Research article

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

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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 H₂ 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 H₂/kWh and 1.2 mol H₂/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 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 H₂ 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...
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 $\mu$S/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 mesh 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 Merc-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.](image-url)
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 purity (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].

\[
\begin{align*}
\text{CH}_3\text{OH} & \rightarrow \text{CH}_3 + \cdot \text{OH} \\
\text{CH}_3\text{OH} & \rightarrow \text{CH}_2\text{OH} + \cdot \text{H} \\
\text{CH}_3\text{OH} & \rightarrow \cdot \text{CH}_3 + \cdot \text{OH}
\end{align*}
\]

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 H₂, HCHO, HCOOH, and HCOOCH₃ 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 CO₂ in our experiment.

\[
\begin{align*}
\text{CH}_3 + \cdot \text{H} & \rightarrow \text{CH}_4 \\
\text{H} + \cdot \text{H} & \rightarrow \text{H}_2 \\
\cdot \text{OH} + \cdot \text{H} & \rightarrow \text{H}_2 \text{O} \\
\text{CH}_3\text{OH} + \cdot \text{OH} & \rightarrow \text{H}_2 \text{O} + \text{CH}_2\text{OH} \\
\cdot \text{CH}_3\text{OH} + \cdot \text{H} & \rightarrow \text{H}_2 + \text{HCHO} \\
\cdot \text{CH}_2\text{OH} + \cdot \text{OH} & \rightarrow \text{H}_2 \text{O} + \text{HCHO} \\
\text{CH}_3\text{OH} + \cdot \text{H} & \rightarrow \text{CH}_2\text{OH} + \text{H}_2 \\
\cdot \text{CH}_3\text{O} + \cdot \text{H} & \rightarrow \text{CH}_2\text{OH} + \cdot \text{H} \\
2\text{H}_2 + \text{O}_2 & \rightarrow 2\text{H}_2\text{O} \\
\cdot \text{OH} + \cdot \text{H} & \rightarrow \text{H}_2 \text{O} \\
\text{H}_2 + \cdot \text{OH} & \rightarrow \text{H}_2 \text{O} + \cdot \text{H} \\
\end{align*}
\]

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 10⁵ 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...
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 Ctot. The slopes of the lines representing discharge transitions are equal to Cdiel 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, 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 C0 and Ct as the initial and final concentrations of methanol solution at reaction time t respectively. Now, Ct/C0 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).

\[ \ln \frac{C_t}{C_0} = -kt \]  

(15)

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.

Figure 4. Methanol degradation (Ct/C0) 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 [27, 28]. For a methanol to hydrogen and other products [27]. This attains a maximum 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$_3$O 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

| 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                      |
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 ($\lambda_{\text{max}}$) 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

| 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.
Dey et al. reported H2 production using DBD plasma technique with an inbuilt Cu electrode [79]. El-Shafee 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 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 H2/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.

| 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       |

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).

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

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