upon the amount of methanol concentration. If the concentration of methanol decreases, the rate of hydrogen production also decreases. The effect of outer electrode material on the yield of hydrogen cannot be overlooked. These electrodes do not come in contact with the reactive material i.e. methanol and connected as grounded electrode. So, it may be claimed that there is no catalytic influence of this electrode on methanol degradation [48]. But, in our case we have observed the highest concentration and better hydrogen yield % for water electrode as compared to copper mesh. So, it may be stated that uniform and stable electric field is provided by the water electrode inducing methanol conversion and showing better yield. This is not achieved by copper mesh which has lesser surface area and a porous structure [48]. The surface intactness is also an important parameter for energy dissipation and generation of plasma which is more in case of water electrode. This may be another reason for better filamentary discharge taking place in case of water electrode which is not achieved by the porous copper mesh.

During the discharge, decomposition of methanolic intermediate species of the type OH, O, CO and CH_3O can be proposed [72, 73]. However, the gas chromatographic study indicates the generation of H_2 only which has been confirmed from the value of the residence time at a constant flow rate. There is no carbon deposition found on the electrodes. Formation of hydroxyl radicals (detected by hydrophilic test by polyethylene) prevents the formation of carbonaceous species. When water is used as an additional reactant along with methanol in DBD reactor, species like H_2, CO, CO_2, HCHO, ethylene glycol are also formed as by-products [74, 75, 76]. DBD plasma reactors with different configurations with different types of dielectric material such as alumina and barium titanate have been discussed in terms of energy efficiency [77]. But, in our case feebly conducting sea water used as an outer electrode has shown better energy efficiency than that of the copper electrode. The concentration and volume of by-products are also very less as per gas chromatographic study. The input current is also less for plasma discharge in case of water electrode as compared to the copper outer electrode. The compositional analysis of water taken as outer electrode for the plasma reactor has also been carried out before and after the discharge process. This has been carried out to study the impact of plasma process on the electrode material. The data have been presented in Table 4. It can be noted that the pH value of water slightly changes from 7.76 to 7.62 after plasma treatment like other parameters given in the table. The value of chemical oxygen demand (COD) changes to 1146–1923 mg/l from 1235-2506 mg/l after the completion of the

Table 2. Gas chromatography data at different voltage and input power for Cu electrode.

Sl. No.	Voltage (kV)	Residence time (min)	Area in Chromatogram (sq. unit)	Concentration of H_2 (%)
1	1.9	3.693	75566	94.0
2	2.2	3.701	87613	96.3
3	2.4	3.681	535282	98.1
4	2.6	3.490	106425	93.8
5	2.8	3.497	361333	97.4
6	2.9	3.642	105293	79.2

Table 3. Gas chromatography data at different voltage and input power for water electrode.

Sl. No.	Voltage (kV)	Residence time (min)	Area in Chromatogram (sq. unit)	Concentration of H_2 (%)
1	1.9	3.631	13830	29.6
2	2.2	3.627	16421	37.0
3	2.4	3.681	39462	44.8
4	2.6	3.685	555202	75.7
5	2.8	3.693	501858	98.4
6	2.9	3.681	62868	98.7

