



INVESTIGATION AND APPLICATION OF METHANOL FUEL PRODUCED BY CATALYTIC REDUCTION OF CARBONATED ALKALINE SOLUTION OF POTASSIUM HYDROXIDE AND ELECTROLYSIS OF WATER: PART II:

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ABSTRACT

This study investigates the confirmatory tests and exhaust emissions of methanol fuel produced from carbonated alkaline solution of potassium hydroxide (KOH) and water in an electrochemical process. Cu and Zn electrodes were used to catalyze the electrochemical processes in the cathodic and anodic half-cells respectively. Methanol production involved simultaneous electrolysis of water within the anodic half-cell and catalytic reduction of KHCO_3 within cathodic half-cell. We separated the anodic and cathodic half-cells using a Proton Exchange Membrane (PEM) prepared by mixture of Paraffin Wax, Silica Gel, and Sodium Dodecyl/Lauryl Sulphate. The PEM materials facilitated a unidirectional transportation of protons and electrons produced in anodic to cathodic half-cell of the electrochemical set-up. We used KMnO_4 , FTIR and GC-MS to carry out the confirmatory tests on the synthesized methanol. The emissions test involved the use of methanol-gasoline blend with 5 percent of methanol mixed with 95 percent of gasoline represented as G95, while G100 represents neat gasoline. The experimental engine was naturally aspirated, single cylinder, 4-stroke with port-fueled injector. We operated the engine under constant engine speed of 3000 rpm and varying loads of 1000, 2000, 3000, 4000 and 5000 (kg). The emissions test results showed that, addition of methanol in the gasoline fuel decreased the CO emissions under low-to-moderate loads, but increased under high-load operations

compared to G100. Conversely, the CO₂ emissions increased with increasing engine loads with slight decrease under high-load operations. However, the uHC and oil temperatures of the methanol blended fuel were higher than those of G100 at all the engine operation loads.

KEY WORDS: *Carbon (IV) Oxide (CO₂); Water; Methanol; Proton Exchange Membrane (PEM); SI Engine; and Exhaust Emissions.*

Introduction

The search for alternative energy source to gasoline led the Federal Government of Nigeria to consider the exploitation of methanol fuel technology in transportation, electricity generation and expansion of its chemical industries. In pursuing the innovation, the Honourable Minister of Science and Technology, Dr. Ogbonnaya Onu inaugurated a Technical Committee on Methanol Fuel Technology Implementation Programme in Nigeria. The adoption of methanol fuel technology in Africa would rejuvenate the weak industrial base of the region. This is because, methanol fuel is extensively used in most parts of the developing and developed nations. Therefore, there is need for Africa especially, Nigeria to join the trajectory due to its abundant natural gas resources that are being flared wastefully. Since methanol fuel is relatively cheaper and environmental friendly than gasoline, its adoption as one of the energy sources will eventually reduce the cost of fuel in the Continent. The methanol technology is in line with international resolutions, which primarily includes the Paris Agreement for nations to take step that will significantly reduce carbon emission and pollution. In Nigeria, most of the natural gases being flared during crude oil exploration constitute health risks that negatively affect the social life of the people especially, those living close to the site. The flared gases if harvested can be converted into methanol for transportation and other industrial uses.

The benefits of methanol fuel is innumerable. Example, it is used as an alternative to conventional transportation fuels in most countries of the world; it has high octane rating and cleaner-burning properties than gasoline (Nwovu *et al.*, 2018); it is relatively cheaper to produce than other alternative fuels; lower risk of flammability compared to gasoline; and can be manufactured from a variety of carbon-based feedstock like natural gas and coal. Nevertheless, it

also has disadvantages such that a coal-based methanol economy could increase among others the water shortages, net carbon dioxide emissions, and volatility to regional and global coal prices. Moreover, methanol is toxic in nature (De Schweinitz, 1901). The publication by the chemical company Global Bonds in Chemistry reported that in humans, methanol has high toxicity such that a little quantity of about 10 mL if drunk can destroy the optic nerve. The resultant effect on the human is permanent blindness. Though, the effects of methanol toxicity can take hours before the patient begins to feel the symptoms, the use of effective antidotes if administered to the patient can easily prevent permanent damage.

In terms of characteristics, Methanol is a colorless, volatile, flammable, poisonous and polar liquid at room temperature with the formula CH_3OH (also abbreviated as MeOH). It can also be called methyl alcohol, wood alcohol/spirit and carbinol. As published by National Center for Biotechnology Information; Khirsariya and Mewada, (2013) and Cappelletti *et al.*, (2012), pure methanol was first separated by Robert Boyle in 1661. Mr. Robert Boyle produced the chemical (i.e., Methanol) through the distillation of boxwood. The chemical was then called pyroxylic spirit. Thereafter, French Chemists, Jean-Baptiste Dumas and Eugene Peligot determined its elemental composition in 1834. It is the simplest in the series of alkanol/hydroxyl group of organic compounds known as alcohols. The hydroxyl group (OH) is attached to a methyl group (CH_3). The term methyl came from the word methylene as conceived by Dumas and Peligot in 1840 (Rossi, 1890 and Wisniak, 2009). It was then applied to describe methyl alcohol. The International Conference on Chemical Nomenclature shortened this to methanol in 1892. Thereafter, the German Chemists, Alwin Mittasch and Mathias Pier developed a means to convert synthesis gas into methanol which was patented on January 12, 1926 (Alwin & Mathias, 1926).

However, the primordial Egyptians obtained methanol from pyrolysis of wood. Pyrolysis is a thermal treatment which results in the production of char, liquid and gaseous products (Maschio *et al.*, 1992). They mixed methanol in the substances which they used in embalming process. In the early 1970s, Mobil developed a methanol to gasoline process for producing vehicle ready gasoline with one of the facilities built in New Zealand at Motunui in the 1980s (Available at: <https://thechemco.com/chemical/methanol/>). Astronomers at

Jodrell Bank Observatory used Merlin array of radio telescopes to discover a large-scale of methanol in space, 300 billion miles across (Harvey-Smith and Cohen, 2006).

Due to methanol's combustion characteristics, it is one of the most widely suggested alternative fuels (Bansode and Urakawa, 2014; Olah, 2005; Olah *et al.*, 2008a; Olah *et al.*, 2008b, Goeppert *et al.*, 2018; Sampson *et al.*, 2019a and Sampson *et al.*, 2019b). For instance, methanol produced from wood or other organic materials (bioalcohol) has been recommended as renewable alternative to petroleum-based hydrocarbons. In some countries (e.g., Europe and China), the use of methanol in existing vehicles involves blending it with proper cosolvents and corrosion inhibitors. Consequently, the European Fuel Quality Directive (EFQD) permits up to 3 percent methanol with an equal amount of cosolvent to be blended in gasoline sold in Europe (<https://thechemco.com/chemical/methanol/>). Whereas in China, they use more than one billion gallons of methanol per year as transportation fuel in existing vehicles and vehicles designed to accommodate the use of methanol fuels. Aside from methanol, ethanol, propanol and butanol are also proposed good replacements to gasoline (Vafamehr *et al.*, 2016; Moxey *et al.*, 2014; Stansfield *et al.*, 2012; Nwovu *et al.*, 2018; and Kar *et al.*, 2008).

