

# Sustainable conversion of carbon dioxide into diverse hydrocarbon fuels via molten salt electrolysis

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## Abstract

In recent decades, the unlimited use of fossil fuels mostly for power generation has emitted a huge amount of carbon dioxide in the atmosphere which in return has led to global warming. Here we use green technology, the molten salt electrochemical system comprising of titanium and mild steel as a cathode with graphite anode whereas molten carbonate ( $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ; 43.5:31.5:25 mol%), hydroxide ( $\text{LiOH-NaOH}$ ; 27; 73 and  $\text{KOH-NaOH}$ ; 50:50 mol %) and chlorides ( $\text{KCl-LiCl}$ ; 41-59 mol%) salts as electrolytes This study investigates the effect of temperature, feed gas ratio  $\text{CO}_2/\text{H}_2\text{O}$  and use of different cathode materials on hydrocarbon product along with current efficiencies. Gas chromatography and mass spectroscopy have been applied to

analyze the gas products. According to GC results, more specific results in terms of high molecular weight and long chain hydrocarbons were obtained by using titanium cathodic material rather than mild steel. The results revealed that among all the electrolytes, molten carbonates at 1.5V and 425°C produced higher hydrocarbons as C<sub>7</sub>H<sub>16</sub> while all other produced CH<sub>4</sub>. The optimum conditions for hydrocarbon formation and higher current efficiencies in case of molten carbonates were found to be 500°C under a molar ratio of CO<sub>2</sub>/H<sub>2</sub>O of 15.6. However, the current efficiencies do not change on increasing the temperature from 425 to 500°C and is maintained at 99% under a molar ratio of CO<sub>2</sub>/H<sub>2</sub>O of 15.6. The total current efficiency of the entire cathodic product reduced clearly from 95 to 79% by increasing the temperature under a CO<sub>2</sub>/H<sub>2</sub>O ratio of 9.2 due to the reduction of hydrocarbon generation in this case, despite the formation of C<sub>7</sub>H<sub>16</sub>. Therefore, due to its fast electrolytic conversion rate and low cost (no use of catalyst) the practice of molten salts could be an encouraging and promising technology for future investigation for hydrocarbon fuel formation.

**Keywords:** Renewable energy; CO<sub>2</sub> utilisation; electrochemical conversion; Molten salts electrolysis; Hydrocarbon fuels and CO<sub>2</sub>/H<sub>2</sub>O.

## **Introduction**

With the increasing population, the demand for the energy resources (fossil fuels) have been increased drastically which in turn has resulted in the higher concentration of CO<sub>2</sub> in the atmosphere. Despite the fact that fossil fuels supply almost 80% of earth's energy, they have exacted an enormous toll on the environment, including global warming, as well as on humans<sup>1</sup>. Air pollution due to the burning of fossil fuels has surplus the fatality rate of cardiovascular, pulmonary and other various diseases <sup>2</sup>.Therefore, the approach to minimize CO<sub>2</sub> emission by

using renewable sources of energy including solar, wind, geothermal as well as nuclear have gained much attention in the last few years<sup>3,4</sup>. However, these renewable resources do not include sequestration of CO<sub>2</sub> through their electricity generation. Alternatively, to store the energy in the form of hydrocarbon fuels (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>) CO<sub>2</sub> capture and conversion is a feasible approach. Different carbon capture techniques reported in the literature include cryogenic fractionation, membrane separation, physical adsorption and chemical adsorption, whereas the chemical absorption method is considered as one of the most applied techniques<sup>5</sup>. Aqueous electrolysis, solid oxide electrolysis, photo catalytic reduction, proton exchange membrane, thermochemical cycles and electrolysis using molten salts are the various types of CO<sub>2</sub> conversion techniques explored in recent years<sup>6-8</sup>.

..The electrolysis is considered an effective method for the production of hydrocarbon fuel from CO<sub>2</sub> and H<sub>2</sub>O. The aqueous electrolysis at low temperatures (<100 °C) was employed by scientists<sup>9</sup>, whereas suitable catalyst to reduce energy consumption and increase product selectivity is necessary<sup>10</sup>. Besides the low solubility of CO<sub>2</sub> in the medium, slow kinetics, low productivity due to unseparated products limits its future use<sup>11</sup>. The high-temperature electrolysis offers both thermodynamic as well as kinetic advantages. Solid oxide electrolysis cells (SOEC) and molten salt cells are used in high temperatures. SOEC produces syngas as well as hydrocarbons<sup>12, 13</sup> but the instability of Ni-based electrode, the performance degradation of the electrode structures due to sintering and agglomeration at high-temperature operations results in greater disadvantages of SOEC usage as a promising technique for effective reduction of CO<sub>2</sub><sup>14, 15</sup>.

Different from SOEC, molten salt has relatively high efficiency and a high generation rate by chemical absorption and physical dissolution of carbonates, hydroxides or chlorine, CO<sub>2</sub> in such cells often exists as CO<sub>3</sub><sup>2-</sup> which makes easy to remove CO, H<sub>2</sub> and other gaseous products from reactants<sup>16</sup>. Besides a wide electrochemical window, high electric conductivity, relatively low cost and their reactivity with CO<sub>2</sub>, the possibility of carbon or CO hydrogenation after electrolysis in molten salts is much more significant. Molten salts, therefore, can be employed to convert CO<sub>2</sub> electrochemically to hydrocarbon gas to liquid fuels using renewable energy<sup>17</sup>. Moreover, Cherry and his research group<sup>17</sup> reported different carbonates eutectics Li<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> (62–38%) and Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> (52–48%) using a gold flag as the electrode at 575–650 °C to produce CO and H<sub>2</sub>. Formation of 45.9% methane and 53.1% hydrogen has been shown by using molten carbonates Li<sub>0.43</sub>Na<sub>0.26</sub>K<sub>0.21</sub>CO<sub>3</sub> (61:22:17) mixed with LiOH were used at 550°C using Ni wire as anode and iron wire as cathode using partitioned cell<sup>16</sup>. LiOH-LiCl at 380°C reported as a promising technique for hydrogen supply, however, lack of efficient recycling of by-product has been a limitation to its use. A high yield 63.34% CH<sub>4</sub> and 35.81% H<sub>2</sub> formation have been reported using Fe cathode and Ni anode in Li<sub>0.85</sub>Na<sub>0.61</sub>K<sub>0.54</sub>+0.15Ca(OH)<sub>2</sub> at 575°C and it is also found that replacing LiOH in place of calcium gives 24.36% CH<sub>4</sub><sup>18</sup>.

Despite molten salts types the electrolyser arrangement, electrodes, the variable conditions such as temperature, CO<sub>2</sub>/H<sub>2</sub>O ratio, effects significantly in the conversion of CO<sub>2</sub> to CO and hydrogen. Different electrolyser arrangements have been reported in the literature the electrolysis cell for CO<sub>2</sub> reduction to CO at 900°C using a partitioned compartment for each of the cathode and anode gas products has been reported<sup>19</sup>. Otake et al.,<sup>20</sup> demonstrated a direct reduction of carbon dioxide to CO using molten chloride with molten oxide in partitioned cell electrolyser. Many researchers

have also discussed the effect of different electrodes for hydrogen production as Hu et al.,<sup>21</sup> discussed the electrode kinetics of nickel porous electrode for hydrogen production in molten carbonate electrolysis cell within the temperature range of 600–650 °C.

However, the use of the same electrolyzer arrangement has not been reported for different molten salts. Herein, a new electrolytic cell using partitioned cell approach with ceramic tubes for collection of anodic and cathodic gases has been arranged to generate hydrocarbons using the eutectic mixtures including carbonates ( $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ ; 43.5:31.5:25 mol%), chlorides (KCl and LiCl; 41-59 mol%) hydroxide (LiOH-NaOH; 27;73 and KOH-NaOH; 50:50 mol%). For the first time, the effect of feed gas ratio  $\text{CO}_2/\text{H}_2\text{O}$  at different temperature (425 and 500°C) on electrolysis in molten salt has been taken into consideration. In this study different optimum conditions including the feed gas ratio  $\text{CO}_2/\text{H}_2\text{O}$  (9.2 and 15.6), temperature (275–500°C) and applied voltage (1.5–3V) have been discussed based on the hydrocarbon product content and current efficiency. In addition, the effect of different cathode materials, titanium and mild steel in molten carbonates at 500°C with  $\text{CO}_2/\text{H}_2\text{O}$  ratio of 15.6 in feed gas has also been discussed.