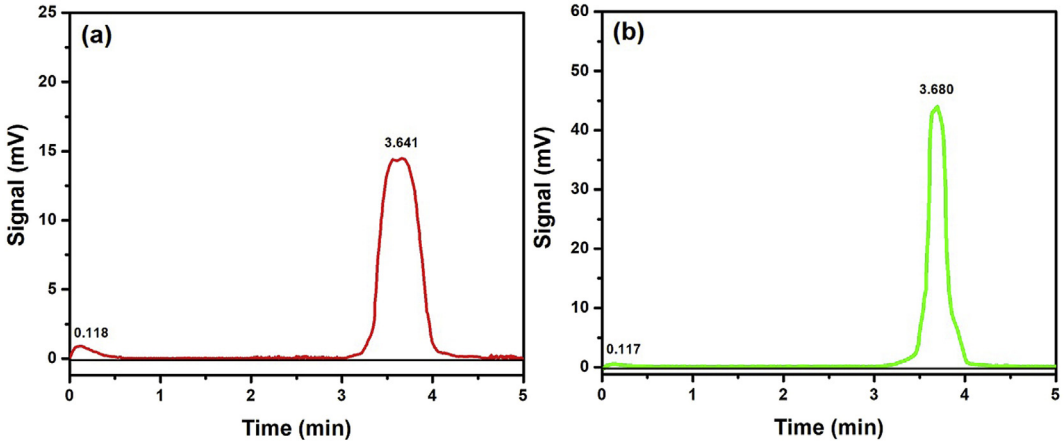

Figure 5. Gas chromatographs recorded for the product gas from DBD reactor using (a) copper and (b) water electrodes.

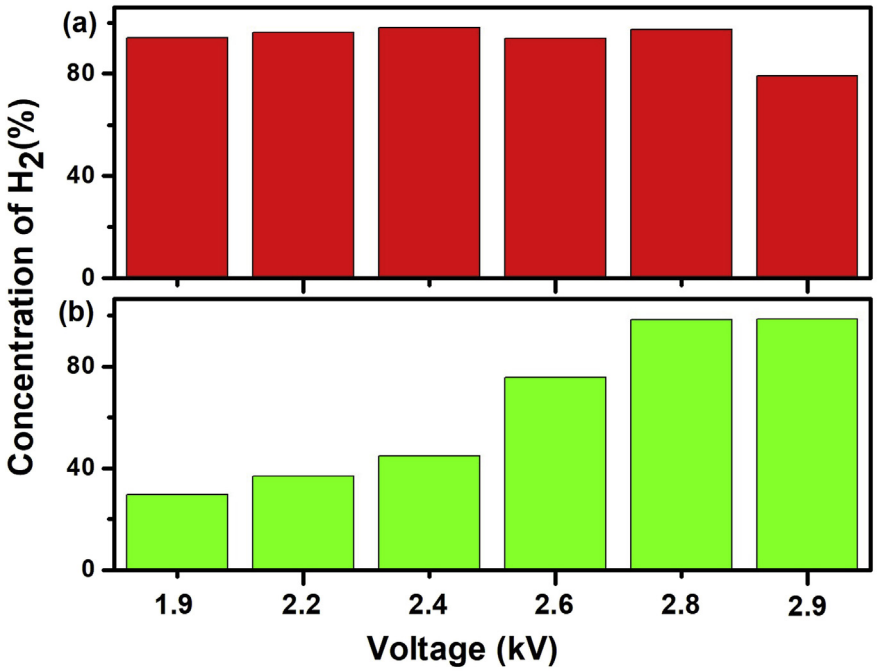

Figure 6. H_2 concentration (%) for different discharge voltages of DBD reactor using (a) copper and (b) water electrodes.

experiment. This may be due to the effect of the plasma process. So, it may be stated that there is a minimal change in the composition of water after the experiment. Methanol degradation study has also been carried out to check for any harmful material produced in the form of residue after the completion of the plasma process. The UV-VIS absorbance spectra of methanol solution before the start of the experiment and for the residue obtained after the treatment have also been recorded which have been shown in Figure 9. The absorption spectrum of untreated methanol shows a peak around 270 nm which apparently remains the same for the residual products obtained from the reactor after completion of the experiment for different applied voltages. Methanol shows absorbance peak (λ_{max}) around 220–280 nm in the UV region [78]. So, it may be understood that the residue also contains untreated methanol as a major part which has not been degraded. As per the recent available

