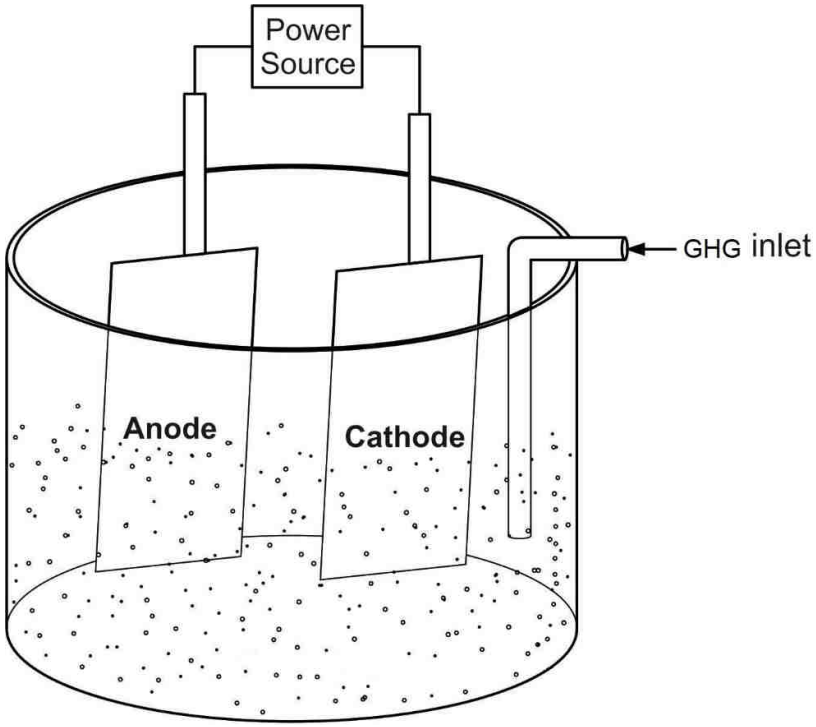

Power Source
GHG inlet
Anode
Cathode

FIG. 1

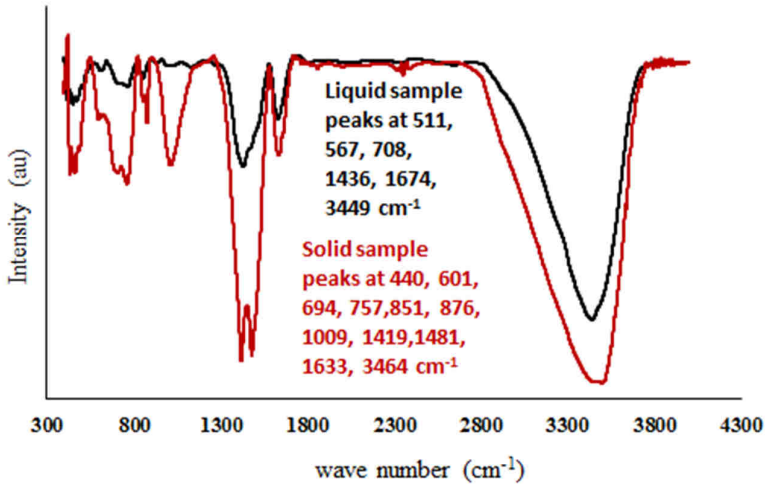

Liquid sample peaks at 511, 567, 708, 1436, 1674, 3449 cm-1
Solid sample peaks at 440, 601, 694, 757,851, 876, 1009, 1419,1481, 1633, 3464 cm-1
Intensity (au)
300
800
1300
1800
2300
2800
3300
3800
4300
wave number (cm-1)

FIG. 2A

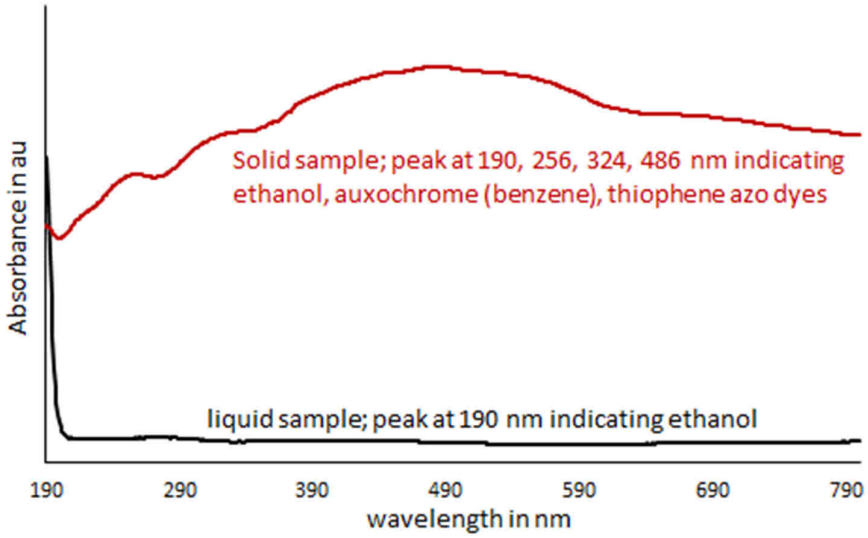


FIG. 2B

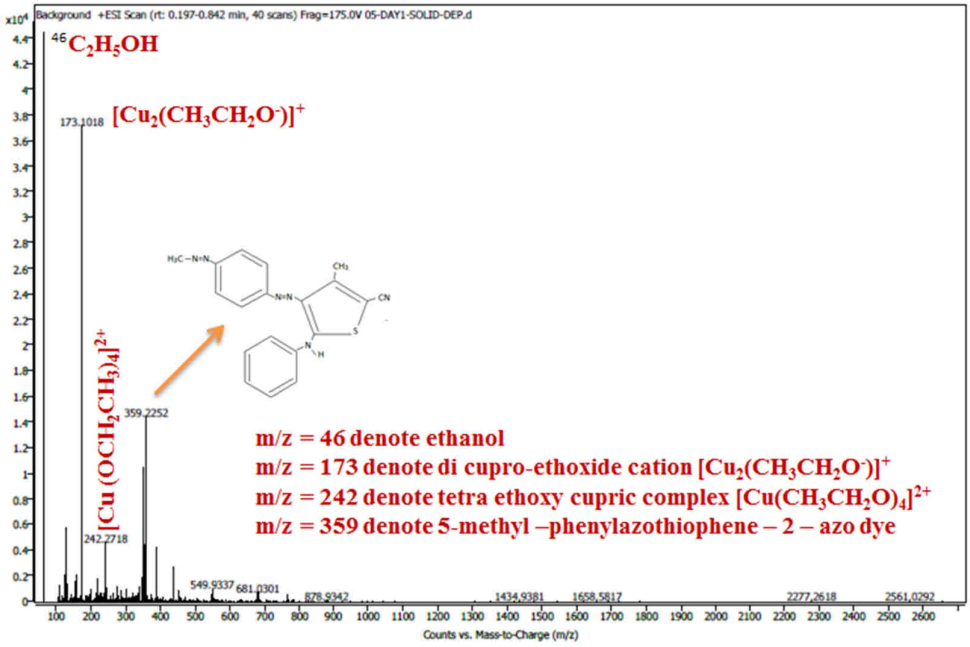


FIG. 2C

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

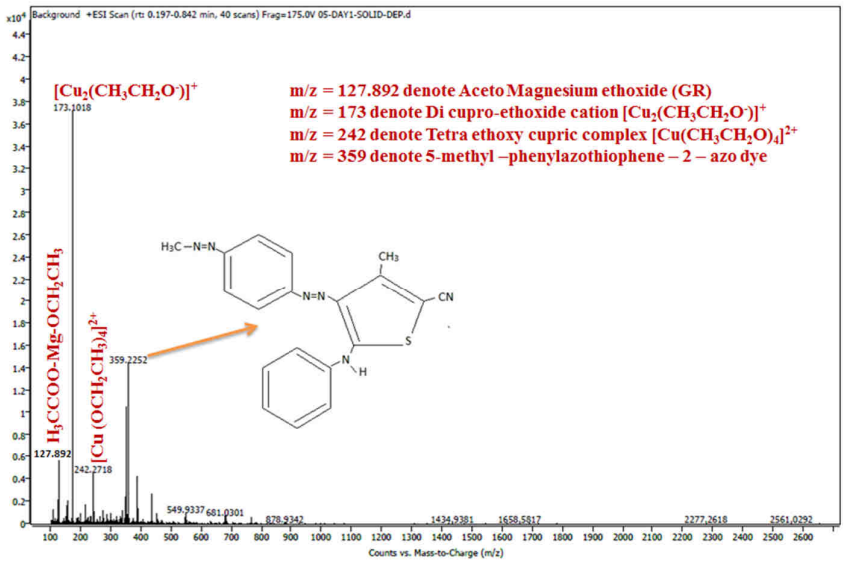


FIG. 2D

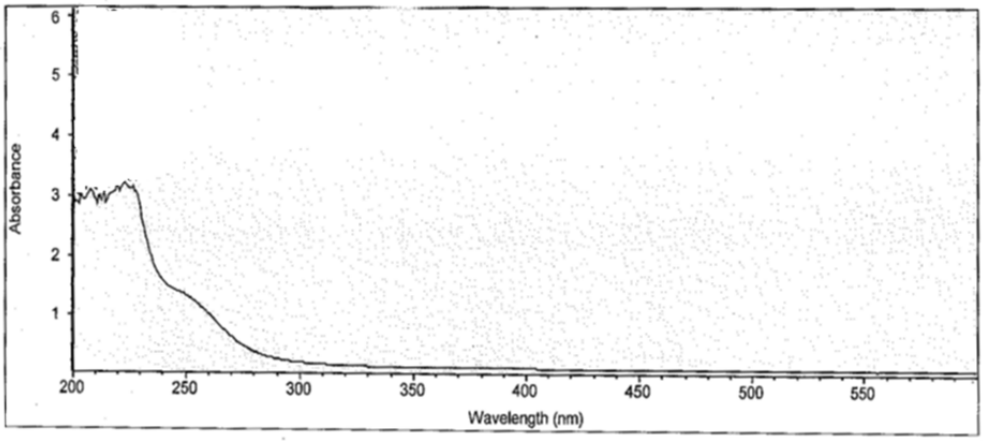


FIG. 3A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

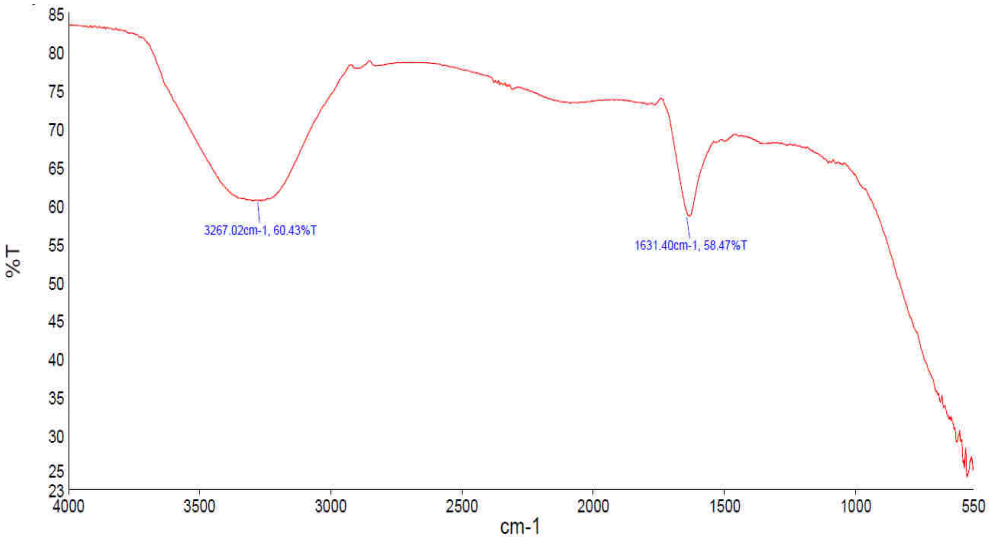

%T
cm-1
3267.02cm-1, 60.43%T
1631.40cm-1, 58.47%T

FIG. 3B

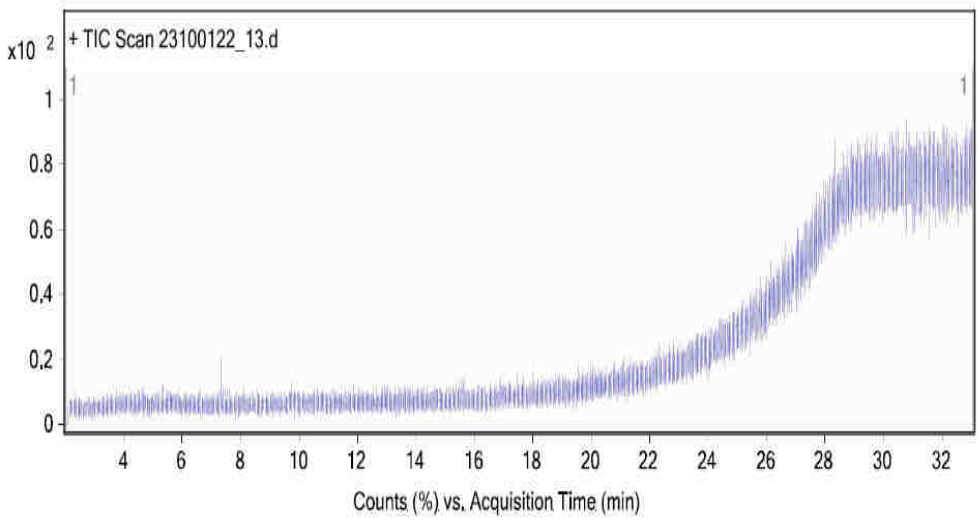

+ TIC Scan 23100122_13.d
x10 2
Counts (%) vs. Acquisition Time (min)

FIG. 3C

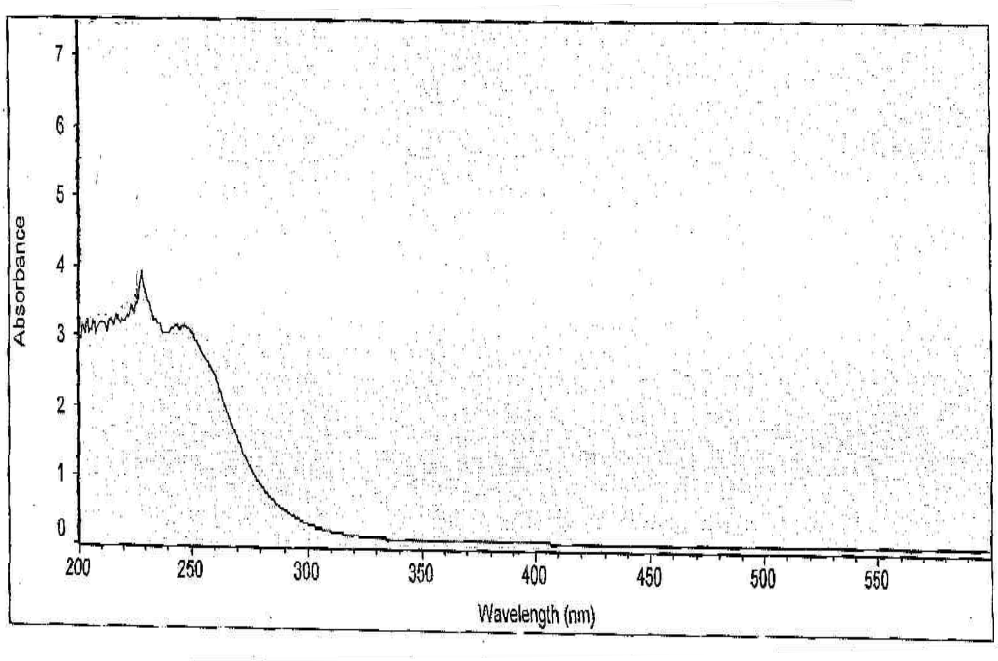


FIG. 3D

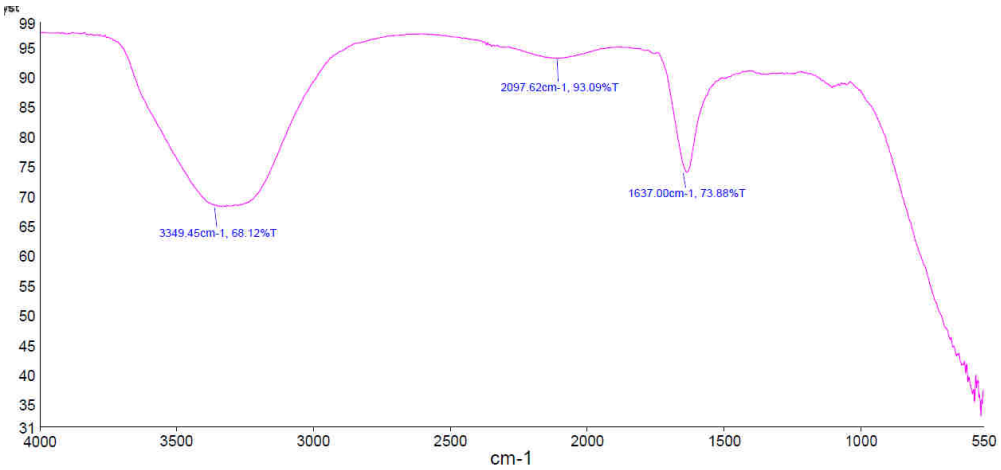


FIG. 3E

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

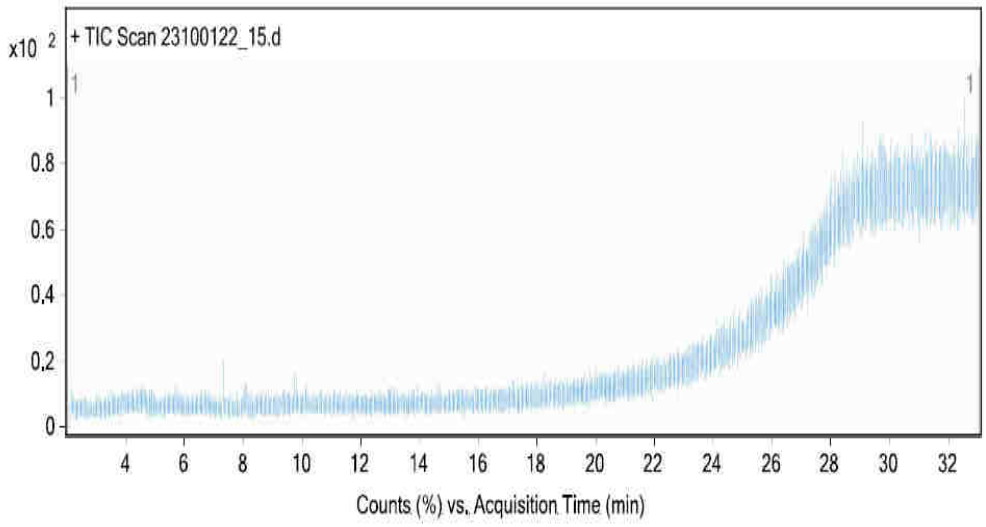


FIG. 3F

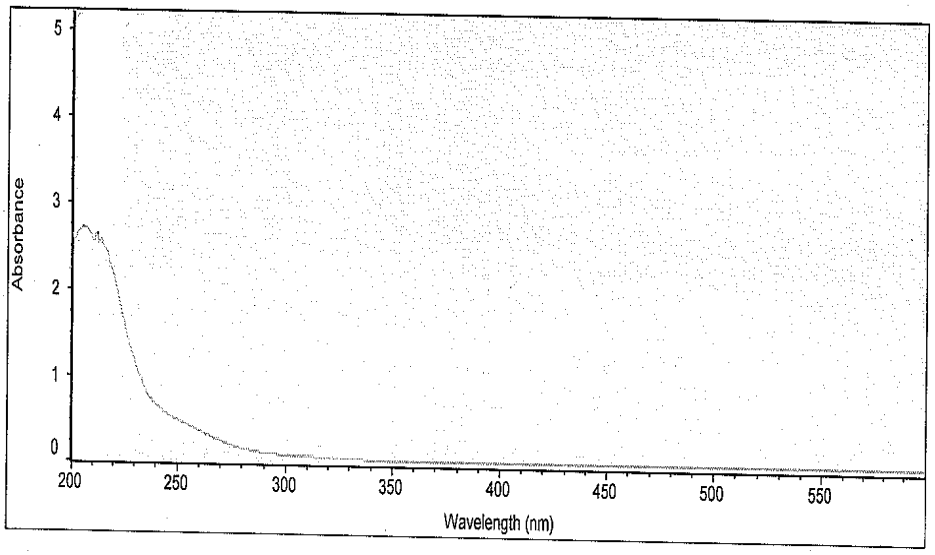


FIG. 4A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

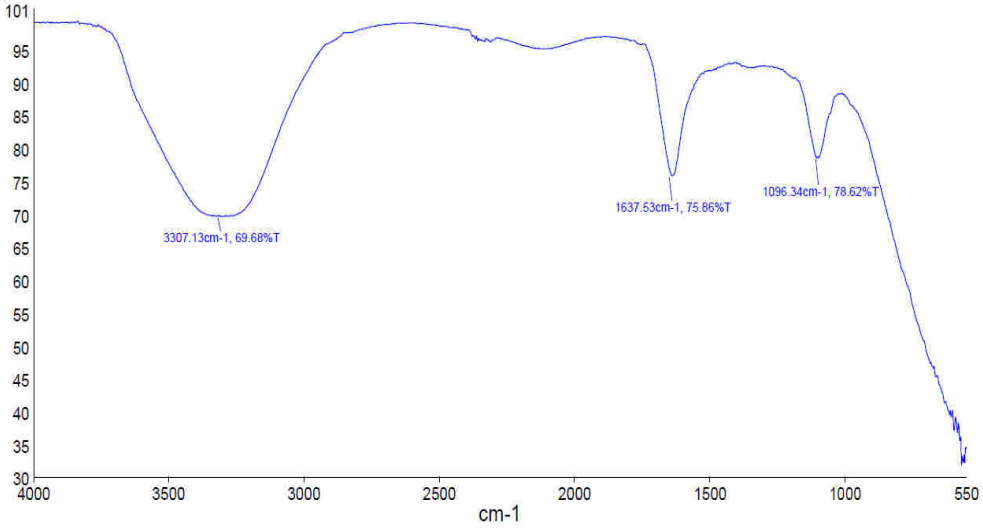


FIG. 4B

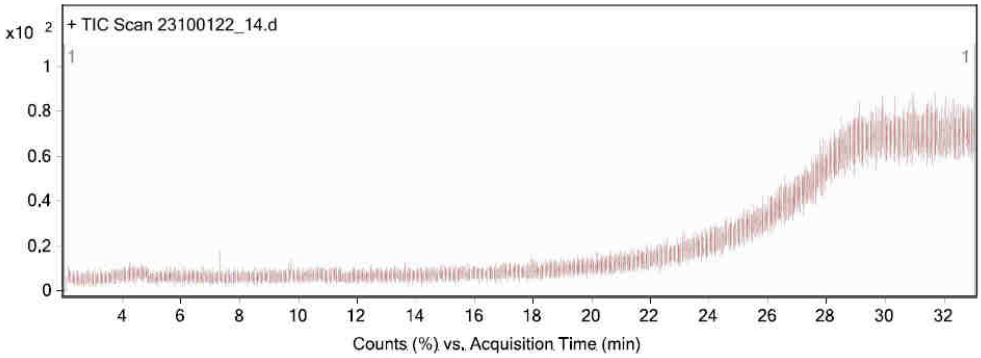


FIG. 4C

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

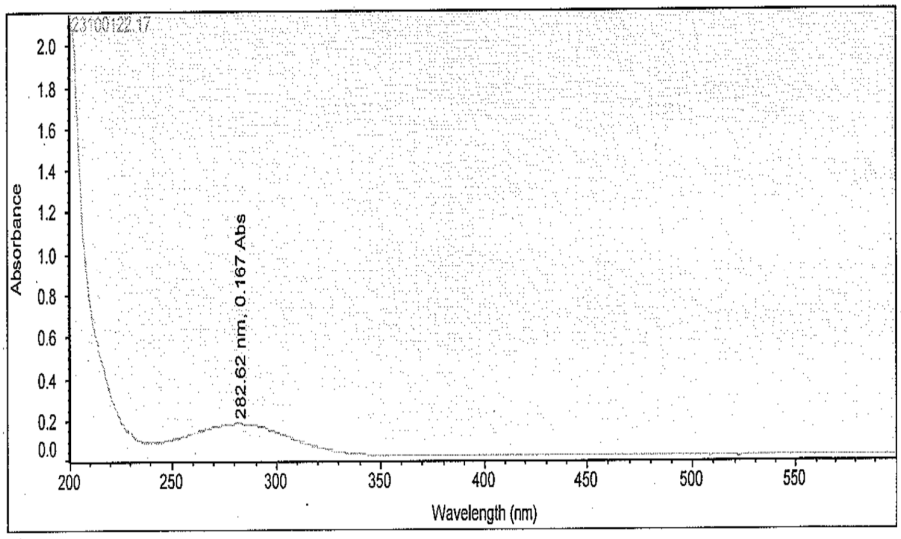


FIG. 5A

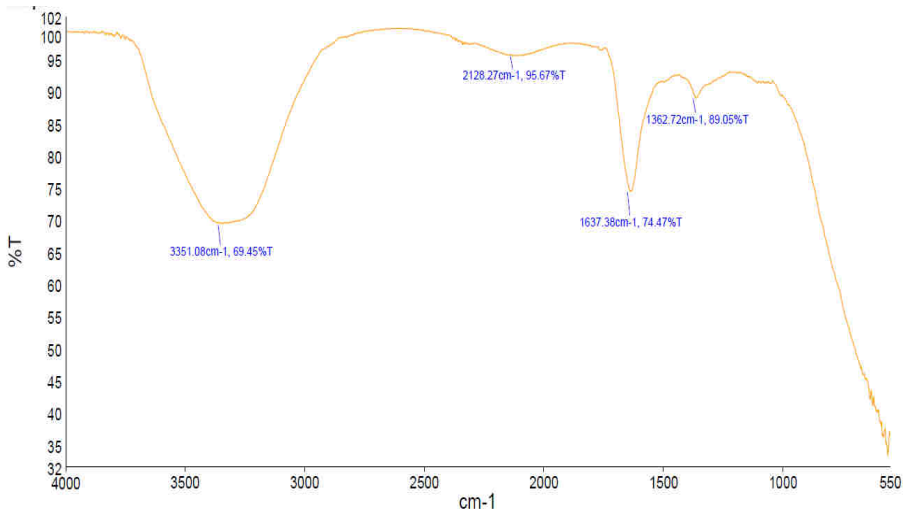


FIG. 5B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

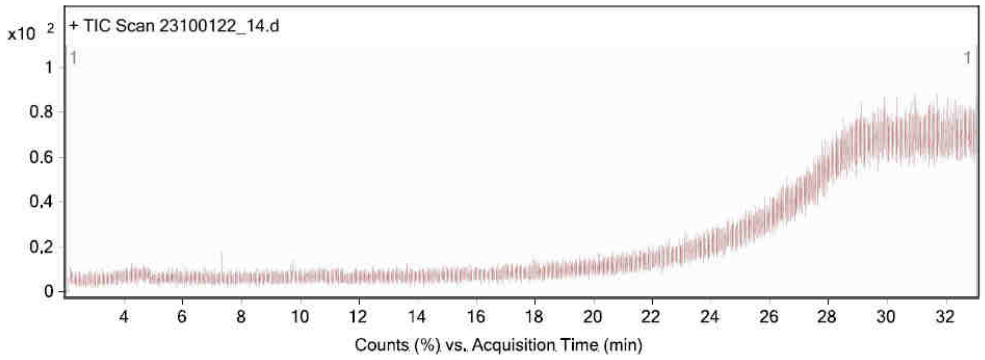


FIG. 5C

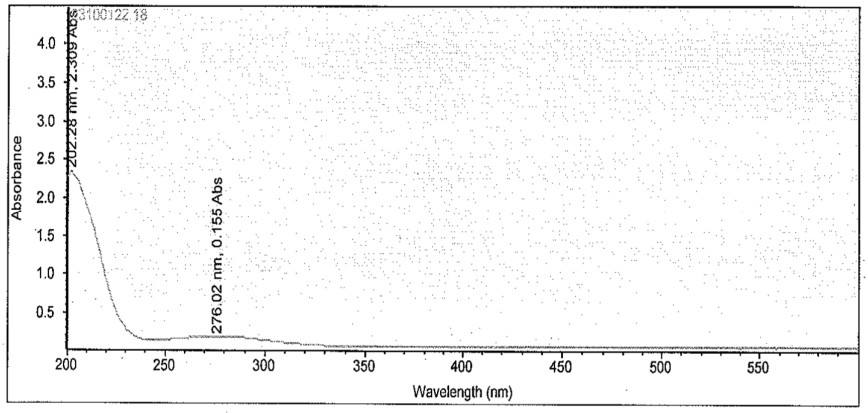


FIG. 6A

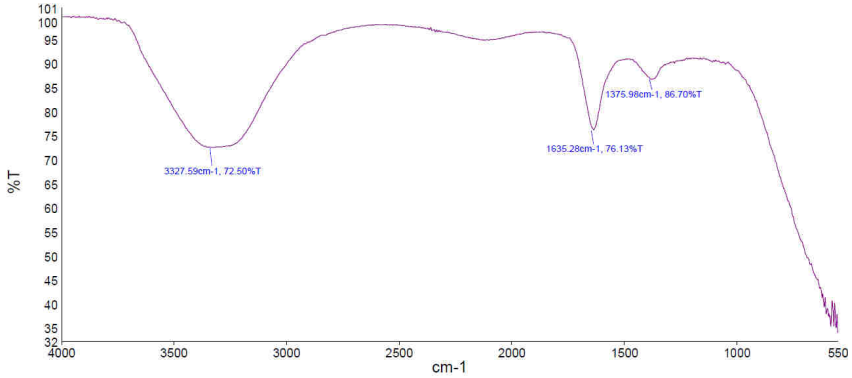


FIG. 6B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

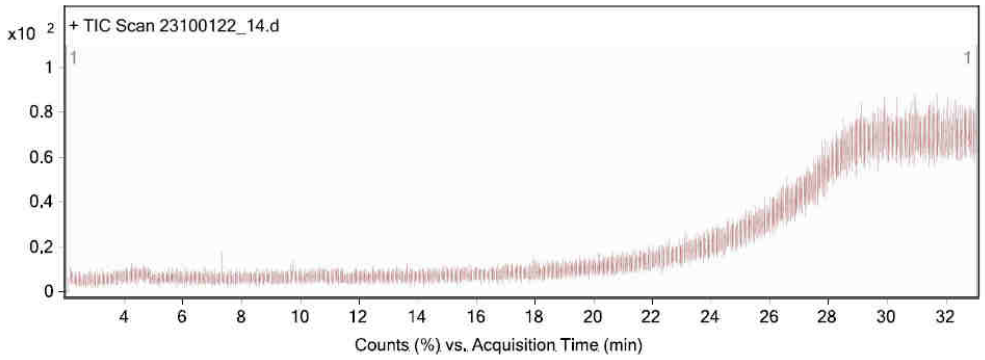


FIG. 6C

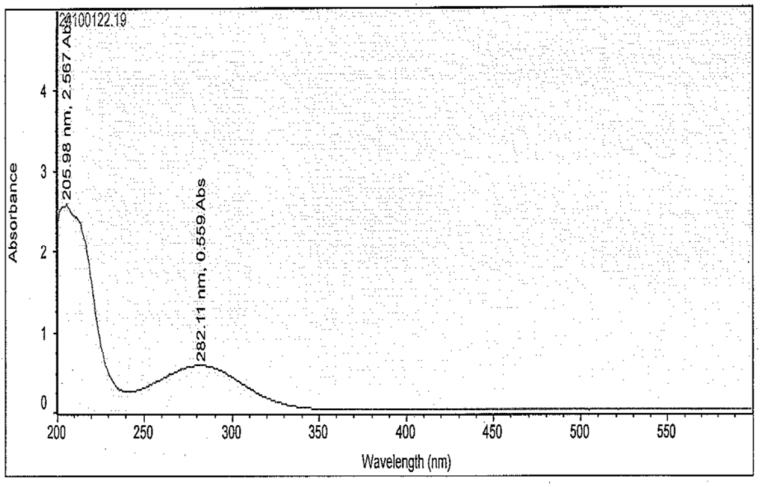


FIG. 7A

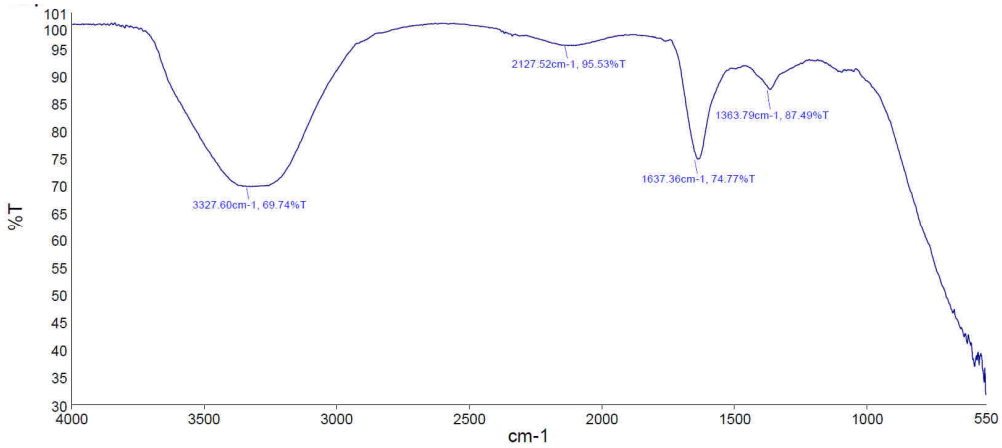
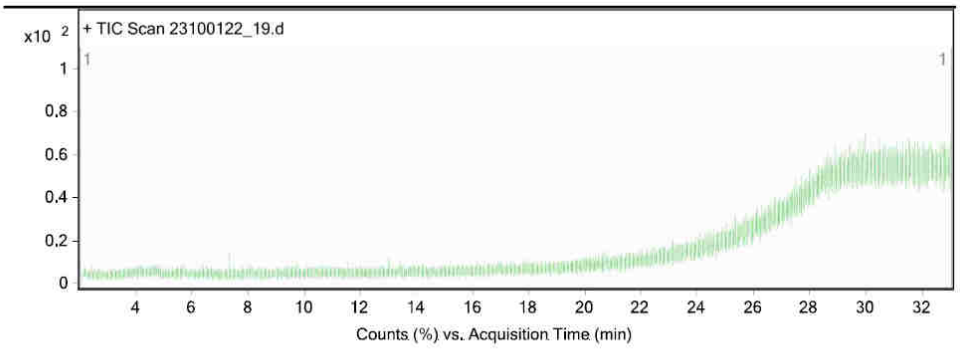


FIG. 7B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)



