

Optimization of Proton Exchange Membrane (Pem) Materials in an Electrochemical Process for Methanol Fuel Synthesis

Sampson Ojon Nwovu^{1*}, O.M.O Etebu² and P. I. Okoye³

^{1&2)}Department of Mechanical Engineering, African Centre of Excellence, Centre for Oilfield Chemical and Research, University of Port Harcourt, Rivers State, P.M.B. 5323, Nigeria;

³⁾Department of Pure and Applied Chemistry, University of Port Harcourt, Rivers State, Nigeria.

Corresponding Author: Sampson Ojon Nwovu

Abstract– This study presents optimum Proton Exchange Membrane (PEM) materials and techniques for synthesis of methanol fuel using electrochemical process. Carbonated alkaline solution of potassium hydroxide (KOH) and water were used as the major feedstocks. To catalyze the reaction processes, Cu and Zn electrodes were adopted for cathode and anode respectively. The electrochemical set-up was a single unit technology that performed electrolysis of water and reduction of KHCO_3 to methanol simultaneously. The PEM was prepared using Paraffin Wax, Silica Gel (SiO_2), and Sodium Dodecyl/Lauryl Sulphate (Surfactant). The paraffin wax repelled water flow across the membrane and also facilitated proton (H^+) transport from anodic half-cell to cathodic half-cell. The SiO_2 served as a pathway for proton transportation while surfactant conducted the electrons through the membrane. Methanol synthesis occurred at cathodic half-cell when the proton produced by water during electrochemical reactions in anodic half-cell reacted with KHCO_3 . The synthesized methanol was separated from its solution by distillation technique, and 2.3 litres were obtained. Potassium Permanganate (KMnO_4) was used to perform qualitative test on the synthesized methanol. Fourier Transform Infrared Spectrophotometer (FTIR) test was used to validate the results by comparing the percentage transformation of the synthesized methanol to existing methanol from chemical suppliers.

Key Words: Carbon (IV) Oxide (CO_2), Water, Potassium Hydroxide (KOH), Methanol Fuel, Proton Exchange Membrane (PEM), Cu & Zn.

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NOMENCLATURE

Symbol & Nomenclature	Description
CH_4	Methane
CH_3OH	Methanol
Cu	Copper
CO_2	Carbon (IV) Oxide
GHSV	Gas Hourly Space Velocity
H^+	Proton
KHCO_3	Potassium Hydrogen Trioxocarbonate (IV) Oxide
KMnO_4	Potassium Permanganate
KOH	Potassium Hydroxide
O_2	Oxygen
PEM	Proton Exchange Membrane
PTDF	Petroleum Technology Development Fund
SDGs	Sustainable Development Goals
SDS	Sodium Dodecyl Sulphate
SLS	Sodium Lauryl Sulphate
H_2O	Water
Zn	Zinc
* Corresponding author. e-mail: ojon.nwovu@aceuniport.org	

I. Introduction

Methanol fuel is among the renewable energy and unconventional fuels presented by researchers and automobile manufacturers as replacement to gasoline in line with Sustainable Development Goals (SDGs). Due to its combustion characteristics, it is one of the most widely suggested alternative fuel (Atul and Atsushi, 2014; Olah 2005; Olah et al. 2008a; Olah et al. 2008b and Goepfert et al. 2018). Accordingly, Olah and co-workers, promoted methanol economy as an excellent replacement to petroleum-based fuels and chemicals. The authors presented methanol and its derivatives as pathway to sustainable development. Methanol fuel has advantages such as high octane rating and cleaner-burning properties than gasoline. It also has some disadvantages. For instance, a coal-based methanol economy could increase amongst others the water shortages, net carbon dioxide emissions, and volatility to regional and global coal prices. Meanwhile, alcohol fuels with carbon atom of C2 to C4 other than methanol as reported (Vafamehr et al. 2016; Moxey et al. 2014; Stansfield et al., 2012; Nwovu et al. 2018; Kar et al. 2008) are also good alternatives to gasoline. Other suggested alternative to gasoline vehicle is electric vehicles. Yet, in electric vehicles, high-cost price and lack of suitable battery remain serious challenges. Meanwhile, the development of Lithium-ion and Lithium-Polymer battery that have two-to-three energy density of lead/acid batteries as reported by (Stone 1999) is an improvement in the battery technology.