## **Material and methods**

### **Chemicals**

Lithium chloride (LiCl; 99%), potassium chloride (KCl; >99.9%), lithium hydroxide (LiOH;  $\geq 98\%$  powder), sodium hydroxide (NaOH;  $\geq 98\%$  pellets), potassium hydroxide (KOH; 90% flakes), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ;  $\geq 99.5\%$ ), lithium carbonate ( $\text{Li}_2\text{CO}_3$ ;  $\geq 99.0\%$ ) and potassium carbonate ( $\text{K}_2\text{CO}_3$ ;  $\geq 99.0\%$ ) were procured from Sigma-Aldrich, USA. Carbon dioxide ( $\text{CO}_2$ ; 99.99%) and argon (Ar; 99.99%) were supplied by Air products.

## Reactor design

The Electrochemical measurements were carried out in house built cylindrical retort comprising of flange type cover using 316- grade stainless steel (17% Ni, 12% Cr, and 2% Mo) to shape the reactor. The dimensions of the retort were 130 mm internal diameter, 7.5 mm wall thickness and 800mm vertical length. A cooling water jacket (Height: 65 mm; Diameter: 200 mm; Thickness: 10 mm) was manually welded to the retort with the flange. On the flange cover, there were some holes drilled for the insertion of ceramics tube. Ceramics tubes are used to collect anode and cathode gases from electrode surface exposed to the molten salt and to guide the gas moving out of the reactor (**Fig. 1**). Two silicon rubber bungs served to hold electrodes inside the ceramic tubes. Another hole in the retort lid was used to insert a smaller ceramic tube for gas feed inlet, the tube was long enough to reach the surface of the molten salt contained in an alumina crucible.

The rotameters of flow range from 20 to 200 mL/min and 5 to 100mL/min at ambient temperature and pressure were connected with the cylinders of CO<sub>2</sub> (99.99%) and Ar (99.99%) that were set to 0.12 MPa. To obtain the desired content of steam (water vapour) in the gas inlet of the reactor, CO<sub>2</sub> and Ar were mixed together before introducing to a dreschel bottle containing 100 mL Millipore grade deionised water. The outlet gas tube was connected to another dreschel bottle having Laboc 10 mineral oil to prevent air entry. A stainless steel stand (Height; 380 mm) was placed and a refractory brick was mounted. In this setup, parts of the cathode and anode rods were deliberately brought out from the tube end inside the salt<sup>19, 20, 22</sup>. In this study combination of four molten salts were used as electrolytes a mixture of molten carbonates (Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>), a mixture of molten chlorides (LiCl-KCl) and two mixtures of molten hydroxides (LiOH-NaOH and KOH-NaOH).

The selection of the molten salt was done based on low melting points and the ability to generate hydrocarbon fuels from the co-reduction of CO<sub>2</sub> and H<sub>2</sub>O. The combination of a hydrocarbon molecule starts ideally from the two known element sources: carbon (C) and hydrogen (H). Both of these elements can be effectively formed from electrochemical conversion via an appropriate molten salt. The electrolyte salts were dried at 200 °C for 4h at atmospheric pressure before their mixing to remove any sort of water impurity and then poured into a corrosion-resistant electrolyser's retort<sup>23</sup>. Different electrode materials have been used for different molten salts, a graphite rod of 5 mm in diameter was used in molten chlorides whereas, a mild steel rod (BDMS, 5 mm diameter) was used as the cathode in both carbonate and hydroxide molten salts. A titanium foil of (25×100×1 mm) dimension and nickel rod of 5 mm diameter were used also as cathode materials in molten carbonate for the selective production of hydrocarbon species. A 6 mm diameter stainless steel rod (304 grade) was used as the counter electrode or anode in the case of both molten carbonate and hydroxide.

The stainless steel exhibits sufficiently good oxidation resistivity and conductivity in addition to its moderate cost. In the case of molten chloride, the counter electrode/anode material was graphite rather than stainless steel because of the relatively high oxidation activity of most of the transition metals such as Fe, Ni, Co, etc. inside molten chloride<sup>21, 23, 24</sup>. Whereas the comparison between two different cathode materials titanium foil 1×20×100 mm<sup>3</sup> and mild steel rod of 5 mm in diameter based on hydrocarbon product content was carried out for electrolysis in the mixed Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> with 43.5-30.5-25 mol% at 500 °C, 1.5 V and a CO<sub>2</sub>/H<sub>2</sub>O ratio of 15.6 in the feed gas.

## Characterization

The PerkinElmer Clarus 580 type instrument was used for gas chromatographic analysis (GC) of general light hydrocarbons ( $<C_6$ ). The Clarus GC has an FID channel to analyse the hydrocarbon gases and the non-hydrocarbon gases were analysed using TCD detector. In this instrument, the gas separation was performed using an RT® Alumina Bond/KCl capillary column (30 m  $\times$  0.32 mm i.d., 5  $\mu$ m) with helium as the carrier gas for hydrocarbon analysis and a Haysep N6 packed column (60–80, 7'  $\times$  1/8" sulfinert) with argon as a carrier gas for non-hydrocarbon analysis. The oven program of 60 °C (hold for 13 min) to 160 °C (hold for 2 min) at 10 °C/min was used for both the TIC and FID channels<sup>25, 26</sup>.

The gas samples were identified and quantified by comparing two different gas calibration standards first which have permanent gas standard with composition of H<sub>2</sub> 10%, CO<sub>2</sub> 10% and CO 40% for TCD detector and the second standard calibration gas for the FID detector contains ethane (C<sub>2</sub>H<sub>4</sub>) 0.2%, propylene (C<sub>3</sub>H<sub>6</sub>) 0.2%, 1-butene (C<sub>4</sub>H<sub>8</sub>) 0.2%, 1-pentene (C<sub>5</sub>H<sub>10</sub>) 0.2%, methane (CH<sub>4</sub>) 20%, ethane (C<sub>2</sub>H<sub>6</sub>) 10%, propane (C<sub>3</sub>H<sub>8</sub>) 5%, n-butane (C<sub>4</sub>H<sub>10</sub>) 2%, n-pentane (C<sub>5</sub>H<sub>12</sub>) 1%. To analyze the feed gas compositions for CO<sub>2</sub> and H<sub>2</sub>O contents gas detecting tubes from GASTEC (ai-cbss Ltd.) were used. With the change in colour from orange to yellow, GASTEC 2HH is characterized to detect the higher contents of CO<sub>2</sub> from 5 to 40% of the feed gas. The water content in the range of 0–18 mg/L can be analyzed by using GASTEC30 tube, and it contains Mg(ClO<sub>4</sub>)<sub>2</sub><sup>27</sup>.



## Results and discussion

### Analysis of electrolyte selection

The molten salt used for electrolysis should possess the ability to be used at low operating temperatures without solidification in order to perform the process in the liquid state. Moreover, salt should have high CO<sub>2</sub> capturing capacity and sufficiently negative cathodic limit in terms of the individual reduction of CO<sub>2</sub> and H<sub>2</sub>O to CO and H<sub>2</sub> respectively<sup>28</sup>.

### Molten Carbonates

The ternary mixture of Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> (43.5, 31.5, and 25.0) mol% has been chosen as it provides the lowest melting point of 397°C amongst all forms of inorganic molten carbonates. The most attractive characteristic of molten carbonate salts, their high capacity for capturing CO<sub>2</sub><sup>29</sup>. The production rates and selectivity for various hydrocarbon species and non-hydrocarbon species including (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>14</sub>, C<sub>7</sub>H<sub>16</sub>, CO, H<sub>2</sub>O, and H<sub>2</sub>) were investigated in molten carbonates (Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>; 43.5:31.5:25 mol%) at 425 °C and 1.5 V by using the gas feed composition of 48.4% (CO<sub>2</sub>) + 3.2% (H<sub>2</sub>O) + 48.4% (Ar) at CO<sub>2</sub>/H<sub>2</sub>O=15.6 and titanium plate as a cathode with the surface area of 5.9 cm<sup>2</sup>. The findings presented in **Fig. 2** and **Table 1** reported that the selectivity for different hydrocarbon species including CH<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, and C<sub>4</sub>H<sub>8</sub> was good at 425 °C due to the lower rates of H<sub>2</sub> and CO in the final products. The presence of CO as clearly noted from **Table 1a** relatively significant amount (in comparison to CH<sub>4</sub>), can be imputed to the individual reduction of CO<sub>2</sub> to CO. On the other hand, some amount of CO<sub>2</sub> was detected in the product using a TCD detector for the non-hydrocarbon channel in the GC **Fig. 2**.