No Compounds Found

FIG. 7C

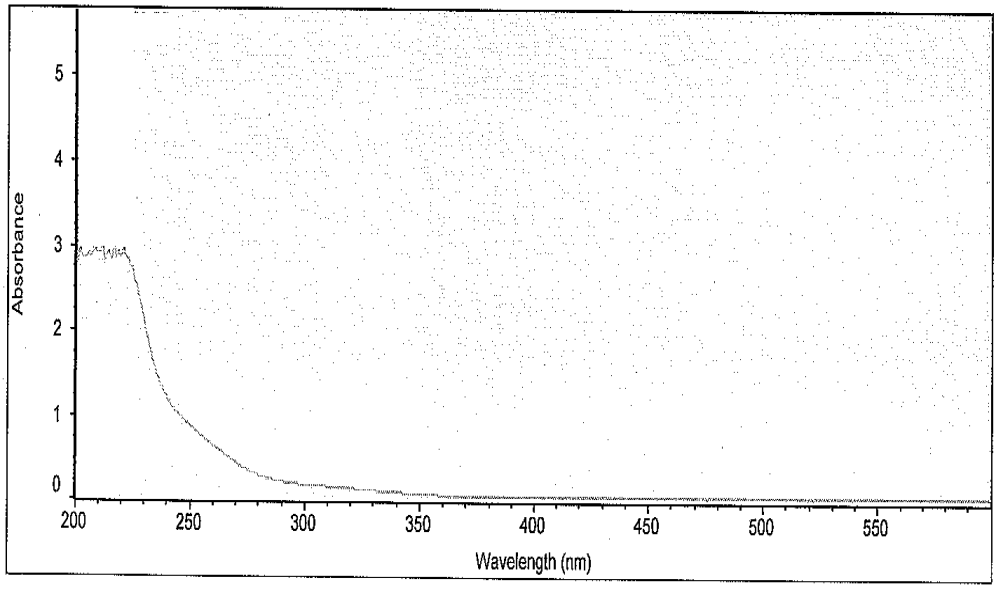


FIG. 8A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

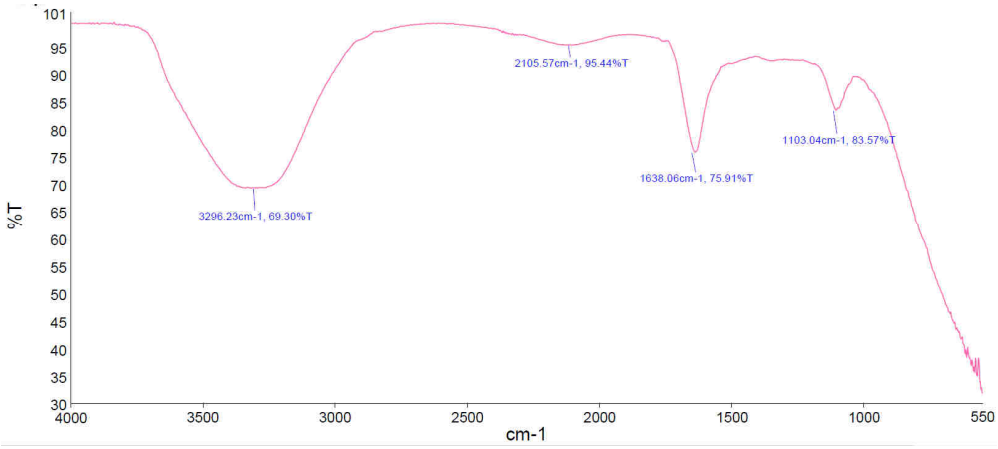
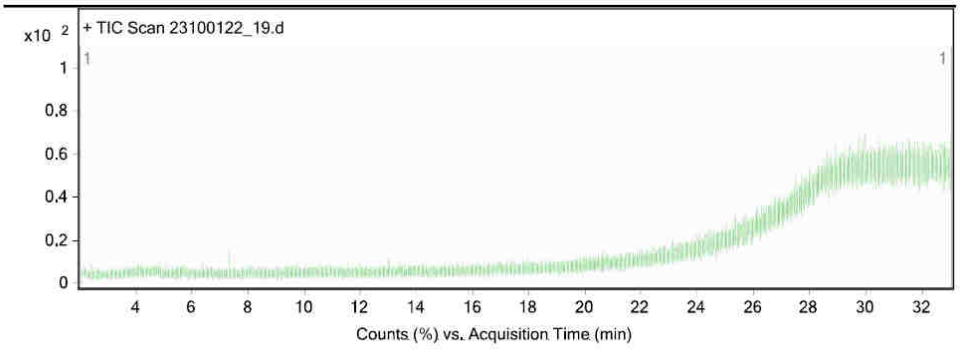