To widely adopt the use of methanol as alternative fuel to petroleum (fossil fuels) and its production to a commercial quantity remain serious setback. To overcome the challenge, many researchers proposed different and promising methanol preparation techniques. Amongst the promising modern technologies are the capturing, recycling, and transformation of CO₂ to methanol and its by-products (example, Dimethyl ether, Alkanes, Alkenes, Dimethyl carbonate, and Olefin). This was reported by (Sorenson, 2001; Atul and Atsushi, 2014). Though, naturally, CO₂ can be transformed to other useful carboxylic products, but such process cannot reduce its emission target to minimal level considering the geometrical growth of global industrialization. However, in 1950s, Grubb introduced the concept of Proton Exchange Membrane (PEM) also called Polymer Electrolytic Membrane. This was not fully given the needed attention by researchers until 20th and 21st Century. Other interesting promising techniques is the heterogeneous catalytic hydrogenation of CO₂ to methanol. Research proved that H₂ required for the hydrogenation process is obtainable by photo-catalytic or electro-catalytic of water (Navarro et al. 2009; Walter et al. 2010). In 2012, Choudhury proposed direct oxidative conversion of natural gas (mainly methane) and reductive hydrogenation conversion of carbon dioxide as two stimulating methods of methanol synthesis. The author also worried about appropriate method that will be employed to synthesize methanol from fossil-fuels by means of syngas chemistry to ensure improved and economic direct oxidative transformation technology. Other concern raised by Choudhury is the additional increase in the atmospheric CO₂ concentration from burning of methanol that is a foremost universal problem.

The use of high-pressure with reduced temperature catalytic techniques as report by (Lee 2007; and Bansode and Urakawa, 2014.) was also a techniques of interest. But the technique negates the economic value associated with a reaction operated at a reduced pressure. The reason is because of higher energy ($\Delta G^\circ = 3.30\text{KJmol}^{-1}$) involved during the high-pressure reaction (Bahruji et al. 2016; Jadhav et al. 2014; and Fujitani et al. 1997). As an improvement to the high-pressure, (Razali et al. 2012) reported that with a high-performance catalyst, the activation energy of CO₂ can be reduced. Nevertheless, the recent report on hydrogenation of CO₂ to methanol by (Tidona, 2013) showed the electrolysis of water as a major stage of high energy demand while the remaining stages are virtually pressure independent. But it is crucial to note that high-pressure and low-temperature techniques are thermodynamically useful in an equilibrium reaction that requires high product yield. Also, for compressive reactants like H₂ and CO₂, high-pressure facilitates reduction in the reactor volume thereby reducing the plant area. Consequently, there will be reduction in capital costs, possibly improved handling of risky chemicals such as hydrogen, and boost in catalytic activity (Atul and Atsushi, 2014).

However, the concept of high-pressure methanol production is not new. In 1923, BASF commercialized the first methanol production using a mixture of syngas at pressure of 250 to 350 bar. Ipatieff and Monroe (1945) carried out CO₂ hydrogenation at high-pressure up to 412 bar using Cu/Al₂O₃ catalysts in a fixed bed reactor. They obtained remarkable selectivity of methanol and high conversion of CO₂. Though, their study yielded an excellent result, but the Gas Hourly Space Velocity (GHSV) that indicates the productivity of a reaction was low (about 1000h⁻¹), thereby requires an improvement. Atul and Atsushi (2014) reported high-pressure up to 360 bar CO₂ hydrogenation to methanol using co-precipitated Cu/ZnO/Al₂O₃ catalysts at high GHSV of 182,000h⁻¹. The authors improved on the catalyst compared to earlier reporters and recorded the first ever outstanding one-pass CO₂ conversion (>95%). Furthermore, they developed a mixed bed that comprised Cu/ZnO/Al₂O₃ and H-ZSM-5 catalysts to achieve a one-step conversion of CO₂ to Dimethyl Ether (DME) with remarkable selectivity (89%). As alternative to high-pressure hydrogenation of CO₂ to methanol, some researchers experimented on low-pressure and temperature techniques. Wang et al. (2013) developed and operated successfully lower reaction pressure of about 50 to 100 bar at comparably lower temperatures in the presence of Cu/Zn-based catalysts. At a pressure of 15 bar and temperature of 250°C, Deerattrakul et al. (2016) achieved methanol productivity of 591mg_{meOH}⁻¹g_{cat}⁻¹h⁻¹ using Nitrogen-doped (N-doped) reduced graphene oxide

(N-rGO) in Cu-Zn catalysts. This is an improvement to the work of Atul and Atsushi, 2014. Subsequently, in 2017, Abdelaziz and co-workers developed an optimum process technology that resulted in methanol production of 0.625 t-per-tonne of CO₂ waste gas supply. The idea led to an annual production of 222,507 tons methanol with a profit of 56.55 M\$/y. Andika, et al., (2018) made a comparison of methanol production from H₂-CO (from co-electrolysis) and H₂-CO₂ mixtures (from electrolysis). In their findings, they projected that methanol production pathways from co-electrolysis and electrolysis if given favourable attention can lead to methanol production in a commercial quantity.