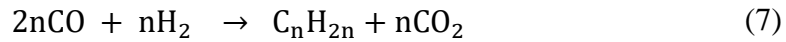
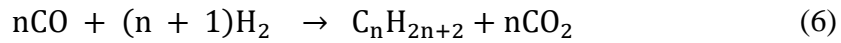
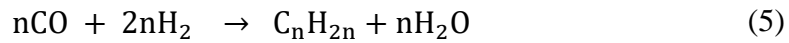
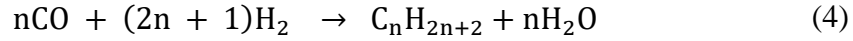
This is because some of the primarily absorbed CO<sub>2</sub> from the molten carbonates can be flushed from the molten salt surface inside the ceramic tube during electrolysis also, a ten-time higher

calorific value as compared to H<sub>2</sub> and CO is offered by the formation of higher molecular weight products (such as C<sub>6</sub>H<sub>14</sub> and C<sub>7</sub>H<sub>16</sub>) with small production rates (2.4 and 1.2 μmol/h cm<sup>2</sup> respectively). The formation of CH<sub>4</sub> can be justified by the reaction of carbon and carbon monoxide with hydrogen. The feasibility of the formation of methane gas from C, CO and hydrogen can be seen from **Eqs. (1) to (3)** as the change in Gibbs free energy at 425 °C is negative indicating the spontaneous reaction. Ji *et al.*,<sup>18</sup> reported CO<sub>2</sub> reduction into CH<sub>4</sub> and H<sub>2</sub> at 575 °C using 20 cm<sup>2</sup> iron and Ni anode with a current efficiency of 92.97%. Wu *et al.*,<sup>30</sup> supported the conversion of CO<sub>2</sub> and H<sub>2</sub>O to methane during molten carbonate electrolysis. Cherry *et al.*,<sup>17</sup> claimed that the adsorption and formation of CO molecules can occur on the cathode by CO<sub>2</sub> reduction at low temperatures (≤650 °C), particularly with lower partial pressures of CO<sub>2</sub> less than 1 bar.



The formation of C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub> was relatively small compared with the corresponding alkenes (**Table 1**). This alkane formation can be confirmed in place of C<sub>2</sub>-C<sub>4</sub> alkenes by mass spectrometric analysis (**Fig. 3**). Peaks 57, 43 and 29 stands for the mass of fragments lost .from C<sub>4</sub>H<sub>10</sub> (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), C<sub>3</sub>H<sub>8</sub> (CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>) and C<sub>2</sub>H<sub>6</sub> (CH<sub>3</sub>CH<sub>3</sub>) respectively. The last peaks (43 and 29) are produced from the further fragmentation of C<sub>4</sub>H<sub>10</sub> and C<sub>3</sub>H<sub>8</sub>. Peaks 55 and 41 stands for the mass of fragments lost from 1-C<sub>4</sub>H<sub>8</sub> (for instance) and C<sub>3</sub>H<sub>6</sub> respectively. The higher intensity of 57 and 43 peaks in **Fig. 3** does not stand for higher content or concentration of certain

compounds (namely C<sub>3</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>) over certain other compounds (namely C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>8</sub>) when compared to the intensity of the corresponding species in standard gas with specified alkane and alkene compositions. The formation of alkene and alkane (C<sub>2</sub>-C<sub>4</sub>) can be seen from **Eqs. (4)-(5)**<sup>31, 32</sup> and **Eqs. (6)-(7)**<sup>33</sup>.



Due to the presence of CO in larger amounts as compared to hydrogen the formation alkene takes place. Generally, the alkenes and alkanes are formed from the CO<sub>2</sub> route because molten carbonates can absorb CO<sub>2</sub> produced during the reaction. The formation of alkenes as C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> at 425°C rather than alkanes occurs due to the partial oxidation of methane as can be seen from **Eqs. ((8)-(9))**.



The oxidation of methane can take place directly by the reaction with the oxygen produced from the anode or its oxygen absorbed inside the molten salt before passing through anode ceramic tube.

On comparing the  $\Delta G$  values of **Eqs. (1) to (3)** to that of **Eqs. (7) to (8)**, it can be concluded that the formation of higher hydrocarbon will be more feasible with alkenes being more favoured rather than alkanes.

### **Molten chlorides**

It is preferable to mix molten chloride salts with oxides or carbonate salts to provide  $O^{2-}$  ions at an adequate concentration for absorbing more  $CO_2$  gas into the molten salt, thereby increasing the product yield from electrolysis. However, the applied or working temperature of the resulting molten salt mixture will also be high, which is not favourable for hydrocarbon production<sup>34</sup>. The production rate of hydrocarbons was investigated in KCl-LiCl molten salt (41–59 mol %) which was continuously flowing through ceramic tubes at the conditions of atmospheric pressure, 2 V and 375°C using feed gas containing  $H_2O$ ,  $CO_2$  and Ar (97.9, 2.1 and 0%). The formation of  $CH_4$ (0.05%) and  $H_2$ (2.4–2.5%) gases were presented in **Fig. 4**. The reaction of  $CO_2$  with  $OH^-$  can be confirmed in the molten chloride for the as the concentration of  $CO_2$  was only 4.8% and the faraday efficiency was found to be 59.3% as presented in **Table 2**.

Comparing the gas product results from the cathode in the molten carbonate with the molten chloride it can be seen that the molar ratio of  $H_2/CH_4$  of product generated in the molten carbonates is about 24. This value is quite half of the ratio calculated for the molten chlorides. To increase productivity in case of molten chlorides high temperature and high voltages are required as reported by Ijije *et al.*,<sup>35</sup> in case of carbon dioxide conversion using LiCl-KCl- $CaCl_2$ - $CaCO_3$  molten salt between the temperature range of 500 to 800 °C. Otake and his research group<sup>20</sup> also used LiCl for the electrolysis of  $CO_2$  at 650 °C. This can be imputed to the higher formation of hydrocarbons in the molten carbonates rather than in the molten chlorides. The current efficiencies of both the

H<sub>2</sub> and CH<sub>4</sub> products generated in the molten chlorides do not reach 60% on the best of occasions whereas the summation of current efficiencies of cathodic products in the molten carbonates can reach 95%. Moreover, the energy consumption was found to be 311 J in case of chlorides which is greater than that of molten carbonates. This can be imputed to the formation of CO in the molten carbonate case, increasing the opportunity of hydrocarbon formation (**Table 2**).

### **Molten hydroxides**

The operating temperature in molten hydroxides can be generally lower than in molten carbonates (200–400°C in the case of molten hydroxides), which is favourable for the formation of hydrocarbons in the gaseous state. However, such investigations are still quite scarce. The process was actually omitted from the literature because of the reactivity of CO<sub>2</sub> with molten hydroxides which results in the production of carbonate ions that are listed as non-electroactive ions in a molten hydroxide<sup>18</sup>. The electrolysis is performed with LiOH-NaOH (27–73 mol%) and KOH-NaOH (50:50 mol%) molten salt at 2 V applied voltage and at 275 °C with a gas feed (17% CO<sub>2</sub> + 3.1% H<sub>2</sub>O by volume). **Table 3** shows a temperature effect on the production of methane, hydrogen and carbon monoxide during the electrolysis of LiOH-NaOH at 2.0 V cell voltage using the composition of CO<sub>2</sub>, H<sub>2</sub>O, and Ar in the feed. Due to the lower melting point (187 °C) KOH-NaOH salt was used at 220°C instead of 1LiOH-NaOH eutectic mixture.

**Table 3** reported that at the constant voltage on increasing the temperature from 220 to 275 °C the H<sub>2</sub> production rate became slightly higher and there was a significant drop to 41.6 μmol/h.cm<sup>2</sup> at 335 °C. However, in molten KOH-NaOH (50:50 mol%) and LiOH-NaOH (27:73 mol%) salts, the production rates for CO and CH<sub>4</sub> were same as 0.00 and 6.12 μmol/hcm<sup>2</sup> when temperature increased from 220 to 275 °C and then inclined to 0.8 μmol/h cm<sup>2</sup> for both fuels at 335 °C in molten

hydroxide. It has been suggested that hydrocarbon, H<sub>2</sub> and CO content does not improve by increasing the electrolytic temperature, in molten hydroxides (KOH-NaOH 50:50 mol%, and LiOH-NaOH 27:73 mol%). Liu *et al.*,<sup>24</sup> revealed that hydrogen formation increases slightly on increasing the temperature due to activity growth while CO decreases due to oxidation. **Fig. 5** confirms the formation of a gaseous product (CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub>) from the GC analysis by using FID and TCD detectors. Ji *et al.*,<sup>16</sup> confirm that CH<sub>4</sub> and syngas are formed due to the co-electrolysis of C<sup>4+</sup> and H<sup>+</sup> in case of molten hydroxide, However, on comparing **Table 1** and **Table 3** it can be concluded that the current efficiencies and the gas product specification are better in molten carbonates than molten hydroxides at low temperature. CH<sub>4</sub> was the main products in case of molten hydroxide while other hydrocarbons such as propane, butane and hexane are not found due to lack of partial oxidation **Fig. 5**.