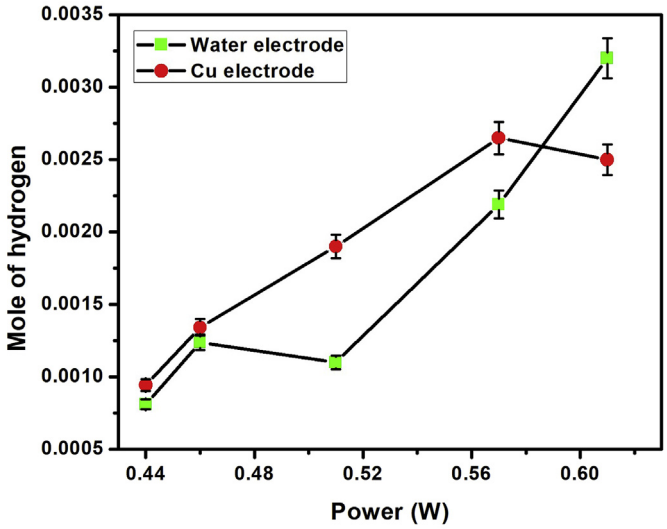

Figure 7. Variation of rate (mole) of hydrogen formation at different discharge powers within discharge time of 5 min.

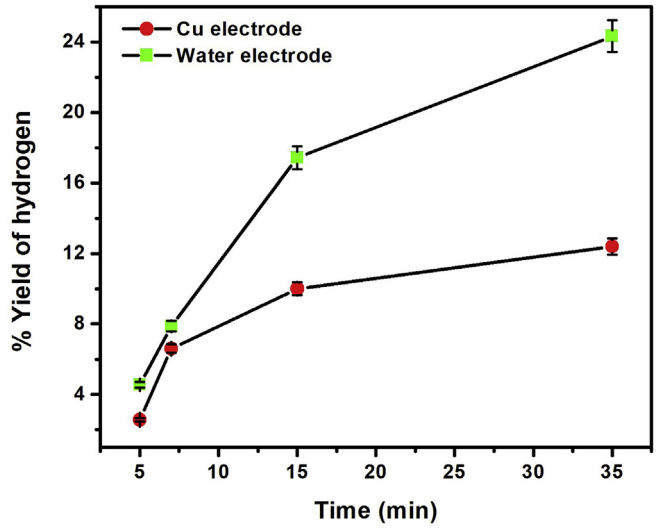

Figure 8. Variation of yield (%) of hydrogen with time (discharge power: 0.5 W).

report, Dey et al. reported H_2 production using DBD plasma technique with an inbuilt Cu electrode [79]. El-Shafie et al. studied the hydrogen generation from water vapour decomposition with application of plasma as energy source [80, 81]. To the best of our knowledge, study on hydrogen production using DBD plasma reactor with water as an

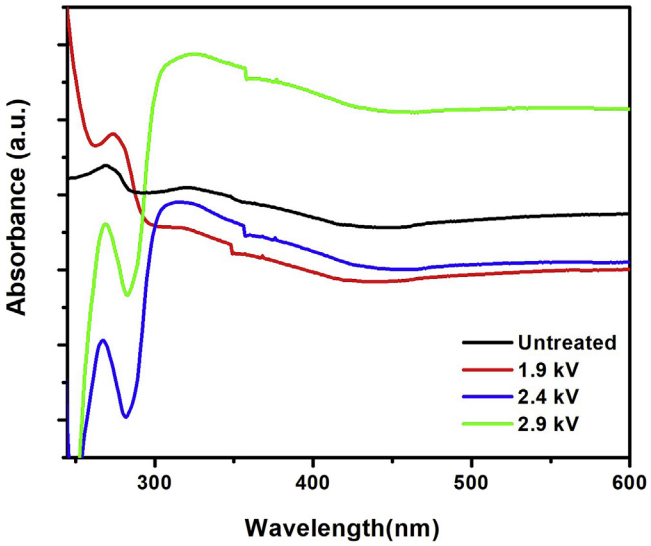

Figure 9. Optical absorption spectra of the residue obtained from the DBD plasma reactor along with untreated methanol.

electrode has not been reported. So, our method is an innovative approach in the generation of renewable hydrogen energy.