The global adoption of methanol as replacement to gasoline and its production to sustainable and commercial quantity are serious challenges facing automobile manufacturers and researchers. To address the challenges, present day researchers adopted diverse and promising methanol preparation techniques. Amongst the technologies are capturing, recycling, and transformation of CO₂ to methanol and its by-products (Sorenson, 2001; Bansode and Urakawa, 2014). In 1950s, Grubb introduced Proton Exchange Membrane (PEM) also called Polymer Electrolytic Membrane whereby the generation of proton (H⁺) and reduction of CO₂ to methanol occur simultaneously in an electrochemical setups (Sampson *et al.*, 2019a and Sampson *et al.*, 2019b). Others are the heterogeneous catalytic hydrogenation of CO₂ to methanol (Navarro *et al.*, 2009; Walter *et al.*, 2010); direct oxidative conversion of natural gas (mainly methane) and reductive hydrogenation conversion of carbon dioxide (Choudhury, 2012); use of high-pressure with reduced temperature catalytic techniques (Ipatieff and Monroe, 1945; Lee, 2007; Razali *et al.*, 2012; Tidona, 2013; Bansode and Urakawa, 2014); low-

pressure and temperature catalytic-based techniques (Sheldon, 2017; Wang *et al.*, 2013; Deerattrakul *et al.*, 2016); Proton Exchange Membrane also called Polymer Electrolytic (PEM) and electrolysis techniques (Andika *et al.*, 2018; Sampson *et al.*, 2019a and Sampson *et al.*, 2019b).

Alcohol fuels additives to gasoline as improvement to combustion characteristics of a an internal combustion engine

The use of alcohol fuels in internal combustion engines started since the onset of mechanically driven automotive transportation (Moxey *et al.*, 2014). Most of the alcohols available in the current SI engines are gasoline-ethanol blends, with 5 to 10% volume alcohol typically allowed. Researches show that alcohol fuel has higher potential to increase engine performance, and ultimately improve knock resistance over gasoline due to its rapid rise in charge temperature during combustion events (Vafamehr *et al.*, 2016 and Nwovu *et al.*, 2018). Other benefits accrued to alcohol fuels are the high latent heat of vaporization and lower unburned gas temperatures which help to cool the charge temperature during combustion compared to gasoline fuels. In terms of injector deposit formation, (Cairns *et al.*, 2009) reported that alcohol blends have a reduced injector deposit formation at an increased compression ratio due to lower nozzle temperatures and single component nature of the fuel.

Nevertheless, in terms of wear and corrosion in fuel pumps for gasoline-alcohol engines, wears due to abrasion may occur with corrosion damage when using higher content of alcohol fuel. Therefore, in the design of modern SI engines that can operate on alcohol fuels, there is need to consider the power cell materials selection, compression ratio and thermodynamic properties. This will validate the prediction by (Turner *et al.*, 2013) that engine output may be raised by 10 to 15% with potential additional gains for dedicated alcohol operation in the future. In both the EU and US, flex-fuel operation via ethanol has gained significant attention in recent years (Moxey *et al.*, 2014). Moreover, Brazil with no oil reserves but plentiful sources of vegetation is already operating an alcohol-fueled policy. Worthy of note is that alcohol fuels suffer cold starting problems due to higher latent heat of vaporization associated with alcohols that causes induction to occur with a partly-liquidized fuel/air mixture. Therefore, alcohol fuels have potential to improve energy security, environmental

concerns, foreign exchange savings, socio-economic issues related to the rural sector, and reduction of greenhouse gases pollution.

Materials and methods

Materials used in methanol production

We used sodium dodecyl sulphate ($\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$) (98.4 % usp cosmetic grade power in a bottle), white silica gel desiccant beads (industrial standard 2-4 mm, dry 5 lbs premium pure & safe), paraffin wax (food grade, 3 lbs/1.36 kg), distilled water bottle pack (Aquapap CPAP water 8 x 12 ounce), sulfuric acid (0.02 N, 0.01M, 500 mL volume, LabChem LC256601), Ajax scientific copper electrode strip (129 mm length x 25 mm width), Ajax scientific zinc electrode strip (100 mm length x 19 mm width), potassium hydroxide (pellets, reagent, A.C.S, 100 g), CO_2 gas in a bottle (>99.9993 %) purchased from a chemical supplier, and carbonated potassium hydroxide solution (KHCO_3) produced by reaction of CO_2 in one molar solution of potassium hydroxide (KOH).

Materials used in emission tests on methanol-gasoline blend with pure gasoline

TD115 MK II 4-Stroke spark ignition engine, TD115 hydraulic dynamometer, TD114 instrumentation unit, stopwatch (for time measurement), thermometer (for temperature measurement), barometer (for pressure measurement), and infralyt exhaust gas analyzer.

Experimental Methods

We adopted two approaches in the experimental methods. The first approach was production of methanol, while the second was emission tests in SI engine using the produced methanol-gasoline blend and pure gasoline fuels under constant engine speed and varying loads.

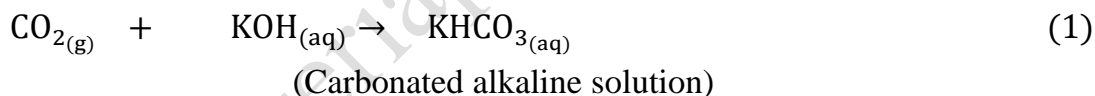
Methanol Synthesis

Before the electrochemical reduction of carbonated Potassium Hydroxide solution (KHCO_3) to methanol, we developed a PEM using mixture of 30 gramme of molten paraffin wax, 15 gramme of silica gel and 5 gramme of SLS/SDS. Presented in Fig. 1. is a sample of the produced PEM after cooling for 30 minutes, while Fig. 2. presents the electrochemical set-up. During the

electrochemical test, the proton (H^+) generated from water within the anodic half-cell moved in a unidirectional mode to the cathodic half-cell through the PEM with the help of electrochemical interactions between the proton and PEM's materials. Within the PEM, paraffin wax prevented flow of water from anodic half-cell to the cathodic half-cell and vice-versa. With the help of control valves, we controlled the amount of water introduced into the anodic half-cell and carbonated potassium hydroxide solution in the cathodic half-cell. We stepped down the voltage supplied to the system using a 5 volt adapter with maximum allowable current of 100 mA. The experimental set-up was such that we connected copper electrode to cathode (negative) terminal and zinc electrode to the anode (positive) terminal of power supply. From the cathodic half-cell, we collected the synthesized methanol in its solution form before separation by fractional distillation to get pure sample. Presented in Fig. 3 is the schematic of the experimental set-up during the methanol fuel production.