### **Optimization of electrodes**

Cathode and anode materials have been chosen based on their resistivity to the molten salt medium and the ability to carry out redox reactions effectively before catalyzing the formation of hydrocarbon fuels. In the case of molten carbonates, the choice of a proper metal for the cathode material is more convenient because the molten salt electrolyte is less aggressive at lower applied temperatures. The temperatures used in CO<sub>2</sub> conversion experiments were significantly lower than 800 °C and can serve dually to reduce metal corrosion while also increasing the hydrocarbon yield. Due to the effective layer of the metal oxide covering the metal when exposed to molten salts, valve metals (Ti, Zr, Hf, V, Nb, Ta, Al) can be used effectively in molten carbonate<sup>16-20, 22</sup>.

A mild steel rod of 5 mm in diameter was used as a cheaper cathode material for electrolysis in the mixed Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> with 43.5-30.5-25 mol% at 500°C, 1.5 V and a CO<sub>2</sub>/H<sub>2</sub>O ratio

of 15.6 in the feed gas. It was observed that the hydrocarbon species in the cathodic gas product ranged qualitatively between C2 and C5 retention times less than 23 minutes from FID analysis by 0.03% of the whole gas product in addition to 0.03% of CH<sub>4</sub>. Some other unidentified species over C5 (retention times over 23 min) were found also by 0.06% of the entire gas product.

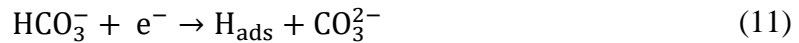
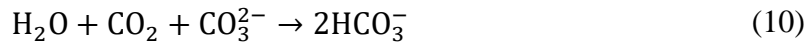
A titanium foil 1×20×100 mm<sup>3</sup> was used as an alternative cathode material for comparison. It was found that the content of C2-C5 species in the gas product in the titanium cathode material case was reduced by 50 to 0.015% while there was an increase in components over C5 by more than 65% over the previous value for mild steel to reach almost 0.1% of the whole gas product. Kalpan *et al.*,<sup>19</sup> confirms that at higher temperatures titanium cathode is insoluble in carbonate molten salt and also does not form an alloy with the lithium, therefore can be used as a cathode for hydrocarbon fuel production using molten carbonate salt. Ossama *et al.*,<sup>36</sup> used Ti cathode for molten carbonates and confirmed the formation of higher hydrocarbons. Further, the GC analysis of both the cathode material **Fig. 6** revealed that the products in the case of titanium cathodic materials were more specific as found in higher molecular weight, long-chain hydrocarbons and thus offer a higher enthalpy of combustion to produce energy or higher heat values. These findings correlate with the literature<sup>9</sup>.

Siambun *et al.*<sup>37</sup> revealed that some amount of carbon formed during electrolysis penetrates in the steel cathode. In order to maintain carbon atom flux in mild steel, a pure carbon layer is important till the end of electrolysis. This thickness depends on two factors: the carbon penetration rate and carbon deposition rate. The penetration rate of carbon is controlled by diffusion and does not depend on applied voltage and temperature. While the carbon deposition rate is controlled by

applied cell voltage. Due to the higher deposition rate, the penetration rate decreases as the deposited layer becomes thicker with time, therefore utilization of carbon is incomplete and hence, low amount of hydrocarbon products. Therefore, the titanium foil is found to be a better cathode material in case of molten carbonates rather than mild steel **Fig. 6**.

### **Effect of gas feed composition and temperature**

The composition of CO<sub>2</sub> and H<sub>2</sub>O in the feed gas depends generally on the type of molten salt itself. Regarding the H<sub>2</sub>O content, it should not exceed 2% of the whole inlet gas (or about 15 mm Hg partial pressure) in any type of molten salt to avoid the high generation of hydrogen gas during electrolysis in addition to the hydrolysis of chloride ions in the molten chloride. For molten carbonates the mechanism of atomic (**Eq.(10)** and **Eq. (11)**) hydrogen formation can only be applicable if the concentration of CO<sub>2</sub> gas is less than 25% of the whole gas inlet.



Regarding hydrocarbon formation, there are two possible mechanisms. The first mechanism is the combination of carbon deposited from CO<sub>2</sub> reduction with the above adsorbed hydrogen (**Eq.(12)**)



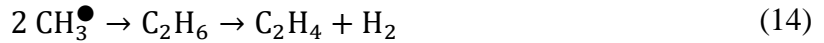
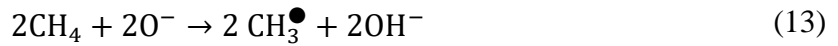
where C<sub>x</sub>H<sub>y</sub> represents the hydrocarbon formula and can be an alkane, alkene or any other type of hydrocarbon molecule. Such produced hydrocarbon fuels can be removed easily from the molten



salt using a carrying gas such as argon, CO<sub>2</sub> or H<sub>2</sub>O or flushed with the feed gas itself through the ceramic tube. The second possible mechanism is the partial oxidation of methane produced by reaction with C<sub>2</sub>-hydrocarbons as shown in **Eq. (13)**.



Therefore, in this case, the melt is a more basic and active form of oxide ions such as peroxide (O<sub>2</sub><sup>2-</sup>) or superoxide (O<sup>-</sup>) present in the basic melt and will play a significant role to perform C<sub>2</sub> gas formation according to **Eqs. (13) to (14)**.



It can be concluded that using a lower CO<sub>2</sub> content in the feed gas (10-25%) in molten carbonates will contribute to higher hydrocarbon formation in terms of higher oxobasicity (**Eq. (16)**) or from the feasibility of H<sub>2</sub> or H formation.



For the molten chloride case, as the minimum concentration of H<sub>2</sub>O should be used, CO<sub>2</sub> gas can be introduced at higher concentrations (>90%) of inlet gas to ensure the high yield of CO or carbon in the product<sup>20</sup>. For molten hydroxide though, CO<sub>2</sub> must be applied with lower concentrations (<10%) of inlet gas to reduce the carbonate ion formation<sup>24</sup>. In this research, it was found (with regards to H<sub>2</sub>O content) that using a CO<sub>2</sub>/H<sub>2</sub>O ratio between 10 and 15 in the feed gas would result in higher current efficiencies. First of all, it can be confirmed that CO and H<sub>2</sub> have been generally produced in molten carbonates by the co-electrolysis of CO<sub>2</sub> and H<sub>2</sub>O at low temperatures (<500

°C) with high current efficiencies, whereas CO (in particular) is conventionally produced or synthesized under higher temperatures (>800 °C) <sup>16</sup>.

The generation of H<sub>2</sub> was performed by the reduction of H<sub>2</sub>O in molten carbonates even without the addition of hydroxide salt (such as NaOH). It can be seen from **Fig. 7** that the highest CO concentration is achieved in the electrolysis at 425 °C under a CO<sub>2</sub>/H<sub>2</sub>O ratio of 15.6. The hydrocarbon species were found in this case in the range C<sub>1</sub>-C<sub>4</sub> with the priority for olefin compounds. Therefore, it can be concluded at this stage that light hydrocarbon (<C<sub>5</sub>) products, particularly CH<sub>4</sub>, can be formulated using electrolysis at a low-temperature condition (425 °C) (**Fig. 8**). Also, the ratio of CO/H<sub>2</sub> production rates can be controlled by the molar ratio of CO<sub>2</sub>/H<sub>2</sub>O in the feed gas to conduct electrolysis at 425 °C. However, apart from the case of a run at 425 °C under a CO<sub>2</sub>/H<sub>2</sub>O ratio of 15.6, it was found that CH<sub>4</sub> amount produced at CO<sub>2</sub>/H<sub>2</sub>O=9.2 at 425 °C was quite high rather than other hydrocarbons due to high rate of H<sub>2</sub>O reduction to hydrogen and lowering the feasibility of hydrocarbon formation.