4. Conclusion

The present study is based on the design of a DBD plasma reactor and production of hydrogen gas through decomposition of methanol by the above reactor. Plasma discharge characteristics have been studied by taking two types of outer electrode such as copper and conducting sea water keeping the inner electrode fixed as copper. Filamentary types of micro-discharge have been observed in the current waveform with the application of voltage which increases with time. The discharge characteristics have been monitored by paying attention to important factors such as; input power, discharge time and types of electrode which have dominant effects on the reaction performance. Electrical characteristics have been carried out to find out the optimal input power of the DBD reactor. Methanol conversion yield has been found out to be higher for the water electrode as compared to metal for higher discharge power. The reactor has been found to show better energy efficiency (1.2 mol H_2/kWh) for water electrode assembly. So, it is possible to use feebly conducting sea water as an electrode in DBD plasma setup which has shown better energy efficiency. Uniform and stable electric field is provided by water electrode to the plasma reactor inducing faster conversion of methanol leading to higher hydrogen yield (%). Compositional analysis of the water used as electrode shows a minimal change after plasma process with no other harmful residue from the reactor other than untreated methanol. It is believed that this investigation will be helpful for modelling and application of discharge plasma in a cost-effective way for hydrogen generation.

Table 4. Composition of water used as electrode before and after the plasma process.

Parameter	Before Treatment	After Treatment
pH	7.76	7.62
Total Hardness (mg/l)	3565	3560
Chloride ion (mg/l)	3088	3075
Conductivity (μS/cm)	730	734
DO (mg/l)	12	10.5
COD (mg/l)	1235–2506	1146–1923

Declarations

Author contribution statement

N. R. Panda, D. Sahu: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Acknowledgements

The authors sincerely thank the esteemed reviewers for their constructive suggestions in improvising the manuscript. One of the authors (DS) is highly thankful to Prof. Supriya Pattanayak, Vice Chancellor, CUTM for constant encouragement to carry out this work.