FIG. 8B



No Compounds Found

FIG. 8C

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

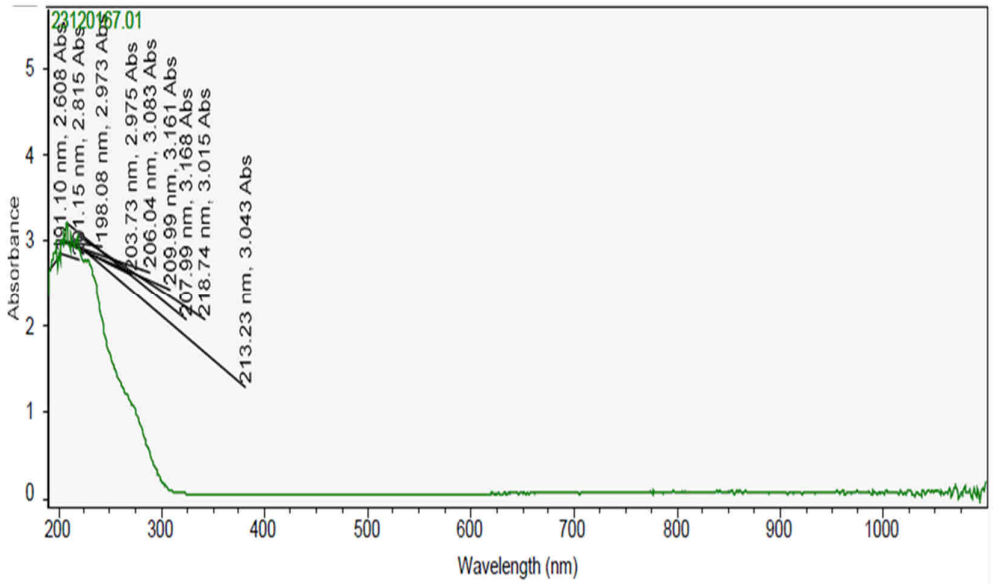


FIG. 9A

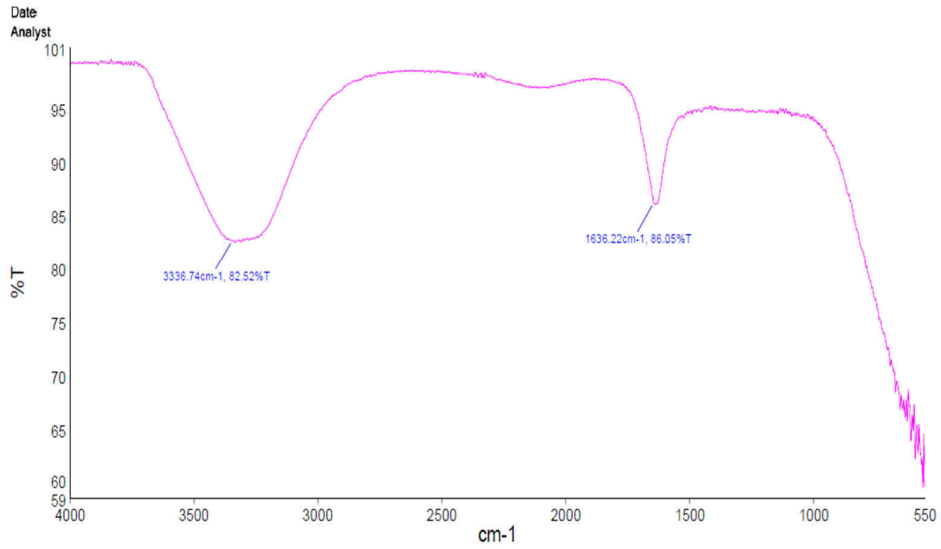


FIG. 9B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

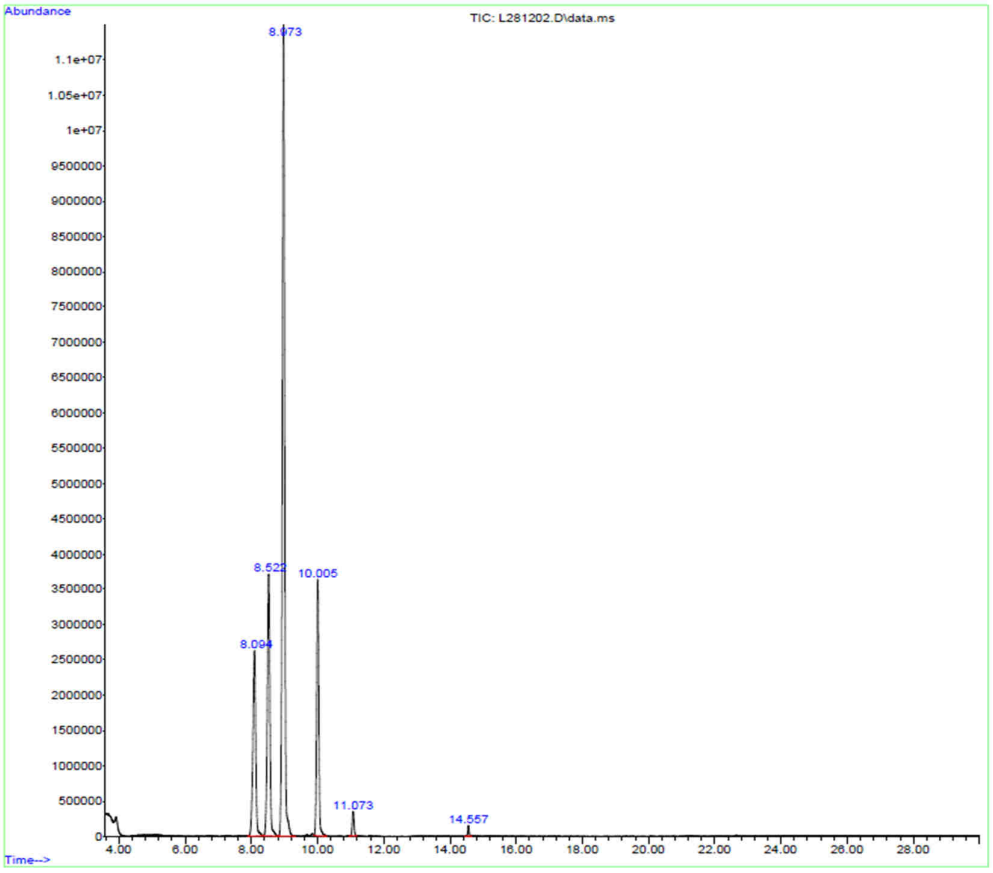


FIG. 9C

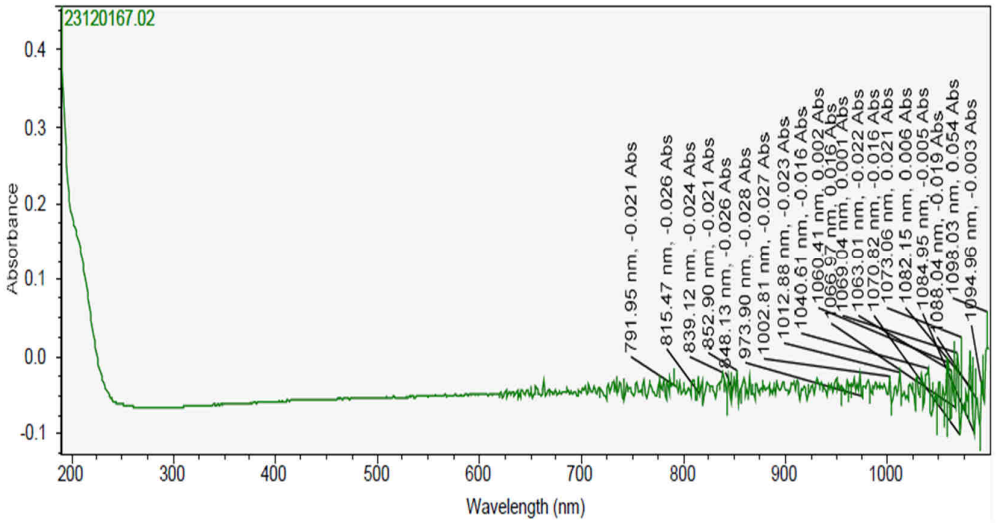


FIG. 10A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

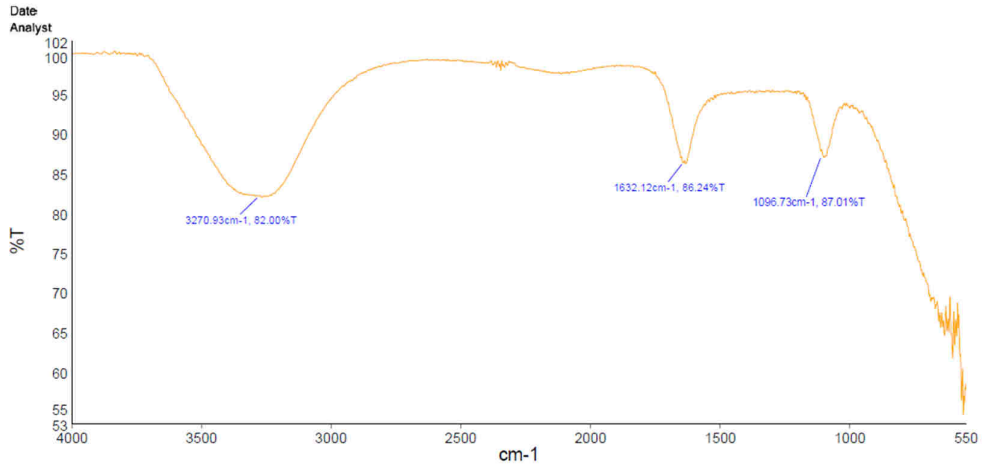


FIG. 10B

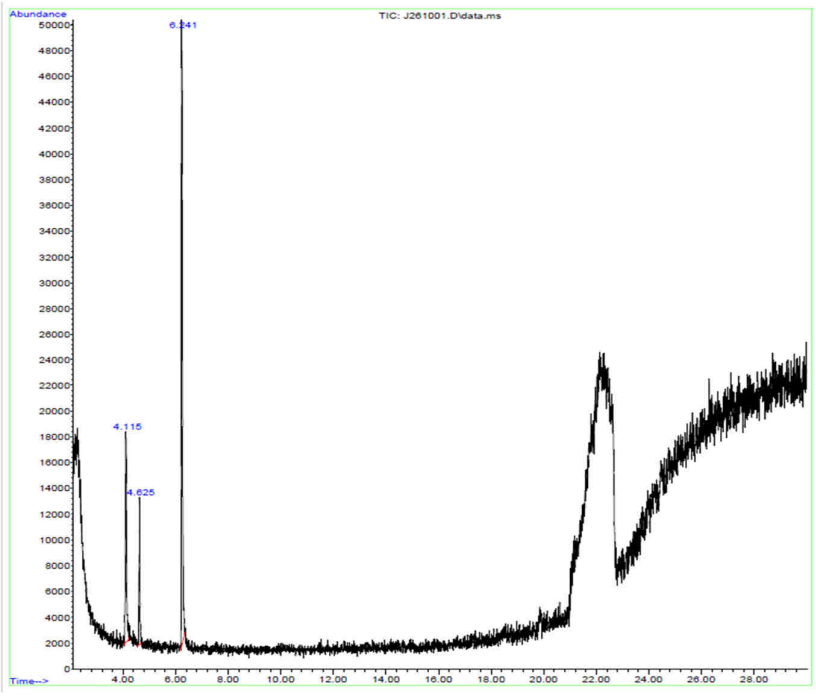


FIG. 10C

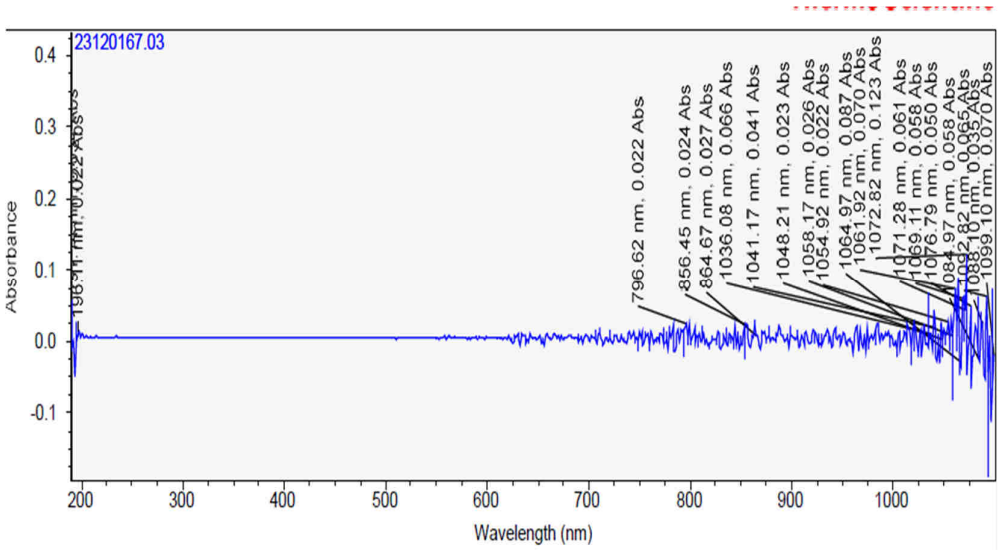


FIG. 11A

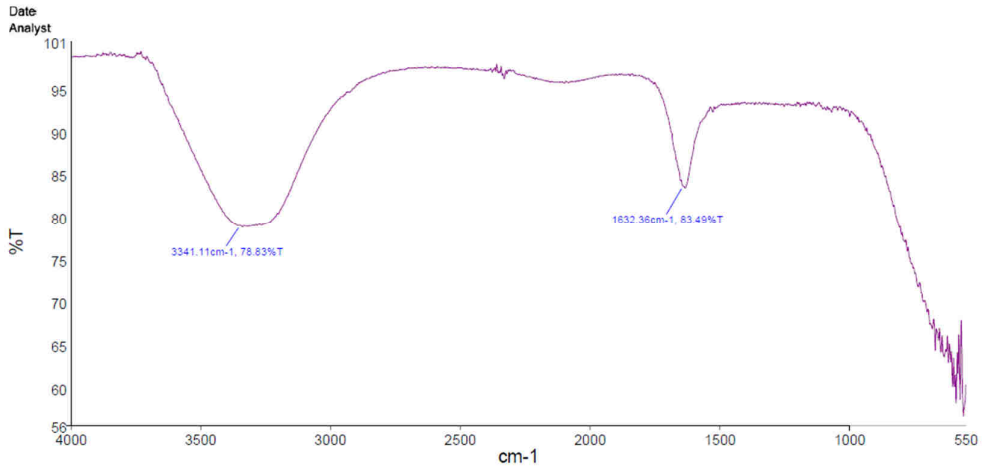


FIG. 11B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

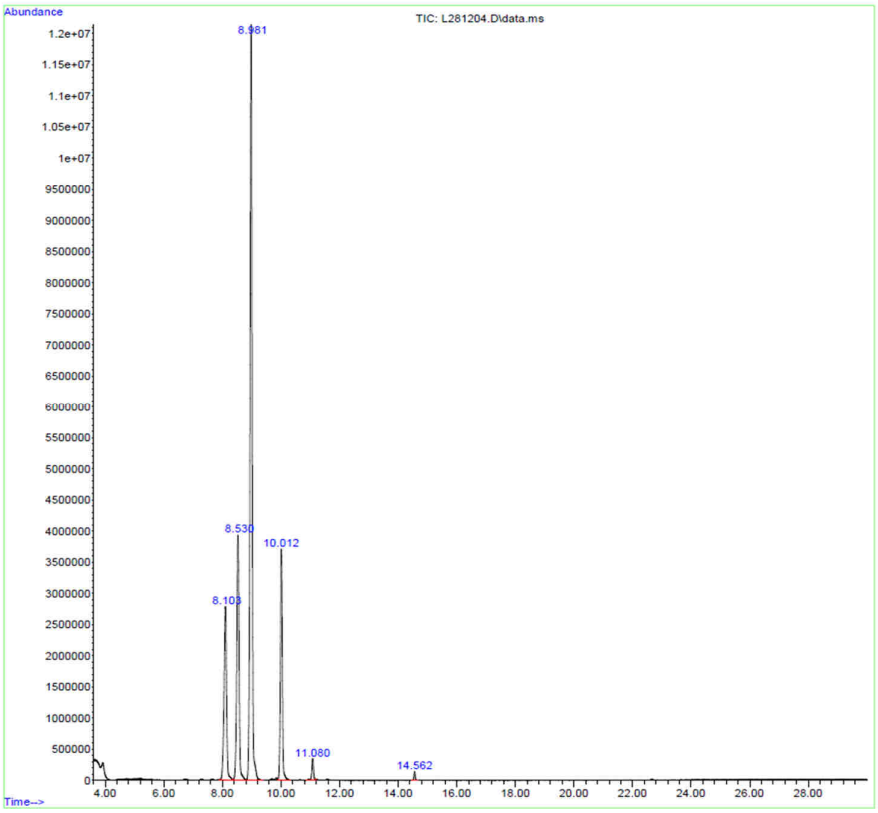


FIG. 11C

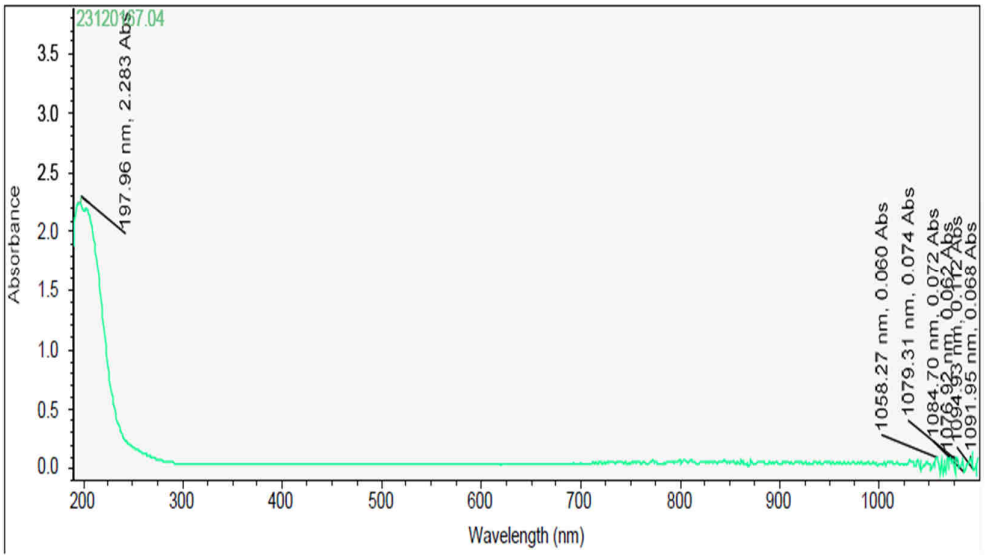


FIG. 12A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

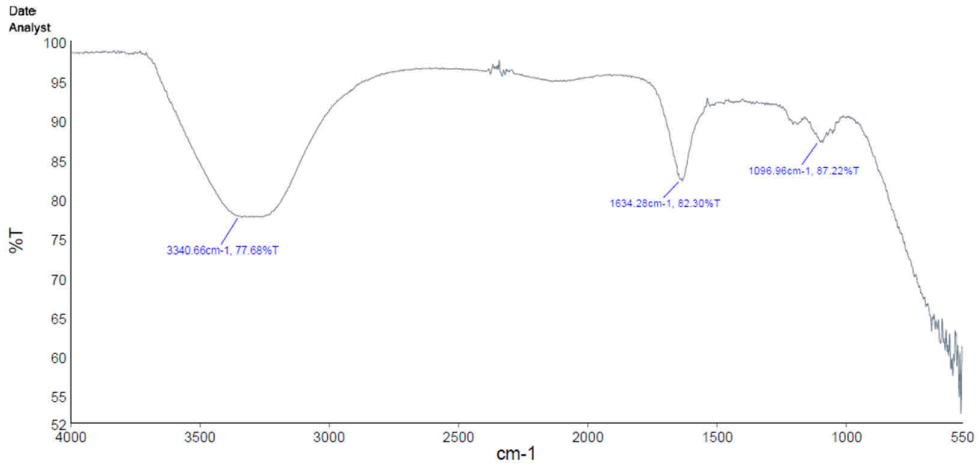


FIG. 12B

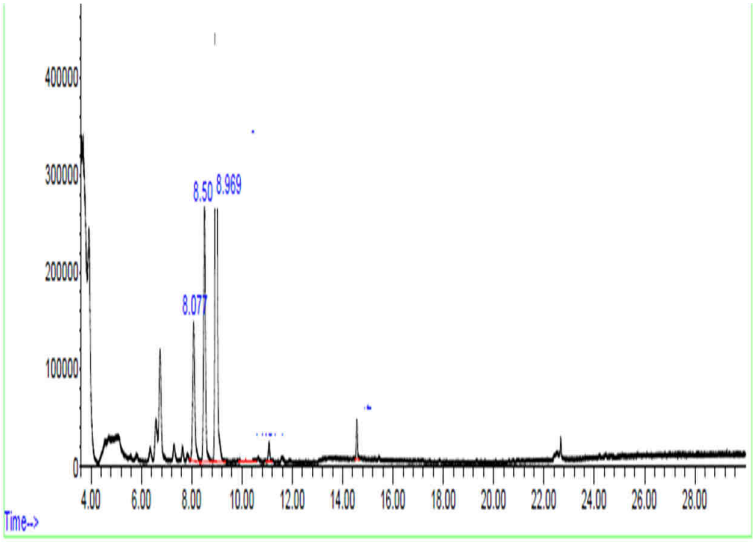


FIG. 12C

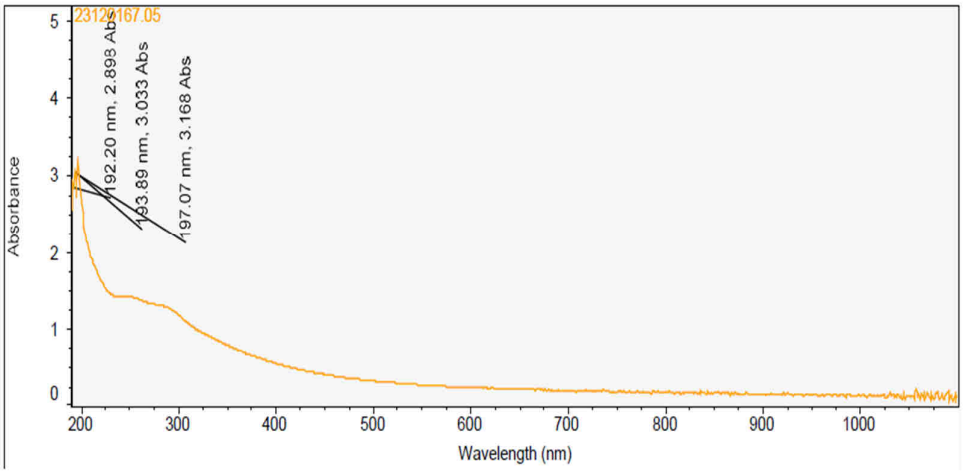


FIG. 13A

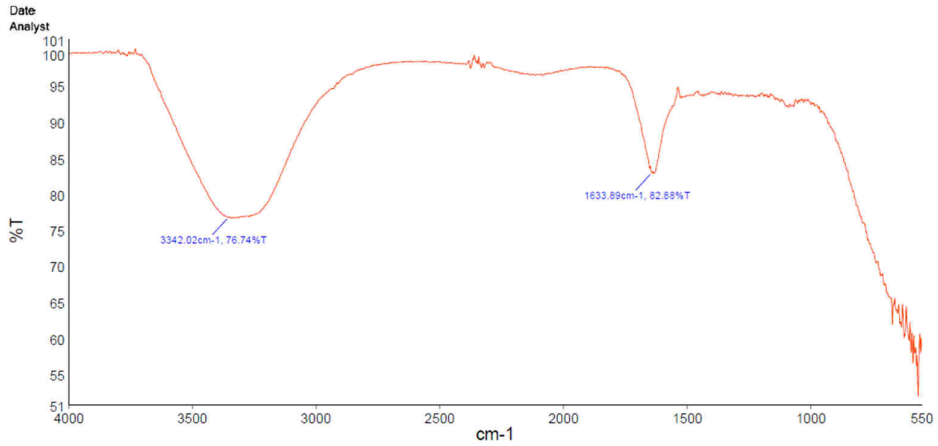


FIG. 13B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

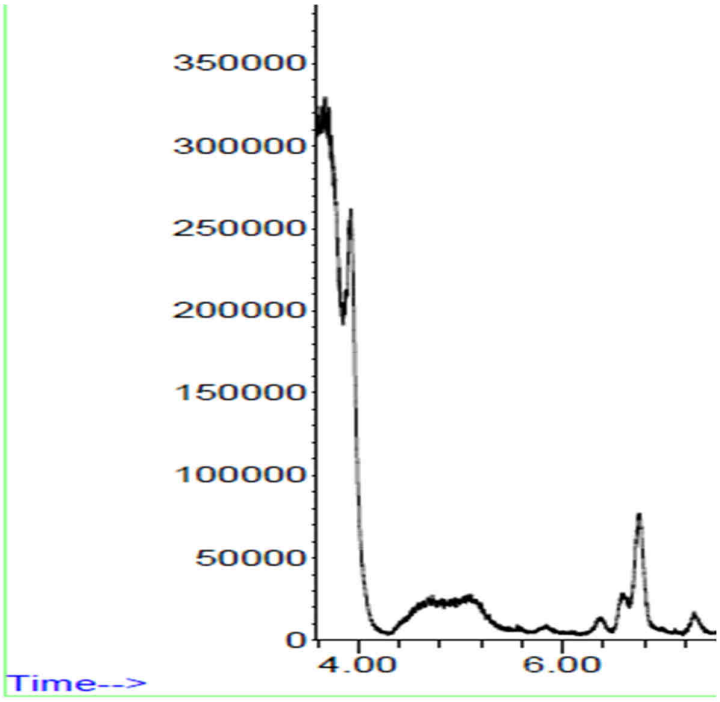


FIG. 13C

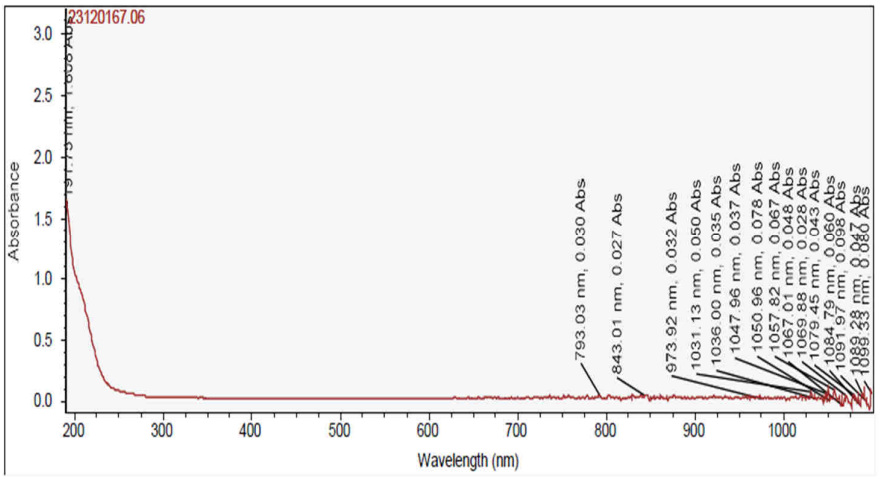


FIG. 14A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

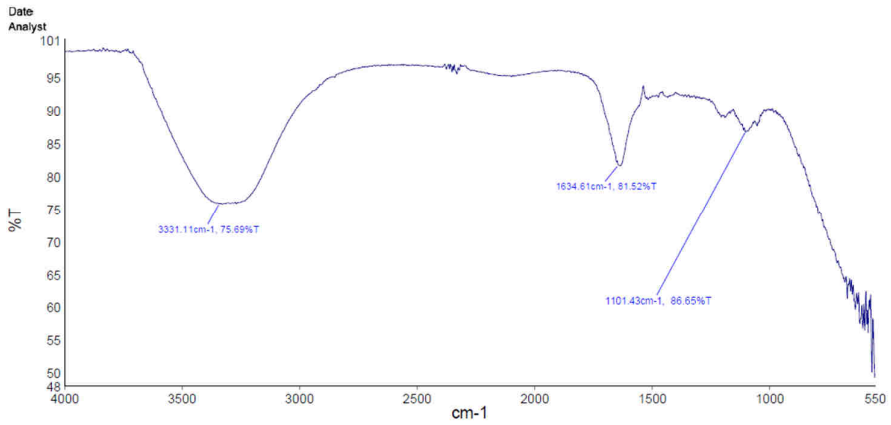


FIG. 14B

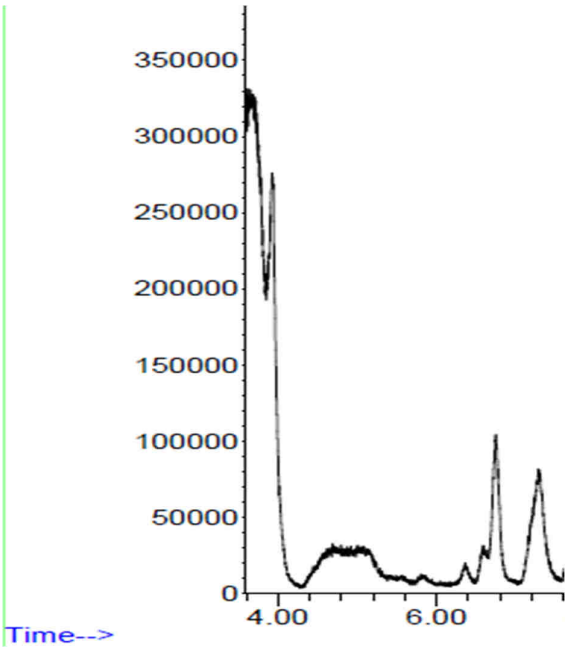


FIG. 14C

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

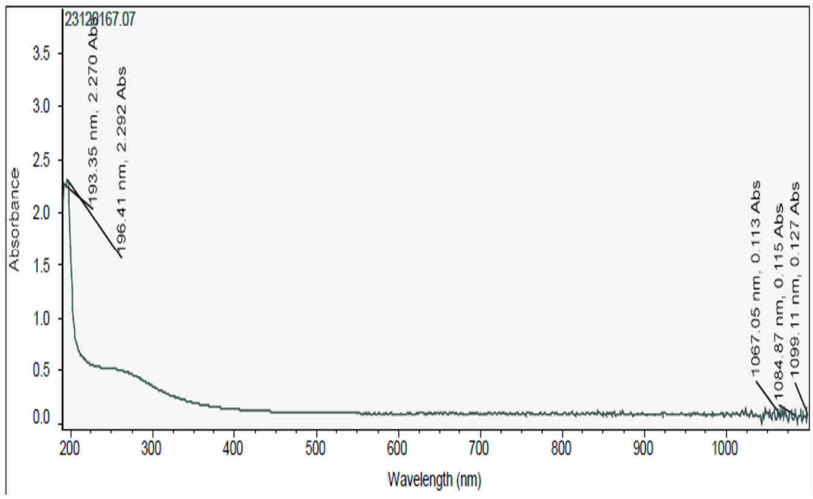


FIG. 15A

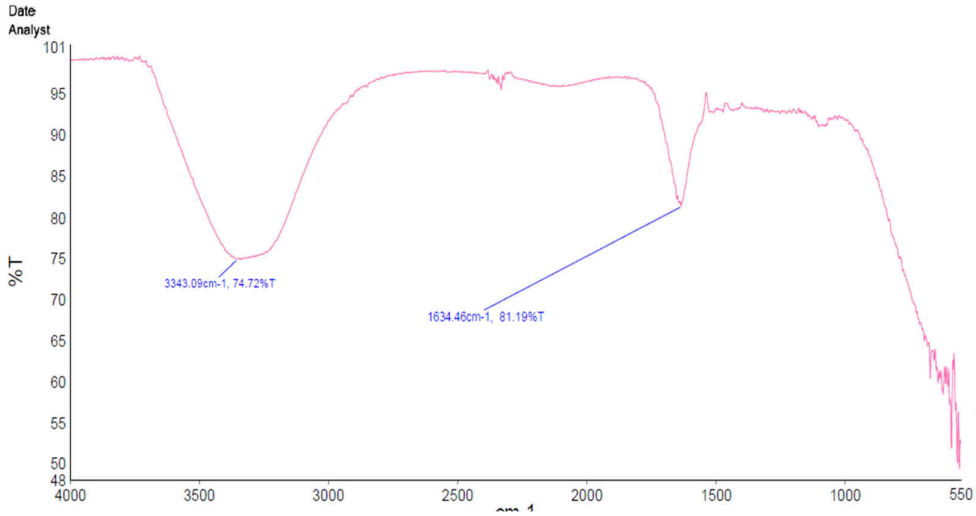


FIG. 15B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

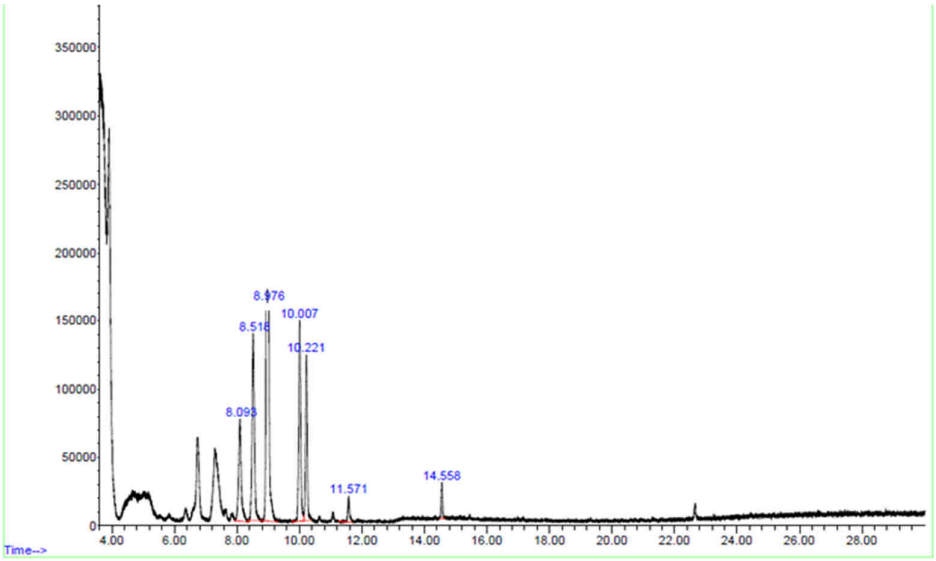


FIG. 15C

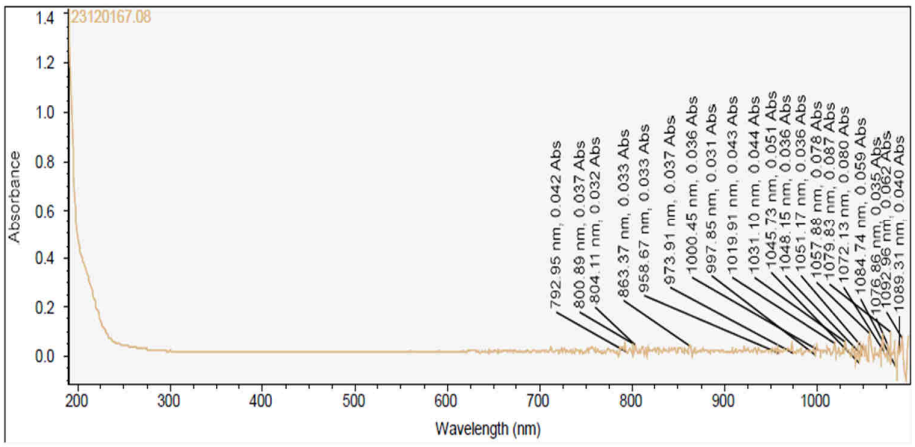


FIG. 16A

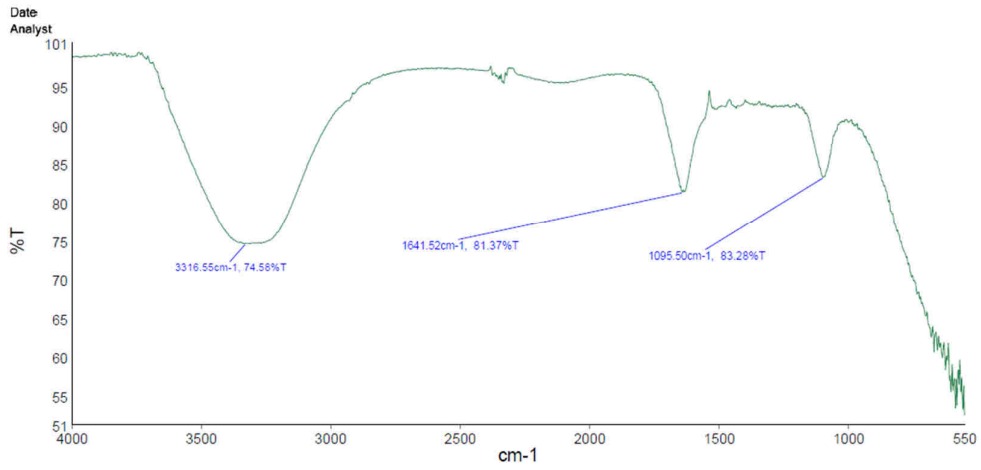


FIG. 16B

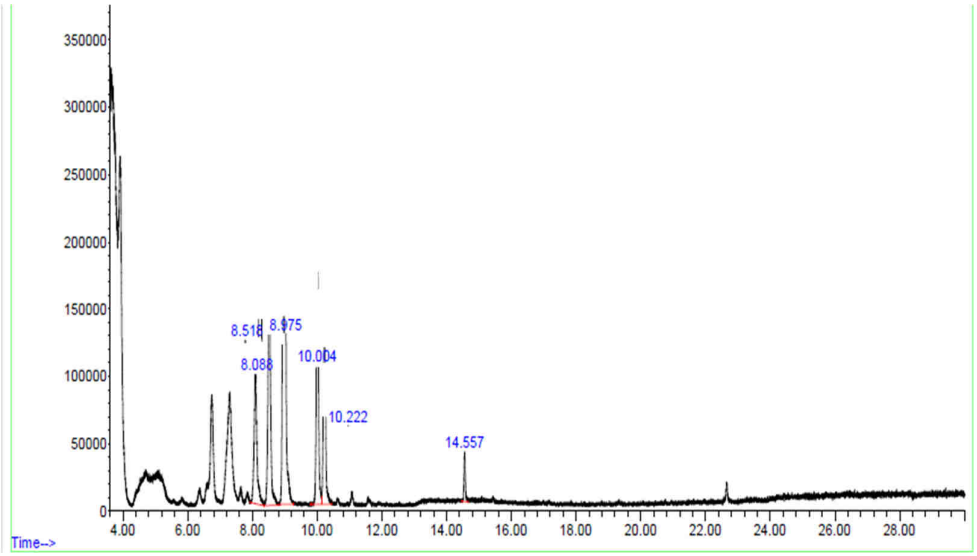


FIG. 16C

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

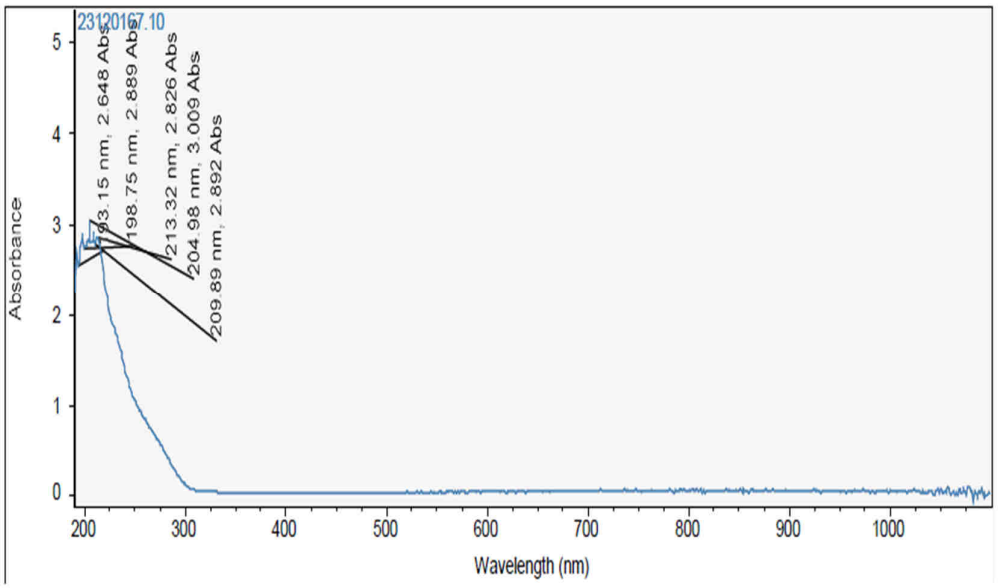


FIG. 17A

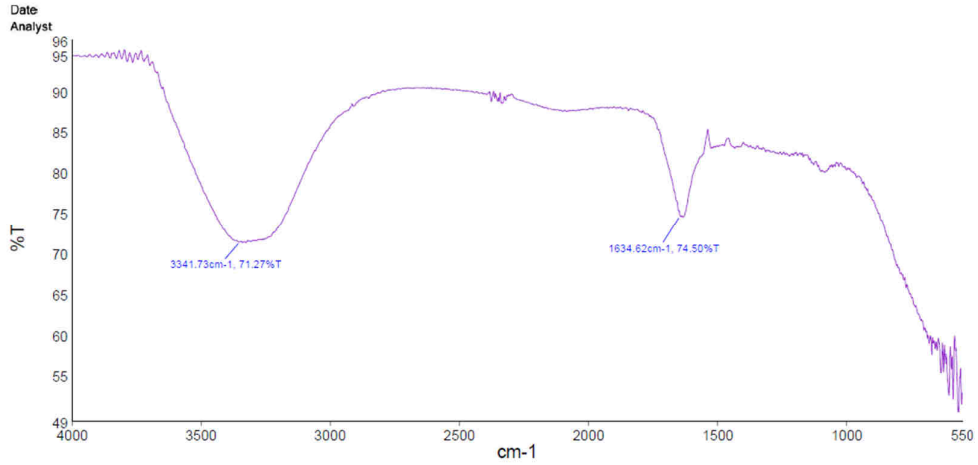


FIG. 17B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

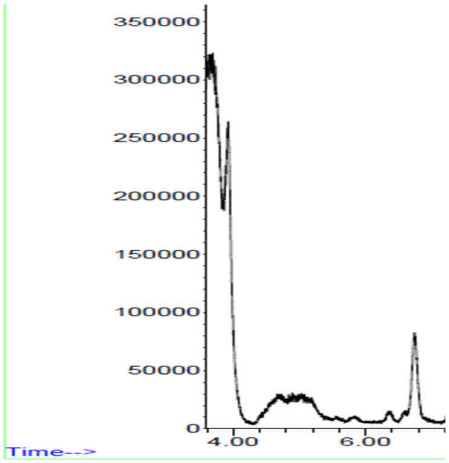


FIG. 17C

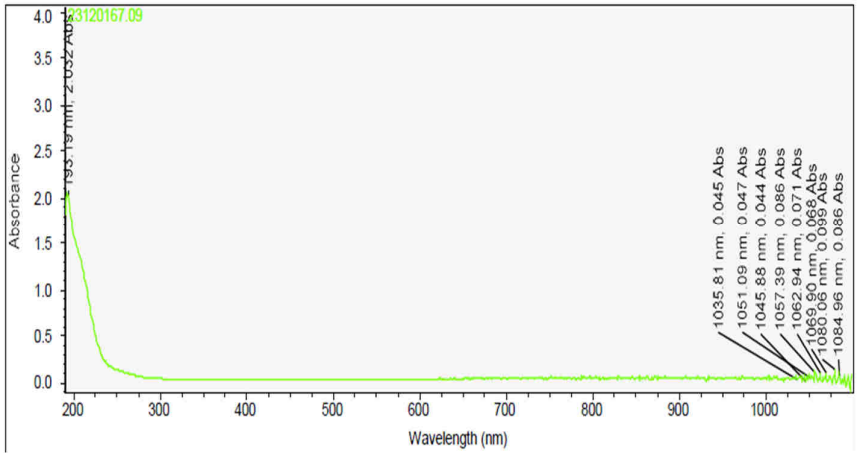


FIG. 18A

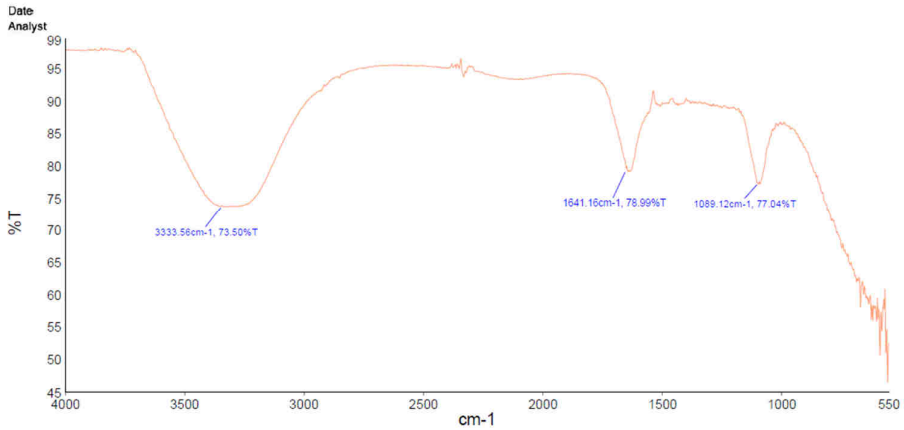


FIG. 18B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

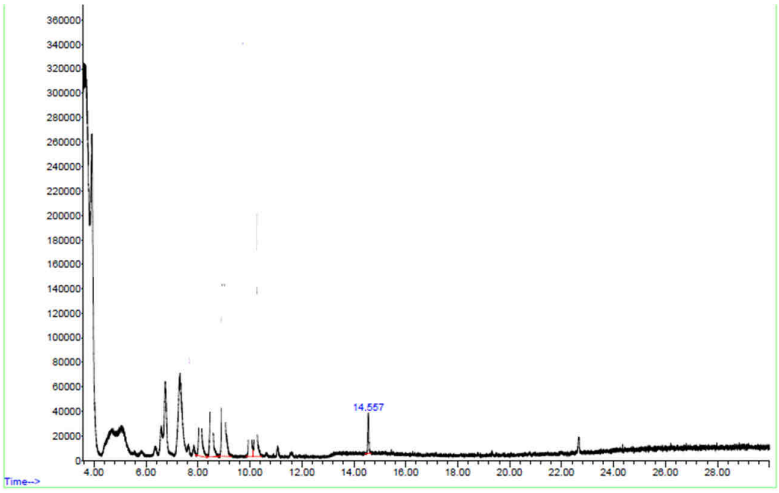


FIG. 18C

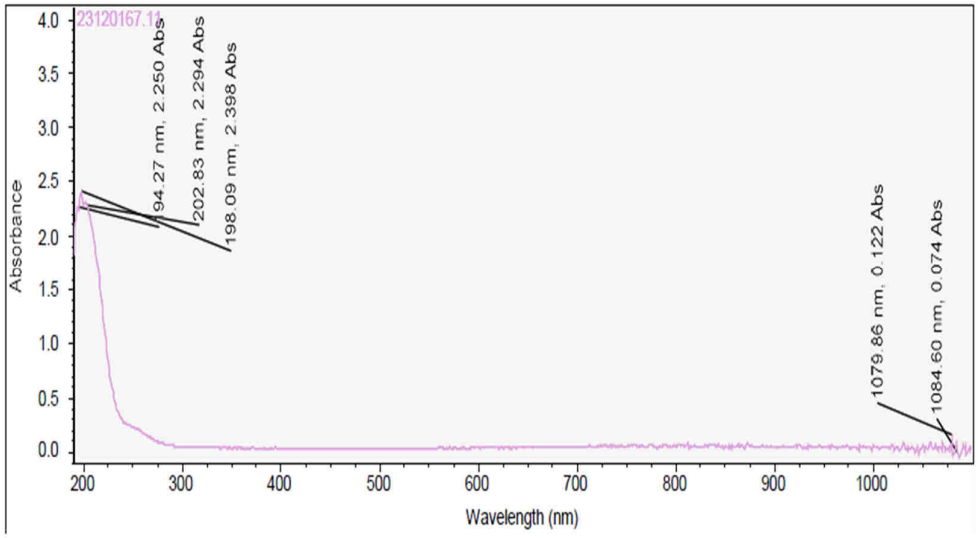


FIG. 19A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