There was a preferential tendency for H<sub>2</sub> generation during electrolysis; particularly in the case of a higher H<sub>2</sub>O content of the feed gas (CO<sub>2</sub>/H<sub>2</sub>O ratio of 9.2) or when the hydroxide mixture with a carbonate salt electrolyte (such as Li<sub>0.85</sub>Na<sub>0.61</sub>K<sub>0.54</sub>CO<sub>3</sub>-2LiOH) was used as confirmed in recent literature<sup>30</sup>. The predominance of CH<sub>4</sub> production was very clear among other hydrocarbon species in this case (**Fig. 8**). Furthermore, it was confirmed that the existence of H<sub>2</sub> in an appropriate amount on the cathode in the molten carbonates, can prevent the formation of solid carbon as an undesired product at low temperatures (<500 °C)<sup>17</sup>. Therefore, there is a clear relationship between the production rate of H<sub>2</sub> and the formation of hydrocarbons at this stage. It can also be noticed

that there is a tangible increase in hydrocarbon production at increasing temperatures, particularly under a CO<sub>2</sub>/H<sub>2</sub>O ratio of 15.6 at 500 °C (**Fig. 7**).

On increasing the temperature to 500 °C, an increase in H<sub>2</sub>O in the gas feed does not lead to higher H<sub>2</sub> production rates like that in the case of 425 °C possibly because H<sub>2</sub>O solubility is lower, and HCO<sub>3</sub><sup>-</sup> ions reduction that were formed from H<sub>2</sub>O conversion to H<sub>2</sub>. It was recorded that CO<sub>2</sub> solubility increased in the molten carbonates by increasing the temperature whereas, the H<sub>2</sub>O solubility was lower. Therefore, partial oxidation of CH<sub>4</sub> can occur even at CO<sub>2</sub>/H<sub>2</sub>O ratio of 9.2. The higher hydrocarbon formation in the case of CO<sub>2</sub>/H<sub>2</sub>O=15.6 is because of the high partial pressure of carbon dioxide which leads to high deposition of CO<sub>2</sub> at the cathode as Ijije *et al.*,<sup>35</sup> confirmed it. Cherry and his research group<sup>17</sup> showed with increase in CO<sub>2</sub> partial pressure both cathodic peaks and current densities increased, the partial pressure dependencies were also confirmed by Hu *et al.*,<sup>38</sup>

### **Current efficiency**

The optimization of each electrolyte can be done in the gas feed introduction method (GFOE and GFIE) for obtaining more fuel production. The formation of hydrocarbon species increases the combined current efficiency of cathodic products. It can be noticed from **Fig. 7** that the current efficiency does not change and is maintained at the high level of ~ 99% (despite a significant rise in current density) when the temperature was increased from 425 to 500 °C under a molar ratio of CO<sub>2</sub>/H<sub>2</sub>O of 15.6. Ijije *et al.*,<sup>35</sup> confirm that the current efficiencies were found to be 95% using molten carbonates at different temperature. This action can be imputed to increasing hydrocarbon formation in general and the evolution of new and long-chain (high molecular weight) hydrocarbon species at high temperatures (**Fig. 9**). Therefore, the combined current efficiency of hydrocarbon

products increased from 55 to 92% at this stage in contrast with the efficiencies of H<sub>2</sub> and CO which remained reduced. Ji *et al.*,<sup>18</sup> confirmed the current efficiency was found to be 93% in the molten carbonates at 500 °C and 1.8V.

However, the total current efficiency of the entire cathodic product reduced clearly from 95 to 79% by increasing the temperature under a CO<sub>2</sub>/H<sub>2</sub>O ratio of 9.2 due to the reduction of hydrocarbon generation in this case, despite the formation of C<sub>7</sub>H<sub>16</sub> (**Fig. 7**). This is because increasing the temperature in case of CO<sub>2</sub>/H<sub>2</sub>O ratio of 15.6 there was a drastic increase in the formation of C<sub>6</sub>H<sub>14</sub> and C<sub>7</sub>H<sub>16</sub> while on increasing the temperature when CO<sub>2</sub>/H<sub>2</sub>O ratio is 9.2 CH<sub>4</sub> decreases and C<sub>7</sub>H<sub>16</sub> was formed but not up to that extent. Alternately, the combined current efficiencies of the hydrocarbon species (due to C<sub>7</sub>H<sub>16</sub> formation), increased from 12% at 425 °C to 24% at 500 °C (**Fig. 9**). Subsequently, the plot of current efficiencies with temperatures (**Fig. 9**), offers another proof for confirming the optimum conditions for hydrocarbon formation at 500°C under a molar ratio of CO<sub>2</sub>/H<sub>2</sub>O of 15.6.

## Conclusions

In the present electrochemical system, molten salt electrolyser used included ceramic tubes for collecting the cathodic and anodic gases in molten carbonates (Li<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>; 43.5:31.5:25 mol %), hydroxide (LiOH-NaOH; 27; 73 and KOH-NaOH; 50:50 mol %) and chlorides (KCl-LiCl; 41-59 mol %) to investigate the formation of hydrocarbon fuel using different electrode material. Mass spectroscopy in the case of molten carbonate confirmed the formation of many hydrocarbon species (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>8</sub>, C<sub>7</sub>H<sub>16</sub>) along with CO and H<sub>2</sub>. The formation of alkene was found in case of molten carbonates at 425°C and CO<sub>2</sub>/H<sub>2</sub>O ratio of 15.6. The production of CH<sub>4</sub> was found to be 0.67 μmol/h.cm<sup>2</sup> and H<sub>2</sub> 32 μmol/h.cm<sup>2</sup> using KCl-LiCl (41-59

mol%). Apart from hydrocarbon content, the current efficiency for molten carbonates was 99% while for molten hydroxide and molten chloride the value comes out to be 87.7% and 59.3% respectively. The GC results for CO<sub>2</sub>/H<sub>2</sub>O ratio of inlet gas reported that H<sub>2</sub> and CH<sub>4</sub> were the predominant product at lower CO<sub>2</sub>/H<sub>2</sub>O ratios (9.2) at 500 °C in molten carbonates under 1.5V. However, the higher molecular hydrocarbon products (C<sub>6</sub>H<sub>14</sub>, and C<sub>7</sub>H<sub>16</sub>) were generated when electrolysis was carried out at higher ratios of CO<sub>2</sub>/H<sub>2</sub>O (15.6) in the feed gas at 500 °C. The GC results for the effect of cathode material in molten carbonates showed that the hydrocarbon species produced in the case of a titanium foil cathode were specifically higher in molecular weight with higher production rates than the products obtained using a mild steel rod cathode. However, it is recommended to analyze the effect of anode material in the case of molten carbonates. While the study of the effect of electrode material, feed gas ratio can also be performed for hydroxides and chlorides for better results.

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## List of Tables

**Table 1.** Specifications of the cathodic gas product during electrolysis using molten carbonates at 1.5 V and different temperature obtained from GC analysis.

Product	Gas product composition (vol%)		Product rate ( $\mu\text{mol/h cm}^2$ )		Selectivity (%)		Current efficiency (%)		Heating value (J)		Total energy consumption (J)	
	425 °C	500 °C	425 °C	500 °C	425 °C	500 °C	425 °C	500 °C	425 °C	500 °C	425 °C	500 °C
H <sub>2</sub>	0.22	0.210	4.40	4.00	-	-	11.90	5.10	11.40	7.30	114.20	171.00
CH <sub>4</sub>	0.06	0.02	1.10	0.40	6.80	7.00	12.50	2.00	10.40	2.60		
C <sub>2</sub> H <sub>4</sub>	0.04	0.00	0.80	-	5.00	-	13.20	-	12.00	-		
C <sub>3</sub> H <sub>6</sub>	0.03	0.00	0.50	-	3.10	-	12.70	-	11.00	-		
C <sub>4</sub> H <sub>8</sub>	0.03	0.00	0.50	-	3.10	-	17.00	-	14.50	-		
C <sub>6</sub> H <sub>14</sub>	0.00	0.12	-	2.40	-	42.10	31.80	58.00	35.30	75.00		
C <sub>7</sub> H <sub>16</sub>	0.00	0.06	-	1.20	-	21.00	-	32.40	-	43.30		
CO	0.58	0.100	11.70	1.70	-	-	-	2.20	-	3.70		
CO <sub>2</sub>	52.70	40.30	-	-	-	-	-	-	-	-		
H <sub>2</sub> O	2.40	3.10	-	-	-	-	-	-	-	-		
Ar	44.00	56.10	-	-	-	-	-	-	-	-		