References

[1] Y. Luo, L. Tang, U. Khan, Q. Yu, H.-M. Cheng, X. Zou, B. Liu, Morphology and surface chemistry engineering toward pH-universal catalysts for hydrogen evolution at high current density, Nat. Commun. 10 (269) (2019) 1–9.
[2] P. Kumar, P. Devi, R. Jain, S.M. Shivaprasad, R.K. Sinha, G. Zhou, R. Notzel, Quantum dot activated indium gallium nitride on silicon as photoanode for solar hydrogen generation, Communications Chem. 2 (4) (2019) 1–7.
[3] H. Zhang, Q. Ding, D. He, H. Liu, W. Liu, Z. Li, B. Yang, X. Zhang, L. Lei, S. Jin, A p-Si/NiCoSe$_x$ core/shell nanopillar array photocathode for enhanced photoelectrochemical hydrogen production, Energy Environ. Sci. 9 (2016) 3113–3119.
[4] P.M. Carraro, K. Sapag, M.I. Oliva, G.A. Eimer, Comparative study of hydrogen storage on metal doped mesoporous materials, Chem. Phys. Lett. 701 (2018) 93–97.
[5] A. Kumar, R. Prasad, Y.C. Sharma, Ethanol steam reforming study over ZSM-5 supported cobalt versus nickel catalyst for renewable hydrogen generation, Chin. J. Chem. Eng. 27 (3) (2019) 677–684.
[6] S.-L. Li, Q. Xu, Metal–organic frameworks as platforms for clean energy, Energy Environ. Sci. 6 (2013) 1656–1683.
[7] S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, Nature 488 (2012) 294–303.
[8] J.A. Turner, Sustainable hydrogen production, Science 305 (2004) 972–974.
[9] V.A. Goltsov, T.N. Veziroglu, L.F. Goltsova, Hydrogen civilization of the future—A new conception of the IAHE, Int. J. Hydrogen Energy 31 (2006) 153–159.
[10] M. Ni, D.Y.C. Leung, M.K.H. Leung, K. Sumathy, An overview of hydrogen production from biomass, Fuel Process. Technol. 87 (2006) 461–472.
[11] B. Wang, Y. Lu, X. Zhang, S. Hu, Hydrogen generation from steam reforming of ethanol in dielectric barrier discharge, J. Nat. Gas Chem. 20 (2011) 151–154.
[12] A. Zuttel, A. Borgschulte, L. Schlapbach, Hydrogen as a Future Energy Carrier, WILEY-VCH, Verlag GmbH & Co. KGaA, Weinheim, 2008.
[13] S. Rumpel, J.F. Siebel, C. Fares, J. Duan, E. Reijerse, T. Happe, W. Lubitz, M. Winkler, Enhancing hydrogen production of microalgae by redirecting electrons from photosystem I to hydrogenase, Energy Environ. Sci. 7 (2014) 3296–3301.
[14] O. Kruse, B. Hankamer, Microalgal hydrogen production – A review, Curr. Opin. Biotechnol. 21 (3) (2010) 238–243.
[15] H. Jae, A. Hwang, N. Kabra, J.R. Kim, B.-H. Jeon, Photoheterotrophic microalgal hydrogen production using acetate- and butyrate-rich wastewater effluent, Energy 78 (2014) 887–894.
[16] X.S. Li, A.M. Zhu, K.J. Wang, Y. Xu, Z.M. Song, Methane conversion to C_2 hydrocarbons and hydrogen in atmospheric non-thermal plasmas generated by different electric discharge techniques, Catal. Today 98 (2004) 617–624.
[17] A. Indarto, Hydrogen production from methane in a dielectric barrier discharge using oxide zinc and chromium as catalyst, J. Chin. Inst. Chem. Eng. 39 (2008) 23–28.
[18] S. Sa, H. Silva, J.M. Sousa, A. Mendes, Hydrogen production by methanol steam reforming in a membrane reactor: palladium vs. carbon molecular sieve membranes, J. Membr. Sci. 339 (1–2) (2009) 160–170.