Presently, it is on record that China is in the frontrunner towards actualization of methanol economy (Chi-Jen and Robert, 2011). This is because from 2006 to 2011, China built an industry of coal-based methanol and dimethyl ether (DME) that is competitive in price with petroleum-based fuels (Chi-Jen and Robert, 2011). Interestingly, (Li-Wang et al., 2013) reported that, in China most of the methanol is primarily consumed in the synthesis of formaldehyde, alternative fuels and acetic acid, with the equivalent percentages of 35.0%, 33.0% and 8.0%. Similarly, in 2011, out of about 22.27 million tons of methanol generated on site, 63.7%, 23.0% and 11.3% were produced by coal, natural gas and coke-oven gas respectively. In terms of transportation, (Li-Wang et al., 2013) reported that China transported approximately 82.6% of methanol by overland freight, 9.0% by sea and 8.4% by train. Further interesting trends in methanol fuel production and utilization is reported by Gong, et al., (2018); Iaquaniello, et al., (2017); Liu, et al., (2017); Liu, et al., (2019); Śliwińska, et al., (2017); Luu et al., (2015); Milani, et al., (2015); Szima and Cormos, (2018); Toyir, et al., (2009); Yang, et al., (2012); and Yao, et al., (2018).

Therefore, this study optimized the use of PEM material technology to synthesis methanol fuel by simultaneous electrolysis of water and reduction of carbonated alkaline solution.

II. Materials and Method

2.1 Materials

The materials used during the study are described below.

Code A Distilled water

Function – Distilled water was used to generate proton (H⁺) at the anodic half-cell during electrolysis.

Code B – Carbonated Potassium Hydroxide (KOH) Solution (i.e., Potassium Hydrogen Trioxocarbonate (IV) – KHCO₃) produced by the reaction of CO₂ and KOH.

Function – Carbonated Potassium Hydroxide (KOH) Solution was used to synthesize the methanol at the cathodic half-cell when reacted with the H⁺ from the anodic half-cell.

Code C Proton Exchange Membrane (PEM) Materials.

Function – PEM promoted transport of H⁺ from anodic half-cell to cathodic half-cell. The PEM consists of the following materials:

I. Paraffin Wax.

Functions:

- i. Repelled flow of water from anodic half-cell to the cathodic half-cell and vice-versa.
- ii. Acted as a good binder.
- iii. Attracted/captured the produced proton from water as a result of hydrogen bond interaction.
- iv. Facilitated the transport of H⁺ from anodic half-cell to cathodic half-cell through “domino effect”.

II. Silica Gel (SiO₂).

Functions:

- i. Worked together with paraffin wax to improve H⁺ transport.
- ii. Provided pathway for proton transport. This is because, during the electrochemical reactions, the lone pair electron of Oxygen atom in the covalently bonded molecules of silica gel tends to attract a proton from the anodic half-cell. To attain suitability, it releases the attraction proton to the cathodic half-cell on continuous basis till the reaction is completed.

III. Sodium Dodecyl/Lauryl Sulphate (SDS/SLS) (Surfactant) – CH₃(CH₂)₁₀CH₂(OCH₂CH₂)_nOSO₃Na.

Functions:

- i. Served as an electron conductor through the membrane. This is because of the release of Na⁺ from its molecule during the electrochemical reactions.
- ii. Improved the conductivity of the membrane since paraffin wax and silica gel are not conductors.

Code D Acidified Potassium Permanganate (KMnO₄).

Function – Acidified potassium permanganate was used to carryout qualitative and confirmatory test for presence of methanol.

Code E Polypropylene Container

Function – Acted as a lid to the component parts and also houses the solid electrolyte pile (i.e., proton exchange membrane).

Code F Cell

Function – The material cell was adopted to hold the carbonated KOH solution (i.e., KHCO_3) and water which served as the electrolytes.