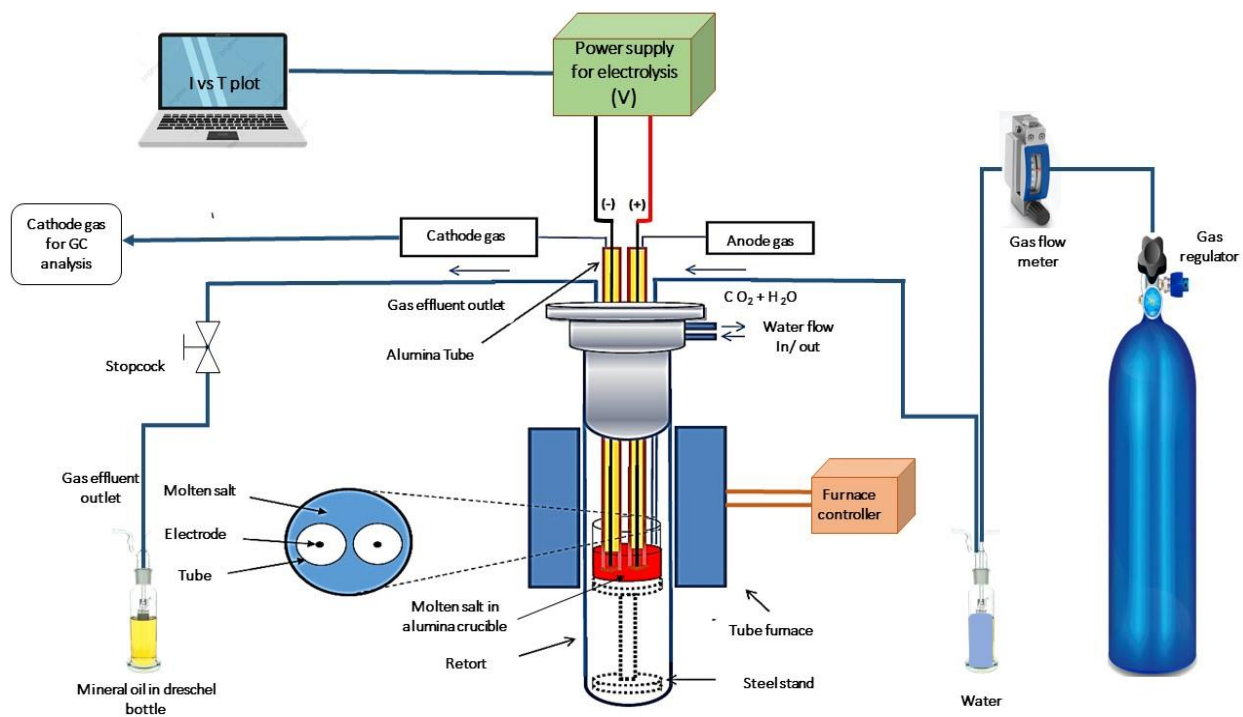
**Table 2.** Cathodic product gas compositions and the current efficiency of the individual components after electrolysis in molten chlorides at different voltage and 375 °C.

Product	Gas Product Composition (vol %)		Product rate ( $\mu\text{mol/h cm}^2$ )		Current efficiency (%)		Total energy Consumption (J)	
	1.5 V	2 V	1.5 V	2 V	1.5 V	2 V	1.5 V	2 V
H <sub>2</sub>	2.40	2.48	32.00	19.10	54.80	28.20		
CH <sub>4</sub>	0.05	0.05	0.67	0.38	4.50	2.30		
CO	0.00	0.00	0.00	0.00	0.00	0.00		
CO <sub>2</sub>	34.80	4.84	-	-	-	-		
H <sub>2</sub> O	2.00	2.00	-	-	-	-	278.00	311.00
Ar	60.80	90.63	-	-	-	-		

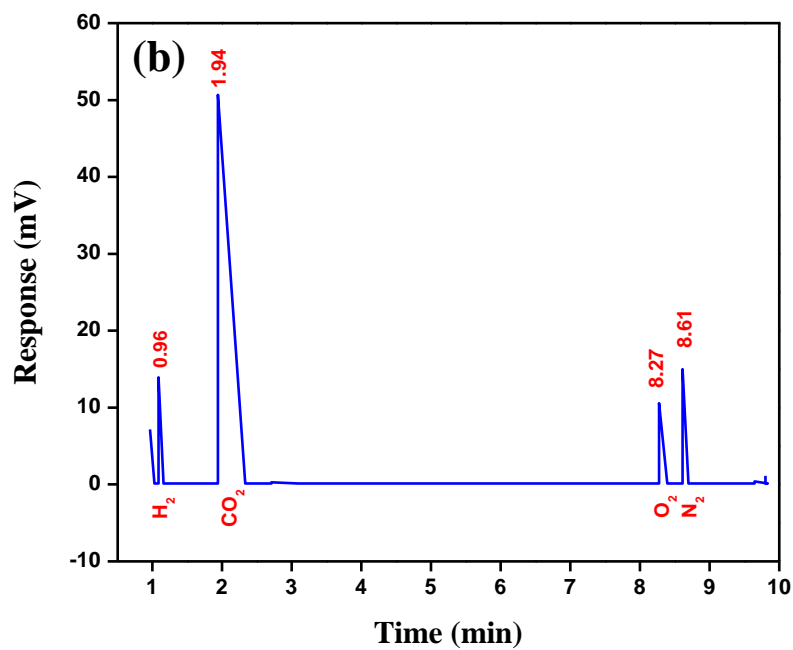
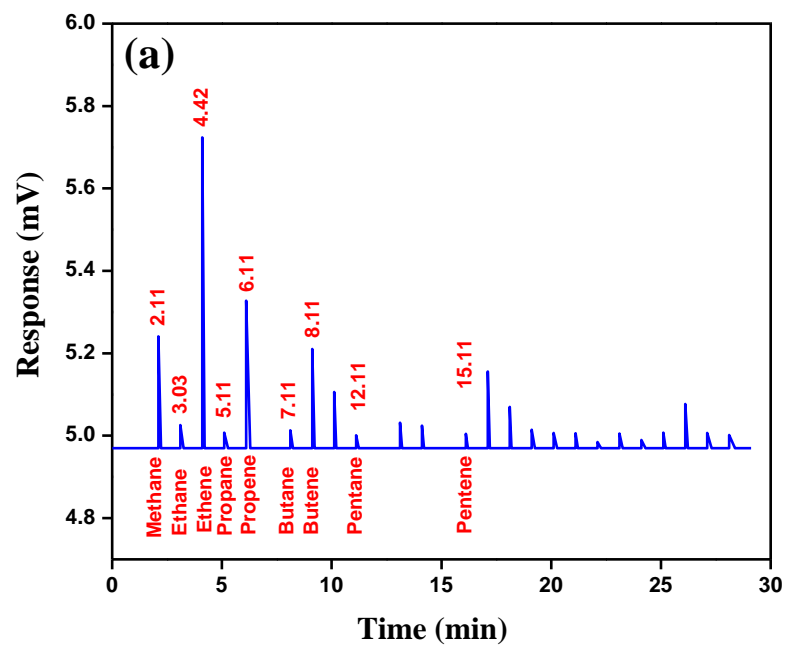
**Table 3.** The cathodic gas product during electrolysis in the molten hydroxides at 2 V and different temperatures obtained from GC analysis.