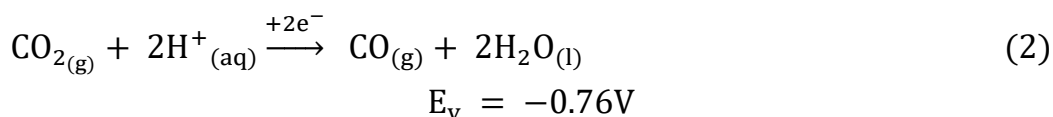
The electrochemical reactions during the methanol fuel synthesis

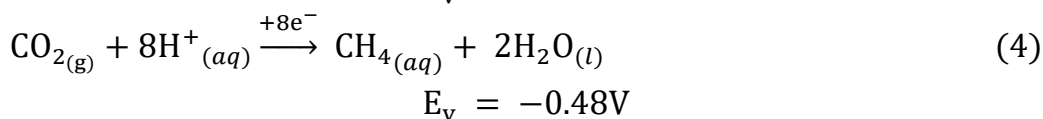
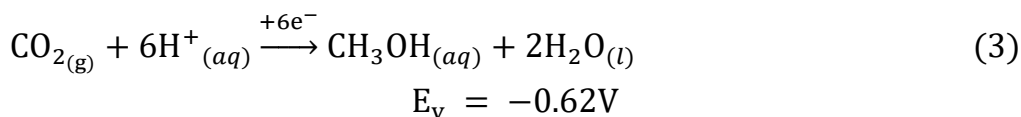
We introduced the CO_2 gas into a beaker that contained 1 molar concentration of potassium hydroxide solution (1.0M KOH) using a delivery tube. The mixture of the CO_2 and KOH produced carbonated alkaline solution ($KHCO_3$) that we fed into cathodic half-cell. Illustrated in equation (1) below is the chemical reaction of the CO_2 gas and the KOH.



Scheme 1 – Solvation of CO_2 in an Alkaline Solution

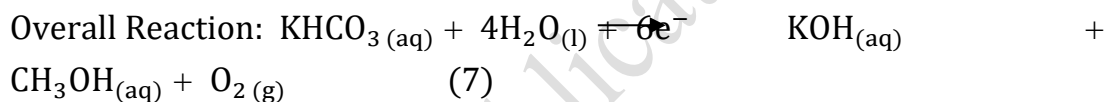
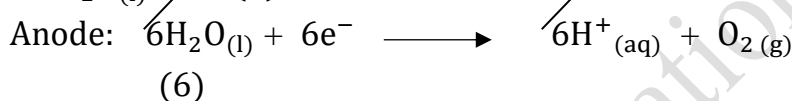
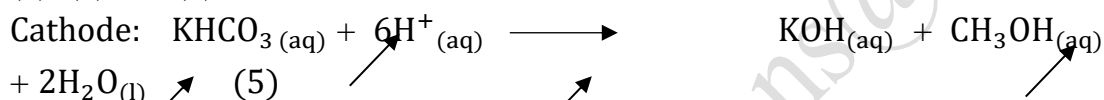
At the cathodic half-cell, the carbonated alkaline solution represented as $KHCO_3$ for the purpose of simplification can selectively reduce to any of the product shown in equations (2), (3) and (4) below (Olah *et al.*, 2008b and Kuhl *et al.*, 2014). The availability of protons and electrons that act as limiting factors determine the preferred products obtained at the end of each reaction. The protons and electrons are from the anodic half-cell during the electrolysis of water.





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 anodic half-cell to cathodic half-cell. Therefore, we achieved the proton transfer using the PEM.

Test engine set-up and fuel preparation

Before the test, the experimental rig setting was such that the engine and dynamometer were on the same bench. To prevent vibration from the engine and dynamometer to the instrumentation unit, we mounted the instrumentation unit on a separate bench. The position of instrumentation unit was higher than that of the engine and dynamometer to aid gravitational flow of the fuel supplied to the engine. We connected the exhaust system to the engine with the air intake connected to the instrumentation unit airbox using a flexible pipe. The torque transducer, tachometer optical head and exhaust thermocouple connections were to the correct inputs slots on the instrumentation unit. The water supply connection was to the inlet of the needle valve mounted on the engine bed. We pushed a flexible PVC pipe in the drain pipe with the end set to discharge into a collection tank without being submerged as the water flew into the tank.

Thereafter, we filled the damper and engine sump with oil without overfill. To measure the exhaust gas emissions and the oil temperature, we connected the gas analyzer to the engine exhaust. When introducing different fuel from that in the tank, we flushed out the fuel system before filling the new fuel into the tank. We switched on the instrumentation unit to enable us set the zero and span control with the scale on the airflow manometer adjusted until it read zero. We turned on the water supply to the dynamometer with the needle valve adjusted to allow for maximum flow of water. The dynamometer seals were all lubricated. The water flow was then reduced to trickle so that the load on the engine was not too high when starting. To enable access to all controls, we removed all tools, weights and obstructions from around the engine. Presented in Table 1 is the geometry of the engine. To prepare the methanol-gasoline fuel blend, we added 5 percent of methanol to 95 percent of gasoline. We represented the resultant blended mixture as G95, while G100 represents neat gasoline. The properties of the experimental fuels are tabulated in Table 2.

Table 1. Basic Engine Geometry

Engine Parameters	Specification
Number of Cylinders	Single
Bore (mm)	63.5
Stroke (mm)	54.34
Swept Volume (cc)	195
Clearance Height (mm)	9
Geometric Compression Ratio	6:1
Maximum Torque (Nm)	15
Maximum Power (kW)	2.5 – 7.5
Maximum Speed (rpm)	6000

Table 2. Properties of the experimental fuels (Sources: Okoro *et al.*, 2012; Wallner *et al.*, 2013; Fonger *et al.*, 2014; Yusri *et al.*, 2017 and PubChem Database)

Property	Gasoline	Methanol
Chemical Formula	C ₈ H ₁₈	CH ₃ OH
Composition (C, H, O) (Mass %)	84.16, 0	37.5, 12.5, 50

Molecular Weight (g/mol)	114.23	32.40
Density @ atm. Press. and Temp. (Kg/M³)	0.692	796.00
Stoichiometric AFR	15.13	6.40
RON	100.00	133.00
MON	88.00	100.00
Heat of Vaporization (kJ/kg)	308.00	920.70
% Contribution of Oxygen by Weight	0.00	50.00
Volumetric Energy Density (mJ/litre)	30.60	15.60
Boiling Point (°C)	99.30	64.70
Flash Point (°C)	-12.00	11.10
Auto-Ignition Temperature (°C)	396.00	470.00

Starting and test for reliability of the engine

Before starting the engine, we turned on the fuel tank tap to enable fuel reach the carburettor from the fuel tank. To ensure availability of fuel within the inlet runner, we slightly opened the throttle before switching on the ignition. We held the engine base and pulled the starting handle rapidly outwards and repeatedly until the engine started. The engine warm-up took five minutes under half throttle. Thereafter, we returned the choke to the open position as soon as the engine started running smoothly without choke. At this stage, we confirmed the engine reliable for the experiment.