Code G Zinc electrode (positive/anode electrode)

Function – The electrode in which water was electrolyzed to generate hydrogen ion (H^+)/proton in the anodic half-cell.

Code H Copper electrode (negative/cathode electrode)

Function – The electrode in which carbonated KOH solution (i.e., KHCO_3) reacted with H^+ from the zinc electrode to produce methanol.

III. Experimental Procedures

3.1 First Step: Preparation of the Proton Exchange Membrane (PEM)

- i. 30g of paraffin wax was weighed into a beaker and heated until it melted.
- ii. 15g of silica gel was weighed into another beaker.
- iii. 5g of SLS/SDS was added into “ii” above and mix properly to obtain a homogenous mixture.
- iv. The mixture in “iii” above was poured into the molten paraffin wax and stirred for 5minutes to ensure proper mixture.
- v. The mixture in “iv” above was poured into a mould and allowed to cool/solidify for 30minutes.
- vi. The mould was removed to obtain the formed PEM. See the Figure 1 below.



Figure 1: PEM made of paraffin wax/SLS/silica gel

3.2 Second Step – The cells were arranged as shown in Figure 2 below.



Figure 2: View of the half-cell compartments with Zinc and Copper electrodes

3.3 Third Step – The complete set up was packaged as shown in the Figure 3 below.

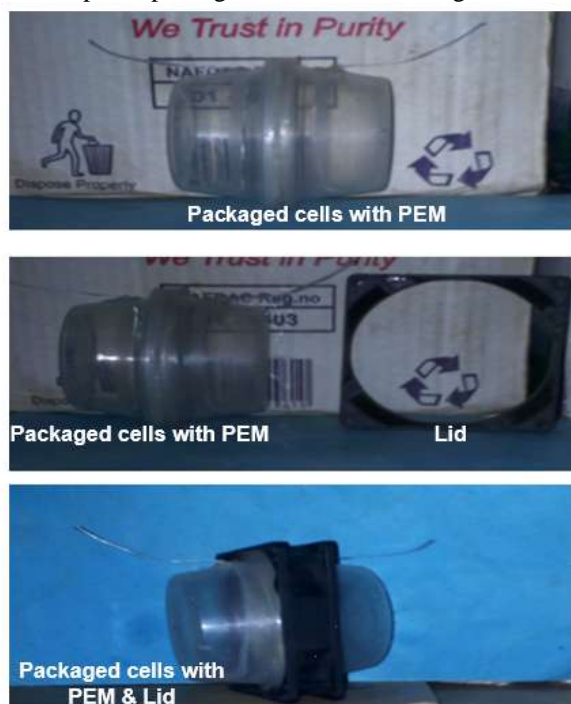


Figure 3: Packaging of the electrochemical set-up

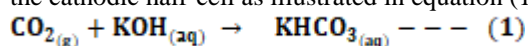
3.4 Fourth Step – The Electrochemical Test was carried out as shown in Figure 4 below



Figure 4: Electrochemical set up

3.5 The Reaction Processes

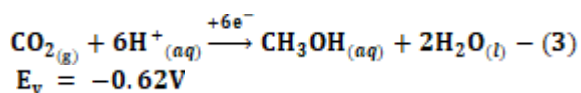
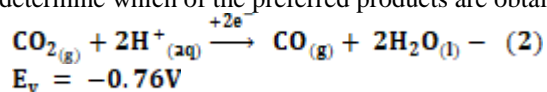
In the electrochemical set up, the CO₂ was fed into the electrochemical cell as a carbonated alkaline solution in the cathodic half-cell as illustrated in equation (1) below.

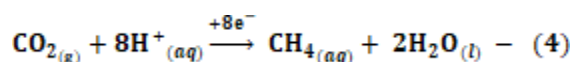


(Carbonated alkaline solution)

Scheme 1: Solvation of CO₂ in an Alkaline Solution

The carbonated alkaline solution which is represented as KHCO₃ for the purpose of simplification can be selectively reduced into any of the product shown in the scheme below (i.e., equations 2, 3 & 4) as reported by (Kuhl et al. 2014 and Olah et al. 2009). The availability of protons and electrons that act as limiting factors determine which of the preferred products are obtained.