<b>Molten salt</b>	<b>Temperature (°C)</b>	<b>Product gas</b>	<b>Gas composition (Vol %)</b>	<b>Production rate (μmol/h cm<sup>2</sup>)</b>	<b>Current efficiency (%)</b>	<b>Total energy Consumption (J)</b>
KOH-NaOH (50-50 mol%)	220	H <sub>2</sub>	3.94	164.70	15.60	1000.00
		CH <sub>4</sub>	0.15	6.12	2.30	
		CO	0.00	0.00	0.00	
		CO <sub>2</sub>	0.58	-	-	
		H <sub>2</sub> O	0.00	-	-	
		Ar	95.30	-	-	
LiOH-NaOH (27-73 mol%)	275	H <sub>2</sub>	4.44	185.70	13.00	1200.00
		CH <sub>4</sub>	0.15	6.12	2.00	
		CO	0.00	0.00	0.00	
		CO <sub>2</sub>	0.75	-	-	
		Ar	94.70	-	-	

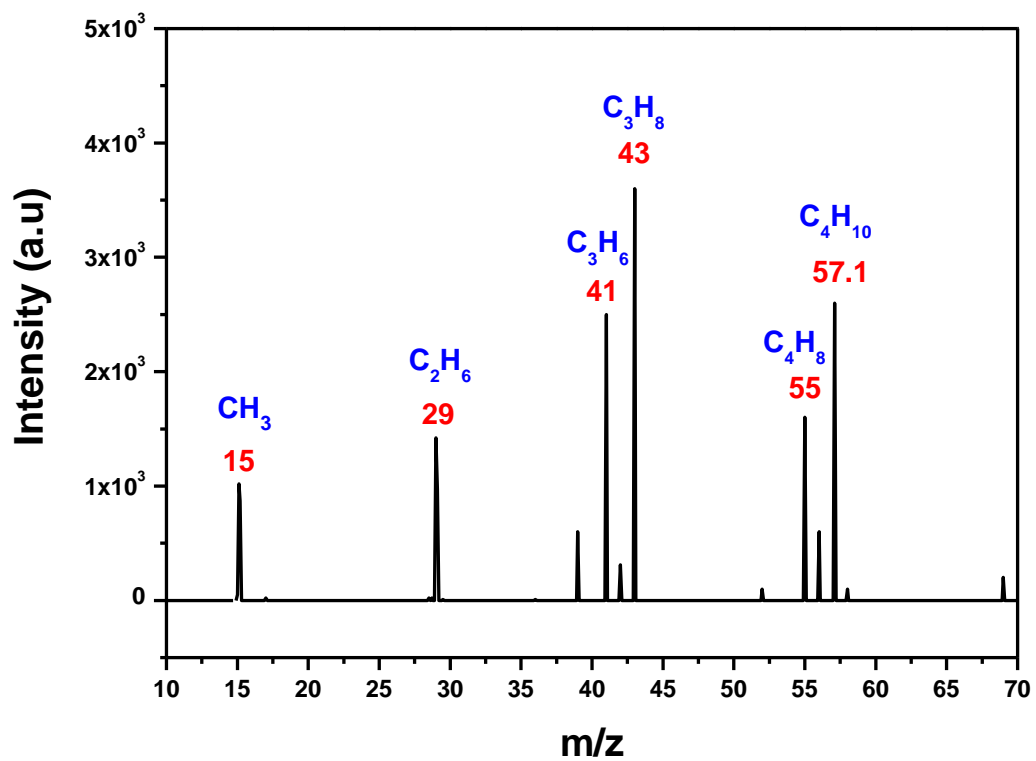
## List of Figures



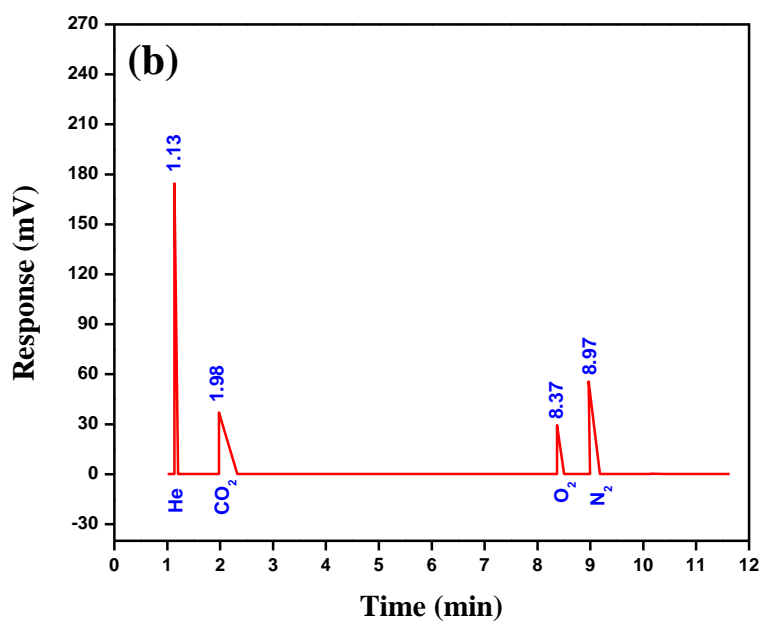
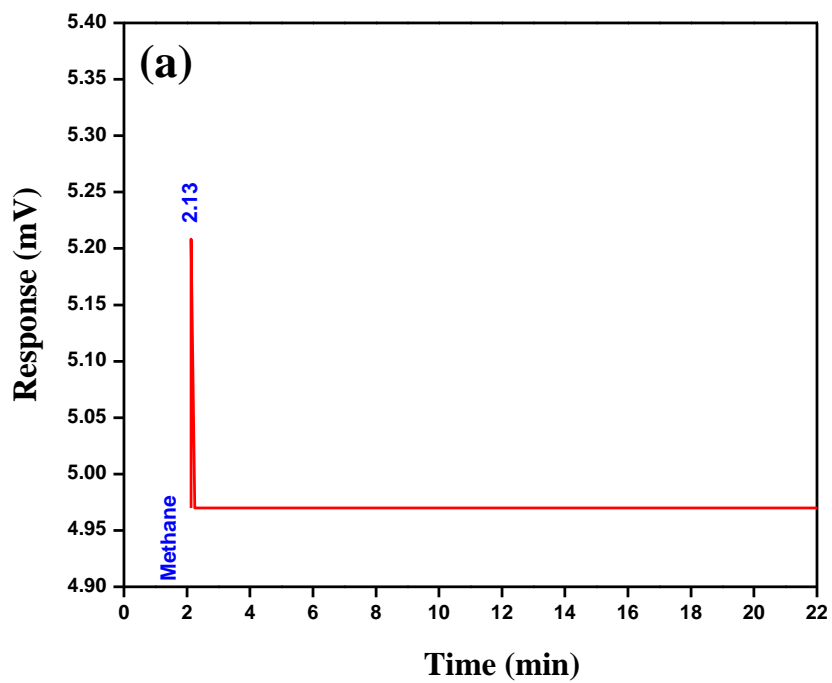
**Fig. 1.** The schematic representation of the electrolytic cell experimental setup.



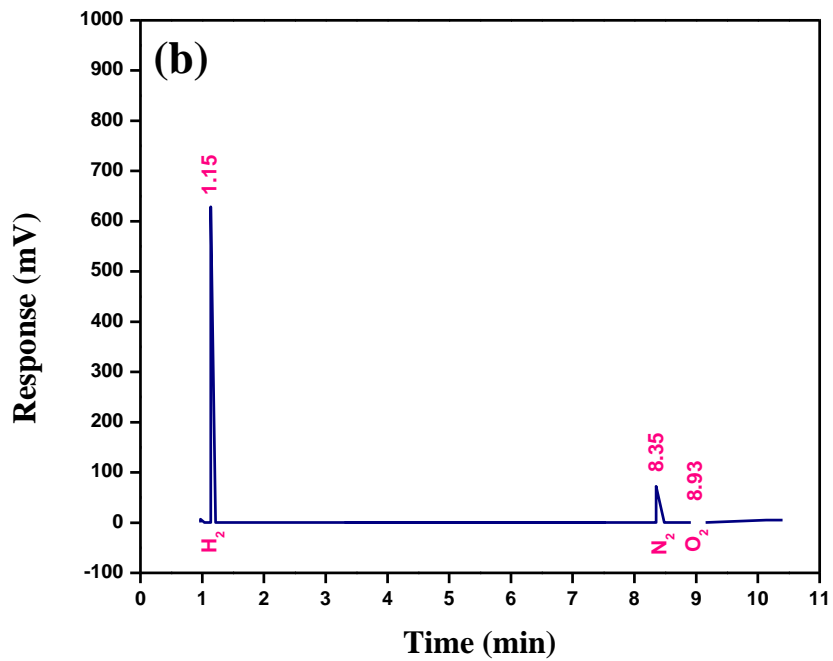
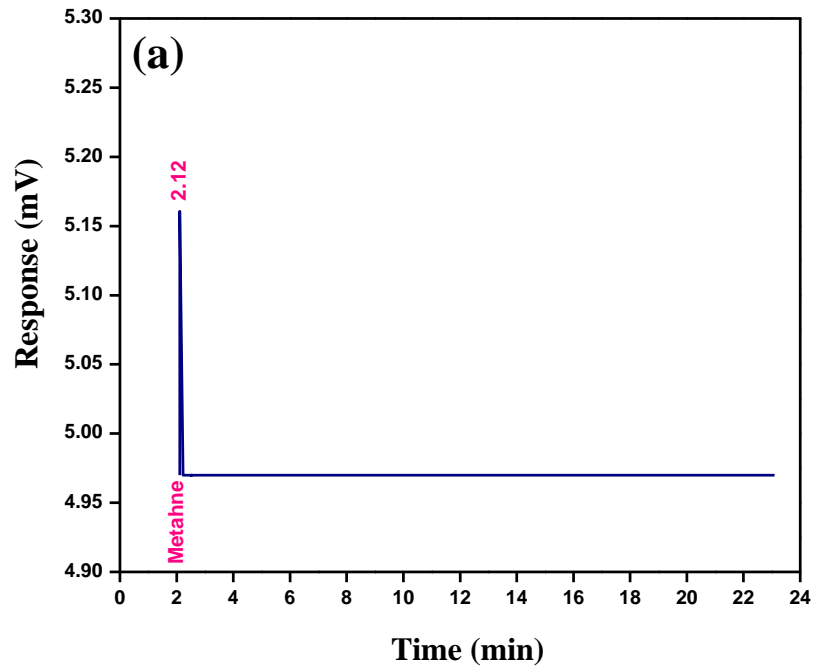
**Fig. 2.** The gas chromatography analysis of cathodic gas using molten carbonates at 1.5V and 425°C; (a) FID detector and (b) TCD.