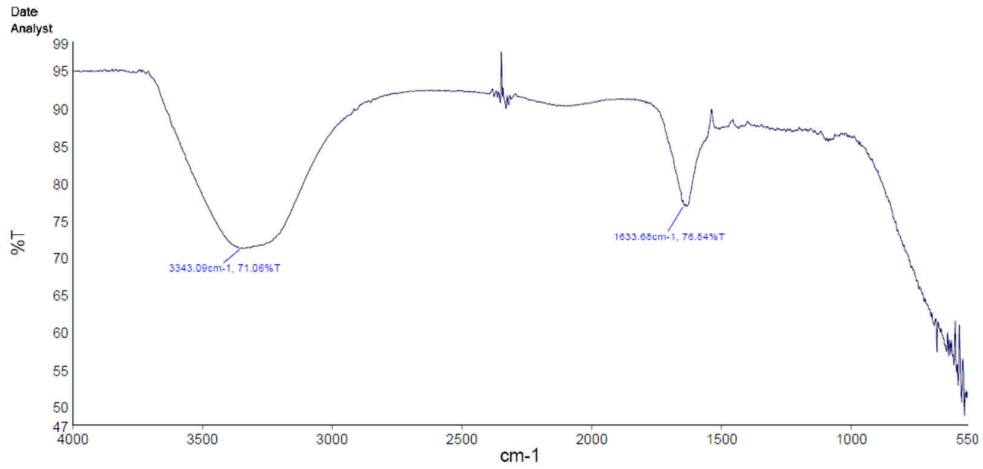


FIG. 19B

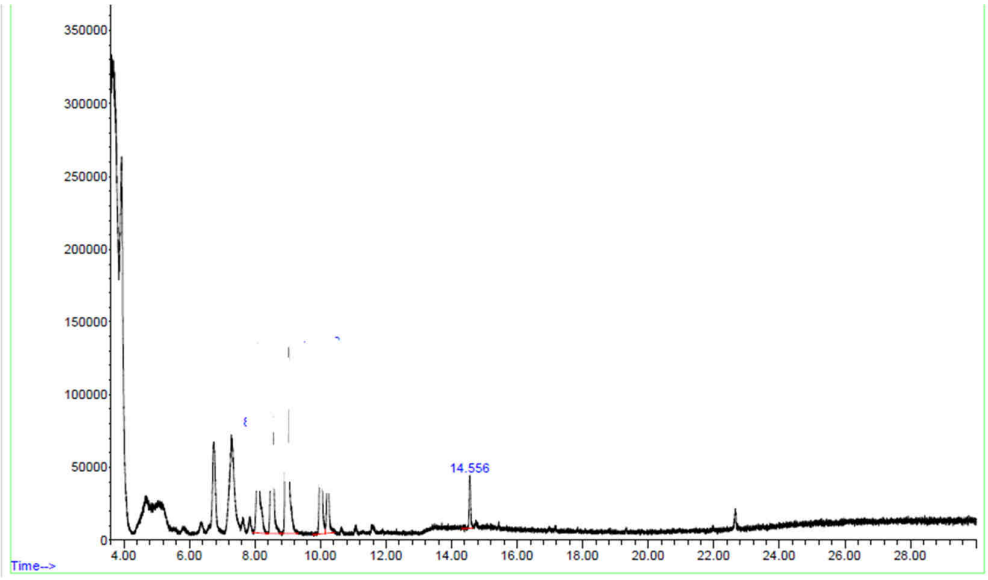


FIG. 19C

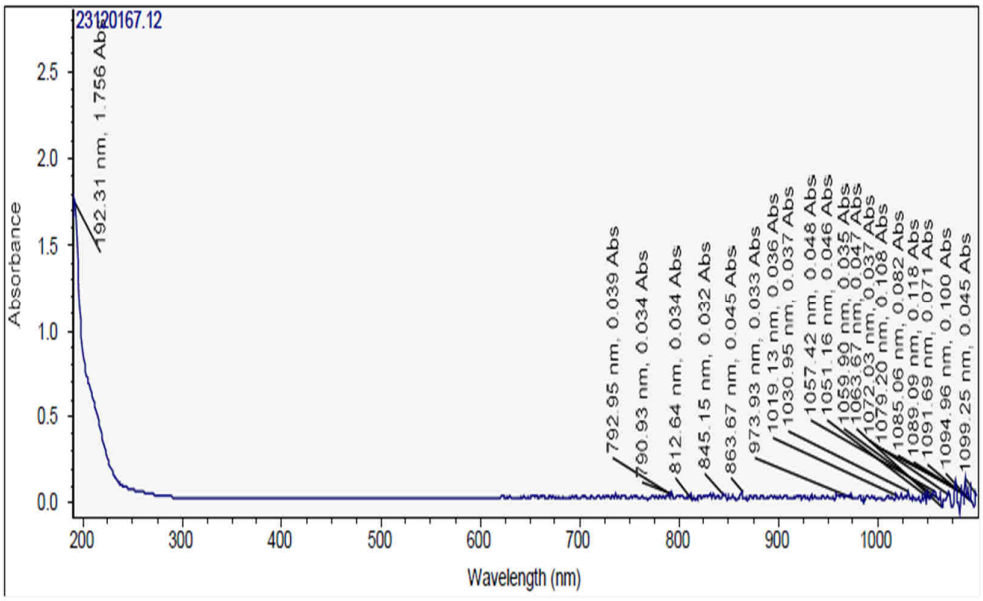


FIG. 20A

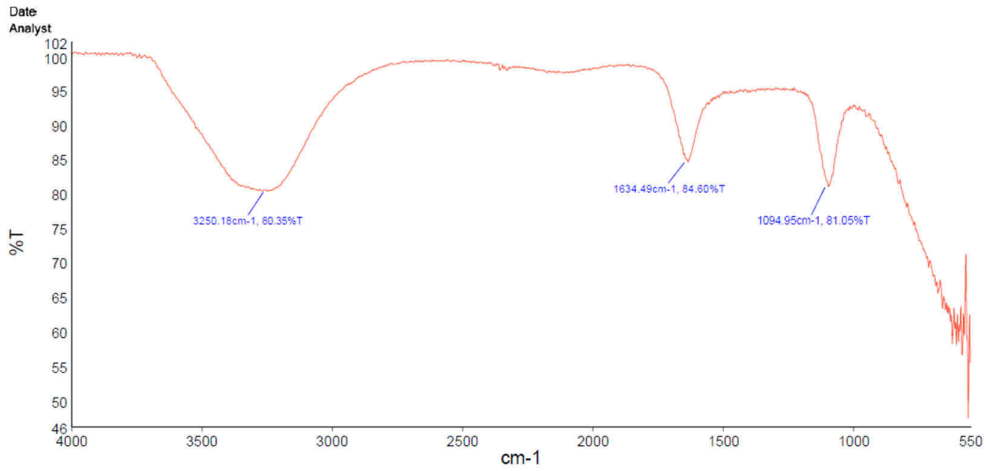


FIG. 20B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

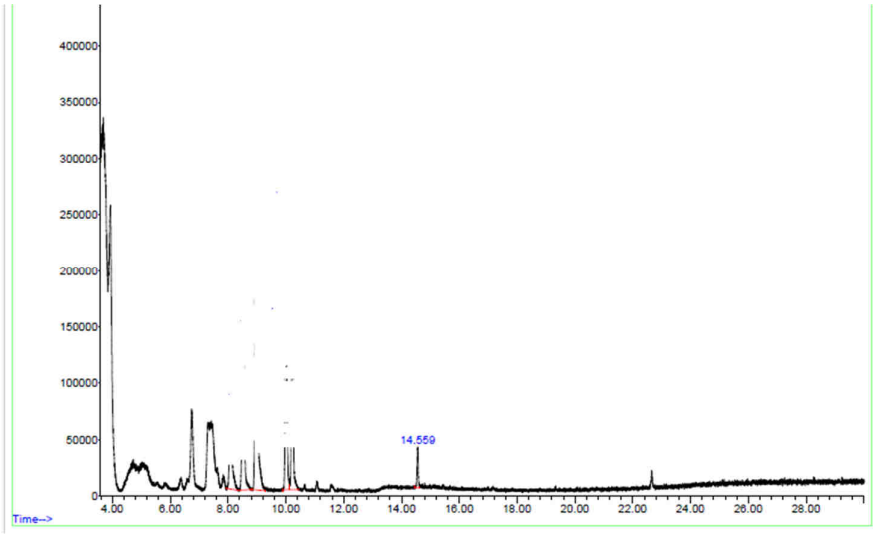


FIG. 20C

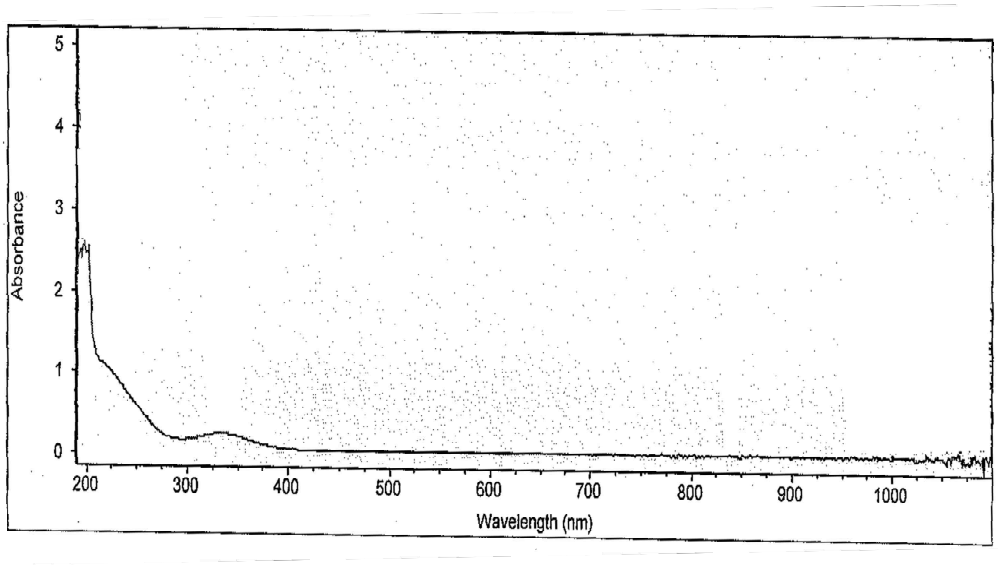


FIG. 21A

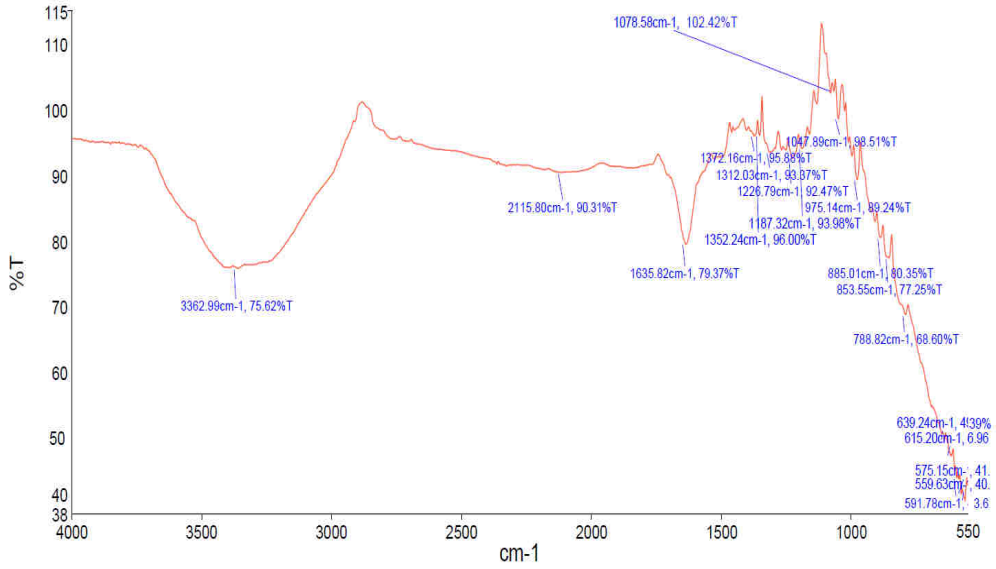


FIG. 21B

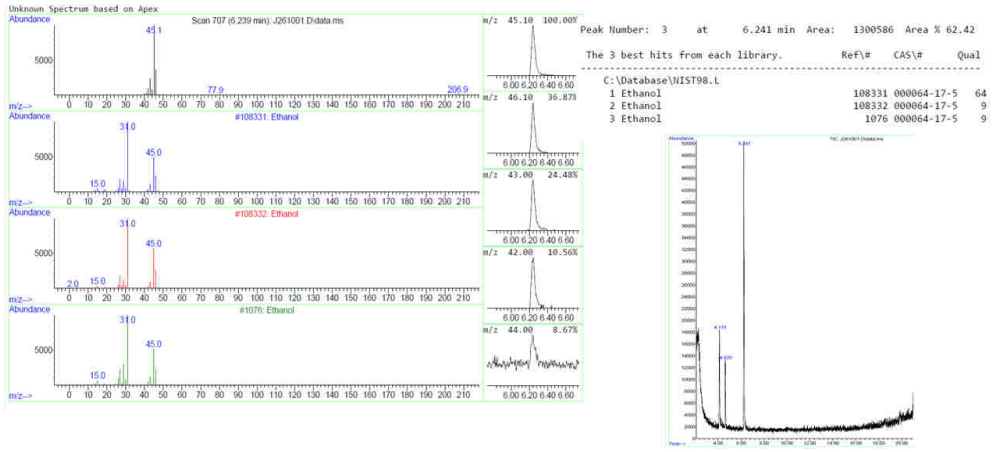


FIG. 21C

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

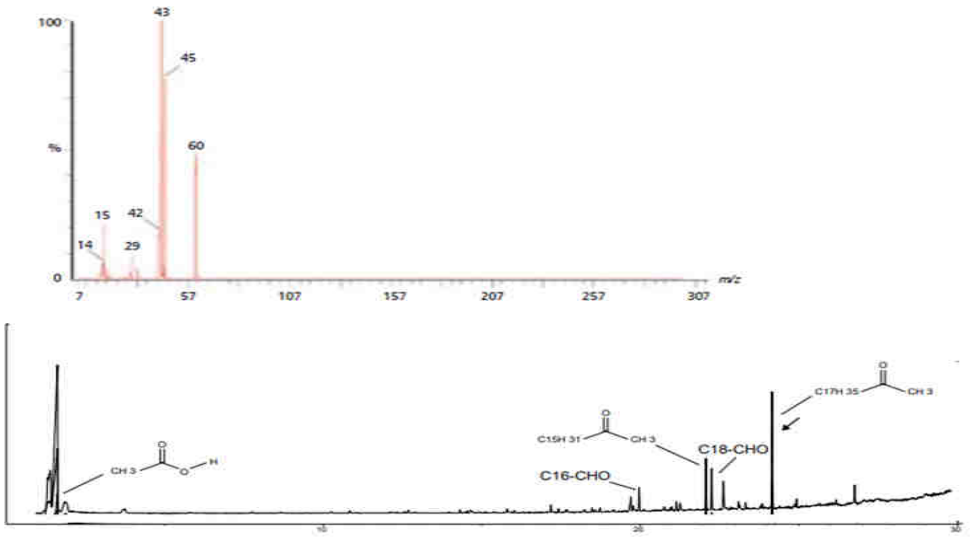


FIG. 21D

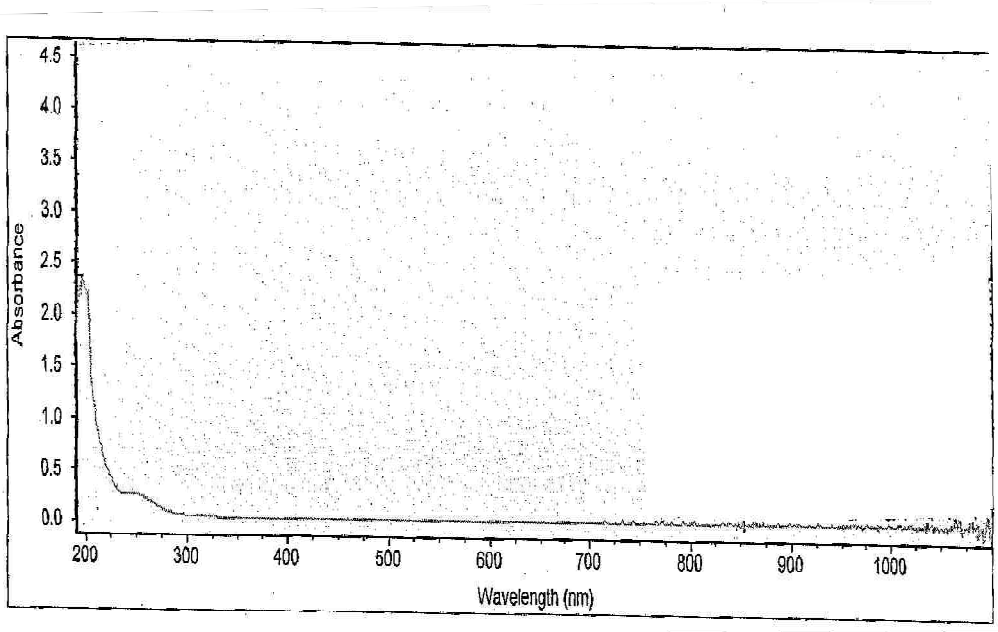


FIG. 21E

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

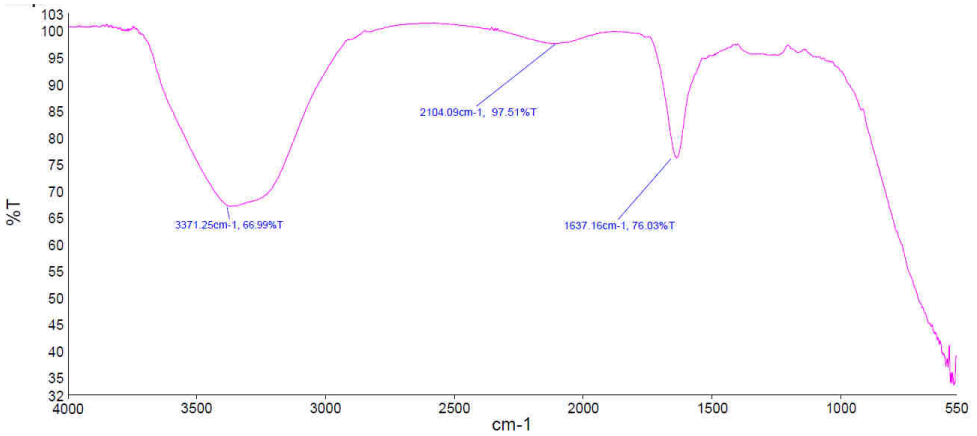


FIG. 21F

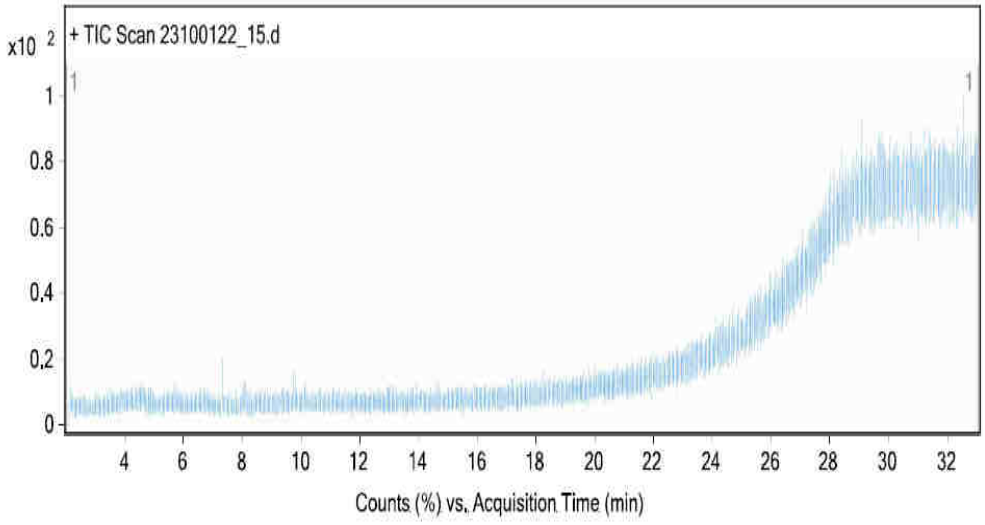


FIG. 21G

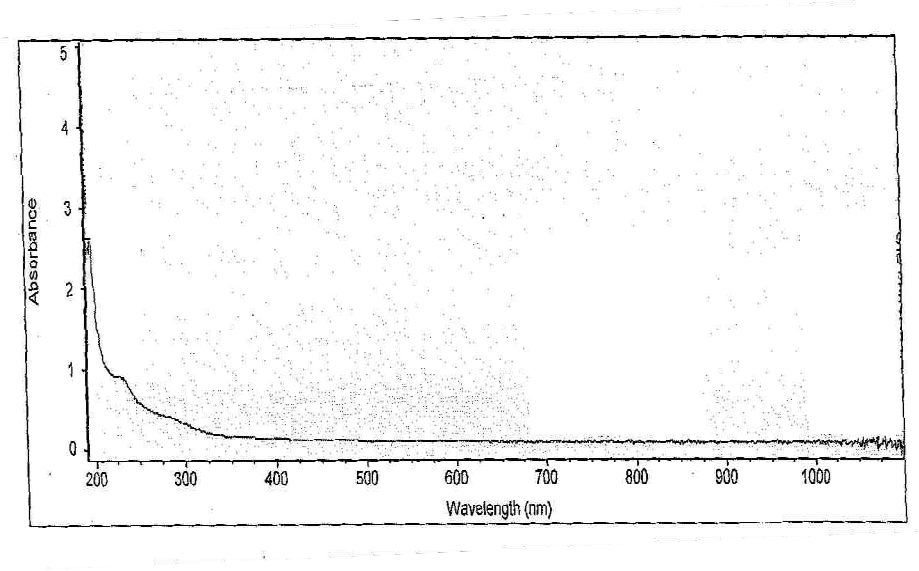


FIG. 22A

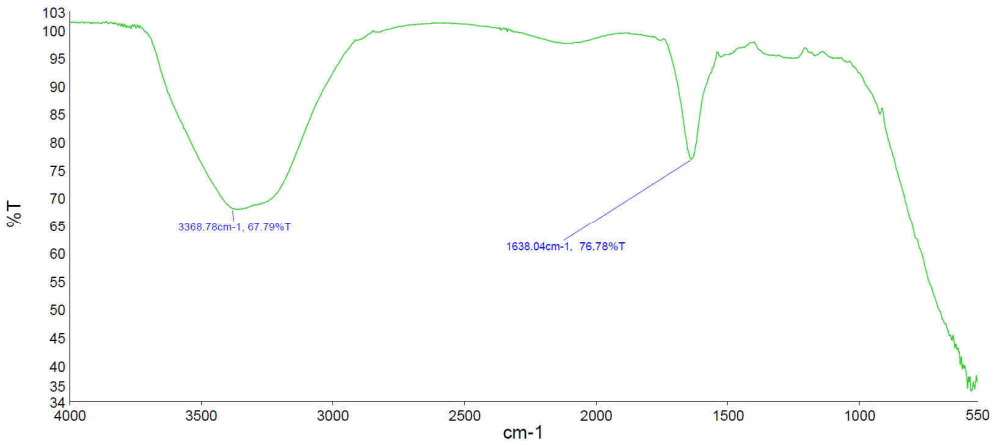


FIG. 22B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

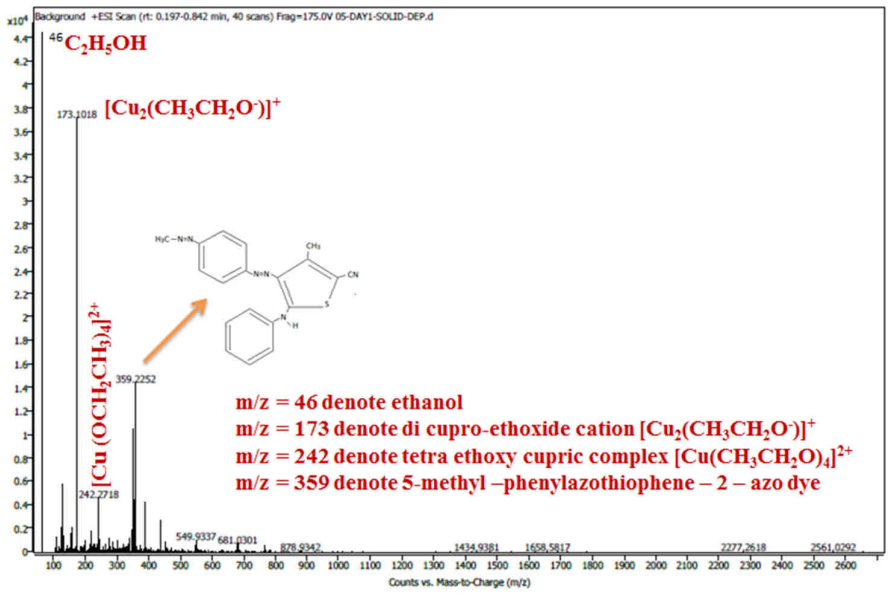


FIG. 22C

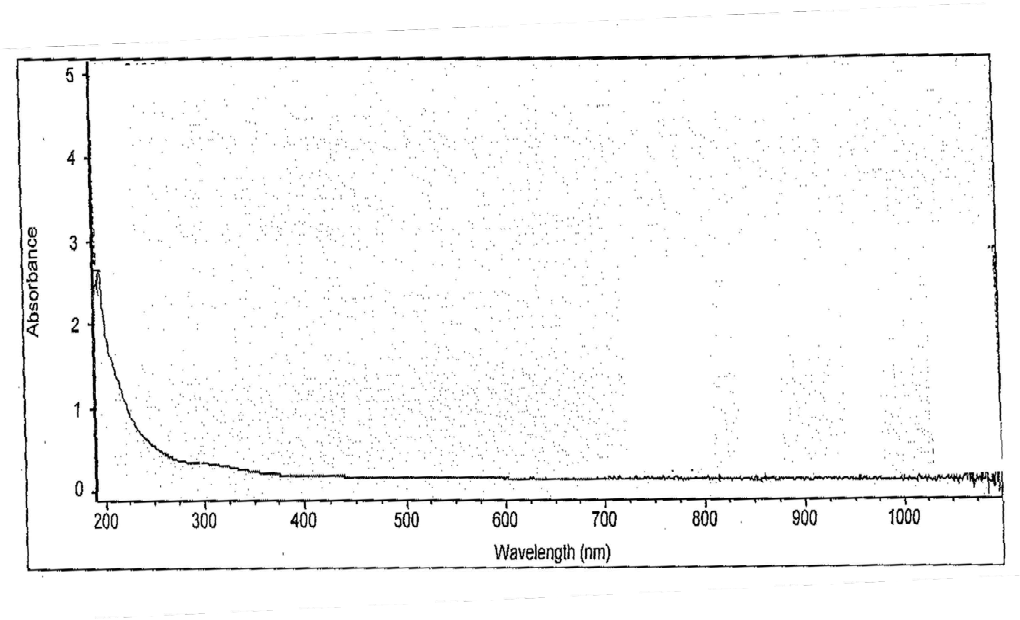


FIG. 23A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

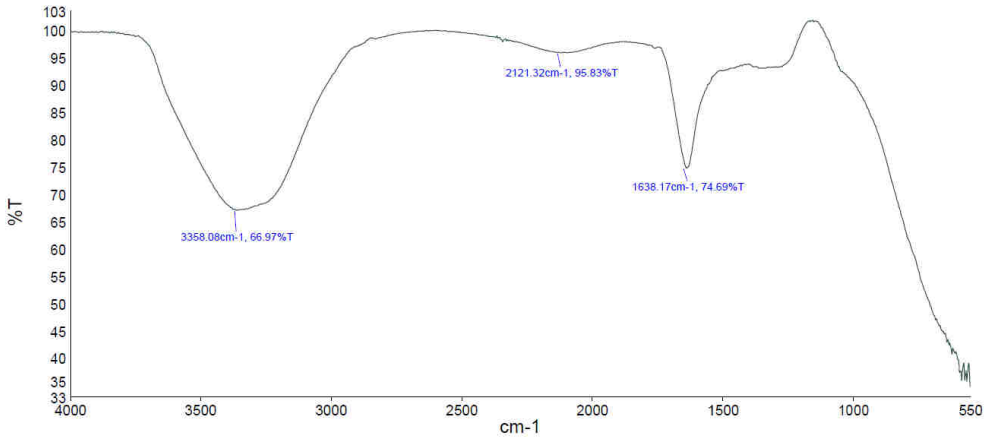


FIG. 23B

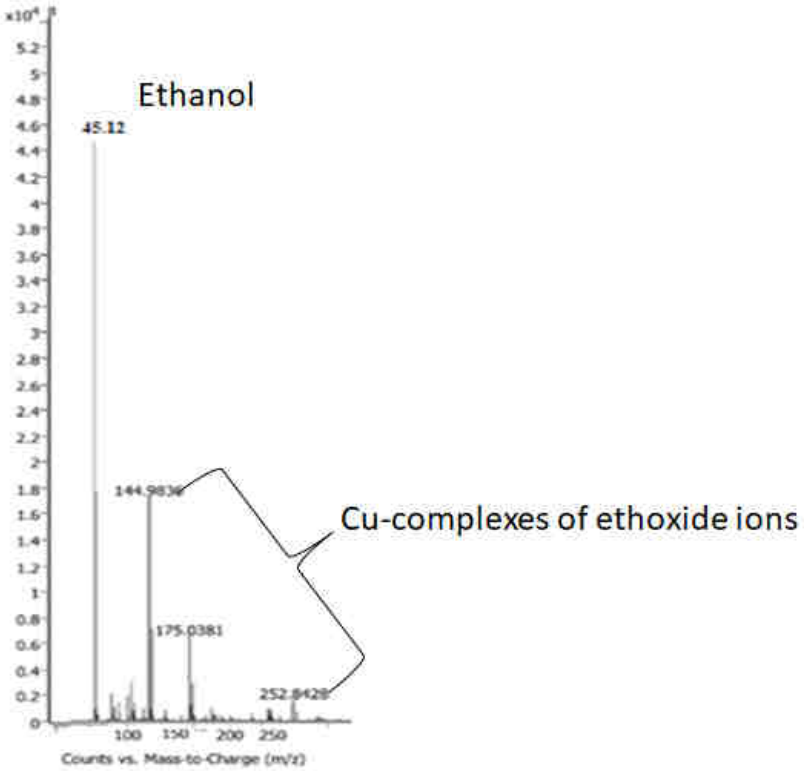


FIG. 23C

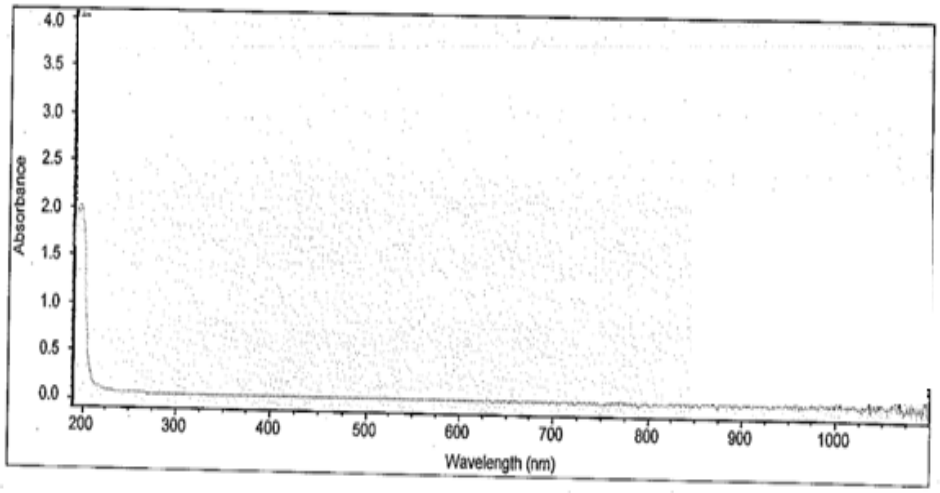


FIG. 24A

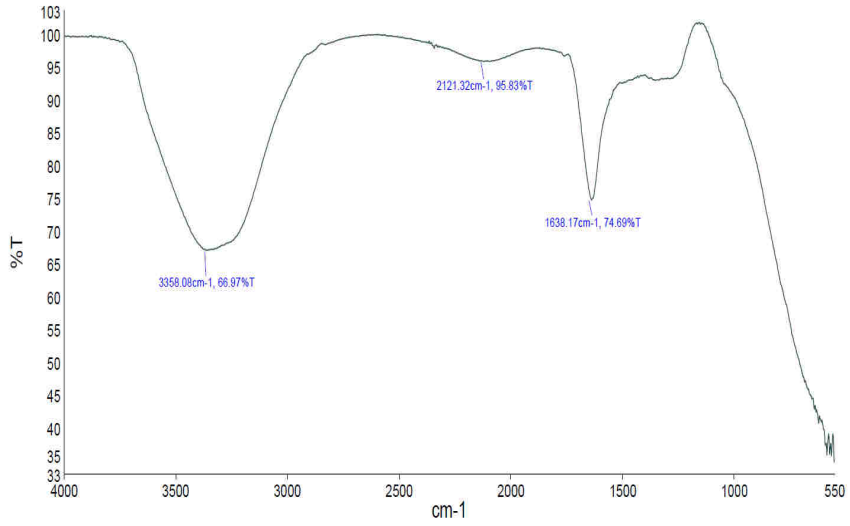


FIG. 24B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

Peak Number: 3 at 6.241 min Area: 1300586 Area % 62.42

The 3 best hits from each library.	Ref\#	CAS\#	Qual
C:\Database\NIST98.L			
1 Ethanol	108331	000064-17-5	64
2 Ethanol	108332	000064-17-5	9
3 Ethanol	1076	000064-17-5	9

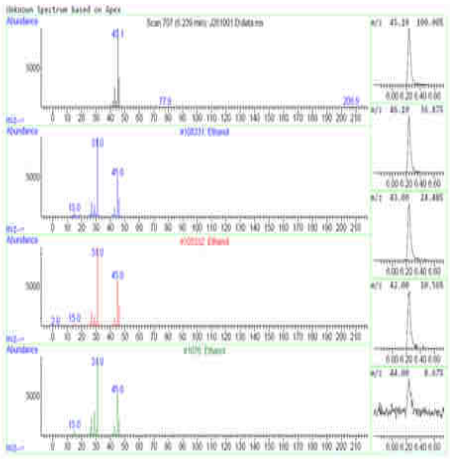


FIG. 24C

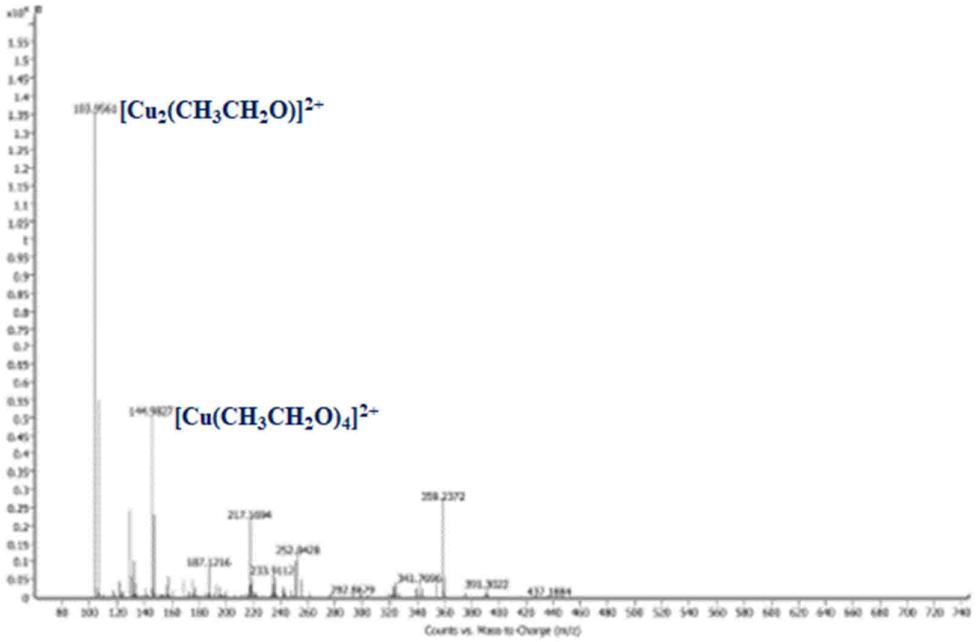


FIG. 24D

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

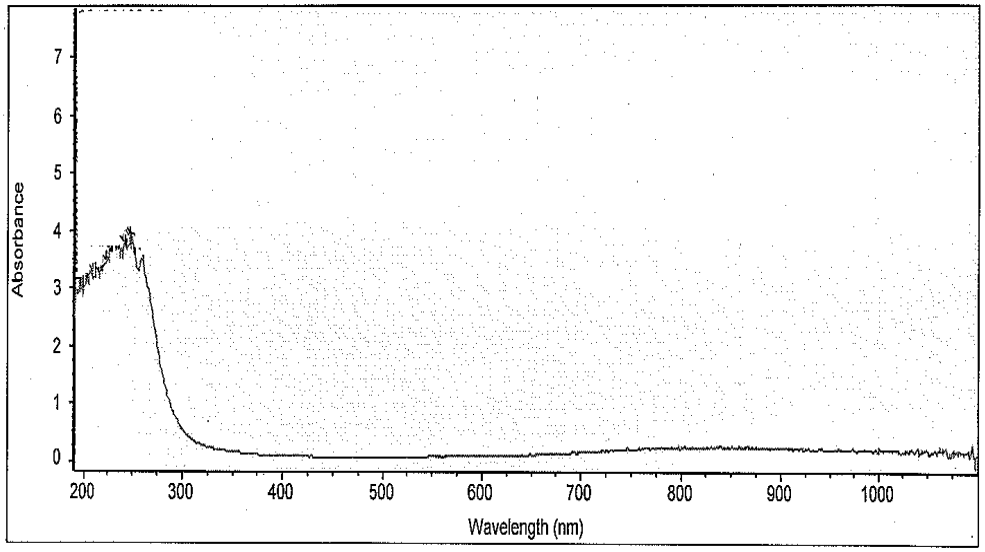


FIG. 25A

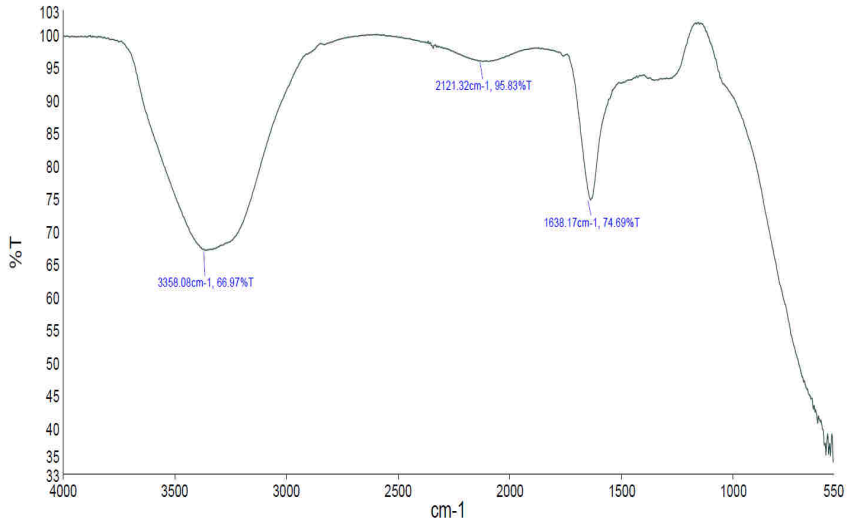


FIG. 25B

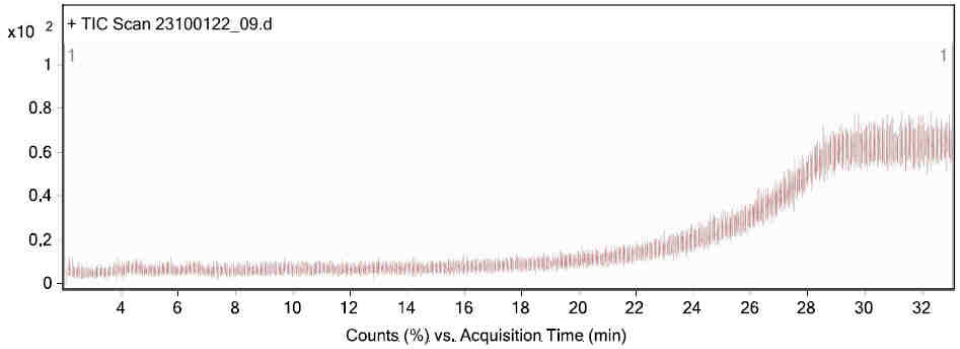


FIG. 25C

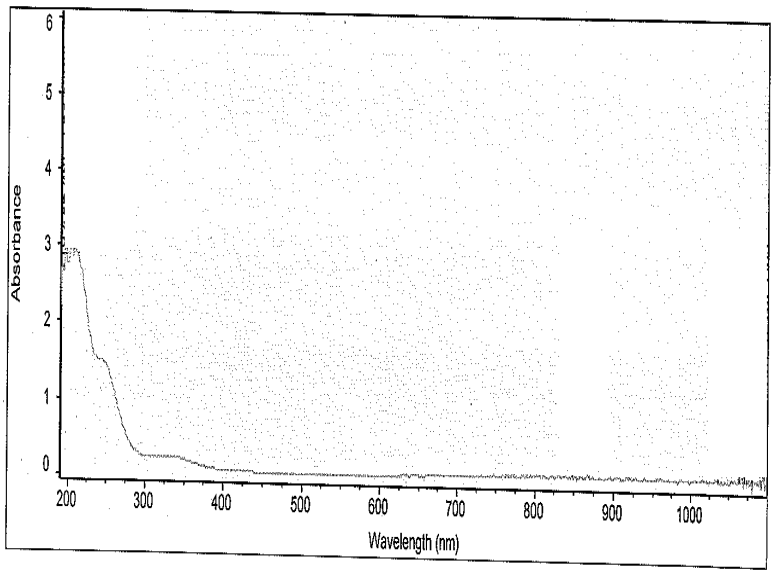


FIG. 26A

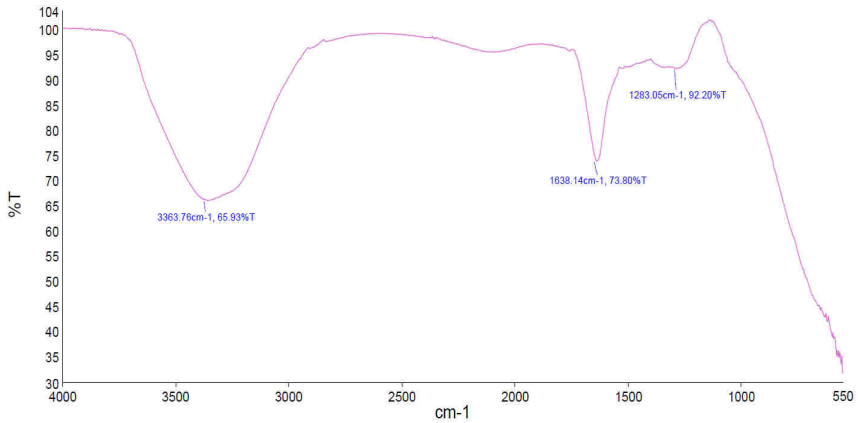


FIG. 26B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

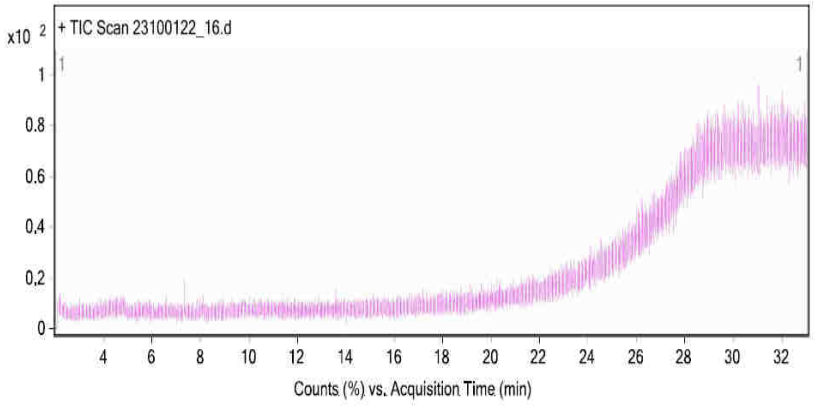


FIG. 26C

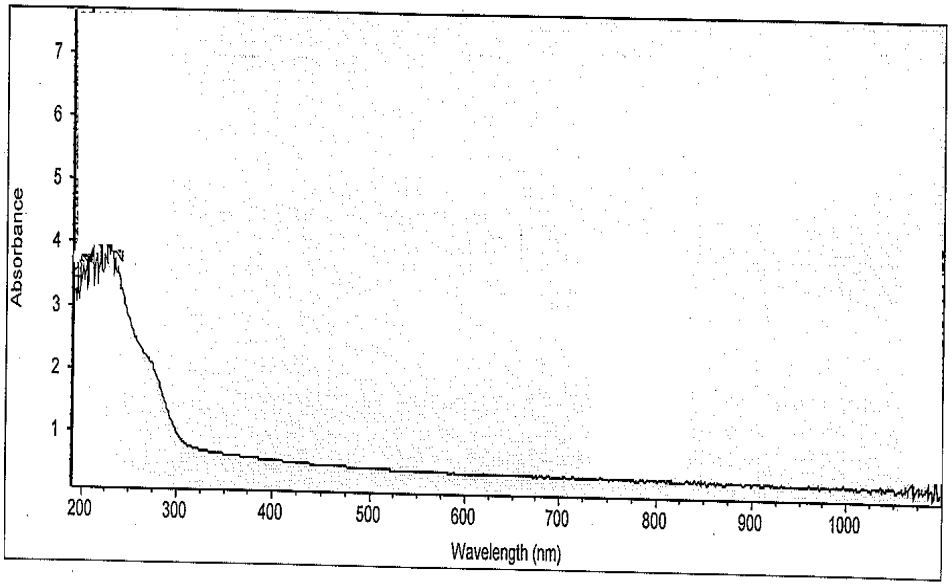


FIG. 27A

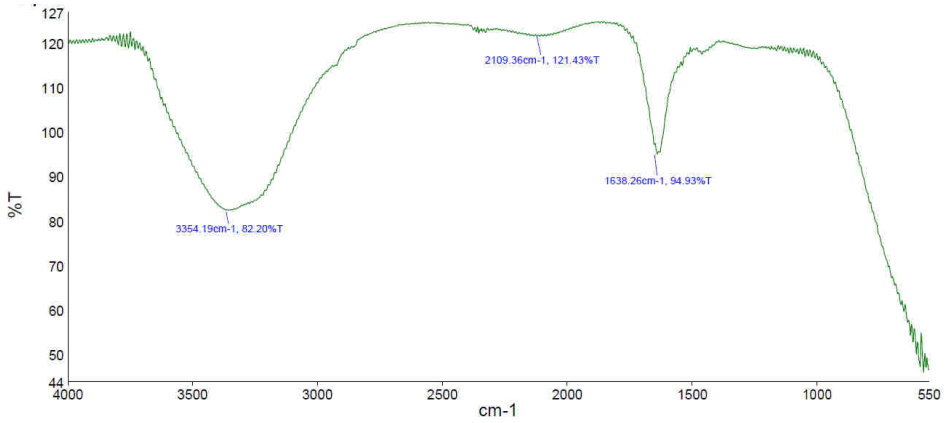


FIG. 27B

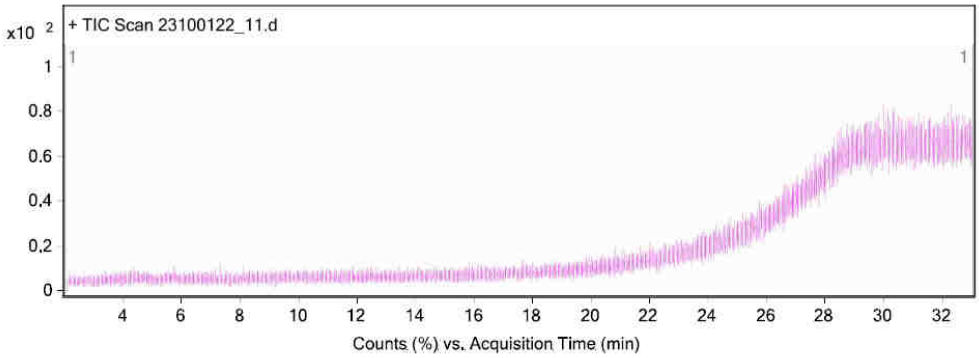
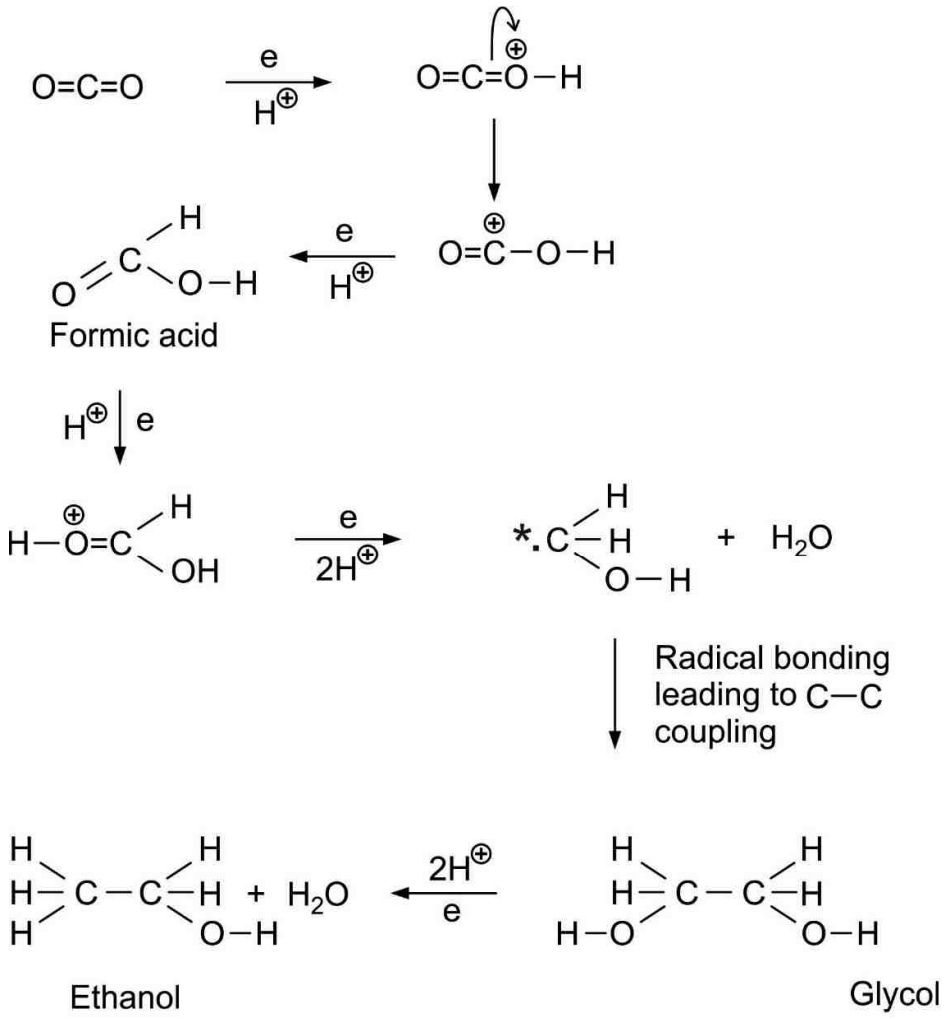


FIG. 27C



Ethanol formation via (i) Formic acid, (ii) Glycol stable intermediates.