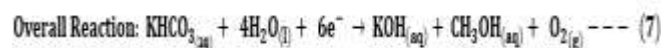
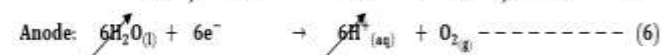




$$E_v = -0.48\text{V}$$

Scheme 2: Overall electrochemical equations for the reduction of carbonated alkaline solution into methanol.

From the electrochemical point of view, the overall reaction for the conversion of the carbonated alkaline solution into methanol is presented in the equations 5, 6 and 7 below:



As demonstrated in scheme 1, the efficiency of this process is grossly dependent on the transfer of protons from one half-cell to another. The proton transfer was achieved using the Proton Exchange Membrane (PEM).

3.6 Schematic of the Experimental Set-Up

Figure A in the Appendix shows the schematic of the experimental set-up.

IV. Experimental Observations and Results

The experiment was allowed to run for 1 hour and the following trends were observed:

- i. For the first 10 to 15 minutes, there was an observable concentration of a yellowish spot within the cathodic half-cell electrolyte.
- ii. After 30 minutes, the yellowish spot disappeared thereby leaving the electrolyte solution in its initial colourless state.
- iii. After 1 hour, we disconnected the power source and poured some sample of the electrolytic solution from the cathodic half-cell into a beaker shown in Figure 5 below for a qualitative test to confirm the presence of methanol.



Figure 5: Sample of KHCO₃ solution after the electrochemical reaction

- iv. Acidified KMnO₄ was added in drops and then in excess to the collected sample of KHCO₃ solution and the colour changes were observed for 4 minutes. At different time intervals, different colour changes were recorded till the sample solution became completely “yellowish” which confirmed the presence of “methanol fuel”. Presented in Figures 6(a to f) are various stages of the colour changes.



Figure 6a: Acidified KMnO₄ solution



Figure 6b: Sample solution of KHCO₃ without addition of acidified KMnO₄ solution



Figure 6c: Sample solution of KHCO_3 when acidified KMnO_4 solution was added.



Figure 6d: Colour change after 1 minute



Figure 6e: Colour change after 2minutes



Figure 6f: Colour change after 4minutes

4.1 Quantitative Comparison of the Synthesized Methanol and Analytical Methanol purchased from Chemical Suppliers.

For more confirmatory test on the synthesized methanol, quantitative test was carried out using Fourier Transform Infrared Spectrophotometer (FTIR). At this stage, the percentage transformation of the synthetic methanol was compared to that of analytical methanol and the results demonstrated equivalent characteristics (see Table 1 below and the graphical representations in Figures 7, 8 and 9).

Table 1: Comparison of Synthetic and Analytic Methanol using FTIR

1/X (1/cm)	% Transform (%T)	
	Synthetic Methanol	Analytical Methanol
1149.612	94.66730831	94.60954862
1249.914	96.02039085	94.30284523
1350.216	91.091953	92.84191431
1450.518	92.48699577	93.34207285
1550.82	98.19361738	93.45452069
1651.121	93.25210838	84.83426685
1751.423	99.06593892	95.15736277
1851.725	100.4076045	100.5299036

1952.027	100.8583288	100.2600021
2052.328	100.06423	98.35921323
2152.63	99.70142008	97.09995
2252.932	100.094501	98.11808877
2353.234	100.4276505	98.67437023
2453.535	100.1006739	100.0601135
2549.979	98.90376275	100.0439407
2646.423	97.68594092	99.670833
2746.725	94.29677123	96.81644092
2847.027	87.90094662	90.42060008
2947.329	82.40153915	83.50185262
3047.63	86.86646023	81.723685
3147.932	79.57331962	71.78944146
3248.234	71.39098446	62.93321323
3348.536	68.72072508	61.08308692
3448.837	70.90820169	64.88092831
3549.139	78.30310723	73.78023254
3649.441	85.21394454	83.42226462
3749.743	90.92839154	90.39270338
3850.044	91.723837	91.041507
3950.346	91.43076454	90.97683438
4004.355	91.766507	91.580963