[19] C.Y. Zong, L. Chen, H.L. Wang, Hydrogen generation by glow discharge plasma electrolysis of methanol solutions, Int. J. Hydrogen Energy 34 (1) (2009) 48–55.
[20] F.W. Chang, L.S. Roselin, T.C. Ou, Hydrogen production by partial oxidation of methanol over bimetallic Au–Ru/Fe_2O_3 catalysts, Appl. Catal. A Gen. 334 (1–2) (2008) 147–155.
[21] A. Indarto, D.R. Yang, J. Palgunadi, J.W. Choi, H. Lee, H.K. Song, Partial oxidation of methane with Cu–Zn–Al catalyst in a dielectric barrier discharge, Chem. Eng. Process 47 (5) (2008) 780–786.
[22] B.M. Besancon, V. Hasanov, R. Imbault-Lastapis, R. Beneschb, M. Barrio, M.J. Molnvikc, Hydrogen quality from decarbonized fossil fuels to fuel cells, Int. J. Hydrogen Energy 34 (5) (2009) 2350–2360.
[23] D. Das, T.N. Veziroglu, Hydrogen production by biological processes: a survey of literature, Int. J. Hydrogen Energy 26 (1) (2001) 13–28.
[24] T. Take, K. Tsurutani, M. Umeda, Hydrogen production by methanol–water solution electrolysis, J. Power Sources 164 (1) (2007) 9–16.
[25] M.A. Gondal, A. Hameed, Z.H. Yamani, Hydrogen generation by laser transformation of methanol using n-type WO_3 semiconductor catalyst, J. Mol. Catal. Chem. 222 (1–2) (2004) 259–264.
[26] M.A. Medinsky, D.C. Dorman, Recent development in methanol toxicity, Toxicol. Lett. 82–83 (1995) 707–711.
[27] B. Wang, X. Zhang, H. Bai, Y. Lu, S. Hu, Hydrogen production from methanol through dielectric barrier discharge, Front. Chem. Sci. Eng. 5 (2) (2011) 209–214.
[28] Y.-F. Wang, Y.-S. You, C.-H. Tsai, L.-C. Wang, Hydrogen production by methanol decomposition using gliding arc gas discharge, Int. J. Hydrogen Energy 35 (2010) 9637–9640.
[29] T. Durka, G.D. Stefanidis, T.V. Gerven, A.I. Stankiewicz, Microwave-activated methanol steam reforming for hydrogen production, Int. J. Hydrogen Energy 36 (2011) 12843–12852.
[30] Z.C. Yan, C. Li, W.H. Li, Hydrogen generation by glow discharge plasma electrolysis of methanol solutions, Int. J. Hydrogen Energy 34 (2009) 48–55.
[31] K. Ghasemzadeh, S.M.S. Tilebon, A. Basile, Reforming and partial oxidation reactions of methanol for hydrogen production, in: A. Basile, F. Dalena (Eds.), Methanol; Science and Engineering, Elsevier, 2018, pp. 239–278.
[32] H.-S. Wang, K.-Y. Huang, Y.-J. Huang, Y.-C. Su, F.-G. Tseng, A low-temperature partial-oxidation-methanol micro reformer with high fuel conversion rate and hydrogen production yield, Appl. Energy 138 (2015) 21–30.
[33] M. Toledo, F. Gonzalez, J. Ellzey, Hydrogen production from methanol and ethanol partial oxidation, Energy Fuels 28 (5) (2014) 3453–3459.
[34] W.-H. Chen, C.-T. Shen, B.-J. Lin, S.-C. Liu, Hydrogen production from methanol partial oxidation over Pt/Al_2O_3 catalyst with low Pt content, Energy 88 (2015) 399–407.
[35] M. Meyyappan, Plasma nanotechnology: past, present and future, J. Phys. D Appl. Phys. 44 (2011) 174002.
[36] K. Ken Ostrikov, U. Cvelbar, A.B. Murphy, Plasma nanoscience: setting directions, tackling grand challenges, J. Phys. D Appl. Phys. 44 (2011) 174001.