FIG. 28

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

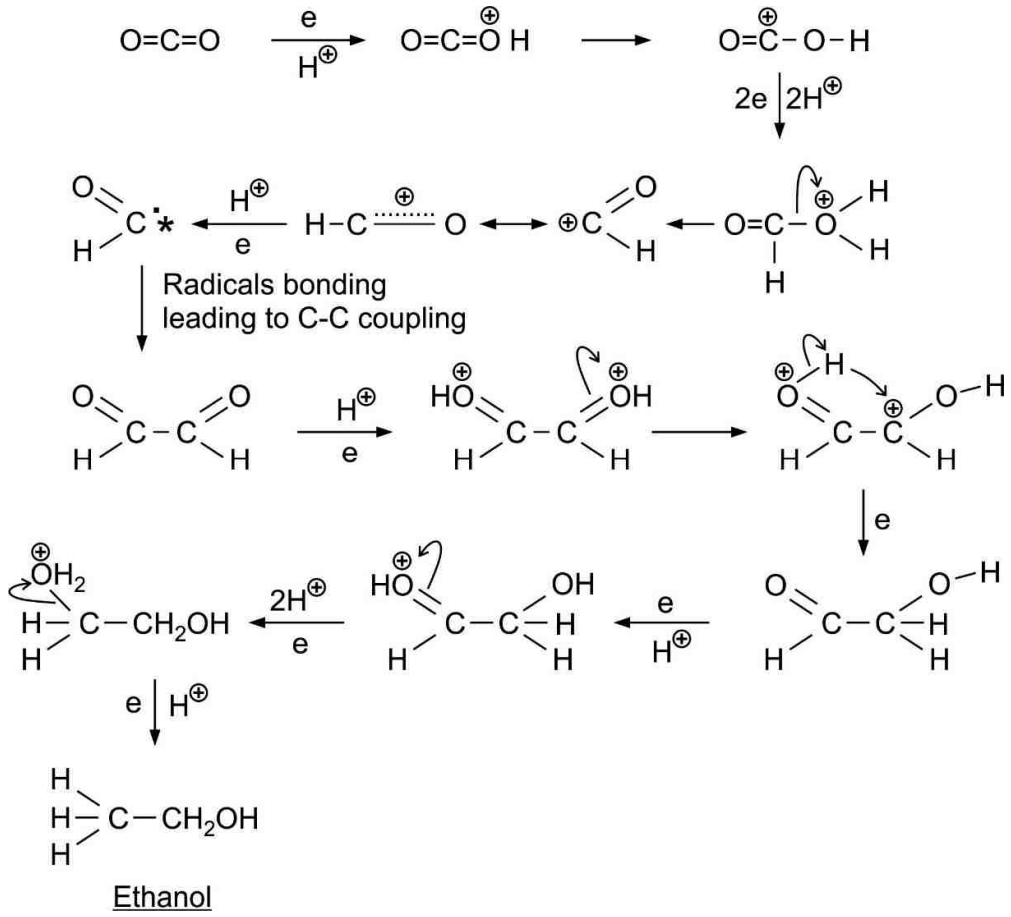


FIG. 29

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

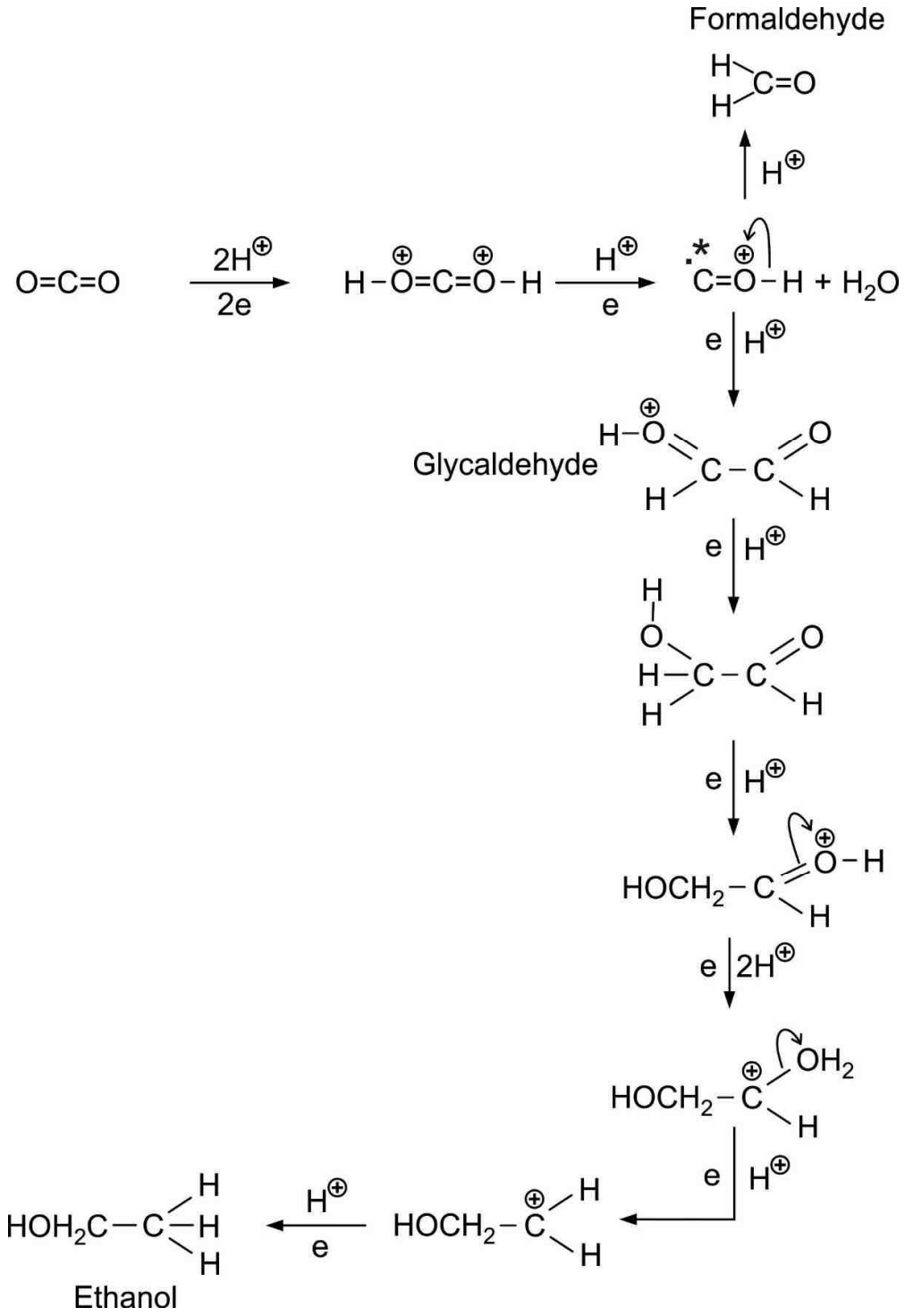


FIG. 30

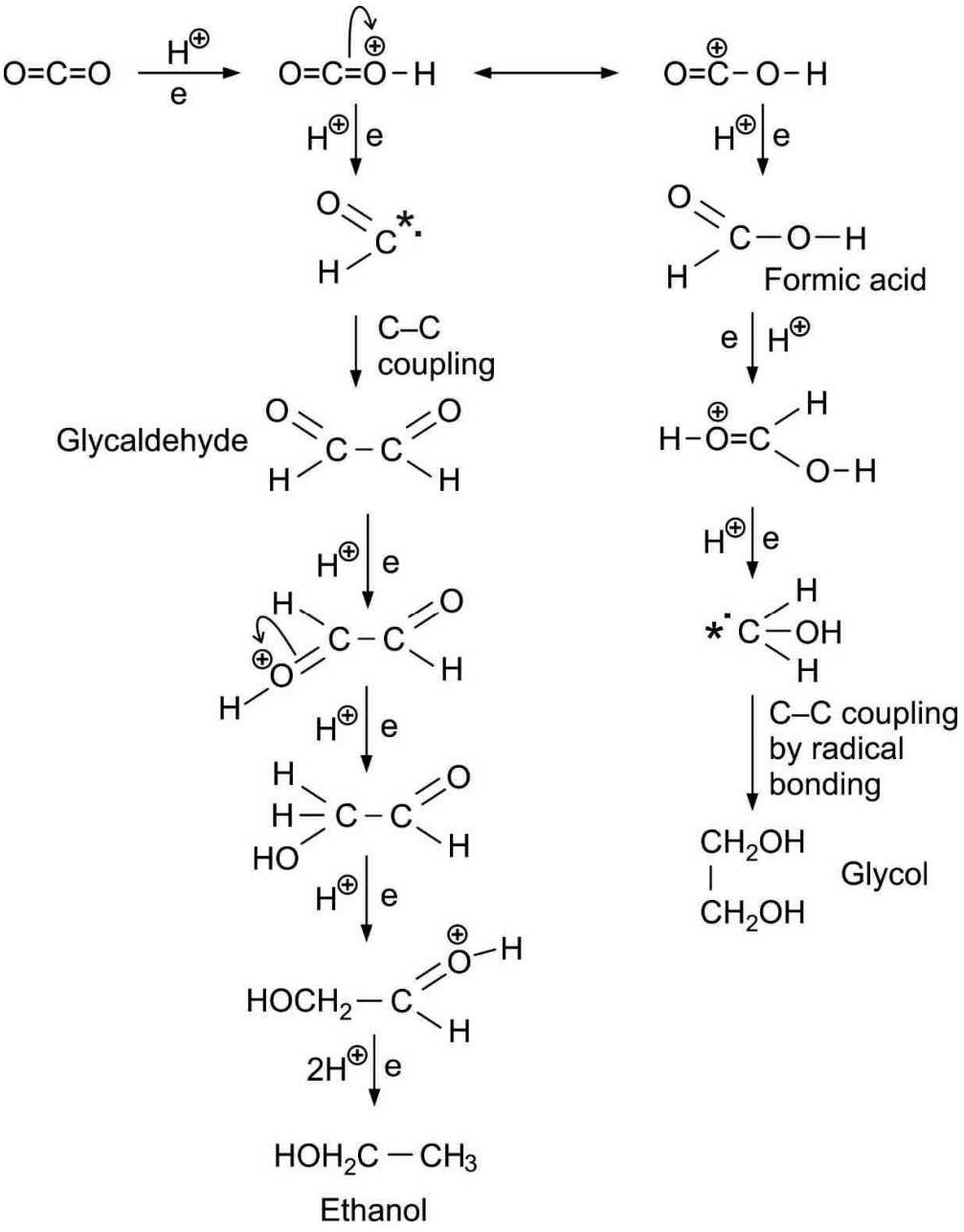


FIG. 31

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

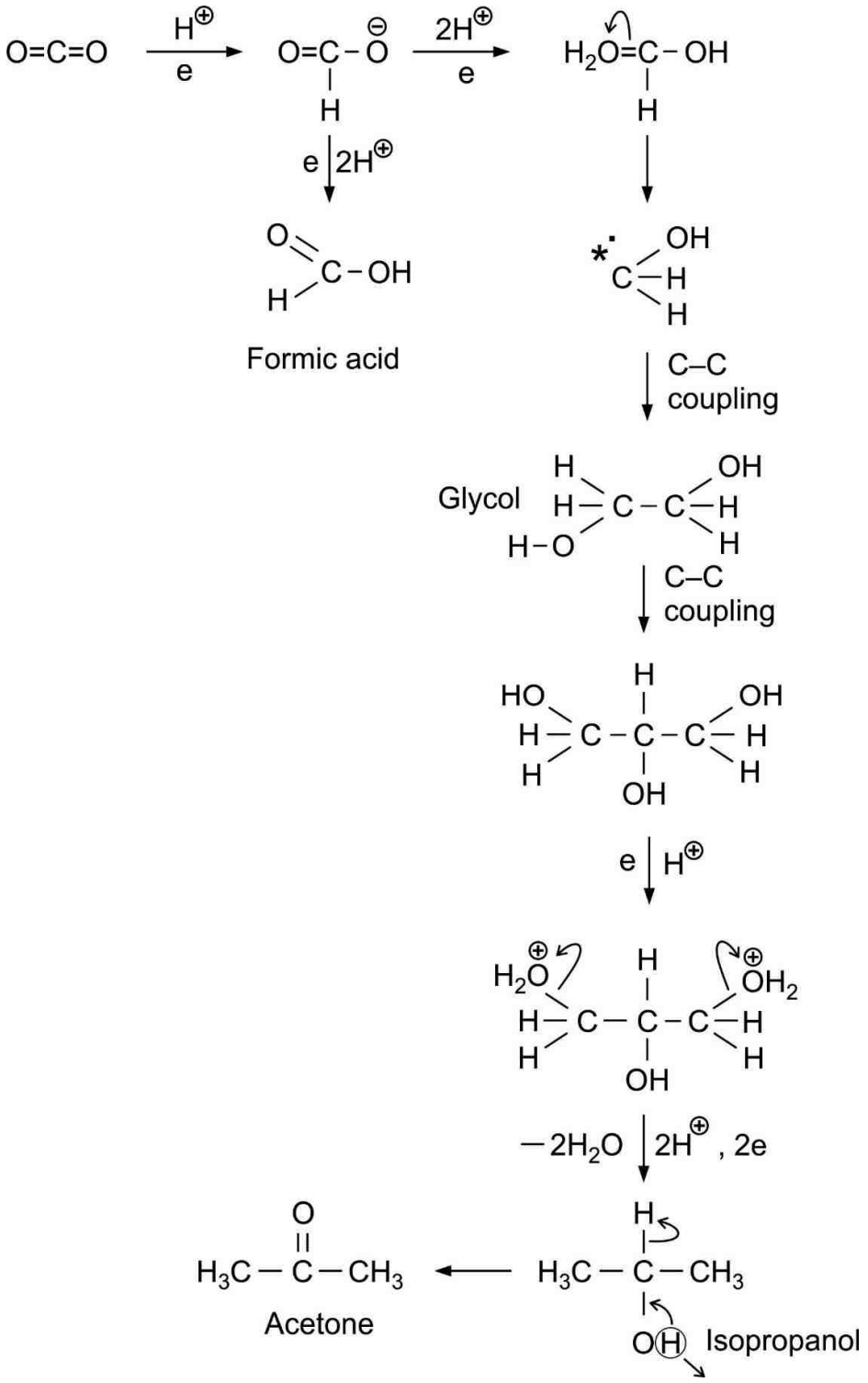
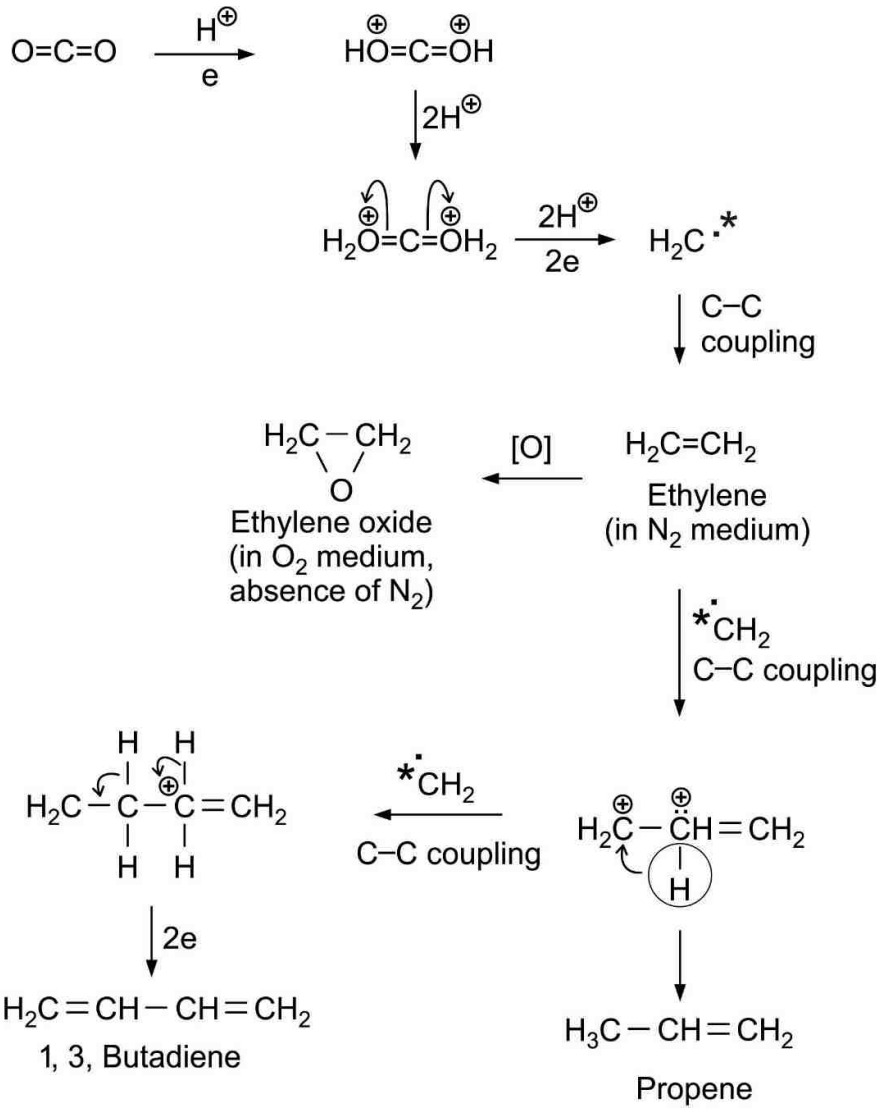


FIG. 32

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)



Unsaturated hydrocarbons are formed in the presence of N_2 atmosphere. If N_2 is the part of the composition of GHG emissions, it acts as inert gas without taking part in the electrochemical reaction, but eliminates oxygen in the medium.

FIG. 33

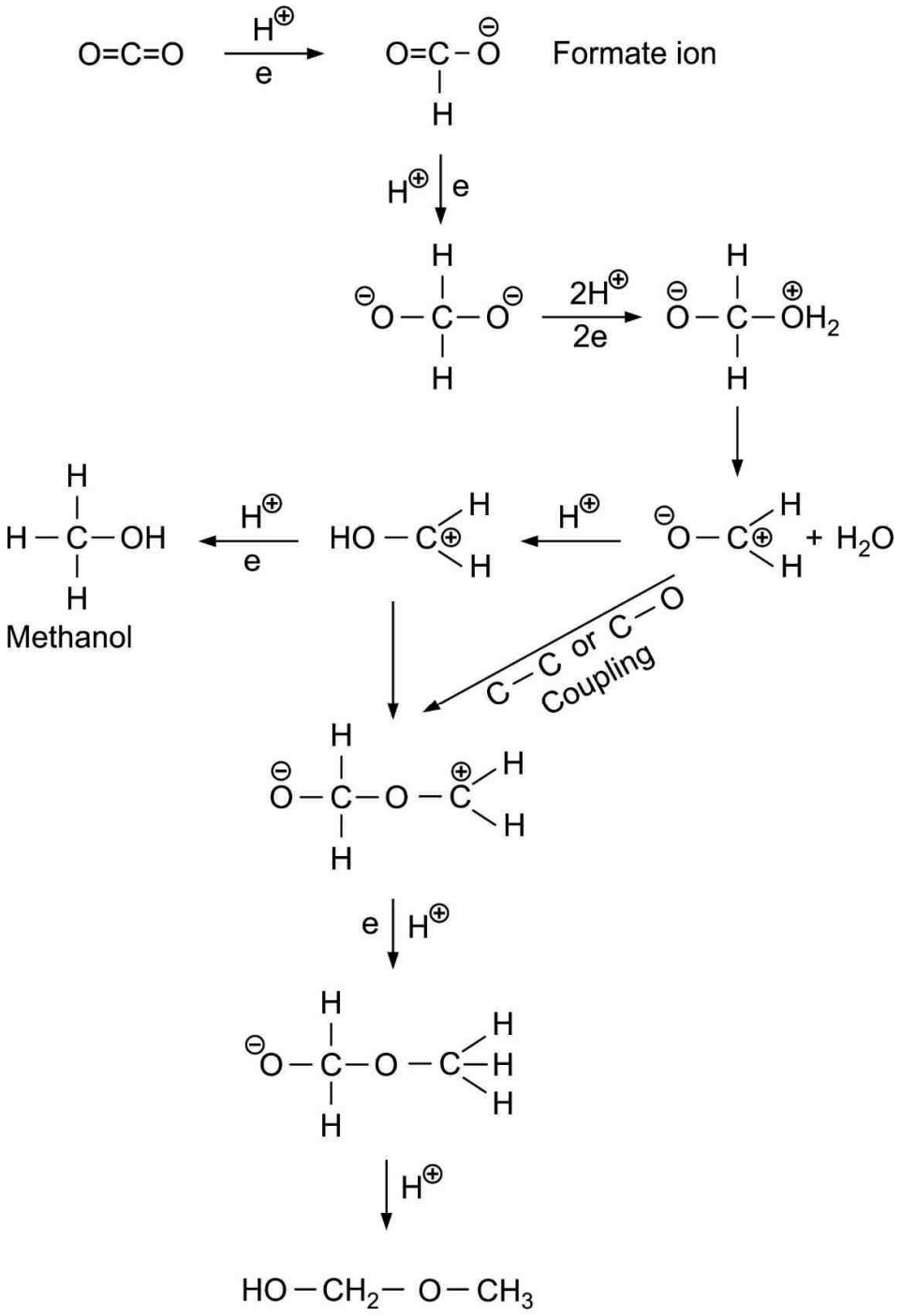


FIG. 34

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

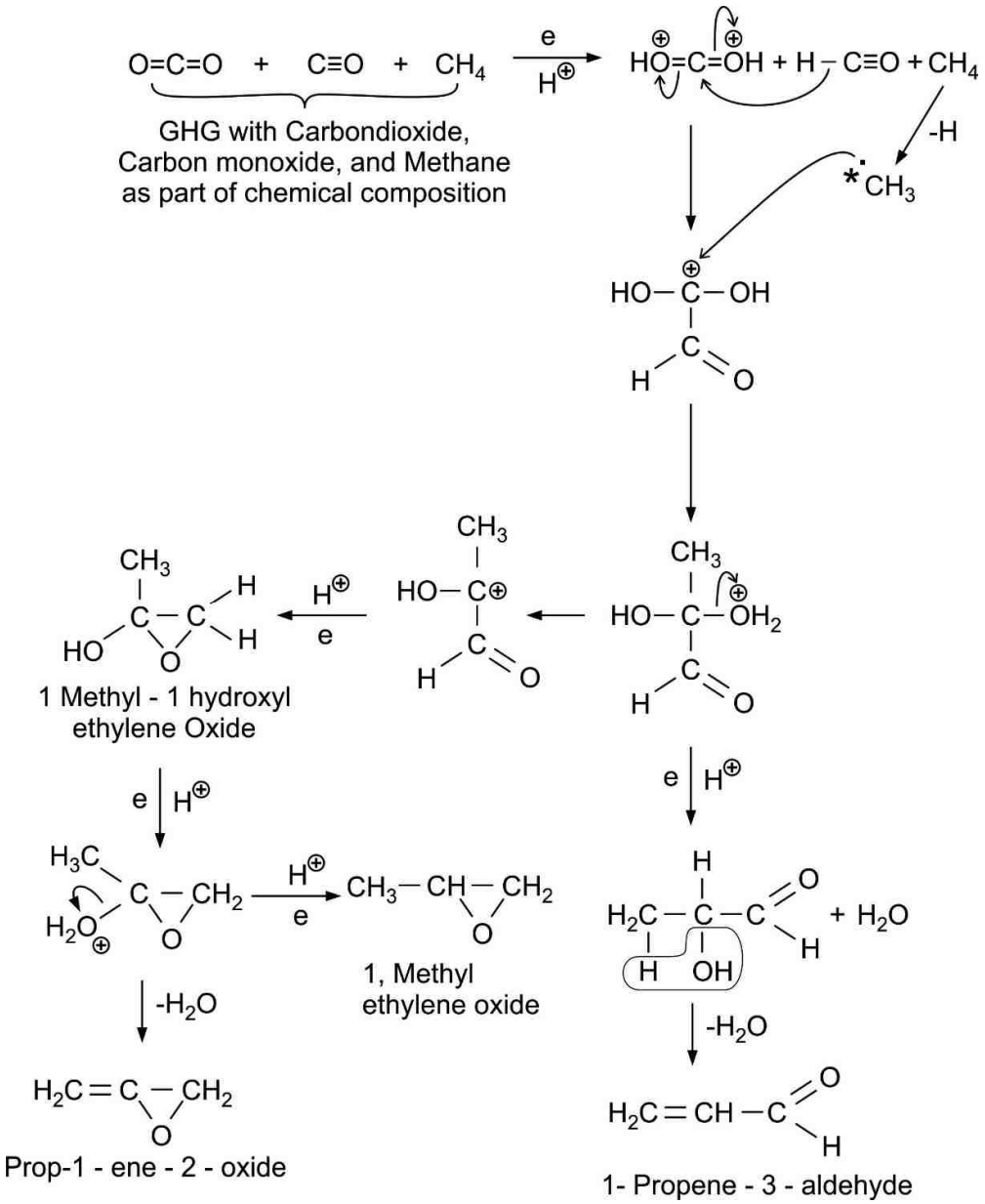

O=C=O + C≡O + CH4
GHG with Carbondioxide, Carbon monoxide, and Methane as part of chemical composition
e
H⊕
HO=C=OH + H – C≡O + CH4
-H
*CH3
HO – C – OH
C
H
O
CH3
HO – C⊕
C
H
O
CH3
HO – C – OH2
C
H
O
H⊕
e
CH3
C – C
H
HO
O
H
1 Methyl - 1 hydroxyl ethylene Oxide
e H⊕
H3C
C – CH2
H2O⊕
O
H⊕
e
CH3 – CH – CH2
O
1, Methyl ethylene oxide
-H2O
H2C = C – CH2
O
Prop-1 - ene - 2 - oxide
e H⊕
H
H2C – C – C
O
H
+ H2O
H OH
-H2O
H2C = CH – C
O
H
1- Propene - 3 - aldehyde

FIG.35

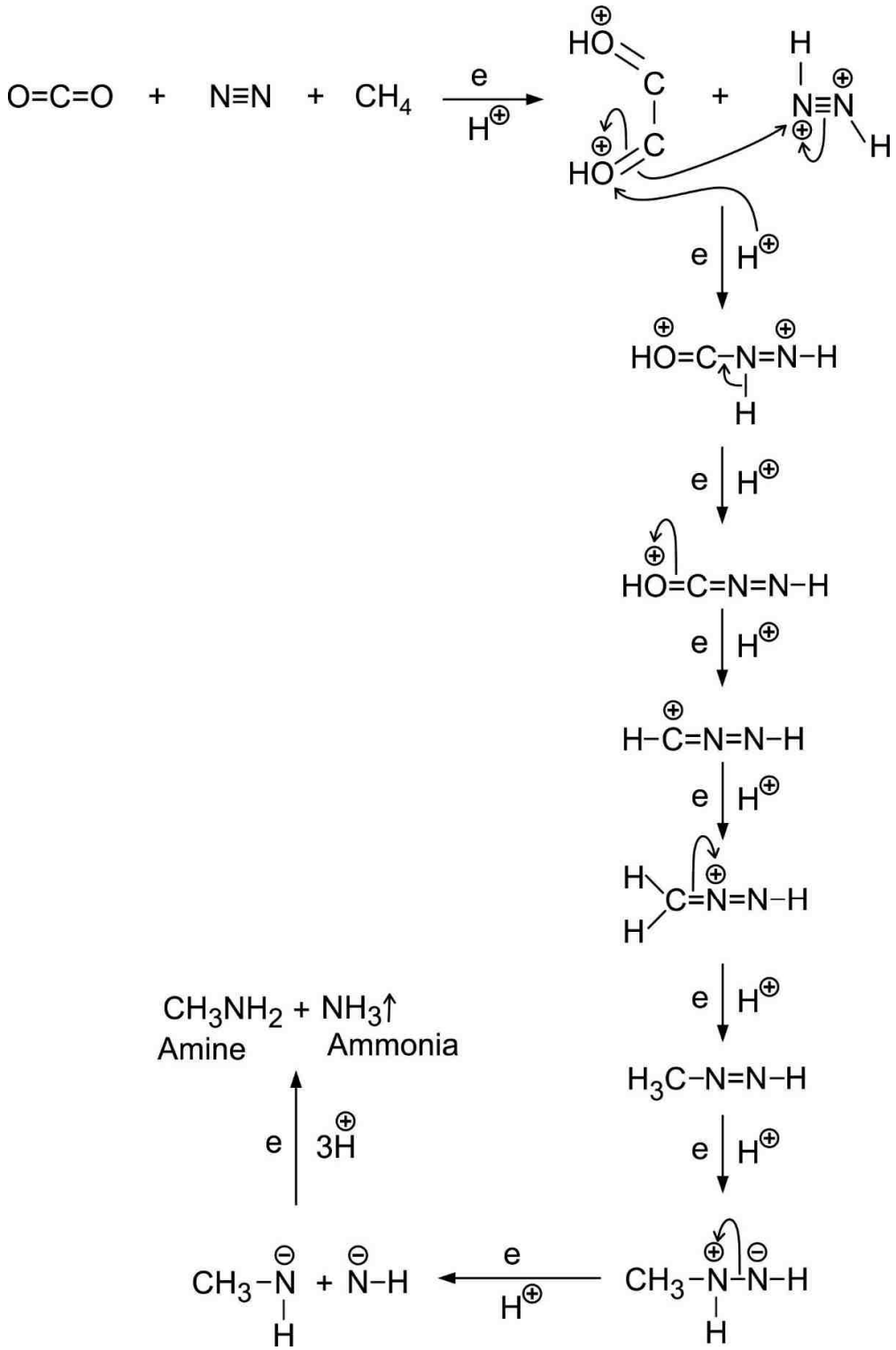


FIG. 36A

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

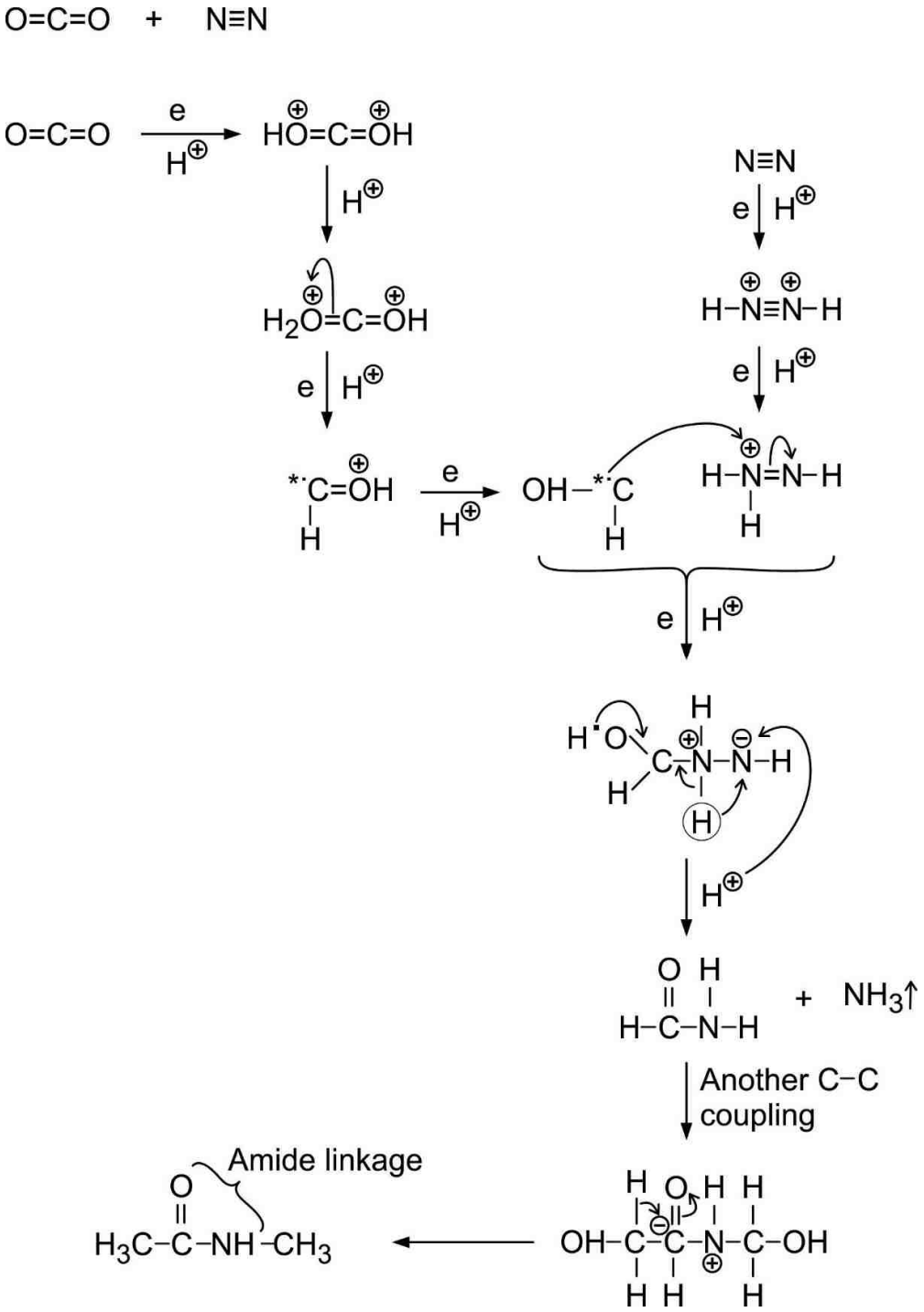


FIG. 36B

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

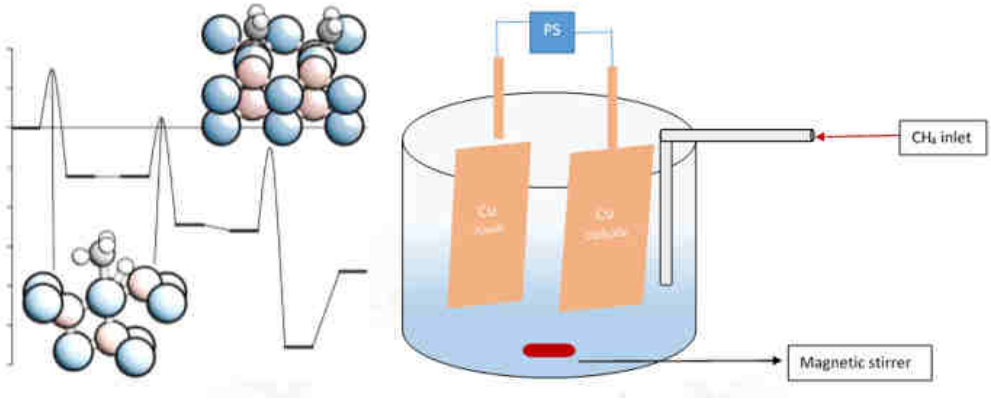


FIG. 1

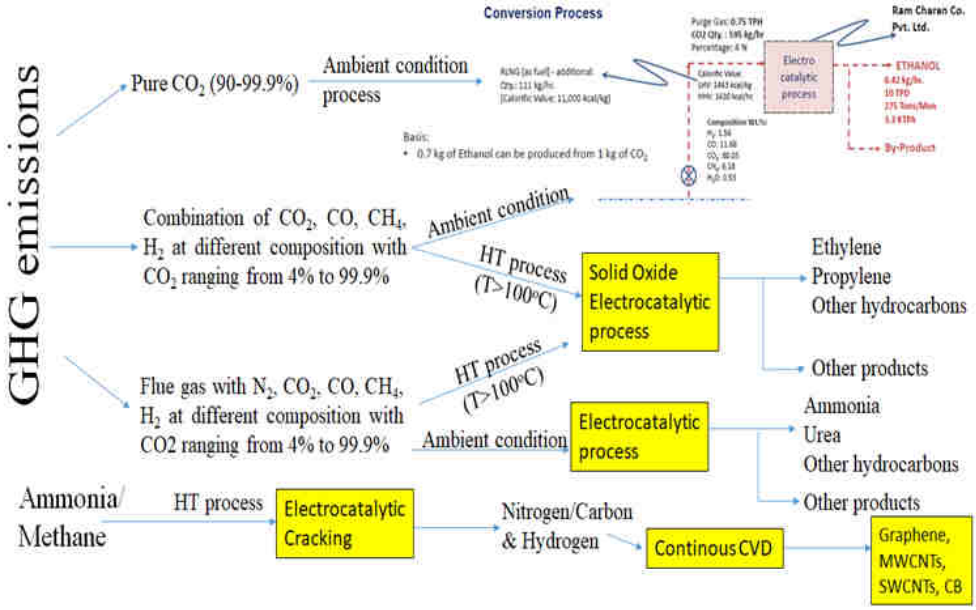


FIG. 2

Tigmakar Tapan Kumar Brahma (IN/PA 3027)
Of ExiLyze Intellectual Services (Agent for the Applicants)

FORM 2

THE PATENTS ACT 1970

(39 OF 1970)

and

The Patents Rules, 2003

COMPLETE SPECIFICATION

[See Section 10 and Rule 13]

TITLE OF THE INVENTION

"ELECTROCATALYTIC REACTOR AND METHOD FOR ELECTROCATALYTIC REDUCTION OF GREEN-HOUSE GAS (GHG) EMISSIONS INTO USEFUL CHEMICALS"

APPLICANT(S):

Name	**Nationality**	**Address**
PALICHA, Kaushik	Indian	505, Fifth Floor Delta Wing, Raheja Towers, Anna Salai, Chennai, Tamil Nadu - 600002
SESHADRI, Harinipriya	Indian	505, Fifth Floor Delta Wing, Raheja Towers, Anna Salai, Chennai, Tamil Nadu - 600002

The following specification particularly describes the invention and the manner in which it is to be performed.