FTIR ANALYSIS RESULT

NATIONAL RESEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA



FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

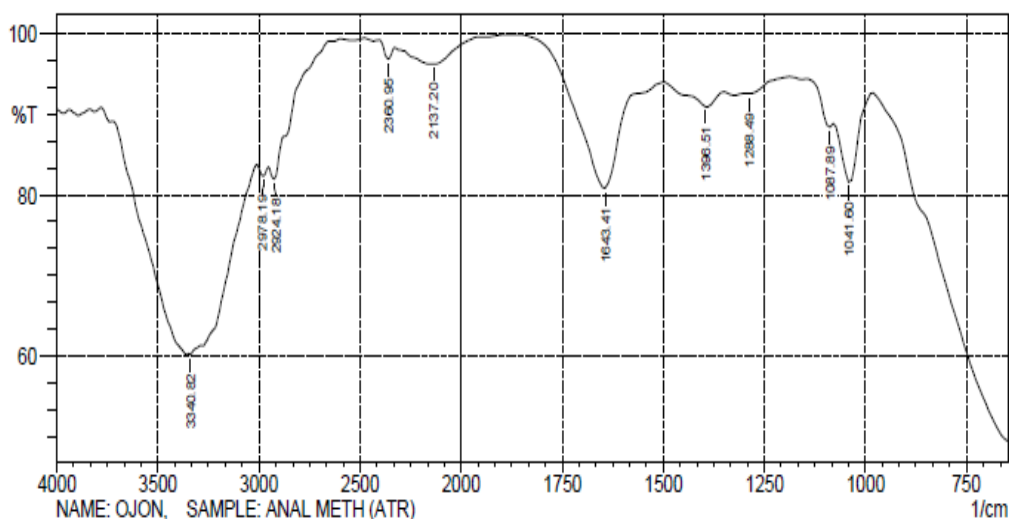


Figure 7: FTIR Test Result for Analytical Methanol

FTIR ANALYSIS RESULT

NATIONAL RESEARCH INSTITUTE FOR CHEMICAL TECHNOLOGY, ZARIA

SHIMADZU
FTIR-8400S FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER

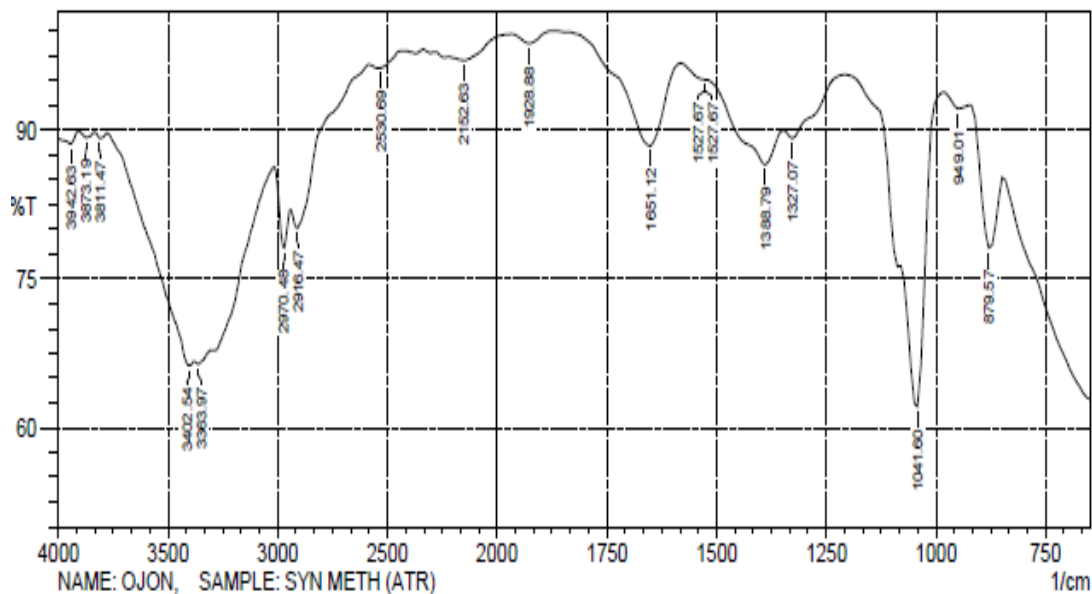


Figure 8: FTIR Test Result for Synthetic Methanol

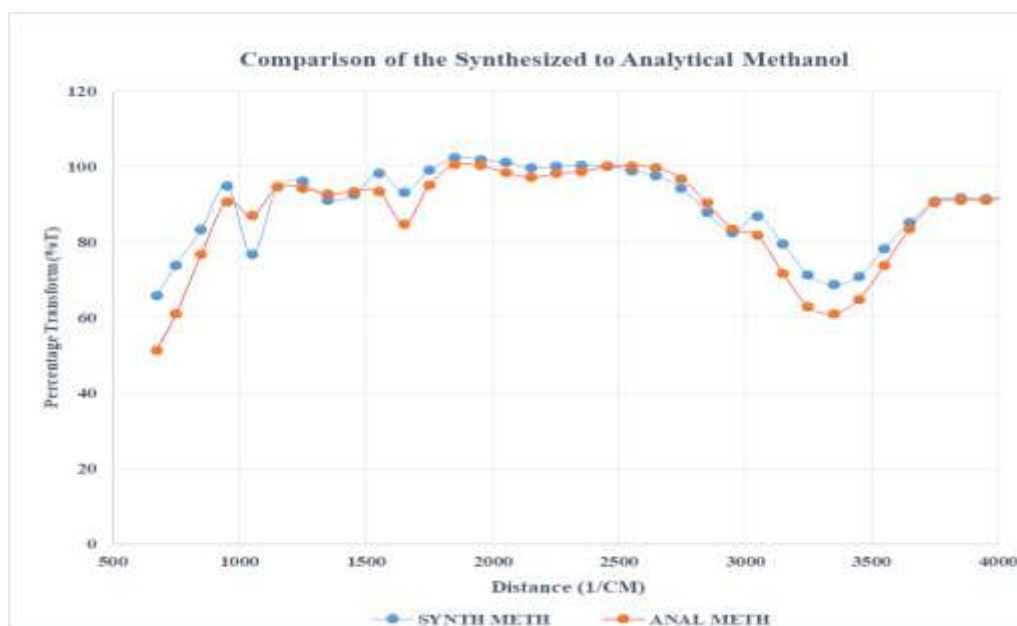


Figure 9: Comparison of the Synthesized to Analytical Methanol

V. Conclusion

From the observations and results, the conclusion drawn are as follows:

- I. Methanol can be synthesized from carbonated alkaline solution and water using electrochemical reaction with the help of appropriate Proton Exchange Membrane (PEM).
- II. PEM made up of combination of paraffin wax, silica gel and sodium lauryl/dodecyl sulphate (SDS) provides suitable pathway for proton and electron transport in an electrochemical process of methanol synthesis. Hence, this study discovered that paraffin wax, silica gel and sodium lauryl/dodecyl sulphate (SDS) are optimum materials for PEM preparation.