[37] A. Bogaerts, E. Neyts, R. Gijbels, J. Spectrochim, Gas discharge plasmas and their applications, Acta, Part B 57 (2002) 609–658.
[38] M. Ma, L. Yang, L. Ouyang, H. Shao, M. Zhu, Promoting hydrogen generation from the hydrolysis of Mg-Graphite composites by plasma-assisted milling, Energy 167 (2019) 1205–1211.
[39] Z. Yan, L. Chen, H. Wang, Experimental study of plasma under-liquid electrolysis in hydrogen generation, Chin. J. Proc. Eng. 6 (3) (2006) 398–401.
[40] O.V. Polyakov, A.M. Badalyan, L.F. Bakhturova, The Water Degradation Yield and Spatial Distribution of Primary radicals in the near-discharge volume of an electrolytic cathode, High Energy Chem. 36 (5) (2002) 280–284.
[41] V.J. Rico, J.L. Hueso, J. Cotrino, A.R. Gonzalez-Elipe, Evaluation of different dielectric barrier discharge plasma configurations as an alternative technology for green C_1 chemistry in the carbon dioxide reforming of methane and the direct decomposition of methanol, J. Phys. Chem. 114 (11) (2010) 4009–4016.
[42] A. Chirokov, A. Gutsol, A. Fridman, Atmospheric pressure plasma of dielectric barrier discharges, Pure Appl. Chem. 77 (2) (2005) 487–495.
[43] U. Kogelschatz, Dielectric-barrier discharges: their history, discharge physics, and industrial applications, Plasma Chem. Plasma Process. 23 (1) (2003) 1–46.
[44] M.G.D. Giorgi, A. Ficarella, A. Sciolti, E. Pescini, S. Campilongo, G.D. Lecce, Improvement of lean flame stability of inverse methane/air diffusion flame by using coaxial dielectric plasma discharge actuators, Energy 126 (2017) 689–706.
[45] B. Sarmient, J.J. Brey, I.G. Viera, A.R. Gonzalez-Elipe, Hydrogen production by reforming of hydrocarbons and alcohols in a dielectric barrier discharge, J. Power Sources 169 (2007) 140–143.
[46] S. Tanabe, H. Matsuguma, K. Okitsu, H. Matsumoto, Generation of hydrogen from methanol in a dielectric-barrier discharge-plasma system, Chem. Lett. 29 (10) (2000) 1116–1117.
[47] L. Wang, S.Y. Liu, C. Xu, X. Tu, Direct conversion of methanol to n-C_4H_{10} and H_2 in a dielectric barrier discharge reactor, Green Chem. 18 (2016) 5658–5666.
[48] X. Zhang, B. Wang, Y. Liu, G. Xu, Conversion of methane by steam reforming using dielectric-barrier discharge, Chin. J. Chem. Eng. 17 (4) (2009) 625–629.
[49] H. Ghomi, N.N. Safa, S. Ghasemi, Investigation on a DBD plasma reactor, IEEE Trans. Plasma Sci. 39 (11) (2011) 2104–2105.
[50] A. Indarto, A review of direct methane conversion to methanol by dielectric barrier discharge, IEEE Trans. Dielectr. Electr. Insul. 15 (4) (2008) 1038–1043.
[51] J. Xue, L. Chen, H.L. Wang, Degradation mechanism of Alizarin Red in hybrid gas–liquid phase dielectric barrier discharge plasmas: experimental and theoretical examination, Chem. Eng. J. 138 (1–3) (2008) 120–127.
[52] H.E. Wagner, R. Brandenburg, K.V. Kozlov, A. Sonnenfeld, P. Michel, J.F. Behnke, The barrier discharge: basic properties and applications to surface treatment, Vacuum 71 (3) (2003) 417–436.
[53] B. Sun, M. Sato, A. Harano, J.S. Clements, Non-uniform pulse discharge-induced radical production in distilled water, J. Electrost. 43 (20) (1998) 115–126.