Test procedure

Upon entering the test cell every day, we carried out checks on the fuel lines to confirm that all connections were tight and that no visible perishing or leakages had occurred to the fuel lines. We carried out similar inspection on all other connections within the experimental rig. The dynamometer power supply was activated as was in the Engine Control Unit (ECU) power supply. The exhaust gas analyzer was also powered on using the power button. After the diagnostic system warm-up period, the fuel level was also checked to confirm that there was enough for the day's test. Thereafter, we advanced the throttle control to its peak position bearing in mind the 6000 rpm highest speed of the engine while the dynamometer water flow was still the trickle used for starting the engine. The throttle was kept open while the needle valve was slowly adjusted to

increase the flow of water through the dynamometer until the needle valve was fully opened. We tested six different engine speed range of 2200, 2600, 3000, 3400, 3800 and 4200 (rpm) for both G100 and G95 under constant engine load of 1000 kg. We obtained optimum performance of the engine at 3000 rpm. The throttle was kept open with reduced water flow to trickle so that the engine returned to its maximum speed.

Engine operating parameters' measurements

As soon as the engine settled down to a steady output, we took the readings for the transmitted torque and exhaust temperature from the instrumentation unit. The fuel tap was beneath the pipette to enable the engine take its fuel from the pipette. We obtained the time taken by the engine to burn 8 ml of the fuel using stop watch. The fuel tap was then turned on to fill up the pipette again.



Fig. 1. PEM made of paraffin wax, SLS and silica gel

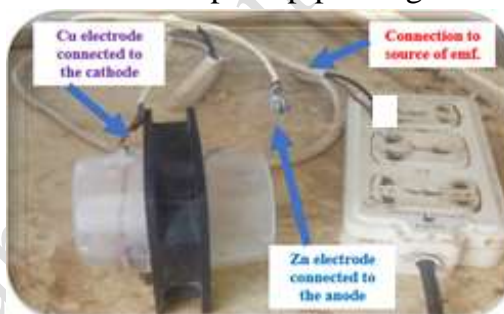


Fig. 2. Electrochemical set-up

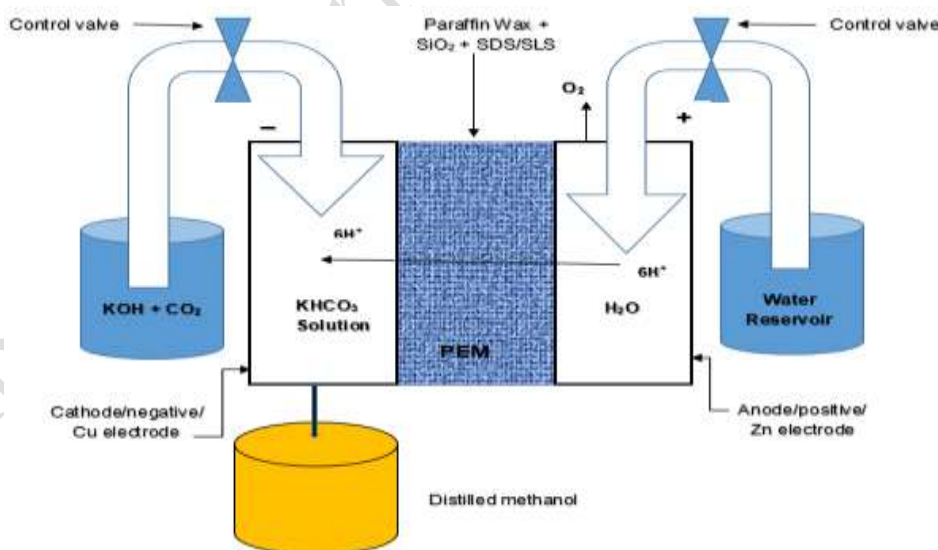


Fig. 3. Schematic of the PEM experimental set-up

Results and Discussions

We allowed the simultaneous electrolysis of water and reduction of carbonated alkaline solution of potassium hydroxide experiment to run for 1 hour. Thereafter, we collected a sample solution of KHCO_3 from the cathodic half-cell in a beaker for qualitative test using KMnO_4 to confirm the presence of methanol. Addition of KMnO_4 in drops and then in excess to the collected sample changed the colourless solution of KHCO_3 to yellowish.

Characterization of the Synthesized Methanol by Comparison with the Analytical Methanol purchased from Chemical Suppliers.

Gas Chromatography – Mass Spectrometry (GC-MS) Test Results

Tentatively Identified Compounds (TIC) in the Library

The calibration of the machine (SHIMADZU GC-MS - QP2010 PLUS) used for the GC-MS test could only analyze and detect organic compounds from butanol (C4) and above. However, from the library results, the Tentatively Identified Compounds (TIC) were butanol and pentanol with highest Similarity Indices (SI) of 97% and 95% respectively to the unknown tested sample. The library results recorded for butanol at retention time of 1.542 minutes and pentanol at retention time of 2.142 minutes are presented in Tables 3 and 4 respectively, while Table 5 presents the peak report of library values of the Tentatively Identified Compounds (TIC). The mass spectra of the TIC with SI of 97, 96 and 95 (%) are shown in Figs. 4, 5 and 6 respectively for butanol, while that of pentanol with SI of 95% is shown in Fig. 7.

From Tables 3 and 4; and Figs. 4, 5, 6 and 7, the high SI of the TIC to the tested sample indicates that if worked backwards using their respective molecular structures, the original structure of methanol can be determined. The reason is that interpretation of GC-MS library results is similar to crime detection by detectives who compares the fingerprint of an unknown crime suspect to a library of known fingerprint.

Fourier Transform Infrared Spectrophotometer (FTIR) Test

During the test, we compared the percentage transmissions of the synthetic methanol to that of analytical methanol and the results were approximately the same as shown Table 6.0. Graphically, we compared the test results in Table 6.0 using Fig. 8. The results in Table 6.0 and Fig. 8 are confirmation that the

synthesized unknown sample belongs to alcohol family. The reason is because of the observable strong intensity/peak and broad band in the spectra between frequency range of 3650 and 3200 cm^{-1} which is the transformation frequency range of hydroxyl group.