CROSS REFERENCE TO RELATED APPLICATIONS

The present application is based upon and claims priority to India provisional patent application number 202341066700 filed on October 05, 2023, titled "METHOD OF ELECTROCATALYTIC REDUCTION OF GREEN-HOUSE GAS (GHG) EMISSIONS", the entire contents of which is herein incorporated by reference.

FIELD:

The present disclosure relates to conversion of green-house gas (GHG) emissions into value added products (VAPs), more particularly relates to electrocatalytic C-C coupling and C-O coupling reduction of green-house gas (GHG) emissions into VAPs.

BACKGROUND:

Gases that trap heat in the atmosphere are called greenhouse gases (GHG). During the daytime, the sun warms the earth's surface by shining through the atmosphere, and at night, the earth's surface cools, releasing the heat back into the air. But some of the heat is trapped by the greenhouse gases in the atmosphere. That's what keeps the earth's temperature at an average 14˚C (57˚F). The gases act like the glass walls of a greenhouse – hence the name, greenhouse gases. Without this greenhouse effect, temperatures would drop to as low as -18˚C (-0.4˚F); too cold to sustain life on earth. But human activities are changing earth's natural greenhouse effect with a dramatic increase in the release of greenhouse gases. Scientists agree greenhouse gases are the cause of global warming and climate change. Since the Industrial Revolution, humans have been releasing larger quantities of greenhouse gases into the atmosphere. In the past century that amount has increased dramatically, with the knock-on effect of global warming. Global temperatures have accelerated in the past 30 years and are now the highest since records began. Greenhouse gases include carbon dioxide, methane, ozone, nitrous oxide, chlorofluorocarbons, and water vapor.

The urgency of the climate crisis and the increase in natural gas production accelerate the need for an efficient way to convert GHG such as methane into

liquid fuels and other commodity chemicals.

Methane is normally sourced from feedstocks from natural gas, coal bed, methane hydrate due to their less cost and abundance. As conversion of GHG emissions such as methane to ethylene or any other value-added products is a high temperature operated process i.e. about 700-850°C, a direct conversion of methane without forming syngas as intermediate makes the process more economical and environmentally benign. Therefore, design and development of process and technology for selective conversion of methane and GHG emissions to high-value-added chemicals under room temperature and ambient conditions becomes a challenging task. It had been demonstrated at R&D scale that metal complexes of Hg, Pt, Pd, Au, Ru, Rh, and V acts as catalyst for selective oxidation of GHG emissions comprising of methane, CO_2, CO, H_2, N_2, H_2S, SOx, NOx, etc in a strong acid medium, such as oleum, trifluoroacetic acid, hydrochloric acid, or hydrobromic acid at 80°C–500°C. Other methods involved molecule-sieve-based catalysts, such as ZSM-518–21 and MOR, to convert GHG emissions with methane to methanol at much lower temperatures like 50°C–225°C. But all the said methods or catalysts converted methane and/or CO_2 with low yield. Thus, the major bottleneck involves (i) the direct room-temperature conversion of GHG emissions without other energy input and (ii) replacement of precious-metal catalysts.

IN202341047481 discloses a method of electrochemical conversion of carbon dioxide into value-added products, wherein the method utilises an electrochemical reactor having metallic Copper (Cu) or Cu-alloy symmetric electrodes (cathode and anode).

US9816035B2 discloses a process and system for producing a synthetic hydrocarbon having a desired H/C ratio is disclosed. Organic material is biochemically digested in a two stage biodigester for separately producing a hydrogen containing biogas substantially free of methane in a first stage and a methane containing biogas in a second stage. The methane containing biogas is reformed in a first reformer to generate hydrogen gas and carbon monoxide gas,

which are then combined in a mixer with the hydrogen containing biogas into a syngas in amounts to achieve in the syngas an overall H/C ratio substantially equal to the desired H/C ratio. The syngas is reacted with a catalyst in a second reformer, a Fischer-Tropsch (FT) reactor, to produce the hydrocarbon. Using a two stage biodigester allows for the generation of separate hydrogen and methane streams, a more economical generation of the FT syngas and reduced fouling of the FT catalyst.

US9163180B2 discloses a process for the conversion of carbon-based material to fuel bases by a hybrid route combining direct ebullent bed liquefaction and indirect liquefaction by gasification followed by a Fischer-Tropsch synthesis, including a stage of production of hydrogen resulting from non-fossil resources and a reverse water gas reaction stage.

US20230287286A1 discloses processes for producing high biogenic concentration Fischer-Tropsch liquids derived from the organic fraction of municipal solid wastes (MSW) feedstock that contains a relatively high concentration of biogenic carbon (derived from plants) and a relatively low concentration of non-biogenic carbon (derived from fossil sources) wherein the biogenic content of the Fischer-Tropsch liquids is the same as the biogenic content of the feedstock.

WO2020176575A1 discloses method of electrochemical reduction of CO2 includes the use of a catalyst of Cu/Cu_2O particles including Cu/Cu_2O interfaces, which is included in an electrochemical cell for the conversion of CO_2 to value-added products. The electrochemical cell may include an anode, a cathode including the Cu/Cu_2O particles including Cu/Cu_2O interfaces, and an aqueous medium containing CO_2 or $CO3^{(-2)}$. The CO_2 or $CO3^{(-2)}$ is reduced by contacting the Cu/Cu2O particles with the aqueous medium while supplying electricity to the cell.

Journal article, “Oxide Derived Copper for Electrochemical Reduction of CO2 to C^{2+} Products”, Nanomaterials, 2022, 12(8):1380; doi:10.3390/nano12081380,

discloses a study directed to electrochemical reduction of CO_2 on copper electrode derived from cupric oxide (CuO), named oxide derived copper (ODCu), in the potential range of -1.0 V to -1.5 V versus RHE. The CuO nanoparticles were prepared by the hydrothermal method. The ODCu electrode was used for carbon dioxide reduction and the results revealed that this electrode is highly selective for C^{2+} products with enhanced current density at significantly less overpotential.

Journal article "Electroreduction of carbon dioxide to hydrocarbons using bimetallic Cu-Pd catalysts with different mixing patterns", J. Am. Chem. Soc. 2017, vol. 139, issue.1, pages: 47-50; doi:10.1021/jacs.6b10740, discloses bimetallic Cu-Pd catalysts for reduction of carbon dioxide to C_1 or C_2 chemicals.

CN104321293A discloses a process for the preparation of methanol having the process a carbon oxides per-pass conversion equal to or higher than 65%, and a selectivity to methanol formation equal to or higher than 75% by submitting carbon dioxide, carbon monoxide or a mixture of carbon monoxide and carbon dioxide to a hydrogenation reaction using a specific metal compound and specific reaction conditions of temperature, pressure, space velocity and a specific range of molar ratio of hydrogen to carbon dioxide, of hydrogen to carbon monoxide, or of hydrogen to the mixture of carbon monoxide and carbon dioxide. It further relates to a process for converting the methanol obtained into dimethyl ether or into a mixture of (C2-C8) alkene and (C1-C8) alkane.

Journal article "Chong Wang et al. Silver-modified copper foam electrodes for enhanced reduction of CO_2 to C2+ products, Mater. Adv., 2022, 3, 4964-4972, DOI: 10.1039/D2MA00188H" discloses an Ag-modified Cu/CuO–Ag catalyst with a porous structure via a galvanic replacement reaction method, which reduced CO_2 to C2+ products with the faradic efficiency (FE) of 52.5% at 1.1 V (vs. RHE). D1 states that the experimental results and density functional theory (DFT) calculations show that the addition of Ag in Cu is beneficial to increasing the coverage of *CO on the Cu surface, which can decrease the potential barrier energy of the C–C coupling reaction and favour the generation of C2+ products.

Journal article "Mun, Yeongdong et al. (2019). Cu-Pd Alloy Nanoparticles as Highly Selective Catalysts for Efficient Electrochemical Reduction of CO_2 to CO. Applied Catalysis B: Environmental, (), S0926337319300219. doi:10.1016/j.apcatb.2019.01.021" discloses alloying of Cu with Cu-Pd in 1:1 ratio achieves CO_2 to CO electrochemical reduction of 87% CO faradic efficiency (FE). D2 discloses that this increase in the FE of CO_2 to CO conversion suppresses the formation of hydrocarbons from CO_2.

Journal article "M. Watanabe, M. Shibata, A. Kato, M. Azuma, T. Sakata, J. Electrochem. Soc. 1991, 138, 3382–3389" discloses Cu based alloys such as Cu-Zn, Cu-Cd, Cu-Ag, Cu-Sn and Cu-Pb as electrocatalyst for CO_2 electrochemical reduction into CH_3OH, HCOOH, and CO in highly selective approach via low overpotentials on Cu-alloy catalysts.

US2022119966A1 discloses a method of electrochemical reduction of CO_2 involving the use of a catalyst of Cu/Cu_2O nanoparticles including Cu/Cu_2O interfaces wherein the catalyst may be included in an electrochemical cell for the conversion of CO_2 to value-added products. The electrochemical cell may include an anode, a cathode including the Cu/Cu_2O nanoparticles including Cu/Cu_2O interfaces.

GB202202262D0 discloses a catalyst for the electrochemical conversion of carbon dioxide or carbon monoxide to a C2+ product wherein the catalyst comprises copper and a metal (M) selected from the group consisting of: yttrium (Y), zinc (Zn), lanthanum (La) and gadolinium (Gd); wherein the molar ratio of Cu: M is from 100: 1 to 100: 10.

SUMMARY:

The present disclosure provides an electrocatalytic reactor for conversion of Green House Gas (GHG) emissions into value-added products (VAPs), wherein the electrocatalytic reactor is equipped with symmetric or asymmetric electrodes (cathode and anode), wherein the cathode is selected from metallic Copper (Cu), Cu-alloy, or Cu-doped Ti mesh, and the anode is selected from metallic Copper

(Cu), Cu alloy, Ti Mesh, Cu-doped Ti Mesh, Carbon felt, or Cu-doped carbon felt, wherein these electrodes act as electrocatalyst, and acidified deionised water (H_3O^+) as electrolyte for generation of H_2 gas through bulk electrocatalysis, wherein a catalyst initiator is included in the acidified deionised water (H_3O^+).

The method of electrocatalytic reduction operation occurs at ambient temperature, and 1 atm pressure. The application of the current density is continued for 3 to 5 hours. An external current of 1 to 5 A was applied to the electrodes in a voltage range of 1 to 5 V, which initiates C-C coupling or C-O coupling reactions on the cathode surface forming short-lived cation radical intermediates, wherein the short-lived cation radical intermediates react among themselves, or the short-lived cation radical intermediates react with the *in-situ* produced H_2 gas, or both, leading to the formation of the VAPs.

The concentrated acid is selected from HCl, H_2SO_4, HNO_3, H_3PO_4.

The initiator mixture includes a mixture of 60% by weight of carbonates or bicarbonates of Mg or Na or K or a combination of carbonates and bicarbonates of Mg, Na and K with 40% by weight of MgO.

When the carbon containing gases in the GHG include CO_2, CO, CH_4, the VAPs produced are unsaturated hydrocarbons, ethanol, acetic acid, acetone, acetaldehyde, glycols, ethylene oxide, propionaldehyde, ethyl vinyl acetate, chloro acetyl chloride so on and so forth.

When the carbon containing gases in the GHG also include H_2, N_2, H_2S, SOx, NOx, the VAPs produced are primary amines, amides, thiophene azo dyes etc.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS:

Fig. 1 illustrates the design of the electrocatalytic reactor to convert GHG to VAPs.

Fig. 2A illustrates FTIR spectra of liquid and Solid sample obtained by the electrocatalytic reduction of GHG in Example 1 with Conc. HCl as acidifying agent.

Fig. 2B illustrates UV-Vis spectra of liquid and solid sample obtained by the electrocatalytic reduction of GHG in Example 1 with Conc. HCl as acidifying agent.

Fig. 2C illustrates High Resolution Mass Spectroscopy (HR-MS) spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 1 with Conc. HCl as acidifying agent.

Fig. 2D illustrates High Resolution Mass Spectroscopy (HR-MS) of solid sample obtained by the electrocatalytic reduction of GHG in Example 1 with Conc. HCl as acidifying agent.

Fig. 3A illustrates UV-Vis spectra of solid sample obtained by the electrocatalytic reduction of GHG in Example 2 with Conc. HCl as acidifying agent.

Fig. 3B illustrates FTIR spectra of solid sample obtained by the electrocatalytic reduction of GHG in Example 2 with Conc. HCl as acidifying agent.

Fig. 3C illustrates GC-MS scan of the solid precipitate obtained by the electrocatalytic reduction of GHG in Example 2 with Conc. HCl as acidifying agent.

Fig. 3D illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 2 with Conc. HCl as acidifying agent.

Fig. 3E illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 2 with Conc. HCl as acidifying agent.

Fig. 3F illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 2 with Conc. HCl as acidifying agent

Fig. 4A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 3 with Conc. H_2SO_4 as acidifying agent.

Fig. 4B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 3 with Conc. H_2SO_4 as acidifying agent.

Fig. 4C illustrates GC-MS scan of the solid precipitate obtained by the electrocatalytic reduction of GHG in Example 3 with Conc. H_2SO_4 as acidifying agent.

Fig. 5A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 4 with Conc. HCl as acidifying agent.

Fig. 5B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 4 with Conc. HCl as acidifying agent.

Fig. 5C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 4 with Conc. HCl as acidifying agent

Fig. 6A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 5 with Conc. H_2SO_4 as acidifying agent.

Fig. 6B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 5 with Conc. H_2SO_4 as acidifying agent.

Fig. 6C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 5 with Conc. H_2SO_4 as acidifying agent.

Fig. 7A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 6 with Conc. HCl as acidifying agent.

Fig. 7B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 6 with Conc. HCl as acidifying agent.

Fig. 7C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 6 with Conc. HCl as acidifying agent

Fig. 8A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 7 with Conc. H_2SO_4 as acidifying agent.

Fig. 8B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 7 with Conc. H_2SO_4 as acidifying agent.

Fig. 8C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 7 with Conc. H_2SO_4 as acidifying agent.

Fig. 9A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 8 with Conc. HCl as acidifying agent.

Fig. 9B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 8 with Conc. HCl as acidifying agent.

Fig. 9C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 8 with Conc. HCl as acidifying agent

Fig. 10A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 9 with Conc. H_2SO_4 as acidifying agent.

Fig. 10B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 9 with Conc. H_2SO_4 as acidifying agent.

Fig. 10C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 9 with Conc. H_2SO_4 as acidifying agent.

Fig. 11A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 10 with Conc. HCl as acidifying agent.

Fig. 11B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 10 with Conc. HCl as acidifying agent.

Fig. 11C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 10 with Conc. HCl as acidifying agent

Fig. 12A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 11 with Conc. H_2SO_4 as acidifying agent.

Fig. 12B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 11 with Conc. H_2SO_4 as acidifying agent.

Fig. 12C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 11 with Conc. H_2SO_4 as acidifying agent.

Fig. 13A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 12 with Conc. HCl as acidifying agent.

Fig. 13B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 12 with Conc. HCl as acidifying agent.

Fig. 13C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 12 with Conc. HCl as acidifying agent

Fig. 14A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 13 with Conc. H_2SO_4 as acidifying agent.

Fig. 14B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 13 with Conc. H_2SO_4 as acidifying agent.

Fig. 14C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 13 with Conc. H_2SO_4 as acidifying agent.

Fig. 15A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 14 with Conc. HCl as acidifying agent.

Fig. 15B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 14 with Conc. HCl as acidifying agent.

Fig. 15C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 14 with Conc. HCl as acidifying agent

Fig. 16A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 15 with Conc. H_2SO_4 as acidifying agent.

Fig. 16B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 15 with Conc. H_2SO_4 as acidifying agent.

Fig. 16C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 15 with Conc. H_2SO_4 as acidifying agent.

Fig. 17A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 16 with Conc. HCl as acidifying agent.

Fig. 17B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 16 with Conc. HCl as acidifying agent.

Fig. 17C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 16 with Conc. HCl as acidifying agent

Fig. 18A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 17 with Conc. H_2SO_4 as acidifying agent.

Fig. 18B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 17 with Conc. H_2SO_4 as acidifying agent.

Fig. 18C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 17 with Conc. H_2SO_4 as acidifying agent.

Fig. 19A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 18 with Conc. HCl as acidifying agent.

Fig. 19B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 18 with Conc. HCl as acidifying agent.

Fig. 19C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 18 with Conc. HCl as acidifying agent

Fig. 20A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 19 with Conc. H_2SO_4 as acidifying agent.

Fig. 20B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 19 with Conc. H_2SO_4 as acidifying agent.

Fig. 20C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 19 with Conc. H_2SO_4 as acidifying agent.

Fig. 21A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 21B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 21C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 21D illustrates High temperature GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 21E illustrates UV-Vis spectra of solid sample obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 21F illustrates FTIR spectra of solid sample obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 21G illustrates GC-MS scan of the solid precipitate obtained by the electrocatalytic reduction of GHG in Example 20 with Conc. HCl as acidifying agent.

Fig. 22A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 21 with Conc. HCl as acidifying agent.

Fig. 22B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 21 with Conc. HCl as acidifying agent.

Fig. 22C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 21 with Conc. HCl as acidifying agent.

Fig. 23A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 22 with Conc. H_2SO_4 as acidifying agent.

Fig. 23B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 22 with Conc. H_2SO_4 as acidifying agent.

Fig. 23C illustrates HR-MS spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 22 with Conc. H_2SO_4 as acidifying agent.

Fig. 24A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 23 with Conc. HCl as acidifying agent.

Fig. 24B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 23 with Conc. HCl as acidifying agent.

Fig. 24C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 23 with Conc. HCl as acidifying agent.

Fig. 24D illustrates GC-MS scan of the solid sample obtained by the electrocatalytic reduction of GHG in Example 23 with Conc. HCl as acidifying agent.

Fig. 25A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 24 with Conc. HCl as acidifying agent.

Fig. 25B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 24 with Conc. HCl as acidifying agent.

Fig. 25C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 24 with Conc. HCl as acidifying agent.

Fig. 26A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 25 with Conc. HCl as acidifying agent.

Fig. 26B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 25 with Conc. HCl as acidifying agent.

Fig. 26C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 25 with Conc. HCl as acidifying agent.

Fig. 27A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 26 with Conc. HCl as acidifying agent.

Fig. 27B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in Example 26 with Conc. HCl as acidifying agent.

Fig. 27C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in Example 26 with Conc. HCl as acidifying agent.

DETAILED DESCRIPTION:

The subject matter of the present disclosure is described in detail with reference to the accompanying drawings. Unless otherwise specified, all the technical and scientific terms used herein have the same meaning as is generally understood by a person skilled in the art pertaining to the present disclosure. Headings are used solely for organizational purposes, and are not intended to limit the disclosure in any way.

The use of the singular includes the plural unless specifically stated otherwise. As used herein, the singular forms “a,” “an” and “the” are intended to include the plural forms as well. The use of “or” means “and/or” unless stated otherwise. Unless otherwise indicated, all numbers used herein to express quantities, dimensions, and so forth used should be understood as being modified in all instances by the term "about." It is to be understood that wherein a numerical range is recited, it includes all values within that range, and all narrower ranges within that range, whether specifically recited or not. As used herein, "including," "containing" and like terms are understood to be synonymous with "comprising" and are therefore open-ended and do not exclude the presence of additional undescribed or unrecited elements, materials, phases or method steps.

In addition, it should be appreciated that any figures are provided herewith, they are for explanation purposes to persons ordinarily skilled in the art and that the drawings of them are not necessarily drawn to scale.

Any method/process steps and/or operations and/or instructions used in this disclosure, are for illustrative purposes in a particular order and/or grouping. Other orders and/or grouping of the process steps or its portions and/or operations or its portions and/or instructions or its portions are possible and, one or more of the process steps and/or operations and/or instructions can be combined and/or deleted.

The present disclosure provides an electrocatalytic reactor and method for electrocatalytic reduction of Green House Gases (GHG) that includes carbon containing gases such as CO_2, CO, CH_4, as well as non-carbon containing gases such as H_2, N_2, H_2S, S, SOx, NOx into value-added products (VAPs) such as ethanol, ethylene, propylene, other hydrocarbons, ammonia, urea, amines, acetic acid, Butadiene, Propionaldehyde, ethyl acetate, ethyl acetate esters, metal ethanoates, azo-dyes, ethylene vinyl acetate, chloro acetyl chloride etc.

The electrocatalytic reactor and method of the present disclosure also is able to perform electrocatalytic cracking of CH_4 and NH_3 gas into C, H_2 gas, and N_2 gas at High temperature, wherein the obtained Carbon can be converted to graphene, MWCNTs, SWCNTs, and carbon black through continuous CVD.

Based on the GHG emission feed, and the products desired, the process parameters of the electrocatalytic reduction operation can be suitably customised by varying the electrochemical parameters, and the proportion of the catalyst initiator.

When the GHG emission feed is pure CO_2 or a mixture of CO_2, CO, CH_4, H_2, the electrocatalytic reduction of CO_2 by the electrocatalytic reactor of the present disclosure, predominantly produces ethanol under ambient reaction conditions (i.e. at room temperature),

When the GHG emission feed contains a mixture of CO_2, CO, CH_4, H_2 having CO_2 in the range of 4% to 99.9%, or a mixture of N_2, CO_2, CO, CH_4, H_2 having CO_2 in the range of 4% to 99.9%, the electrocatalytic reduction of the mixture by

the electrocatalytic reactor of the present disclosure predominantly produces ethylene, propylene, other hydrocarbons under ambient reaction conditions, which may form other products such as higher carbon alkenes, alkynes under high temperature (>100°C) conditions.

When the GHG emission feed contains flue gas i.e. a mixture of N_2, CO_2, CO, CH_4, H_2 having CO_2 in the range of 4% to 99.9%, the electrocatalytic reduction of the mixture by the electrocatalytic reactor of the present disclosure predominantly produces ammonia, Urea, hydrocarbons under ambient reaction conditions, which may form other products such as higher chain saturated and unsaturated hydrocarbons, long chain hydrocarbon based amines (primary, secondary and tertiary) etc under high temperature (>100°C) conditions.

In an aspect CH_4 in the GHG is electrocatalytically reduced to ethylene through the following reaction pathway:

$$2CH_4 \rightarrow C_2H_6 + 4H^+ + 2e^-$$

The pathway of the elementary steps involves

$$2[CH_4 + Cu^{2+} - O^{2-} \rightarrow CH_3^- - Cu - OH^-]$$

$$2[CH_3^- - Cu - OH^- \rightarrow CH_2 - Cu - O^{2-} + 2H^+ + 2e]$$

$$2CH_2 - Cu - O^{2-} \rightarrow O^{2-}\text{-}Cu\text{-}CH_2\text{-}CH_2\text{-}Cu\text{-}O^{2-}$$

$$O^{2-}\text{-}Cu\text{-}CH_2\text{-}CH_2\text{-}Cu\text{-}O^{2-} \rightarrow CH_2\text{-}CH_2 + 2CuO$$

<u>The electrocatalytic reactor:</u>

The electrocatalytic reactor of the present disclosure for conversion of Green House Gas (GHG) emissions that include carbon containing gases as well as non-carbon containing gases into value-added products (VAPs), wherein the electrocatalytic reactor is equipped with symmetric or asymmetric electrodes (cathode and anode), wherein the cathode is selected from metallic Copper (Cu), Cu-alloy, or Cu-doped Ti mesh, and the anode is selected from metallic Copper (Cu), Cu alloy, Ti Mesh, Cu-doped Ti Mesh, Carbon felt, or Cu-doped carbon felt, wherein these electrodes act as electrocatalyst, and acidified deionised water

(H_3O^+) as electrolyte for generation of H_2 gas through bulk electrocatalysis, wherein a catalyst initiator is included in the acidified deionised water (H_3O^+).

A representation of the electrocatalytic reactor is shown in **Fig. 1.**

The catalyst initiator:

The catalyst initiator for of the present disclosure is a mixture of 60% by weight of carbonates or bicarbonates of Mg or Na or a combination of carbonates and bicarbonates of Mg and Na with 40% by weight of MgO in distilled water to facilitate the reaction of the short-lived cation radical intermediates formed by C-C coupling or C-O coupling reactions on the cathode surface leading to hydrolysis and VAPs formation with high specificity and selectivity.

In preferred embodiments of the present disclosure, the catalyst initiator mixture can be the following combinations:

- 60% by weight of $MgCO_3$ with 40% by weight of MgO.
- 60% by weight of a mixture of $MgCO_3$ and one or more of Na_2CO_3, K_2CO_3, $NaHCO_3$, or $KHCO_3$ with 40% by weight of MgO.

The method of electrocatalytic conversion of GHG into VAPs:

The method of electrocatalytic conversion of Green House Gas (GHG) emissions that include carbon containing gases as well as non-carbon containing gases into value-added products (VAPs) includes:

- adding deionised water to an electrocatalytic reactor vessel and dipping a cathode, and an anode in the deionised water;
- purging GHG into the deionised water in the reactor vessel from an external GHG source;
- applying current density to the cathode and anode through an external power source; wherein the power source set at voltage of up to 5V and current of up to 5A;

- adding a catalyst initiator to the deionised water in the reactor vessel forming an initiator solution; and
- adding a concentrated acid to the initiator solution in the reactor vessel with constant stirring to form an electrolytic reaction solution, which produces H_2 gas *in-situ* from the electrolytic reaction solution on the cathode surface,

wherein the applied current density initiates the C-C coupling or C-O coupling reactions on the cathode surface forming short-lived cation radical intermediates, wherein the short-lived cation radical intermediates react among themselves, or the short-lived cation radical intermediates react with the *in-situ* produced H_2 gas, or both, forming organic acid anions and alkoxides,

wherein, on the anode, when the anode contains proton formation, oxygen evolution occurs, wherein the evolved oxygen reacts with the cation radical resulting in the oxidization of the same to form the value-added products (VAPs) such as acetone, acetaldehyde, acetic acid, ethylene oxide,

wherein, additionally, on the anode, when the anode contains Cu, dissolution of Cu occurs forming Cu^{2+} ions, wherein, the organic acid anions and alkoxides react with the Cu^{2+} ions forming metallorganic complexes; wherein, the metallorganic complexes are left for hydrolysis for about 24 hours at 35º to 45º C to form the value-added products (VAPs),

wherein, on the anode, when the anode contains Ti Mesh or Carbon felt i.e. in the absence of Cu, the VAPs formed include Ethylene Vinyl Acetate, Chloro Acetyl Chloride.

The application of the current density to the electrodes is continued for 3 to 5 hours.

The Cu-alloy for the electrodes can be selected from Cu/CuO, Cu/Ag, Cu/Ti, Cu/Pt, and Cu/Pd, wherein the alloying substance i.e., CuO, Ag, Ti, Pt, and Pd is present in an amount of less than or equal to 2.5% by weight.

In the Cu-doped Ti Mesh electrodes, the dopant Cu is present in an amount of less than or equal to 2% by weight.

Similarly, in the Cu-doped carbon felt, the dopant Cu is present in an amount of less than or equal to 2% by weight.

The concentrated acid added to the initiator solution in the reactor vessel is selected from HCl, H_2SO_4, HNO_3, H_3PO_4.

In an aspect, the purging of GHG into the deionised water in the reactor vessel from an external GHG source at a flow rate of 30-50 Litre/hour (LPH).

An external current of 1 to 5 A was applied to the electrodes in a voltage range of 1 to 5 V, which facilitates the formation of organic cation radical intermediates, which lead to the formation of the VAPs.

The obtained reaction solution can be analysed by techniques such as Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis spectroscopy, High Resolution Mass Spectrometry (HR-MS) and Gas chromatography-mass spectrometry (GC-MS) to understand the compounds formed and their % yield. The formed compounds can be recovered by a suitable distillation technique.

The plausible mechanisms of formation of the VAPs have been provided in **Fig. 28 to Fig. 36B.**

Examples:

The present disclosure will now be explained in further detail by the following examples. These examples are illustrative of certain embodiments of the disclosure without limiting the scope of the present disclosure.

Electrocatalytic reactor details used in all the examples:

As the representation shown in **Fig. 1,** the electrocatalytic reactor vessel, which is a lab scale prototype made of Borosil glass of capacity 5 litres with applied current and voltage. An inlet is provided on the cap of the reactor is the provision to pass GHG. The electrodes are in form of a slab with rectangular handle. The handle of the electrode acts as the current collector that is connected to the power source (PS). The dimensions of the slab of each electrode is 10cm*7cm*2cm (length*breadth*thickness).

The power source (from Won-a-Tech, Korea) with 20 V and 10 A capacity. The power source is provided with software interface to acquire the dynamic data of the voltage (V) and Current (I) during the course of the reaction.

The electrodes are connected to the power source via cables (one terminal acts as anode, and the other acts as cathode). The power source is set at the upper voltage of 5V and current up to 5A for the reaction to proceed.

The ratio of the ingredients in the catalyst initiator mixture used in all the examples are by their weight percentage.

Example 1

Reduction of GHG emissions from petrochemical exhaust from Chennai Petroleum Corporation (CPCL), Manali, Chennai, Tamil Nadu with Conc. HCl.

- Feed source: GHG emissions collected from CPCL, Manali, Chennai, Tamil Nadu in bladders of two litres capacity each. Four bladders of 2L of GHG emissions (8L in total) was used as the feed source.
- GHG Feed includes Carbon containing gases: CO_2, CO, CH_4, ethane.
- GHG Feed includes non-carbon containing gases: N_2, SOx, NOx, S, H_2S.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 60% $MgCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. The experiment was carried out at ambient of 28^oC. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 3 hours. A brown-coloured precipitate is formed on the copper anode surface during the reaction and fell into the solution. The experimental solution is left at 40^0C for 24 hrs for the completion of the reaction.

After the completion of the reaction, the solution and solid products are tested by Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis spectroscopy, High Resolution Mass Spectrometry (HR-MS) to understand the products formed.

Fig. 2A illustrates FTIR spectra of liquid and Solid sample obtained by the electrocatalytic reduction of GHG in **Example 1**.

Six peaks of varying intensities were noticed in the FTIR spectrum of the liquid samples

1. A broad high intense peak around 3449 cm^{-1} attributed to the absorption peak of hydroxyl group, alcoholic in nature and due to the symmetric stretching mode of O-H bonds and are intermolecular bonded; also, attributes to N-H stretching frequency
2. A sharp small peak at 1674 cm^{-1} representing the C=C stretching vibration mode of aromatic moiety or C=N stretching vibrations
3. A broad medium intense peak at 1436 cm^{-1} depicting O-H bending as in alcohol, CH_3 and CH_2 bending frequencies
4. A small weak peak around 708 cm^{-1} represents the vibrational modes of benzene derivatives
5. A very small weak peak at 567 & 511 cm^{-1} corresponds to the presence of Cu-O coordination mostly hydroxyl or alkoxy group attachment

Hence, the FTIR of the liquid samples indicate formation of ethanol as well as aromatic derivatives with C=N, N-H moieties.

Eleven peaks of varying intensities were observed for the solid samples in the FTIR spectrum.

1. A broad high intense peak around 3464 cm^{-1} attributed to the absorption peak of hydroxyl group, alcoholic in nature and due to the symmetric stretching mode of O-H bonds and are intermolecular bonded; which also attributes to N-H stretching frequency
2. A sharp medium peak at 1633 cm^{-1} representing the C=N stretching vibrations
3. A sharp high intense peak between 1400 to 1500 cm^{-1} is split into a doublet at 1419 and 1481 cm^{-1}. This is a overlapped frequencies of CH_2 bending and C=C aromatic stretching vibrations

4. A medium intense peak around 1009 cm^{-1} represents the vibrational modes of C-N stretching mode
5. A broad peak between 750 to 900 cm^{-1} seen as triplet at 757, 851, 876 cm^{-1} corresponds to the presence of C=C alkene bending or aromatic C=C stretching modes of vibrations with intermolecular bonding
6. A sharp medium triplet peak between 400 – 700 cm^{-1}, C=C bending or Cu-O coordination mostly hydroxyl or alkoxy group attachment

Hence, FTIR of solid samples provide evidence for the presence of ethanol, and aromatic and aliphatic groups substituted C-N bonds.

Fig. 2B illustrates UV-Vis spectra of liquid and solid sample obtained by the electrocatalytic reduction of GHG in **Example 1**.

From **Fig. 2B**, the UV-Vis spectra of the liquid samples obtained from the experiment has two peaks one at 190 nm caused by the ethanol in the solution, whereas the broad peak at 281 nm indicates the amide linkage expected in the other compounds present in the solution.

The UV-Vis spectra of solid samples showed four peaks at 190, 256, 3244 and 486 nm. The peaks correspond to the presence of ethanol, auxochromes such as benzene derivatives or phenyl group, substituted thiophene moiety respectively.

Fig. 2C illustrates High Resolution Mass Spectroscopy (HR-MS) spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 1**.

Fig. 2D illustrates High Resolution Mass Spectroscopy (HR-MS) spectra of solid sample obtained by the electrocatalytic reduction of GHG in **Example 1**.

As shown in **Fig. 2C**, the HR-MS spectra of the liquid sample indicated m/z fragments at 46, 173.1018, 359.2252. The peak at m/z=46 represents ethanol, m/z=173.1018 denote the presence of di-cupro-ethoxide cation

($[Cu_2(CH_3CH_2O)]^+$, m/z=242.2718 indicate the presence of coordination compound such as Tetra ethoxy cupric anion $Cu(CH_3CH_2O)_4]^{2-}$; the peak at m/z=359.2252 represents the presence of single molecule of 5-methyl-phenylazothiphene-azo dye. The presence of azo dye is also corroborated by the presence of aromatic C=C, benzene derivative, N-H bending etc. peaks of FTIR and 281nm peak in UV-Vis spectroscopy. Thus, from the HR-MS of liquid sample, the products obtained are identified as ethanol and 5-methyl-phenylazothiphene-azo dye.

As shown in **Fig. 2D** the HR-MS spectra of solid samples with m/z fragments at 127.892 due to Aceto magnesium ethoxide (Grignard reagent), m/z=173.1018 attributed to Di-cupro-ethoxide cation $[Cu_2(CH_3CH_2O^-)]^+$, m/z = 242.2718 representing the tetra ethoxy cupric coordination complex of tetrahedral geometry $[Cu(CH_3CH_2O)_4]^{2-}$ and m/z = 359.2252 denoting the thiophene azo dye (5-methyl-phenyl azo thiophene- 2- azo dye).