- III. Water is a good feedstock for proton synthesis using electrochemical techniques.

- IV. Potassium permanganate (KMnO₄) solution is a good reagent for a qualitative/confirmatory test for the presence of methanol in a given solution.
- V. Copper and zinc electrodes serve as good catalyst for reductive hydrogenation of carbonated alkaline solution in an electrochemical reaction to synthesize methanol fuel.

VI. Recommendation

From the observations in the tabular and graphical comparisons of the synthetic and analytical methanol (i.e., Table 1.0 and Figures 7.0, 8.0 & 9.0), it is recommended that further studies should aim at improving the capacity and effectiveness of the proton exchange membrane to achieve methanol production in commercial quantity.

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APPENDIX

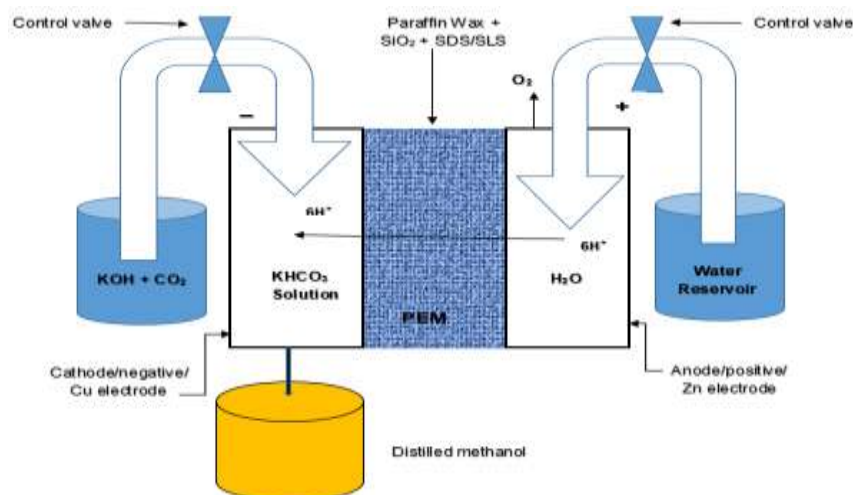


Figure 10: Schematic of the experimental set-up

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