Comparison of Engine Emissions Characteristics when Operated on G95 and G100 under Constant Speed of 3000 rpm and varying Loads

Comparison of Oil Temperatures by the G100 and G95 Fuels under Constant Speed and varying Loads

The oil temperature of both G100 and G95 fuels increased as the engine load increased. The results are presented in Table 7 and Fig. 9. However, the oil temperatures of G100 were higher than that of G95 under high-load engine operations. The reason was due to the increased in-cylinder temperature of the engine when operated on G100 compared to G95. But under low-to-moderate load engine operations, the oil temperatures of G95 were higher than those of G100 due to improved combustion of the fuel mixture as a result of presence of oxygen atom in the methanol structure.

Comparison of CO Emissions by the G100 and G95 Fuels under Constant Speed and varying Loads

The CO emissions by G100 increased as the engine load increased until it attained a maximum value of 2.14 percent under a load of 3000 kg as shown in Table 7 and Fig. 10. Under higher-loads of 4000 and 5000 (kg), the CO emissions decreased to 1.38 and 1.26 (%) respectively. The result shows that the combustion events during the engine operation on G100 improved under higher-load than lower-load operations. For G95, the CO emissions decreased continually at all the engine loads due to the presence of oxygen in methanol structure which improved the combustion events compared to that of G100. The increased CO emissions of the G95 under low-to-moderate engine load was as a result of rich fuel-air mixture, but under high-load operation, the mixture became leaner thereby reduced the CO emissions.

Comparison of CO₂ Emissions by the G100 and G95 Fuels under Constant Speed and varying Loads

The CO₂ emissions of G100 increased with the engine loads and attained highest value of 4.0 percent under 4000 kg. Further increase in the load to 5000 kg decreased the CO₂ emissions to 3.52 percent as shown in Table 7 and Fig. 11. The result shows that the optimum load required to achieve best combustion

process by the engine when operated on G100 was 4000 kg. Similarly, the CO₂ emissions of G95 increased with the engine loads and attained a maximum value of 3.82 percent under 3000 kg before it decreased to a least value of 3.61 percent under higher-load operation of 5000 kg. The results show that the optimum load required to achieve best combustion process by the engine when operated on G95 was 3000 kg. Thereafter, further increase in load resulted in incomplete combustion of the fuel mixture within the combustion chamber. The resultant effect of the incomplete combustion was reduction in the CO₂ emissions as observed when the engine loads were 4000 and 5000 (kg). Overall, the CO₂ emissions of G95 were lower under low-load operation than that of G100 but increased under high-load compared to that of G100 due to increased cooling losses associated with G95 under low-load operations.

Comparison of uHC Emissions by the G100 and G95 Fuels under Constant Speed and varying Loads

The uHC emissions of G100 increased with the engine load and attained a maximum value of 292 ppm under 3000 kg as shown in Table 7 and Fig. 12. Further increase in the load to 4000 and 5000 (kg) resulted in decreased uHC emissions to 260 and 242 (ppm) respectively. The increased uHC emissions under low-to-moderate loads could be attributed to engine misfire that led to an incomplete combustion of the fuel mixture within the combustion chamber. For the G95, the engine recorded highest uHC emission of 368 ppm under 1000 kg. The result could be attributed to poor atomization of the fuel. However, under moderate-to-high loads operation, the uHC emissions decreased due to better fuel air mixture that resulted in a more homogenous combustion events. Overall, Table 7 and Fig. 12 show that the uHC emissions of G95 were higher than those of G100 at all the engine operation loads considered because of its leaner fuel-air mixture within the combustion chamber.

Table 3 GC-MS library results recorded for butanol at retention time 1.542 minutes

Library								
<< Target >>								
Line#:		1						
R.Time:		1.542						
Mass Peaks:		13						
Raw Mode:		Single 1.542						
Base Peak:		43.10 (79910)						
Hit No.	Entry	Library	LIB SI	Formula	CAS	Mol Weight	Ret Index	Compound Name

1	444	NIST08s	97	C ₄ H ₁₀ O	78-83-1	74	597	1-Propanol, 2-methyl- Isobutyl alcohol Isobutanol Isopropylcarbinol 2-Methyl-1-propanol iso-C ₄ H ₉ OH Fermentation butyl alcohol.
2	445	NIST08s	96	C ₄ H ₁₀ O	78-83-1	74	597	1-Propanol, 2-methyl- Isobutyl alcohol Isobutanol Isopropylcarbinol 2-Methyl-1-propanol iso-C ₄ H ₉ OH Fermentation butyl alcohol.
3	446	NIST08s	96	C ₄ H ₁₀ O	78-83-1	74	597	1-Propanol, 2-methyl- Isobutyl alcohol Isobutanol Isopropylcarbinol 2-Methyl-1-propanol iso-C ₄ H ₉ OH Fermentation butyl alcohol.
4	391	NIST08s	95	C ₄ H ₁₀ O	78-83-1	74	597	1-Propanol, 2-methyl- Isobutyl alcohol Isobutanol Isopropylcarbinol 2-Methyl-1-propanol iso-C ₄ H ₉ OH Fermentation butyl alcohol.

Table 4 GC-MS library results recorded for pentanol at retention time 2.142 minutes

Library								
Line#:		2						
R.Time:		2.142						
Mass Peaks:		9						
Raw Mode:		Single 2.142 (78)						
Base Peak:		55.10						
Hit No.	Entry	Library	LIB SI	Formula	CAS	Mol Weight	Ret Index	Compound Name

1	1060	NIST08s	95	C ₅ H ₁₂ O	123-51-3	88	597	1-Butanol, 3-methyl- Isopentyl alcohol Fermentation amyl alcohol Fusel Oil Isoamyl alcohol Isoamylol Isobutyl carbinol
2	1061	NIST08s	94	C ₅ H ₁₂ O	123-51-3	88	697	1-Butanol, 3-methyl- Isopentyl alcohol Fermentation amyl alcohol Fusel Oil Isoamyl alcohol Isoamylol Isobutyl carbinol
3	1039	NIST08s	93	C ₅ H ₁₂ O	123-51-3	88	697	1-Butanol, 3-methyl- Isopentyl alcohol Fermentation amyl alcohol Fusel Oil Isoamyl alcohol Isoamylol Isobutyl carbinol
4	1062	NIST08s	91	C ₅ H ₁₂ O	123-51-3	88	697	1-Butanol, 3-methyl- Isopentyl alcohol Fermentation amyl alcohol Fusel Oil Isoamyl alcohol Isoamylol Isobutyl carbinol

Table 5 Peak report of library values of the Tentatively Identified Compounds (TIC)

Peak #	R.Tim e	I.Tim e	F.Tim e	Area	Area %	Height	Height %	A/H	Mar k	Name
1	1.544	1.517	1.617	453838	65.25	226754	71.75	2.00		Fermentati on butyl alcohol \$
2	2.143	2.092	2.233	241737	34.75	89287	28.25	2.71		Fermentati on amyl alcohol \$