Based on the variation in constituents and composition of the input GHG emissions, the yield of the VAPs such as ethanol, 5-methyl-phenyl azo thiophene-2-azo dye, acetic acid, Ethylene Vinyl Acetate, Chloro Acetyl Chloride, amides, amines can be fine-tuned by varying the electrochemical parameters and the proportion of the catalyst initiator to be the major product.

Example 2

Reduction of GHG emissions from Steel plant (Coke Oven – Battery No. 10) in Chhattisgarh with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant in Chhattisgarh – the GHG emission samples were collected from Coke Oven – Battery No. 10.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).

- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 2 hours. After completion of the electrocatalytic reaction, the solution turned to a greenish yellow suspension. The probe used to extract GHG emissions in the present case was a short probe.

Fig. 3A illustrates UV-Vis spectra of solid sample obtained by the electrocatalytic reduction of GHG in **Example 2**.

The product solution is filtered and dried to obtain solid precipitate powder. The solid sample is subjected to analysis via UV-Vis spectroscopy in the wavelength range of 190 to 1100 nm.

As shown in **Fig. 3A**, the UV-Vis specta showed nine peaks in the wavelength range of 200 to 260 nm. The first and second peaks at 201.724 & 204.176 nm are attributed to ethanol with H-bonded compounds. Third peak at 208.137 nm is due

to n→π* and π→π* transitions of propionaldehyde (H_2C=CH-CH=O), as propionaldehyde has aldehydic C=O functional group, it creates H-bonds with ethanol, shifting the UV finger print of ethanol to wavelength > 200 nm. Fourth and fifth peaks at 212.088 & 213.965 nm correspond to presence of ethanol and primary amines. Sixth & seventh peaks at 220.004 & 223.155 nm represents C=O and HC=O functional groups. The peak at 226.872 nm is due to C=C of 1,3 Butadiene (H_2C=CH–CH=CH_2). The ninth peak in the form of hump at 260 nm is due to alcohol and primary amine groups. First eight peaks merge together and are seen as spikes due to short interval in the wavelength whereas ninth peak is seen prominently as a hump due to primary amine and ethanol H-bonded product.

Fig. 3B illustrates FTIR spectra of solid sample obtained by the electrocatalytic reduction of GHG in **Example 2**.

The solid sample is subjected to analysis via FTIR spectroscopy in the wavenumber range of 4000 to 400 cm^{-1}.

As shown in **Fig. 3B**, six peaks were noticed in FTIR spectra. First peak at 3267.02cm^{-1} is a broad peak with 60.43% transmittance and attributed to the presence of alcoholic OH group, H-bonded. Second peak is a sharp peak at 1631.4 cm^{-1} with 58.47% transmittance corresponds to the presence of alkyl group or C=C stretching mode of vibrations. Third peak at 675 cm^{-1} is a small peak with 34.11% transmittance and depicts the presence of C=C bending vibrations of cis configured disubstituted moiety. Fourth peak is again a small peak at 614.31 cm^{-1} with 28.91% transmittance due to the presence of C-Cl bond stretching vibrations. Peak at 583.09 & 574.22 cm^{-1} are small peaks with 24.78 to 25.55% transmittance and is attributed to the presence of C-Cl bond. Thus, from FTIR analysis it is demonstrated that the products in the solid phase are ethanol bonded to compounds with C=C & C-Cl moieties.

Fig. 3C illustrates GC-MS scan of the solid precipitate obtained by the electrocatalytic reduction of GHG in **Example 2**.

Fig. 3C indicates the absence of any metallo-organic compounds or free organic molecules in the solid precipitate. The inference from the GC-MS of the solid precipitate is an organic H-bonded molecule which upon dispersing in the solvent for UV-Vis or FTIR analysis had showed peaks of ethanol, ethylene, 1,3 Butadiene, Propionaldehyde and not in free state, so not seen in GC-MS studies.

Fig. 3D illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 2**.

As shown in **Fig. 3D**, the peaks at 202.205 & 204.021 nm accounts for ethanol H-bonded to other compounds. The $\pi \rightarrow \pi^*$ transitions of propionaldehyde is seen at 206.979 nm. Since the GHG is a gaseous combination of SOx, NOx, S, H_2S and N_2, under the operating conditions of the electrocatalytic reduction of the GHG emissions, nitrogen-based products like primary amines are found at 210.175 & 214.404 nm. Alkenes like 1,3, Butadiene is seen at 217.284 nm whereas 224.117 nm indicates presence of -N=N- group in azo dye. Peaks at 228.947, 243.778, 247.427nm are due to presence of C-Cl bond. Thus, from UV-Vis analysis of the liquid sample from electrocatalytic reduction of GHG emissions from coke oven Batt-10 involves ethanol as major product and few alkenes and azo products as minor product.

Fig. 3E illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 2**.

As in **Fig. 3E**, the following inference is arrived at from the analysis of the liquid sample obtained by the electrocatalytic reduction of GHG emissions by FTIR spectroscopy.

1. Peak at 3349.45cm^{-1} broad with 68.12% transmittance is attributed to the presence of alcoholic OH group.

2. Peak at 2097.62 cm^{-1} broad with 93.09% transmittance depicts the presence of vinyl C=C.

3. Peak at 1637.00 cm^{-1} sharp peak with 73.88% transmittance corresponds to the presence of alkyl group or C=C stretching.

4. Small peaks at 615.32, 606.98, 583.01, 575.30, 559.65 cm^{-1} with 39.19% transmittance represents the presence of C-Cl stretching mode.

Thus, from UV-Vis and FTIR we can infer that the compound formed as VAPs are ethanol as major product with alkenes as minor products

Fig. 3F illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 2**, which indicates the liquid sample is a mixture of ethanol, ethylene, 1,3 Butadiene, Propionaldehyde & azo dyes.

Example 3

Reduction of GHG emissions from Steel plant (Coke Oven – Battery No. 10) in Chhattisgarh with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant in Chhattisgarh - the GHG emission samples were collected from Coke Oven – Battery No. 10.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to

deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 2 hours. The physical observation of the solution shows that the solution turned blue from colourless. The probe to extract GHG emissions was a short probe.

Fig. 4A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 3**. Three peaks are noticed in the UV-Vis spectra at 205.334, 211.944 & 213.927 nm, which are attributed to the presence of ethanol and primary amines.

Fig. 4B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 3**.

From **Fig. 4B**, the following inference is arrived at:

1. Peak at 3307.02cm^{-1} broad with 69.68% transmittance is attributed to the presence of alcoholic OH group.
2. Peak at 1637.53 cm^{-1} sharp peak with 75.86% transmittance is attributed to the presence of alkyl group or C=C stretching.
3. Peak at 1096.34 cm^{-1} a small peak with 78.62% transmittance is attributed to the presence of C-N stretching mode.
4. Peak at 606.18, 594.89, 582.39, 566.83, 560.23, 555.23 cm^{-1} small peak with 39.19% transmittance is attributed to the presence of Cu-Cl stretching mode.

Thus, from UV-Vis and FTIR we can infer that the compound formed as VAPs are ethanol with primary amines as minor products.

Fig. 4C illustrates GC-MS scan of the solid precipitate obtained by the electrocatalytic reduction of GHG in **Example 3**, which indicates the absence of any metallo-organic compounds or free organic molecules in the solid precipitate. The inference of the present case is the liquid sample is a mixture of ethanol & primary amines.

A consolidated data of VAPs obtained from the electrocatalytic reduction of GHG emissions as in **Example 3** is provided in **Table 1**.

Table 1

Composition	Volume	VAPs obtained and Remarks			
		In HCl		In H_2SO_4	
		Major	Minor	Major	Minor
O_2	6.8%	Ethanol	Propionaldehyde 1,3 Butadiene Primary amines	Ethanol	Primary amines
CO_2	7.85%				
CO	2509 ppm				
NO	194 ppm				
NOx	204 ppm				
SO_2	29 ppm				

Example 4

Reduction of GHG emissions from Steel plant (Blast Furnace - 7) in Chhattisgarh with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant in Chhattisgarh - the GHG emission samples were collected from Blast Furnace - 7.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 2 hours. The physical observation is that the solution turned brownish in colour from colourless. The probe to extract GHG emissions employed was a long probe.

Fig. 5A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 4**. Two peaks are noticed in the UV-Vis spectra at 201.075 nm of ethanol with impurity at 282.62 nm due to amide linkage.

Fig. 5B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 4**.

The following inference is arrived at from the analysis of the liquid sample obtained by the electrocatalytic reduction of GHG emissions by FTIR spectroscopy.

1. Peak at 3351.08 cm^{-1} broad with 69.45% transmittance is attributed to the presence of alcoholic OH group.
2. Peak at 2128.27 cm^{-1} broad with 95.67% transmittance is attributed to the presence of N=C=N stretching mode.

3. Peak at 1637.38 cm^{-1} sharp peak with 74.47% transmittance is attributed to the presence of alkyl group or C=C stretching.

4. Peak at 1362.72 cm^{-1} sharp peak with 89.05% transmittance is attributed to the presence of O-H bending mode.

5. Peak at 633.7 cm^{-1} very small peak with 42.06% transmittance is attributed to the presence of Cu-O bond.

Fig. 5C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 4**, which indicates the absence of any metallo-organic compounds or free organic molecules in the solid precipitate. The inference of the liquid sample is a mixture of ethanol & amide.

Example 5

Reduction of GHG emissions from Steel plant (Blast Furnace - 7) in Chhattisgarh with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant in Chhattisgarh - the GHG emission samples were collected from Blast Furnace - 7.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the

electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 2 hours. The physical observation being the solution turning brownish in colour from colourless. The probe to extract GHG emissions was a long probe.

Fig. 6A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 5**. Two peaks are noticed in the UV-VIS spectra at 202.28 nm of ethanol with impurity at 276.02 nm due to amide linkage.

Fig. 6B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 5**.

The following inference is arrived at from the analysis of the liquid sample obtained by the electrocatalytic reduction of GHG emissions by FTIR spectroscopy.

1. Peak at 3327.59 cm^{-1} broad with 72.50% transmittance is attributed to the presence of alcoholic OH group.
2. Peak at 2118.07 cm^{-1} broad with 95.67% transmittance is attributed to the presence of N=C=N stretching mode.
3. Peak at 1635.28 cm^{-1} sharp peak with 76.13% transmittance is attributed to the presence of alkyl group or C=C stretching.
4. Peak at 1375.98 cm^{-1} sharp peak with 86.70% transmittance is attributed to the presence of O-H bending mode.
5. Peak at 610 to 557 cm^{-1} very small peak with 35 % transmittance is attributed to the presence of Cu-O bond.

Fig. 6C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 5**, which indicates the absence of any metallo-organic compounds or free organic molecules in the solid precipitate. The inference in the present case is the liquid sample is a mixture of ethanol & amide.

A consolidated data of VAPs obtained by electrocatalytic conversion of the GHG emissions as in **Example 5** is provided in **Table 2**.

Table 2

Composition	Volume	VAPs obtained and Remarks			
		In HCl		In H_2SO_4	
		Major	Minor	Major	Minor
O_2	7.61%	Ethanol	Carbamides Amides Amines	Ethanol	Carbamides Amines
CO_2	7.42%				
CO	2111 ppm				
NO	20 ppm				
NOx	21 ppm				
SO_2	26 ppm				

Example 6

Reduction of GHG emissions from Steel plant (Plate Mill) in Chhattisgarh with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant in Chhattisgarh - the GHG emission samples were collected from Plate Mill.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).

- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 2 hours. The physical observation of the solution being turned bluish in colour from colourless. The probe to extract GHG emissions in the present case was a long probe.

Fig. 7A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 6**. Two peaks are noticed in the UV-VIS spectra at 205.98 nm of ethanol with impurity at 282.11 nm due to amide linkage.

Fig. 7B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 6**.

The following inference is arrived at from the analysis of the liquid sample obtained by the electrocatalytic reduction of GHG emissions.

1. Peak at 3327.60 cm^{-1} broad with 69.74% transmittance is attributed to the presence of alcoholic OH group.

2. Peak at 2127.52 cm^{-1} broad with 95.53% transmittance is attributed to the presence of N=C=N stretching mode.

3. Peak at 1637.36 cm^{-1} sharp peak with 74.77% transmittance is attributed to the presence of alkyl group or C=C stretching.

4. Peak at 1363.79 cm^{-1} sharp peak with 87.49% transmittance is attributed to the presence of O-H bending mode.

5. Peak at 620 to 557 cm^{-1} very small peak with 33 % transmittance is attributed to the presence of C-Cl bond.

Fig. 7C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 6**, which indicates the absence of any metallo-organic compounds or free organic molecules in the solid precipitate. The inference of the liquid sample is a mixture of ethanol & amide.

Example 7

Reduction of GHG emissions from Steel plant (Plate Mill) in Chhattisgarh with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant in Chhattisgarh - the GHG emission samples were collected from Plate Mill.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the

reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 2 hours. The physical observation of the solution being turned bluish in colour from colourless. The probe to extract GHG emissions in the present case was a long probe.

Fig. 8A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 7**. The broad peak noticed in the UV-Vis spectra from 202.95 to 220 nm is that of ethanol with impurity.

Fig. 8B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 7**.

The following inference is arrived at from the analysis of the liquid sample obtained by the electrocatalytic reduction of GHG emissions.

1. Peak at 3296.23 cm^{-1} broad with 69.30% transmittance is attributed to the presence of alcoholic OH group.
2. Peak at 2105.57 cm^{-1} broad with 95.44% transmittance is attributed to the presence of N=C=N stretching mode.
3. Peak at 1638.06 cm^{-1} sharp peak with 74.77% transmittance is attributed to the presence of alkyl group or C=C stretching.
4. Peak at 1103.04 cm^{-1} sharp peak with 83.57% transmittance is attributed to the presence of C-O stretching.

5. Peak at 610 to 557 cm^{-1} very small peak with 34 % transmittance is attributed to the presence of Cu-O bond.

Fig. 8C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 7**, which indicates the absence of any metallo-organic compounds or free organic molecules in the solid precipitate. The inference is that the liquid sample is a mixture of ethanol & amide.

A consolidated data of VAPs from the electrocatalytic reduction of the GHG emissions as in **Example 7** is represented in **Table 3**.

Table 3

Composition	Volume	VAPs obtained and Remarks			
		In HCl		In H_2SO_4	
		Major	Minor		
O_2	15.52%	Ethanol	Carbamides	Ethanol	Carbamides
CO_2	3.10%				
CO	5%				
NO	31 ppm				
NOx	33 ppm				
SO_2	12 ppm				

Table 4 denotes the summary of the VAPs obtained from the electrocatalytic reduction of GHG emissions from **Example 2** – **Example 7**.

Table 4

Example	**VAPs formed**
2	Ethanol, ethylene, 1,3 Butadiene, Propionaldehyde, Azo dyes
3	Ethanol with primary amine impurity
4	Ethanol with amide impurity
5	Ethanol with amide impurity

6	Ethanol with amide impurity
7	Ethanol with amide impurity

Hence the major product is ethanol and the minor products vary from primary amines to amides.

Example 8

Reduction of GHG emissions from Steel plant-1 (Coke Oven – Battery No. 11) in West Bengal - with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant-1 in West Bengal - the GHG emission samples were collected from Coke Oven – Battery No. 11.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 3A, and the electrocatalytic reaction got stabilized at 1V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density

across the electrodes was continued for 70 minutes. The particulate matter is filtered by attaching filter cap to the nozzle of the probe. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 9A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 8**.

The UV-Vis absorption peaks for the VAPs of **Example 8** have been explained in **Table 5**.

Table 5

Wavelength (nm)	Absorbance	Remarks
191.10	2.608	Peaks from 191 to 204 nm accounts for the presence of ethanol
191.15	2.815	
198.08	2.973	
203.73	2.975	
206.04	3.083	Peaks from 206 to 210 nm indicates n→π*, π→π* transitions of propionaldehyde CH_2=CH-CHO
207.99	3.168	
209.99	3.161	
213.23	3.043	213 to 215 nm accounts for CH_3NH- group
218.74	3.015	π→π* transition of 1,3 Butadiene ($_2$HC=CH-CH=CH_2)
280.05	1.083	Presence of amide linkage O=C-N-H

The UV-Vis spectra demonstrates that around 10 peaks were noticed in the UV-Vis spectra of the VAPs obtained from the electrocatalytic reduction of GHG emissions of the **Example 8**. The first set of peaks from 191 to 204 nm represents the signature peaks of ethanol. The second set of peaks from 206 to 210 nm indicates the non-bonding (n) orbital to anti-bonding (π*) transition as well as bonding (π) orbital to anti-bonding (π*) orbital transitions corresponding to the

propionaldehyde moiety (CH_2=CH-CHO). The third set of peaks range from 213 to 215 nm depicting the formation of primary amine especially methyl amine (CH_3NH_2). The ninth peak at 218.74 nm accounts for the $\pi \rightarrow \pi^*$ transition of 1,3 Butadiene, confirming the formation of 1,3, Butadiene ($_2$HC=CH-CH=CH_2). These nine peaks are high absorbance peaks with absorption of the order of 3.168 to 2.608 Au. The tenth peak is a comparatively low absorption and broad peak at 280.05 nm showing the presence of amide linkage (O=C-N-H). Thus, the VAPs formed as concluded by UV-Vis spectroscopy are ethanol, methyl amine, propionaldehyde and 1,3, Butadiene and amide. The high intensity peaks contribute to the major product, in the present scenario, the products obtained are Propionaldehyde, 1,3, Butadiene & ethanol with amide impurities due to the N_2 rich GHG emissions.

Fig. 9B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 8**, which represents three prominent peaks and a set of low intensity peaks. First broad and high intensity peak at 3336.74 cm^{-1} with 82.52% transmittance is attributed to the presence of alcoholic OH group. The second broad peak at 2157.32 cm^{-1} with 97.83% transmittance is attributed to the presence C=C stretching vibration modes. Third sharp peak at 1636.22 cm^{-1} with 86.05% transmittance is attributed to the presence of C=O stretching bonds. The very low intensity peaks from 628 to 558 cm^{-1} small peaks with 70 to 59% transmittance are attributed to the presence of C-Cl bonds. Thus, the FTIR analysis indicates presence of C=C; C=O; Alkanes; O-H; C-O; groups in the liquid sample of the VAPs. This corroborates the UV-Vis conclusion of the 190 to 204 nm, 205 to 210 nm peaks corresponding to ethanol, propionaldehyde and 1,3 Butadiene in the liquid sample.

Fig. 9C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 8**, and the inferences have been presented in **Table 6**.

Table 6

Time (s)	Identified group or compound	Remarks
3.7 to 4.9	ethanol	Low intensity peak, hence the yield is less
8.094	propionaldehyde	Methyl substituted propionaldehyde with three high intensity peaks
8.522	propionaldehyde	
8.973	propionaldehyde	
10.005	Butadiene	Methyl substituted butadiene next intense peak in the product sample
11.073	Butadiene	
14.557	Iso-pentane	Low intensity peak, hence the yield is less

It is understood that seven peaks are seen in the GC-MS analysis of the liquid sample of VAPs obtained from the electrocatalytic conversion of the GHG emissions form Coke Oven Batt – 11 in conc. HCl medium. Low intensity peaks from residence time of 3.7 to 4.9 s is identified as ethanol peak with very less yield. Three high intensity peaks at 8.094, 8.522 and 8.973 s correspond to methyl substituted propionaldehyde. The next high intense peak at 10.005 & 11.073s represents methyl substituted butadiene. Low intensity peak at 14.557s is a low yield isopentane presence in the liquid sample.

Example 9

Reduction of GHG emissions from Steel plant-1 (Coke Oven – Battery No. 11) in West Bengal - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant-1 in West Bengal - the GHG emission samples were collected from Coke Oven – Battery No. 11.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).

- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 3A, and the electrocatalytic reaction got stabilized at 2V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. The particulate matter is filtered by attaching filter cap to the nozzle of the probe. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 10A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 9**.

The UV-Vis absorption peaks for the VAPs of **Example 9** have been explained in **Table 7**.

Table 7

Wavelength (nm)	Absorbance	Remarks
≥ 195	0.4	Ethanol
212.50	0.2	210-215 nm accounts from methyl amine formation (CH_3NH_2)

790 to 1095	≥ 0.1	Very minor amount of $CuSO_4$

From **Table 7**, it can be inferred that three peaks were seen in the UV-Vis spectra. The first peak at wavelength ≥ 195 nm with 0.4 absorbance represents the presence of ethanol. The second peak at 212.50 nm corresponds to the presence of methyl amine (CH_3NH_2). The third peak from 790 to 1095 nm with very low absorbance of 0.1 denotes the presence of $CuSO_4$ salt in minor amounts in the sample. From the UV-Vis analysis no high intensity peaks are noticed in the present scenario, hence the products obtained are ethanol and primary amine with copper sulphate impurities due to the N_2 rich GHG emissions.

Fig. 10B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 9**, which shows four peaks. The peak at 3270.93cm^{-1} broad with 82.00% transmittance is attributed to the presence of alcoholic OH group. Peak at 1632.12 cm^{-1} sharp peak with 87.02% transmittance contributes to the presence of alkyl group or C=C stretching mode. Peak at 1096.73 cm^{-1} sharp peak with 90% transmittance denotes the presence of C-O stretching of primary alcohol. Peaks between 700-560 cm^{-1} with 50-60% transmittance depicted the presence of Cu-O stretching mode. Thus, FTIR indicates the presence of alcohols, Cu salt and corroborates with the UV-Vis results.

Fig. 10C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 9**, and the inferences have been presented in **Table 8**.

Table 8

Time (s)	Identified group or compound	Remarks
4.115 and 4.625	ethanol	Low intensity sharp peak, hence the yield is less

6.241	Primary amine	High intensity peak, major product
22.0	ethyl esters	Minor product that is ethyl acetoacetate ester

From the GC-MS scan, it is concluded that at 4.115 & 4.625 s, two low intensity sharp peaks were seen due to presence of ethanol of very low yield. The peak at 6.241s is the high intensity peak contributed by primary amine especially methyl amine (CH_3NH_2). The broad peak at resident time of 22s is attributed by ethyl acetoacetate esters as minor product. Thus, the liquid sample is primary amine as major product and ethanol, ethyl acetoacetate ester as minor products as confirmed by UV-VIS, FTIR and GC-MS techniques.

Example 10

Reduction of GHG emissions from Steel plant-1 (Blast Furnace stove) in West Bengal - with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant-1 in West Bengal - the GHG emission samples were collected from the Blast Furnace stove.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 2V and current 5A, and the

electrocatalytic reaction got stabilized at 0.44V, 0.5A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 60 minutes. The particulate matter is filtered by attaching filter cap to the nozzle of the probe, passed through the gas analyzer and then into the electrocatalytic reactor. After completion of the electrocatalytic reaction the solution is colourless.

Fig. 11A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 10**.

The UV-Vis absorption peaks for the VAPs of **Example 10** have been explained in **Table 9**.

Table 9

Wavelength (nm)	Absorbance	Remarks
191.10	0.054	Peaks accounts for the presence of ethanol
196.11	0.022	
796 to 1099	0.03	Peaks from 790 to 1100 nm indicates n→π*, π→π* transitions of ethylene

The UV-Vis spectra indicate two peaks at 191.10 & 196.11 nm accounting to ethanol. Peaks between 796 to 1099 nm represents the n→π*, π→π* transitions of ethylene. As no high intensity peaks were noticed, in the present scenario, the products obtained are ethanol and ethylene. Less intensity is because, the GHG is taken from SOx and NOx analyser and not directly from the chimney of Blast furnace Stove.

Fig. 11B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 10**, which shows three peaks. First broad peak at 3341.11cm^{-1} with 78.83% transmittance is attributed to the presence of alcoholic OH group. Second sharp peak at 1632.38 cm^{-1} with 83.49% transmittance denotes the presence of alkyl group attached to C-OH group. The group of small peaks around 614 to 560 cm^{-1} with 39.19% transmittance depicts the presence of C-Cl stretching mode. Therefore, the FTIR analysis results in the confirmation of alcohol and C-Cl bonds in the product.

Fig. 11C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 10**, and the inferences have been presented in **Table 10**.

Table 10

Time (s)	Identified group or compound	Remarks
3.8 to 4.05	ethanol	Low intensity peak, hence the yield is less
8.103	Ethylene trapped in liquid	with three high intensity peaks as major product
8.53		
8.981		
10.012	Butadiene	Methyl substituted butadiene next intense peak in the product sample
11.08	Butadiene	
14.562	Iso-pentane	Low intensity peak, hence the yield is less

From the GC-MS scan, it is concluded that seven peaks are identified. Peaks between 3.80 to 4.05s is a low intensity peak with low yield of ethanol. Three high intensity peaks at 8.103, 8.53 and 8.981s corresponds to the ethylene trapped in the liquid state. The next two intense peak in the liquid sample are seen at 10.012 and 11.08s indicate the methyl substituted butadiene. The low intensity peak at 14.562s with very less yield denote presence of isopentane. Therefore, the

liquid sample is ethanol and ethylene, butadiene as confirmed by UV-VIS, FTIR and GC-MS spectroscopy.

Example 11

Reduction of GHG emissions from Steel plant-1 (Blast Furnace stove) in West Bengal - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant-1 in West Bengal - the GHG emission samples were collected from the Blast Furnace stove.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 1V, 0.5A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. The particulate matter is filtered by attaching filter cap to the nozzle of the probe,

passed through the gas analyzer and then into the electrocatalytic reactor. After completion of the electrocatalytic reaction the solution is light blue in colour.

Fig. 12A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 11**. The UV-Vis absorption peaks have been explained in **Table 11**.

Table 11

Wavelength (nm)	Absorbance	Remarks
197.96	2.283	High intense peak accounts for the presence of ethanol
1050 to 1099	0.05	Peaks indicates $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ transitions of ethylene

The UV-Vis spectra indicate presence of a high intense peak at 197.96 nm with absorbance of 2.283 accounting for the formation of ethanol. The small very less intense peaks from 1050 to 1099 nm with 0.05 absorbance depicts the $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ transitions of ethylene. Hence from UV-Vis spectra the products formed are ethanol (major) and ethylene (minor).

Fig. 12B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 11**, which shows five peaks of different transmittance. Broad high intense peak at 3540.66 cm^{-1} with 77.68% transmittance is attributed to the presence of alcoholic OH group. Broad peak at 2121.57 cm^{-1} with 95.20% transmittance depicts the presence of acetyl C=O group. Sharp peak at 1634.28 cm^{-1} with 82.30% transmittance denotes the presence of alkyl group or C=C stretching. Broad peak at 1283.05 cm^{-1} with 92.20% transmittance represents the presence of C-O stretching vibrations. Sharp peak at 1096.96 cm^{-1} with 87.22% transmittance indicate C-O stretching of primary alcohol. Peaks from 600 to 500 cm^{-1} with 50% transmittance is attributed to the presence of C-O & C-Cl stretching modes. Therefore, FTIR analysis

corroborates with UV-Vis results of C=C (ethylene), C=O and C-O stretching of primary alcohol (ethanol) in the liquid sample.

Fig. 12C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 11**, and the inferences have been presented in **Table 12**.

Table 12

Time (s)	Identified group or compound	Remarks
3.8 to 4.05	ethanol	High intensity peak
8.077	Ethylene trapped in liquid	with three high intensity peaks
8.5		
8.999		

From the GC-MS scan, it is concluded that four peaks in GC-MS spectra of the VAPs obtained, where the high intensity peak form 3.8 to 4.05s corresponds to ethanol, three high intensity peaks at 8.077, 8.5 & 8.999s represents ethylene trapped in liquid. This confirms the formation of ethanol and ethylene in equal proportions as products.

Example 12

Reduction of GHG emissions from Steel plant-1 (plate mill chimney) in West Bengal - with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant-1 in West Bengal - the GHG emission samples were collected from plate mill chimney.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).

- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 1V, 0.5A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 60 minutes. The particulate matter is filtered by attaching filter cap to the nozzle of the probe. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 13A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 12**. The UV-Vis absorption peaks have been explained in **Table 13**.

Table 13

Wavelength (nm)	Absorbance	Remarks
192.20	2.893	High intense peak accounts for the presence of ethanol
193.89	3.033	
197.07	3.168	
280.12	1.523	Presence of amide groups

The UV-Vis spectra indicate four peaks in the UV-Vis spectra of the VAPs produced by the electrocatalytic reduction of the GHG emissions from plate mill in Conc. HCl medium. Three high intensity peaks at 192.20, 193.89 and 197.07 nm with corresponding absorbance at 2.893, 3.033 & 3.168 respectively accounts for the presence of ethanol in the product and one broad peak at 280.12 nm with absorbance of 1.523 depict the presence of amide linkage in the product. Thus, the products formed in the present case is ethanol (major) and amide (minor).

Fig. 13B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 12**, which shows the following peaks.

- Peak at 3342.02 cm^{-1} broad with 76.74% transmittance is attributed to the presence of alcoholic OH group
- Peak at 2109.36 cm^{-1} broad & weak with 98.43% transmittance is attributed to the presence of C=O stretching mode
- Peak at 1633.89 cm^{-1} sharp peak with 82.88% transmittance is attributed to the presence of alkyl group attached to C-O
- Peak at 1098.32 cm^{-1} small peak with 95% transmittance is attributed to the presence of C-O stretching in primary alcohol
- Peaks from 600 to 500 cm^{-1} with 65% transmittance is due to C-Cl and C=O stretching modes

Therefore, both UV-Vis and FTIR corroborate the formation of ethanol and amide.

Fig. 13C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 12**, and the inferences have been presented in **Table 14**.

Table 14

Time (s)	Identified group or compound	Remarks
3.8 to 4.05	Ethanol	High intensity peak

4.885		Ethanol H-bonded to impurities, in the present case it is amide
5.225		
6.621		

From the GC-MS scan, it is concluded that the high intensity peaks from 3.80 to 4.05s indicate presence of ethanol, high intensity peaks ate 4.885, 5.225 and 6.621s denote ethanol H-bonded to the amide formed as minor product. Hence, from the UV-Vis, FTIR and GC-MS spectroscopy, the VAPs obtained from electrocatalytic reduction of GHG emissions from **Example 12** is ethanol with amide impurities.

Example 13

Reduction of GHG emissions from Steel plant-1 (plate mill chimney) in West Bengal - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant-1 in West Bengal - the GHG emission samples were collected from plate mill chimney.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the

electrocatalytic reaction got stabilized at 1V, 0.49A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. The particulate matter is filtered by attaching filter cap to the nozzle of the probe. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 14A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 13**. The UV-Vis absorption peaks have been explained in **Table 15**.

Table 15

Wavelength (nm)	Absorbance	Remarks
191.75	1.608	High intense peak accounts for the presence of ethanol
221	3.033	Ethanol H-bonded to impurity
790 to 1100	0.056	Peaks from 790 to 1100 nm indicates n→π*, π→π* transitions of ethylene

The UV-Vis spectra indicate three peaks. First peak at 191.75 with absorbance of 1.608 accounts for the presence of ethanol. Second peak at 221 nm with absorbance of 3.033 corresponds to H-bonded ethanol with impurities. The small peaks from 790 to 1100 nm with very low absorbance of 0.056 depict the n→π*, π→π* transitions of ethylene. High intensity peak noticed is ethanol. In the present scenario, the products obtained are ethanol and ethylene.

Fig. 14B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 13**.

- Broad peak at 3331.11 cm^{-1} with 75.69% transmittance is attributed to the presence of alcoholic OH group.
- Broad & weak peak at 2122.36 cm^{-1} with 98.43% transmittance is attributed to the presence of C=O stretching mode.
- Sharp peak at 1634.81 cm^{-1} with 81.52% transmittance is attributed to the presence of alkyl group attached to C-O.
- Small peak at 1101.43 cm^{-1} with 86.65% transmittance is attributed to the presence of C-O stretching in primary alcohol.
- Very small peaks from 600 to 500 cm^{-1} with 65% transmittance is due to C-Cl and C=O stretching modes.

Fig. 14C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 13**, and the inferences have been presented in **Table 16**.

Table 16

Time (s)	Identified group or compound	Remarks
3.8 to 4.15	Ethanol	High intensity peak
4.885		Ethanol H-bonded to impurities, in the present case it is ethylene
5.225		
6.621		

From the GC-MS scan, it is concluded that the high intensity peak at 3.8 to 4.15s indicate the presence of ethanol. Three peaks at 4.885, 5.225 and 6.621 s represent the H-bonded ethanol with ethylene. Thus, in the present scenario the VAPs formed are ethanol and ethylene as confirmed by UV-Vis, FTIR and GC-MS spectroscopy.

Table 17 denotes the summary of the VAPs obtained from the electrocatalytic reduction of GHG emissions from **Example 8** – **Example 13**.

Table 17

Example #	VAPs formed
8	Methyl substituted propionaldehyde, butadiene as major product and ethanol, isopentane as minor products
9	Primary amine as major product and ethanol, ethyl acetate ester as minor products
10	Ethanol as minor product and ethylene, butadiene as major products
11	Ethanol and ethylene in equal proportion
12	Ethanol primarily and amide impurity
13	Ethanol as major product and ethylene as minor

Example 14

Reduction of GHG emissions from Steel plant-2 (Coke Oven – Battery No. 6) in West Bengal - with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant-2 in West Bengal - the GHG emission samples were collected from Coke Oven – Battery No. 6.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the

electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 1V, 0.1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 60 minutes. After completion of the electrocatalytic reaction the solution is colourless.

Fig. 15A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 14**. The UV-Vis absorption peaks have been explained in **Table 18**.

Table 18

Wavelength (nm)	Absorbance	Remarks
193.35	2.270	Peaks from 191 to 204 nm accounts for the presence of ethanol
196.41	2.292	
280	0.51	Presence of amides
1050 to 1100	0.115	$\pi \rightarrow \pi^*$ transition of 1,3 Butadiene ($_2HC=CH-CH=CH_2$)

The UV-Vis spectra indicate three prominent peaks and one set of small peaks. The peaks at 193.35 & 196.41 nm with absorbance 2.27 & 2.292 are the high intensity peaks that accounts for the presence of ethanol. Broad peak at 280 nm with 0.51 absorbance shows the presence of amides and the very small peaks from 1050 to 1100 nm with 0.115 absorbance corresponds to $\pi \rightarrow \pi^*$ transition of 1,3

Butadiene ($_2HC=CH-CH=CH_2$). Thus, from UV-Vis spectroscopy, the products formed are ethanol with amides and 1,3 Butadiene as minor products.

Fig. 15B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 14**.

Four peaks were noticed. First broad high intense peak at 3343.09 cm^{-1} with 74.72% transmittance is attributed to the presence of alcoholic OH group. Second broad peak at 2331.64 cm^{-1} with 97.83% transmittance is attributed to the presence C=C stretching. Third sharp peak at 1634.46 cm^{-1} with 86.05% transmittance is attributed to the presence of C=O stretching bonds. The small peaks at 660 to 540 cm^{-1} with 59% transmittance is attributed to the presence of C-Cl bonds. FTIR analysis indicates the formation of ethanol and alkene as the VAPs thus corroborating the results of UV-Vis analysis.

Fig. 15C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 14**, and the inferences have been presented in **Table 19**.