[54] Y. Ma, J. Chen, B. Yang, Q. Yu, Degradation of high concentration methanol in aqueous solution by dielectric barrier discharge, IEEE Transactions on plasma sciences 41 (7) (2013) 1716–1724.
[55] Z. Qi, X. Lin, Y. Zhao, J. Niu, D. Liu, Z. Ding, Y. Xia, L. Ji, Z. Zhao, L. Yang, Interaction of plasma jet with methanol as fundamental processes in solution, IEEE Trans. Plasma Sci. 47 (11) (2019) 4802–4810.
[56] H. Kabashima, H. Einaga, S. Futamura, Hydrogen generation from water, methane, and methanol with nonthermal plasma, IEEE Trans. Ind. Appl. 39 (2) (2003) 340–345.
[57] N. Bundaleska, D. Tsyganov, R. Saavedra, E. Tatarova, F.M. Dias, C.M. Ferreira, Hydrogen production from methanol reforming in microwave "tornado"-type plasma, Int. J. Hydrogen Energy 38 (22) (2013) 9145–9157.
[58] S. Futamura, H. Kabashima, Effects of reactor type and voltage properties in methanol reforming with nonthermal plasma, IEEE Trans. Ind. Appl. 40 (6) (2004) 1459–1466.
[59] H. Zhang, F. Zhu, X. Li, K. Cen, C. Du, X. Tu, Enhanced hydrogen production by methanol decomposition using a novel rotating gliding arc discharge plasma, RSC Adv. 6 (16) (2016) 12770–12781.
[60] X. Chao, T. Xin, Plasma-assisted methane conversion in an atmospheric pressure dielectric barrier discharge reactor, J. Energy Chem. 22 (2013) 420–425.
[61] S. Yao, A. Nakayama, E. Suzuki, Methane conversion using a high-frequency pulsed plasma: discharge features, AIChE J. 47 (2001) 419–426.
[62] M. Magureanu, N.B. Mandache, V.I. Parvulescu, Ch. Subrahmanyam, A. Renken, L. Kiwi-Minsker, Improved performance of non-thermal plasma reactor during decomposition of trichloroethylene: optimization of the reactor geometry and introduction of catalytic electrode, Appl. Catal. B Environ. 74 (2007) 270–277.
[63] M. Krauss, B. Eliasson, U. Kogelschatz, A. Wokaun, CO_2 reforming of methane by the combination of dielectric-barrier discharges and catalysis, Phys. Chem. Chem. Phys. 3 (2001) 294–300.
[64] T. Shibata, H. Nishiyama, Water treatment by dielectric barrier discharge tube with vapor flow, Int. J. Plasma Environ. Sci. Technol. 11 (1) (2017) 112–117.
[65] Z. Falkenstein, J.J. Coogan, Microdischarge behaviour in the silent discharge of nitrogen – oxygen and water – air mixtures, J. Phys. D Appl. Phys. 30 (1997) 817–825.
[66] J.-J. Zou, Y.-P. Zhang, U.-J. Liu, Hydrogen production from partial oxidation of dimethyl ether using corona discharge plasma, Int. J. Hydrogen Energy 32 (2007) 958–964.
[67] Y.S. Nakayama, A.E. Suzuki, Methane conversion using a high-frequency pulsed plasma: discharge features, AIChE J. 47 (2001) 419–426.
[68] A. Lamb, K.A. Larson, E.L. Tollefson, A gas chromatographic method for exhaust gas analysis, J. Air Pollut. Contr. Assoc. 23 (3) (1973) 200–202.
[69] N. Khadir, K. Khodja, A. Belasri, Methane conversion using a dielectric barrier discharge reactor at atmospheric pressure for hydrogen production, Plasma Sci. Technol. 19 (2017) 95502.
[70] Q. Wang, B.-H. Yan, Y. Jin, Y. Cheng, Investigation of dry reforming of methane in a dielectric barrier discharge reactor, Plasma Chem. Plasma Process. 29 (2009) 217–228.
[71] D. Sahu, Degradation of industrial phenolic wastewater using dielectric barrier discharge plasma technique, Russ. J. Appl. Chem. 93 (2020) 905–915.
[72] W. Wang, C. Zhu, Y. Cao, DFT study on pathways of steam reforming of ethanol under cold plasma conditions for hydrogen generation, Int. J. Hydrogen Energy 35 (2010) 1951–1956.
[73] W.J. Wang, Y.Q. Wang, Dry reforming of ethanol for hydrogen production: thermodynamic investigation, Int. J. Hydrogen Energy 34 (2009) 5382–5389.
[74] O. Aubry, C. Met, A. Khacef, J.M. Cormier, On the use of a non-thermal plasma reactor for ethanol steam reforming, Chem. Eng. J. 106 (2005) 241–247.
[75] A. Yanguas Gil, J.L. Hueso, J. Cotrino, A. Caballero, A.R. Gonzalez Elipe, Reforming of ethanol in a microwave surface-wave plasma discharge, Appl. Phys. Lett. 85 (2004) 4004–4006.
[76] Z.C. Yan, C. Li, W.H. Lin, Hydrogen generation by glow discharge plasma electrolysis of methanol solutions, Int. J. Hydrogen Energy 34 (2009) 48–55.
[77] S. Fromille, J. Phillips, Super dielectric materials, Materials 7 (2014) 8197–8212.
[78] C.R. Warren, Rapid measurement of chlorophylls with a microplate reader, J. Plant Nutr. 31 (2008) 1321–1332.
[79] G.R. Dey, S.D. Zode, V. Namboodiri, Application of plasma for efficient H_2 production: a realism of copper electrode in single dielectric barrier discharge reactor, Phys. Plasmas 25 (2018) 103508.
[80] M. El-Shafie, S. Kambara, Y. Hayakawa, Performance evaluation of an industrial absorption system, Energy Rep. 6 (2020) 45–51.
[81] M. El-Shafie, S. Kambara, Y. Hayakawa, T. Miura, Study of the reactor temperature effect on H2 production from steam decomposition using DBD plasma, Int. J. Hydrogen Energy 44 (2019) 20239–20248.