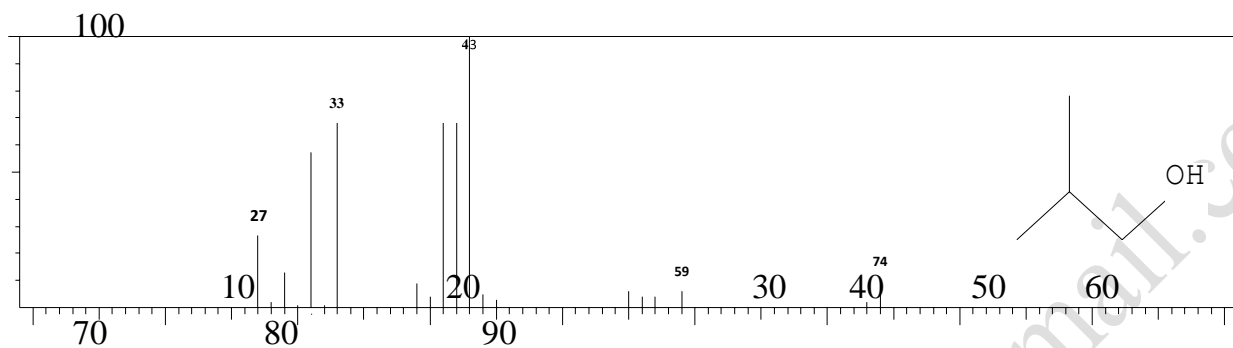


Fig. 4 GC-MS library spectra for butanol with SI of 97% to methanol at retention time of 1.542 minutes

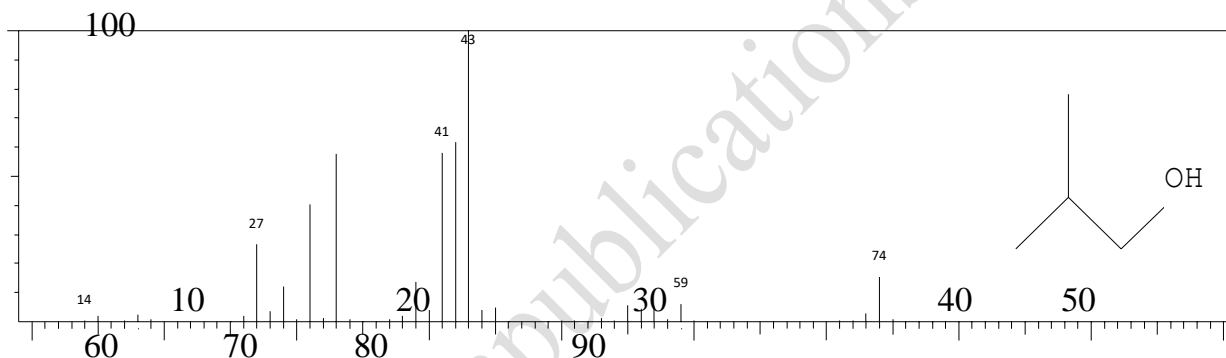


Fig. 5 GC-MS library spectra for butanol with SI of 96% to methanol at retention time of 1.542 minutes

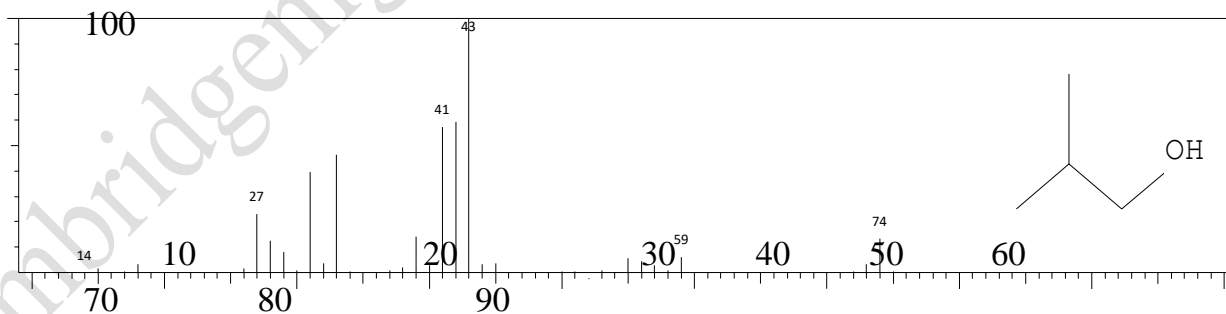


Fig. 6 GC-MS library spectra for butanol with SI of 95% to methanol at retention time of 1.542 minutes

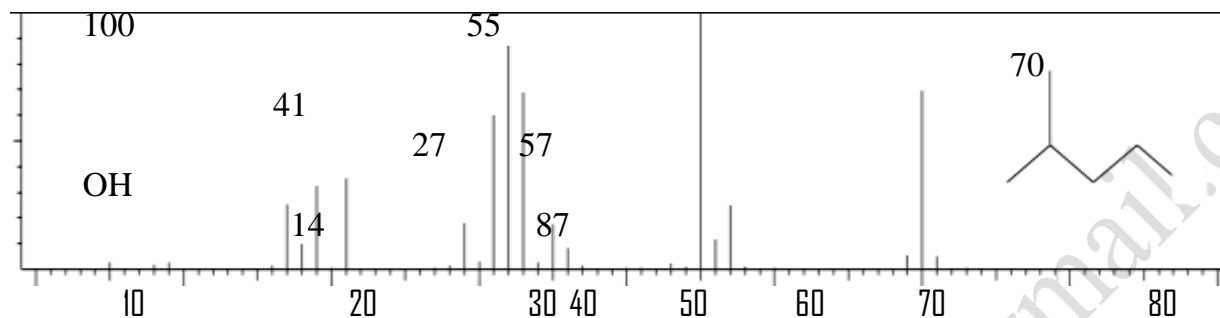


Fig. 7 GC-MS library spectra for pentanol with SI of 95% to methanol at retention time of 2.142 minutes

Table 6.0 Comparison of the percentage transmission of synthetic and analytic methanol using FTIR

Frequencies (l/X) (l/cm)	% Transform (%)	
	Synthetic Methanol	Analytical Methanol
1149.6	94.7	94.6
1249.9	96.0	94.3
1350.2	91.1	92.8
1450.5	92.5	93.3
1550.8	98.0	93.5
1651.1	93.0	84.9
1751.4	99.0	95.2
1851.7	99.4	99.5
1952.1	99.1	99.3
2052.3	100.0	98.4
2152.6	99.7	97.1
2252.9	100.0	98.1
2353.2	99.8	98.7
2453.5	99.9	99.9
2549.9	99.0	100.0
2646.4	97.7	99.7
2746.7	94.3	96.8
2847.1	87.9	90.4

2947.3	82.5	83.5
3047.6	86.9	81.8
3147.9	79.6	71.8
3248.2	71.4	63.0
3348.5	68.7	61.1
3448.8	70.9	64.9
3549.1	78.3	73.8
3649.4	85.2	83.5
3749.7	90.9	90.4
3850.1	91.7	91.1
3950.3	91.4	91.0
4004.3	91.7	91.6

Table 7 Exhaust emissions at a constant engine speed of 3000 rpm and varying loads.