Table 19

Time (s)	Identified group or compound	Remarks
3.7 to 6.21	ethanol	High intensity peak
8.094	propionaldehyde	Methyl substituted propionaldehyde with three less intensity peaks
8.522	propionaldehyde	
8.973	propionaldehyde	
10.007 & 10.221	Butadiene	Methyl substituted butadiene less intense peak
11.073	Butadiene	
14.557	Iso-pentane	Low intensity peak, hence the yield is less

From the GC-MS scan, seven peaks at different residential time were observed. The peak between 3.7 to 6.21 is a high intense peak representing ethanol. The less intense peaks at 8.094, 8.522, 8.973s represent methyl substituted propionaldehyde. The less intense peaks at 10.007, 10.221 and 11.073s correspond to methyl substituted butadiene. The vey less intense peak at 14.557s denote isopentane. Thus, the VAPs formed are ethanol (major), methyl substituted propionaldehyde and butadiene as minor products.

Example 15

Reduction of GHG emissions from Steel plant-2 (Coke Oven – Battery No. 6) in West Bengal - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant-2 in West Bengal - the GHG emission samples were collected from Coke Oven – Battery No. 6.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 1V, 0.1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised

water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 16A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 15**. The UV-Vis absorption peaks have been explained in **Table 20**.

Table 20

Wavelength (nm)	Absorbance	Remarks
≥ 195	1.2	Ethanol
212.50	0.4	210-215 nm accounts from methyl amine formation (CH_3NH_2)
790 to 1095	≥ 0.1	Very minor amount of $CuSO_4$

The UV-Vis spectra indicate three peaks in the UV-Vis spectra of the VAPs. The high intense peak at ≥ 195 nm with 1.2 as absorbance indicate presence of ethanol. The peak at 212.50 nm with absorbance of 0.4 accounts for the presence of methyl amine and very low intense peaks from 790 to 1095 nm account for very minor amounts of $CuSO_4$ salt. In the present scenario, the products obtained are ethanol is major product and primary amine with copper sulphate impurities due to the N_2 rich GHG emissions.

Fig. 16B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 15**, which shows the following peaks.

- Peak at 3316.55 cm^{-1} broad with 74.58% transmittance is attributed to the presence of alcoholic OH group.
- Peak at 2332 cm^{-1} broad with 95.48% transmittance is attributed to the presence of C=C stretching.

- Peak at 1641.52 cm^{-1} sharp peak with 81.37% transmittance is attributed to the presence of alkyl group or C=C stretching.
- Peak at 1095.50 cm^{-1} sharp peak with 83.20% transmittance is attributed to the presence of C-O stretching of primary alcohol.
- Peak at 700-550 cm^{-1} small peak with 50-60% transmittance is attributed to the presence of Cu-O stretching mode.

Fig. 16C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 15**, and the inferences have been presented in **Table 21**.

Table 21

Time (s)	Identified group or compound	Remarks
3.7 to 6.61	ethanol	High intensity peak
8.094	propionaldehyde	Methyl substituted propionaldehyde with three less intensity peaks
8.522	propionaldehyde	
8.973	propionaldehyde	
10.007 & 10.221	Butadiene	Methyl substituted butadiene less intense peak
11.073	Butadiene	
14.557	Iso-pentane	Low intensity peak, hence the yield is less

From the GC-MS scan, it is observed that ethanol is the major product and Propionaldehyde, Butadiene as minor products as confirmed by UV-VIS, FTIR and GC-MS.

Example 16

Reduction of GHG emissions from Steel plant-2 (Blast Furnace-2) in West Bengal - with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant-2 in West Bengal - the GHG emission samples were collected from Blast Furnace-2.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 1V, 0.25A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 60 minutes. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 17A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 16**. The UV-Vis absorption peaks have been explained in **Table 22**.

Table 22

Wavelength (nm)	Absorbance	Remarks
193.16	2.648	Peaks accounts for the presence of ethanol
198.75	2.889	
213.32	2.826	
204.95	3.008	
209.89	2.892	

The UV-Vis spectra indicate that the peaks from 193.16 to 209.89 account for the presence of ethanol as the complete major product. The hump near 280nm depicts presence of amide impurities.

Fig. 17B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 16**, which shows the following peaks.

- Peak at 3341.73 cm^{-1} broad with 78.83% transmittance is attributed to the presence of alcoholic OH group.
- Peak at 1634.62 cm^{-1} sharp peak with 74.50% transmittance is attributed to the presence of alkyl group attached to C-OH group.
- Peaks at 650 to 560 cm^{-1} small peak with 49.19% transmittance is attributed to the presence of C-Cl stretching mode.

Fig. 17C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 16**, wherein the high intense peak between 3.8 to 6.621 s corresponds to ethanol. Hence the VAP obtained is ethanol.

Example 17

Reduction of GHG emissions from Steel plant-2 (Blast furnace-2) in West Bengal - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant-2 in West Bengal - the GHG emission samples were collected from Blast furnace-2.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 2V, 0.69A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 18A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 17**. The UV-Vis absorption peaks have been explained in **Table 23**.

Table 23

Wavelength (nm)	Absorbance	Remarks
193.189	2.032	High intense peak accounts for the presence of ethanol
1030 to 1100	0.08	Peaks indicates n→π*, π→π* transitions of ethylene

The UV-Vis spectra indicate the presence of one high intense peak at 193.189 nm with absorbance of 2.032 denoting ethanol formation and very small less intense peaks between 1030 to 1100 with absorbance of 0.08 indicating n→π*, π→π* transitions of ethylene.

Fig. 18B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 17**, which shows the following peaks.

- Peak at 3333.56 cm^{-1} broad with 73.50% transmittance is attributed to the presence of alcoholic OH group
- Peak at 1641.16 cm^{-1} sharp peak with 78.99% transmittance is attributed to the presence of alkyl group attached to C-O
- Peak at 1089.12 cm^{-1} sharp peak with 77.04% transmittance is attributed to C-O stretching of primary alcohol
- Peak from 600 to 500 cm^{-1} with 50% transmittance is attributed to the presence of C-O & C-Cl stretching

Fig. 18C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 17**, wherein the very high intensity peaks between 3.8 to 6.621 s indicating the formation of ethanol in the VAPs as major product. This is in conjunction with the results of UV-Vis and FTIR analysis.

Example 18

Reduction of GHG emissions from Steel plant-2 (MSM chimney) in West Bengal - with Conc. HCl.

- Feed source: GHG emissions collected from Steel plant-2 in West Bengal - the GHG emission samples were collected from MSM chimney.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the electrocatalytic reaction got stabilized at 1V, 0.69A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 60 minutes. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 19A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 18**. The UV-Vis absorption peaks have been explained in **Table 24**.

Table 24

Wavelength (nm)	Absorbance	Remarks
194.27	2.25	High intense peak accounts for the presence of ethanol
198.09	2.398	
202.83	2.294	
280.12	0.25	Presence of amide groups
1070 to 1090	0.01	Negligible peaks

The UV-Vis spectra indicate five peaks. The first high intense peak at 194.27 nm, second high intense peak at 198.09 nm, third high intense peak at 202.83 nm with corresponding absorbance at 2.28, 2.398 and 2.294 respectively accounts for the presence of ethanol as major VAP. Low intensity peak at 280.12 nm with 0.25 absorbance indicates presence amide impurities. The negligible peaks between 1070 to 1090 nm with absorbance of 0.01 indicate traces of ethylene.

Fig. 19B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 18**, which shows the following peaks.

- Peak at 3343.09 cm^{-1} broad with 71.06% transmittance is attributed to the presence of alcoholic OH group
- Peak at 1633.68 cm^{-1} sharp peak with 76.84% transmittance is attributed to the presence of alkyl group attached to C-O
- Peaks from 600 to 500 cm^{-1} with 65% transmittance is due to C-Cl and C=O stretching modes

Fig. 19C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 18**, and the inferences have been presented in **Table 25**.

Table 25

Time (s)	Identified group or compound	Remarks
3.8 to 4.05	Ethanol	High intensity peak
4.885		Ethanol H-bonded to impurities, in the present case it is amide
5.225		
6.621		

From the GC-MS scan, it is observed that the high intensity peaks between 3.8 to 4.05 s, 4.885s, 5.225s, 6.621s represent H-bonded ethanol with amide impurities in the VAPs**.**

Example 19

Reduction of GHG emissions from Steel plant-2 (MSM chimney) in West Bengal - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Steel plant-2 in West Bengal - the GHG emission samples were collected from MSM chimney.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 3V and current 5A, and the

electrocatalytic reaction got stabilized at 1V, 0.49A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. After completion of the electrocatalytic reaction the solution turned light blue in colour.

Fig. 20A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 19**. The UV-Vis absorption peaks have been explained in **Table 26**.

Table 26

Wavelength (nm)	Absorbance	Remarks
192.31	1.756	High intense peak accounts for the presence of ethanol
221	0.25	Ethanol H-bonded to impurity
790 to 1100	0.056	Peaks from 790 to 1100 nm indicates $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ transitions of ethylene

From the UV-Vis spectra, the high intense peak at 192.31 with absorbance of 1.756 indicate ethanol. Low intensity peak at 221 nm with absorbance of 0.25 accounts for H-bonded ethanol with impurity. Very small peaks between 790 to 1100 nm with 0.056 absorbance indicates $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ transitions of ethylene.

Fig. 20B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 19**, which shows the following peaks.

- Peak at 3250.18 cm^{-1} broad with 80.35% transmittance is attributed to the presence of alcoholic OH group.

- Peak at 1634.49 cm^{-1} sharp peak with 84.80% transmittance is attributed to the presence of alkyl group attached to C-O.
- Peak at 1094.95 cm^{-1} small peak with 81.05% transmittance is attributed to the presence of C-O stretching in primary alcohol.
- Peaks from 600 to 500 cm^{-1} with 65% transmittance is due to C-Cl and C=O stretching modes.

Fig. 20C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 19**, and the inferences have been presented in **Table 27**.

Table 27

Time (s)	Identified group or compound	Remarks
3.8 to 4.15	Ethanol	High intensity peak
4.885		Ethanol H-bonded to impurities, in the present case it is ethylene
5.225		
6.621		

From the GC-MS scan, it is observed that the peaks between 3.8 to 4.15 s are high intense and demonstrates the presence of ethanol. Peaks at 4.885, 5.225 and 6.621s are mainly due to ethanol-ethylene H-bonded interaction.

Table 28 denotes the summary of the VAPs obtained from the electrocatalytic reduction of GHG emissions from **Example 14** – **Example 19**.

Table 28

Example #	VAPs formed
14	Ethanol as major product and Methyl substituted propionaldehyde, butadiene as minor products

15	Ethanol as major product and propionaldehyde, butadiene as minor products
16	Ethanol as major product
17	Ethanol as major product
18	Ethanol primarily and amide impurity
19	Ethanol as major product and ethylene as minor

Example 20

Reduction of GHG emissions from Gas production plant (outlet through pipeline), Uttar Pradesh, India - with Conc. HCl.

- Feed source: GHG emissions collected from Gas production plant, Uttar Pradesh, India.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu-doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Graphite felt of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density

across the electrodes was continued for 180 minutes. After completion of the electrocatalytic reaction the solution turned light yellow in colour.

Fig. 21A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 20**.

The UV-Vis spectra indicate six peaks. The high intensity peak at 193.822 nm is due to formation of ethanol, second peak at 197.984 nm is also due to ethanol, third peak at 201.773 nm is also due to the formation of ethanol. A broad peak at 333.831 nm is mainly due to Ethylene Vinyl Acetate intermolecularly bonded to ethanol and water. Other insignificant peaks at 840 nm, 950-1100 nm shows the vinyl acetate intramolecularly bonded to water and ethanol mixture.

Fig. 21B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 20**, which shows the following peaks.

- Peak at 3382.99 cm^{-1} broad with 75.62% transmittance is attributed to the presence of alcoholic OH group.
- Peak at 2115.80 cm^{-1} broad peak with 90.31% transmittance is attributed to the presence C=C stretching.
- Peak at 1635.82 cm^{-1} a sharp peak with 79.37% transmittance is attributed to the presence of C=O stretching bonds.
- Peak at 1372.16 cm^{-1} small peak with 95.88% transmittance is attributed to the presence of alkane bending mode.
- Peak at 1352.24 cm^{-1} small peak with 96% transmittance is attributed to the presence of alkane bending mode.
- Peak at 1312.03 cm^{-1} small peak with 93.37% transmittance is attributed to the presence of O-H bending mode.
- Peak at 1226.79 cm^{-1} small peak with 92.47% transmittance is attributed to the presence of C-O stretching vinyl ether linkage.
- Peak at 1187.32 cm^{-1} small peak with 93.98% transmittance is attributed to the presence of C-O stretching ester or ether linkage.

- Peak at 1078.58 cm^{-1} small peak with 102.48% transmittance is attributed to the presence of C-O stretching in aliphatic ether or ester linkage.
- Peak at 1047.89 cm^{-1} small peak with 98.51 % transmittance is attributed to the presence of C-O stretching in secondary alcohol.
- Peak at 975.14 cm^{-1} small peak with 89.24% transmittance is attributed to the presence of C=C bending of alkene (monosubstituted).
- Peak at 885.01 cm^{-1} small peak with 80.35% transmittance is attributed to the presence of C=C bending (vinylidene).
- Peak at 853.55 cm^{-1} small peak with 77.25% transmittance is attributed to the presence of C-Cl bending mode.
- Peak at 788.82 cm^{-1} small peak with 68.6% transmittance is attributed to the presence of disubstituted alkene bending.
- Peak at 640 to 550 cm^{-1} with 40% transmittance is attributed to the presence of C-Cl stretching vibrations.

Thus, FTIR indicates C=C; C=O; Alkanes; O-H; vinyl C-O; Alkene C=C; C-Cl groups. This corroborates the 193-202nm; 333nm peak in UV-Vis corresponding to ethanol and EVA.

Fig. 21C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 20**.

From the GC-MS scan, it is observed that peaks of high intensity at m/z of 45 and 45.1 indicating formation of ethanol with yield of 64%.

Fig. 21D illustrates High temperature GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 20**. The peaks represent the following:

- m/z at 60 indicates the release of alkenes from the polyethylene linkage of EVA.
- m/z at 45 represents the release of ethanol from the solution.

– m/z at 43 represents the release of $^{\cdot}CH_2CHO$ radical.

In High temperature GC-MS the peaks for EVA in the solution is identified to have around C_{18} carbon linkage including polyethylene and vinyl linkage and acetic acid peak separately.

Fig. 21E illustrates UV-Vis spectra of solid sample obtained by the electrocatalytic reduction of GHG in **Example 20**, which represents the following peaks.

– 193.797 & 196.685 nm are peaks of ethanol.
– 264.021 nm is peak of HN-C=O linkage intermolecular bonded with ethanol (amide group).

Fig. 21F illustrates FTIR spectra of solid sample obtained by the electrocatalytic reduction of GHG in **Example 20**. The FTIR peaks indicate the following:

– Peak at 3371.25cm-1 broad with 66.99% transmittance is attributed to the presence of alcoholic OH group.
– Peak at 2104.09 cm-1 broad with 97.51% transmittance is attributed to the presence of aromatic C-H bending overtone.
– Peak at 1637.16 cm-1 sharp peak with 76.03% transmittance is attributed to the presence of alkyl group or C=C stretching.
– Peak at 590-560 cm-1 small peak with 39.19% transmittance is attributed to the presence of C-Cl stretching mode.

Fig. 21G illustrates GC-MS scan of the solid precipitate obtained by the electrocatalytic reduction of GHG in **Example 20**. As there is no significant peak noticed in the GC-MS spectra, most of the composition of the solid VAPs is attributed to sulphates and nitrates from any S or SOx and NOx present in the GHG emissions.

Example 21

Reduction of GHG emissions from Gas production plant (outlet through pipeline), Uttar Pradesh, India - with Conc. HCl.

- Feed source: GHG emissions collected from Gas production plant, Uttar Pradesh, India.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu-doped Ti Mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Cu Plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 180 minutes. After completion of the electrocatalytic reaction the solution turned brown in colour.

Fig. 22A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 21**. It is inferred that 194.10 &

197. 85 nm are peaks of ethanol, 250.021 nm is peak of n→π* or π→π* transition of intermolecular bonded ethanol.

Fig. 22B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 21**, which shows the following peaks.

- Peak at 3368.78cm^{-1} broad with 67.79% transmittance is attributed to the presence of alcoholic OH group
- Peak at 1638.04 cm^{-1} sharp peak with 76.78% transmittance is attributed to the presence of alkyl group attached to C-OH group
- Peaks at 614 to 560 cm^{-1} small peak with 39.19% transmittance is attributed to the presence of Cu-Cl stretching mode

Fig. 22C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 21**, which demonstrates that in the presence of Cu and proprietary Cu doped Ti mesh electrodes, with S, H_2S, SOx and NOx impurities (even at ppm level) resulted in the minor quantities of thiophene azo dyes.

Example 22

Reduction of GHG emissions from Gas production plant (outlet through pipeline), Uttar Pradesh, India - with Conc. H_2SO_4.

- Feed source: GHG emissions collected from Gas production plant, Uttar Pradesh, India.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Graphite felt of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. H_2SO_4. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 180 minutes. After completion of the electrocatalytic reaction the solution turned brown in colour.

Fig. 23A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 22**, which depicts two peaks at 193.841 & 196.54 nm with absorbance of 2.75 demonstrating the formation of ethanol as the only product.

Fig. 23B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 22**, which shows the following peaks.

- Peak at 3358.06 cm^{-1} broad with 66.97% transmittance is attributed to the presence of alcoholic OH group.
- Peak at 2121.32 cm^{-1} broad & weak with 95.83% transmittance is attributed to the presence of azide stretching mode.
- Peak at 1638.17 cm^{-1} sharp peak with 74.69% transmittance is attributed to the presence of alkyl group or C=C stretching.

Fig. 23C illustrates HR-MS spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 22**, which indicates formation of ethanol, copper ethanoate.

Table 29 denotes the summary of the VAPs obtained from the electrocatalytic reduction of GHG emissions from **Example 20** – **Example 22**.

Table 29

Example #	**VAPs formed**
20	Ethanol and Ethylene Vinyl Acetate
21	Ethanol, and thiophene azo dyes
22	Ethanol with Copper ethanoate

Example 23

Reduction of GHG emissions from Distillery plant, Uttar Pradesh (the outlet through pipeline) - with Conc. HCl.

- Feed source: GHG emissions collected from Distillery plant, Uttar Pradesh - the GHG emission samples were collected from the outlet through pipeline.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the

cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 300 minutes. After completion of the electrocatalytic reaction the solution is brown in colour with solid precipitates.

Fig. 24A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 23**. The UV-Vis spectra indicate two peaks at 193.90 & 197.828 nm with absorbance of 2.12 demonstrating the formation of ethanol as the major product.

Fig. 24B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 23**, which shows the following peaks.

- Peak at 3358.04 cm^{-1} broad with 66.97% transmittance is attributed to the presence of alcoholic OH group
- Peak at 2121.32 cm^{-1} broad peak with 96.83% transmittance is attributed to the presence C=C stretching
- Peak at 1638.17 cm^{-1} a sharp peak with 74.59% transmittance is attributed to the presence of C=O stretching bonds
- Peak at 1226.79 cm^{-1} small peak with 92.47% transmittance is attributed to the presence of C-O stretching

The FTIR indicates C=C; C=O; Alkanes; O-H; C-O; groups, this corroborates the 193, 197 nm; peak in UV-Vis corresponding to ethanol.

Fig. 24C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 23**. From the GC-MS scan, it is

observed that ethanol is the major product with yield of 62.42% and the remaining as solid products in the form of Cu-ethanoate precipitates.

Fig. 24D illustrates GC-MS scan of the solid sample obtained by the electrocatalytic reduction of GHG in **Example 23**, which indicates that the solid precipitates resulted from the ethoxide ligand-based Cu tetrahedral complexes such as $[Cu_2(CH_3CH_2O)]^{2+}$ and $[Cu_2(CH_3CH_2O)_4]^{2+}$.

Example 24

Reduction of GHG emissions from Distillery plant, Uttar Pradesh (the outlet through pipeline) - with Conc. HCl.

- Feed source: GHG emissions collected from Distillery plant, Uttar Pradesh - the GHG emission samples were collected from the outlet through pipeline.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Metallic Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Cu-doped Ti mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the

initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 90 minutes. After completion of the electrocatalytic reaction the solution is brown in colour.

Fig. 25A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 24**. The UV-Vis spectra indicate a broad peak from 193 to 251 nm due to ethanol. 250.021 nm is peak of $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition of intermolecular bonded ethanol as the major product.

Fig. 25B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 24**, which shows the following peaks.

- Peak at 3360.26cm^{-1} broad with 66.66% transmittance is attributed to the presence of alcoholic OH group
- Peak at 1633.73 cm^{-1} sharp peak with 73.96% transmittance is attributed to the presence of alkyl group attached to C-OH group
- Peaks at 614 to 560 cm^{-1} small peak with 39.19% transmittance is attributed to the presence of Cu-Cl and/or C-Cl stretching mode

The FTIR indicates Alkanes; O-H; C-OH; groups, this corroborates the UV-Vis corresponding to ethanol.

Fig. 25C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 24**. From the GC-MS scan, it is observed that the solid precipitates resulted from the sulphates and nitrate salts.

Example 25

Reduction of GHG emissions from Distillery plant, Uttar Pradesh (the outlet through pipeline) - with Conc. HCl.

- Feed source: GHG emissions collected from Distillery plant, Uttar Pradesh - the GHG emission samples were collected from the outlet through pipeline.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu-doped Ti mesh of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Graphite felt of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Catalyst initiator: 30% $MgCO_3$ + 15% Na_2CO_3 + 15% $KHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 180 minutes. After completion of the electrocatalytic reaction the solution is light yellow in colour.

Fig. 26A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 25**. The UV-Vis spectra indicate 192.827 nm is peak of ethanol, 197.113 nm is peak of ethanol, 205-213 nm is

peak of $\pi \rightarrow \pi^*$ transition, Shoulder peak at 250 nm is due to alkyl chloride, 340nm peak accounts for aceto group attached to chloro and alkyl group.

Fig. 26B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 25**, which shows the following peaks.

- Peak at 3363.76 cm^{-1} broad with 65.93% transmittance is attributed to the presence of alcoholic OH group
- Peak at 2121.57 cm^{-1} broad with 98.20% transmittance is attributed to the presence of acetyl C=O group
- Peak at 1638.14 cm^{-1} sharp peak with 73.80% transmittance is attributed to the presence of alkyl group or C=C stretching
- Peak at 1283.05 cm^{-1} broad peak with 92.20% transmittance is attributed to the presence of C-O stretching
- Peak from 600 to 500 cm^{-1} with 37.36% transmittance is attributed to the presence of C-O & C-Cl stretching

FTIR indicates formation of alkyl chlorides and corroborates with UV-Vis analysis.

Fig. 26C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 25**. From the GC-MS scan, it is observed that the solid precipitates resulted from the sulphates and nitrate salts.

Example 26

Reduction of GHG emissions from Distillery plant, Uttar Pradesh (the outlet through pipeline) - with Conc. HCl.

- Feed source: GHG emissions collected from Distillery plant, Uttar Pradesh - the GHG emission samples were collected from the outlet through pipeline.
- Electrocatalytic reactor capacity: 5 litres.
- Cathode: Cu plate of dimension 10cm*7cm*2cm (length*breadth*thickness).
- Anode: Graphite felt of dimension 10cm*7cm*2cm (length*breadth*thickness).

- Catalyst initiator: 30% $MgCO_3$ + 15% K_2CO_3 + 15% $NaHCO_3$ with 40% MgO in distilled water.
- Flow rate of GHG: 500 ml/min (30L/h).

The electrocatalytic reactor was prepared according to the above specifications. 3 litres of deionised water was taken in the electrocatalytic reactor vessel, and the electrodes (cathode and anode) were dipped into the deionised water through the reactor lid. GHG was purged into the deionised water in the reactor vessel at a flow rate of 500ml/min at 1 atm pressure. Current density was applied to the cathode and anode at an applied potential of 5V and current 5A, and the electrocatalytic reaction got stabilized at 1.5V, 1A. 5 gm of the catalyst initiator was added to deionised water to form the initiator solution, and the initiator solution was acidified with 50 ml of conc. HCl. The acidified solution generated *in-situ* hydrogen gas by bulk electrocatalysis of acidified deionised water, and the initiation of adsorption of CO_2 on electrocatalyst surface by initiator hydrolysis to facilitate the reduction of GHG into VAPs. Application of the current density across the electrodes was continued for 180 minutes. After completion of the electrocatalytic reaction the solution is light yellow in colour.

Fig. 27A illustrates UV-Vis spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 26**. The UV-Vis spectra indicate 195 to 225 nm broad peak of ethanol and 280 nm of amide.

Fig. 27B illustrates FTIR spectra of liquid sample obtained by the electrocatalytic reduction of GHG in **Example 26**, which shows the following peaks.

- Peak at 3354.19 cm^{-1} broad with 82.20% transmittance is attributed to the presence of alcoholic OH group
- Peak at 2109.36 cm^{-1} broad & weak with 121.43% transmittance is attributed to the presence of C=O stretching mode
- Peak at 1638.26 cm^{-1} sharp peak with 94.93% transmittance is attributed to the presence of alkyl group or C=C stretching

- Peaks from 600 to 500 cm^{-1} with 45% transmittance is due to C-Cl and C=O stretching modes

FTIR indicates formation of alcohol and alkyl chlorides and corroborates with UV-Vis analysis.

Fig. 27C illustrates GC-MS scan of the liquid sample obtained by the electrocatalytic reduction of GHG in **Example 26**. From the GC-MS scan, it is observed that the solid precipitates resulted from the sulphates and nitrate salts.

Table 30 denotes the summary of the VAPs obtained from the electrocatalytic reduction of GHG emissions from **Example 23** – **Example 26**.

Table 30

Example #	**VAPs formed**
23	Ethanol
24	metal acetates and metal ethoxides
25	Ethanol
26	Ethanol and Chloro Acetyl chloride

Advantages:

The electrocatalytic reduction of GHG emissions of the present disclosure has the following non-limiting advantages.

- The air-polluting GHG emission converted into useful raw material for industries.
- VAPs produced is a building block for petrochemical industries and monomer for polymer industries, thus the demand is high.
- Cost of ethylene produced is approximately $800 per ton
- Carbon credits due to CH_4 and/or CO_2, SOx & NOx, S utilization – towards carbon neutral.

- The electrodes as electrocatalyst employed is an earth abundant material and hence highly cost effective.
- Recycling of the electrode and electrocatalyst is highly feasible and facile making the process highly closed loop.
- Completely renewables driven – zero waste concept with 5R compliance.
- Flow type electrocatalytic reactor design leads to high selectivity and yield of production of VAPs.
- Excellent Faradaic efficiency (FE) of the process, leading to good yield of ethanol, thus highly economical.
- To process tonnes of GHG per day, continuous flow electrocatalytic reactor can be designed with ease and hence scaling up and mass production is highly feasible
- Less chemical intensive process, easy design and operation.

Applications:

The electrocatalytic reduction of GHG emissions of the present disclosure has the following non-limiting industrial applications.

- Production of VAPs such as ethylene, propylene, butadiene, other hydrocarbons, acetic acid, ethyl acetate, ethyl acetate esters, ethoxides, metal ethanoates, propionaldehyde, ethanol, amides, amines, ammonia, urea, azo-dyes, graphene, MWCNTs, SWCNTs.

Although the present disclosure is described in terms one or more embodiments, it is to be understood that they have been presented by way of example, and are not limiting. Thus, the present disclosure should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims and their equivalents.

CLAIMS

We claim:

1. An electrocatalytic reactor for conversion of Green House Gas (GHG) emissions that include carbon containing gases as well as non-carbon containing gases into value-added products (VAPs) comprising: symmetric or asymmetric electrodes (cathode and anode), wherein the cathode is selected from metallic Copper (Cu), Cu-alloy, or Cu-doped Ti mesh; and the anode is selected from metallic Copper (Cu), Cu alloy, Ti Mesh, Cu-doped Ti Mesh, Carbon felt, or Cu-doped carbon felt, wherein the electrodes act as electrocatalyst, and acidified deionised water (H_3O^+) as electrolyte for generation of H_2 gas through bulk electrocatalysis, wherein a catalyst initiator is included in the acidified deionised water (H_3O^+),
   wherein an external current of 1 to 5 A is applied to the electrodes in a voltage range of 1 to 5 V, which initiates C-C coupling or C-O coupling reactions on the cathode surface forming short-lived cation radical intermediates, wherein the short-lived cation radical intermediates react among themselves, or the short-lived cation radical intermediates react with the *in-situ* produced H_2 gas, or both, leading to the formation of the VAPs.

2. The electrocatalytic reactor as claimed in claim 1, wherein for application of current density to the electrodes, the power source is set at voltage of 1V to 5V and current of 1A to 5A.

3. The electrocatalytic reactor as claimed in claim 1, wherein Cu-alloy for the electrodes can be selected from Cu/CuO, Cu/Ag, Cu/Ti, Cu/Pt, and Cu/Pd, wherein the alloying substance i.e., CuO, Ag, Ti, Pt, and Pd is present in an amount of less than or equal to 2.5% by weight.

4. The electrocatalytic reactor as claimed in claim 1, wherein in the Cu-doped Ti Mesh electrodes, the dopant Cu is present in an amount of less than or equal to 2% by weight.

5. The electrocatalytic reactor as claimed in claim 1, wherein in the Cu-doped carbon felt, the dopant Cu is present in an amount of less than or equal to 2% by weight.

6. The electrocatalytic reactor as claimed in claim 1, wherein the concentrated acid added to the initiator solution in the reactor vessel is selected from HCl, H_2SO_4, HNO_3, H_3PO_4.

7. The electrocatalytic reactor as claimed in claim 1, wherein the catalyst initiator mixture includes a mixture of 60% by weight of carbonates or bicarbonates of Mg or Na or a combination of carbonates and bicarbonates of Mg and Na with 40% by weight of MgO.

8. The electrocatalytic reactor as claimed in claim 1, wherein the catalyst initiator is a mixture of $MgCO_3$ and one or more of Na_2CO_3, K_2CO_3, $NaHCO_3$, or $KHCO_3$ with 40% by weight of MgO.

9. A method of electrocatalytic conversion of Green House Gas (GHG) emissions that include carbon containing gases as well as non-carbon containing gases into value-added products (VAPs) includes:
   - adding deionised water to an electrocatalytic reactor vessel and dipping a cathode, and an anode in the deionised water;
   - purging GHG into the deionised water in the reactor vessel from an external GHG source;
   - applying current density to the cathode and anode through an external power source; wherein the power source set at voltage of 1V to 5V and current of 1A to 5A;
   - adding a catalyst initiator to the deionised water in the reactor vessel forming an initiator solution; and
   - adding a concentrated acid to the initiator solution in the reactor vessel with constant stirring to form an electrolytic reaction solution, which produces H_2 gas *in-situ* from the electrolytic reaction solution on the cathode surface,

   wherein the applied current density initiates the C-C coupling or C-O coupling reactions on the cathode surface forming short-lived cation radical intermediates, wherein the short-lived cation radical intermediates react among themselves, or the short-lived cation radical intermediates react with the *in-situ* produced H_2 gas, or both, forming organic acid anions and alkoxides,

wherein, on the anode, when the anode contains proton generation, oxygen evolution occurs, wherein the evolved oxygen reacts with the cation radical resulting in the oxidization of the same to form the value-added products (VAPs) such as acetone, acetaldehyde, acetic acid, ethylene oxide,

wherein, additionally, on the anode, when the anode contains Cu, dissolution of Cu occurs forming Cu^{2+} ions, wherein, the organic acid anions and alkoxides react with the Cu^{2+} ions forming metallorganic complexes; wherein, the metallorganic complexes are left for hydrolysis for about 24 hours at 35° to 45° C to form the value-added products (VAPs),

wherein, on the anode, when the anode contains Ti Mesh or Carbon felt i.e. in the absence of Cu, the VAPs formed include Ethylene Vinyl Acetate, Chloro Acetyl Chloride.

10. The method as claimed in claim 9, wherein the application of the current density is continued for 3 to 5 hours.

11. The method as claimed in claim 9 operates at ambient temperature, and 1 atm pressure.

12. The method as claimed in claim 9, wherein Cu-alloy for the electrodes can be selected from Cu/CuO, Cu/Ag, Cu/Ti, Cu/Pt, and Cu/Pd, wherein the alloying substance i.e., CuO, Ag, Ti, Pt, and Pd is present in an amount of less than or equal to 2.5% by weight.

13. The method as claimed in claim 9, wherein in the Cu-doped Ti Mesh electrodes, the dopant Cu is present in an amount of less than or equal to 2% by weight.

14. The method as claimed in claim 9, wherein in the Cu-doped carbon felt, the dopant Cu is present in an amount of less than or equal to 2% by weight.

15. The method as claimed in claim 9, wherein the concentrated acid added to the initiator solution in the reactor vessel is selected from HCl, H_2SO_4, HNO_3, H_3PO_4.

16. The method as claimed in claim 9, wherein the initiator mixture includes a mixture of 60% by weight of carbonates or bicarbonates of Mg or Na or a combination of carbonates and bicarbonates of Mg and Na with 40% by weight of MgO.

17. The electrocatalytic reactor as claimed in claim 9, wherein the catalyst initiator is a mixture of $MgCO_3$ and one or more of Na_2CO_3, K_2CO_3, $NaHCO_3$, or $KHCO_3$ with 40% by weight of MgO.

18. The method as claimed in claim 9, wherein when the carbon containing gases in the GHG include CO_2, CO, CH_4, the VAPs produced include ethanol, acetic acid, propanol (primary and secondary), butanol, isoamyl alcohol, acetone, acetic acid, esters, ethers, ethylene, butadiene, propionaldehyde, ethylene glycol, ethylene oxide.

19. The method as claimed in claim 9, wherein when the non-carbon containing gases in the GHG include H_2, N_2, H_2S, S, SOx, NOx, the VAPs produced include ammonia, amines, thiophene azo dyes, ethylene vinyl acetate, chloro acetyl chloride.

Dated this 08th day of March 2024



Tigmakar Tapan Kumar Brahma
IN/PA 3027
ExiLyze Intellectual Services
(Agent for the Applicants)

To,
The Controller of Patents
The Patent Office, at Chennai, India.

ABSTRACT

ELECTROCATALYTIC REACTOR AND METHOD FOR ELECTROCATALYTIC REDUCTION OF GREEN-HOUSE GAS (GHG) EMISSIONS INTO USEFUL CHEMICALS

An electrocatalytic reactor for conversion of Green House Gas (GHG) emissions into value-added products (VAPs), which includes an electrocatalytic reactor equipped with symmetric or asymmetric electrodes (cathode and anode) that act as electrocatalyst, which are dipped in an electrolytic reaction solution that includes acidified deionised water (H_3O^+) and a catalyst initiator. An external current of 1 to 5 A applied to the electrodes in a voltage range of 1 to 5 V for 3 to 5 hours, which initiates C-C coupling or C-O coupling reactions on the cathode surface forming short-lived cation radical intermediates, wherein the short-lived cation radical intermediates react among themselves, or react with *in-situ* produced H_2 gas, leading to the formation of VAPs such as ethylene, propylene, butadiene, acetic acid, ethyl acetate, ethyl acetate esters, ethoxides, propionaldehyde, ethanol, amides, amines, ammonia, urea, azo-dyes, graphene, MWCNTs, SWCNTs.

Fig. 1