Load (kg)	CO (%)		CO ₂ (%)		uHC (ppm)		Oil Temp. (°C)	
	G100	G95	G100	G95	G100	G95	G100	G95
1000	1.96	1.86	2.26	2.08	208	368	32.40	35.60
2000	2.10	1.80	2.60	2.10	280	322	32.70	35.70
3000	2.14	1.76	2.76	3.82	292	330	32.80	35.80
4000	1.38	1.70	4.00	3.72	260	316	36.10	35.90
5000	1.26	1.68	3.52	3.61	242	296	36.20	36.00

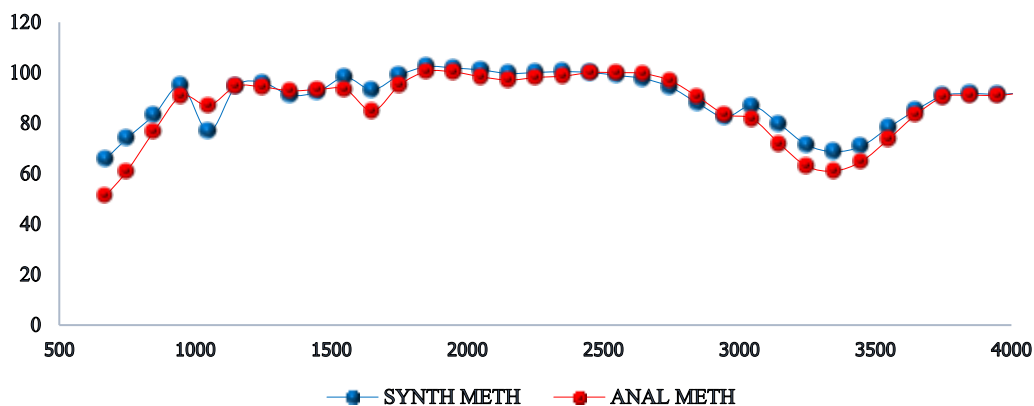


Fig. 8 Graphical comparison of generated data from the FTIR test results of synthetic and analytical methanol

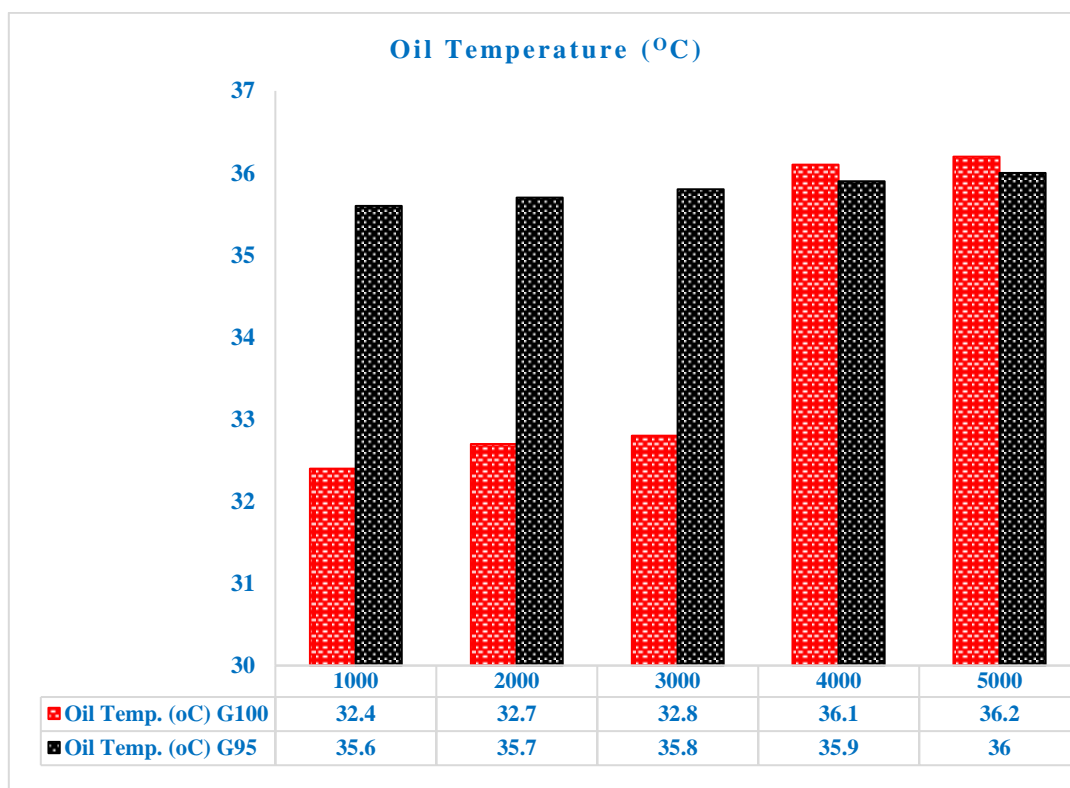


Fig. 9 Comparison of oil temperatures by G100 and G95 under constant engine speed and varying load operations

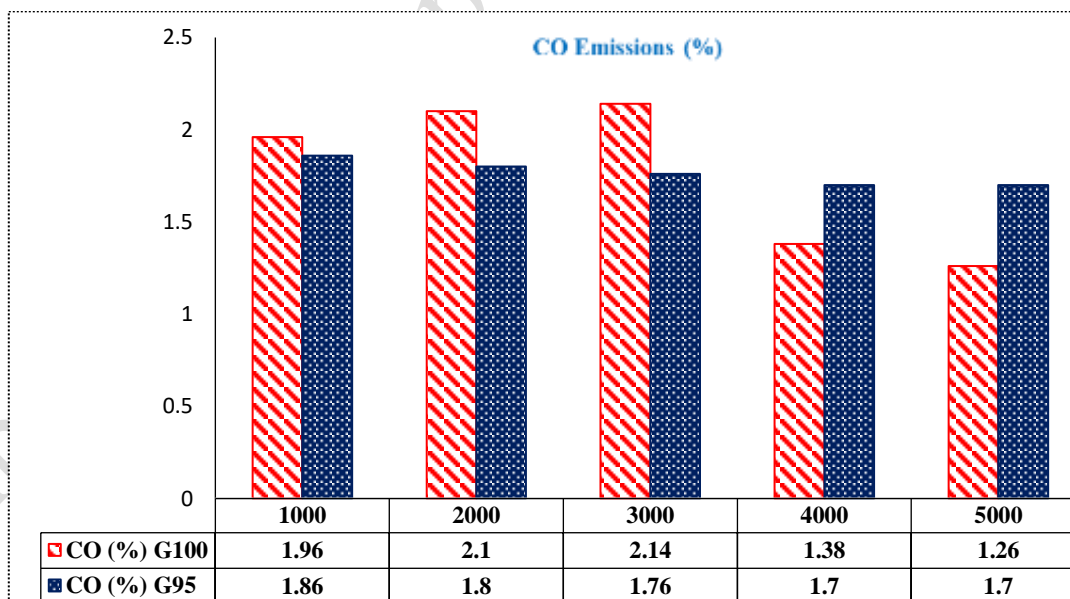


Fig. 10 Comparison of CO emissions by G100 and G95 under constant engine speed and varying load operations.

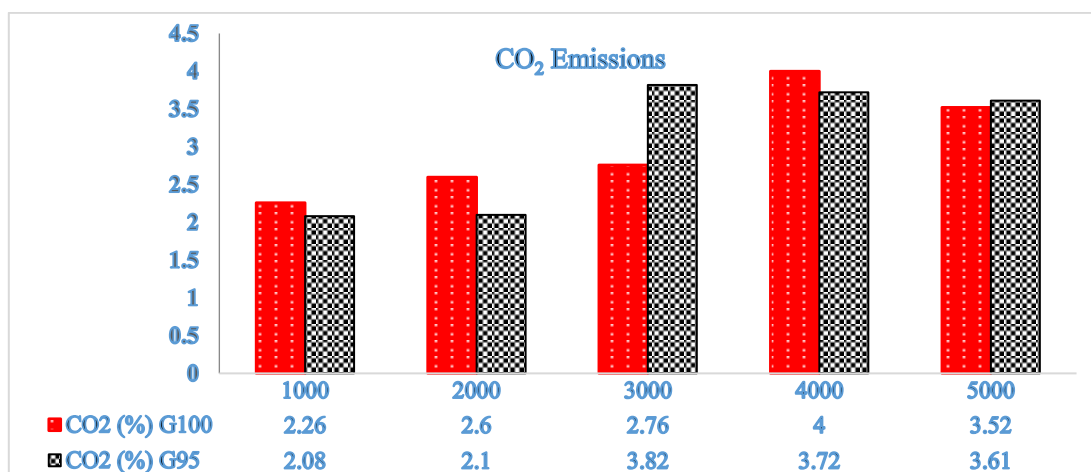


Fig. 11 Comparison of CO₂ emissions by G100 and G95 under constant engine speed and varying load operations.

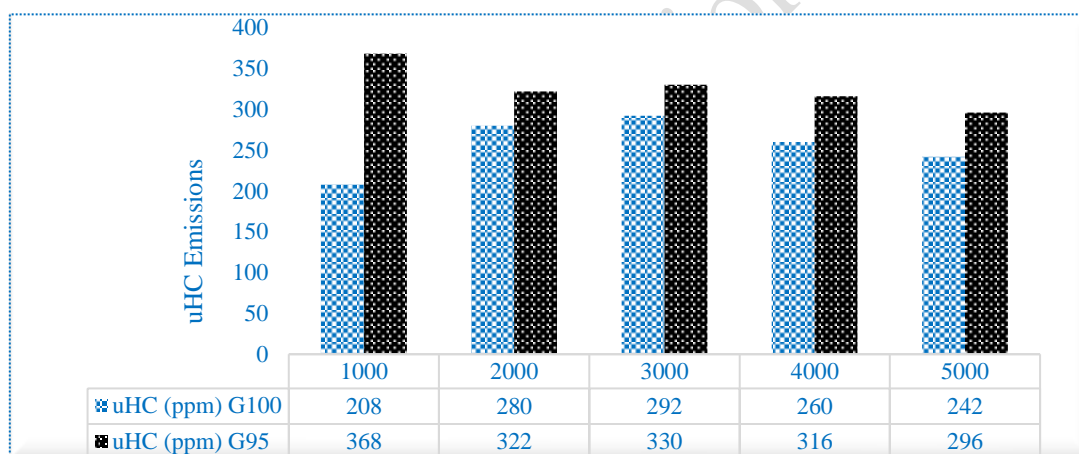


Fig. 12 Comparison of uHC emissions by G100 and G95 under constant engine speed and varying load operations.

Conclusions

From the literature and test results obtained during methanol fuel production and application in spark ignition engine, we conclude that; the use of paraffin wax, silica gel and sodium lauryl/dodecyl sulphate (SDS) in preparation of PEM used in an electrochemical process of methanol production improves the membrane's stability and also promote better electro-osmosis across the membrane. Therefore, increased capacity of the electrochemical set-up plant can lead to production of methanol to a commercial quantity. The use of Potassium permanganate (KMnO₄), Fourier Transform Infrared

Spectrophotometer (FTIR) and GC-MS are good confirmatory tests for the presence of methanol in an unknown sample.

The increased demand for spark ignition engine in transportation industry has led to increased emissions of GHGs that have adverse effects on the environment and human health. Therefore, the global quest for Green technology elicited researchers to intensify studies on alternative automobile fuels to gasoline. The utilization of alcohol fuel plays a crucial role in reduction of the harmful engine exhaust emissions. Consequently, scholars around the globe have studied the effect of alcohol-based fuel on spark ignition engine exhaust emissions over the last decades. But the sustainable method required to produce the alcohol fuel to meet global demand was the major challenge until late 1990s, when many researchers discovered suitable technology that led many nations to commercialize alcohol-based fuel especially the methanol.

It is true that exhaust emissions of an internal combustion engine depend on number of factors. However, the difference in the properties of alcohol leads to an improved exhaust emissions when operated on alcohol-based fuel compared to gasoline.

Recommendation

The study provided a valuable insight into the interaction between Carbon (IV) Oxide and water, paraffin wax, silica gel and sodium lauryl/dodecyl sulphate (SDS) in the presence of Cu and Zn catalysts for methanol fuel production. Therefore, to gain more understanding of methanol fuel production in a larger scale using PEM technique, we recommend that a complete setup with higher capacity that contains all the processes be established in a designated research centre.

The study also provided an understanding between the emissions of blended methanol fuel with gasoline when compared to pure gasoline in a port-fueled SI engine. Therefore, a better understanding of the performance and emissions characteristics of the methanol fuel in a SI engine could be achieved if the experiment is carried out in an engine that has multiple fuel injection ports as seen in the literature section of this paper.

As part of the solutions to harmful effects of GHGs emissions from combustion of gasoline to the atmosphere and human health, it is further recommended that

the present day automobile fuel should be blended with alcohol fuel since it has potential to reduce exhaust emissions.

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