**Fig. 3.** Mass spectrum of compounds showing hydrocarbons after electrolysis in the molten carbonate electrolyte at 1.5 V at 425 °C.

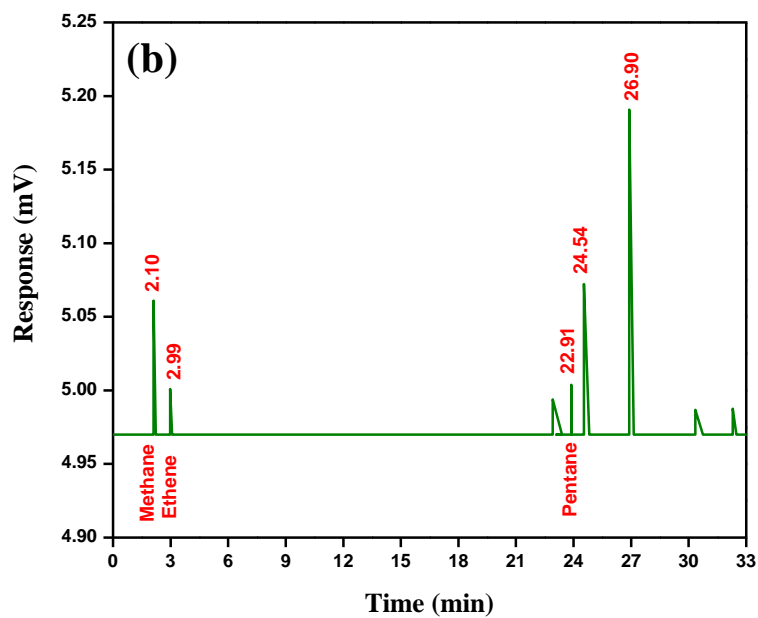
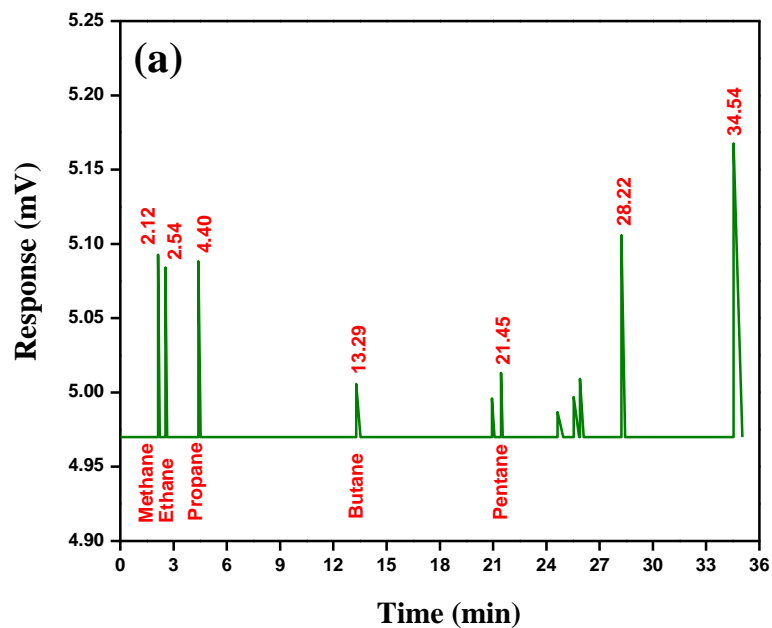


**Fig. 4.** The gas chromatography analysis of gaseous products in molten chlorides at 375 °C and 2 V; (a) FID detector and (b) TCD detector.

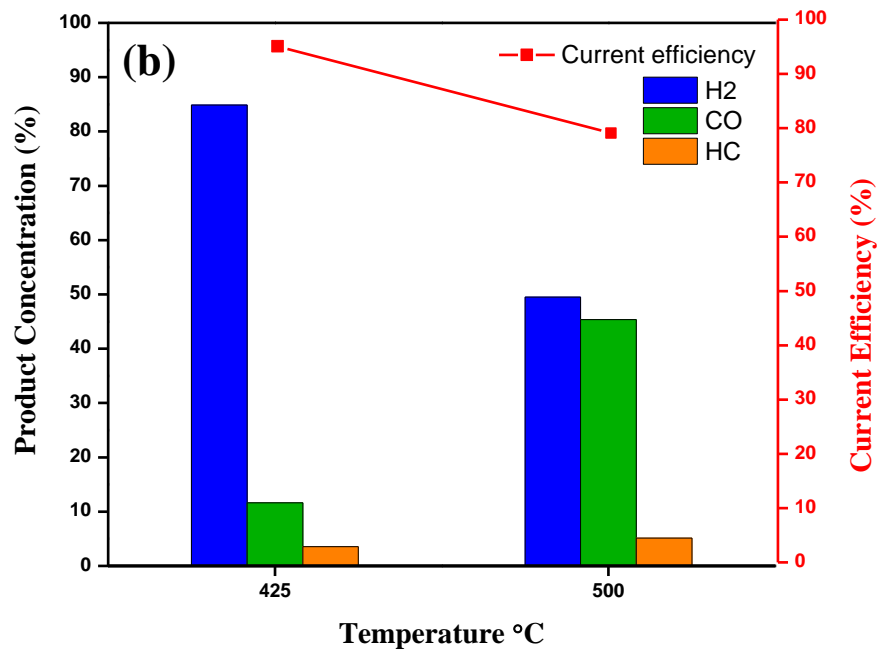
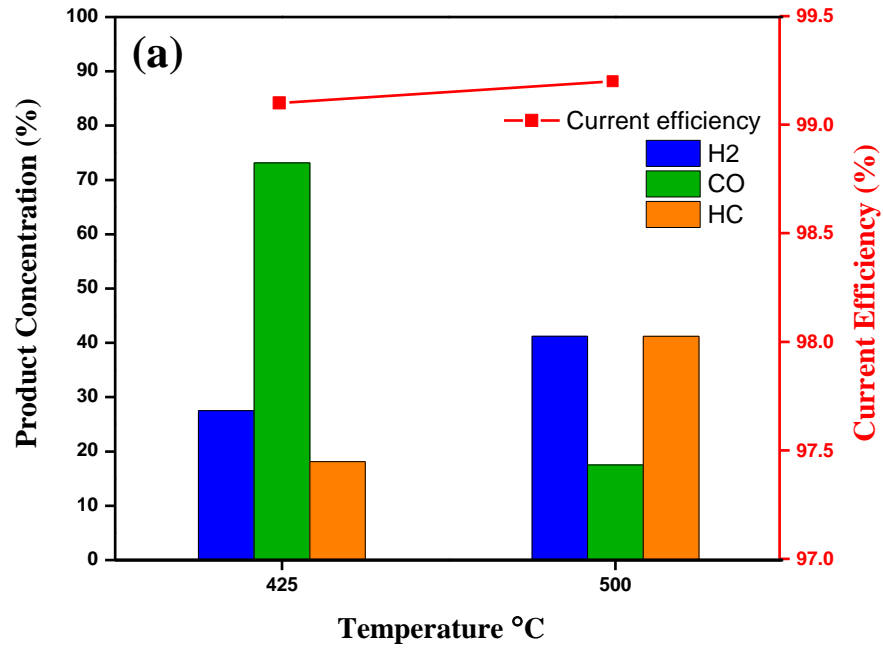


**Fig. 5.** Gas chromatography analysis of gaseous product in molten hydroxide at 2 V and 275 °C; (a) FID detector and (b) TCD detector.

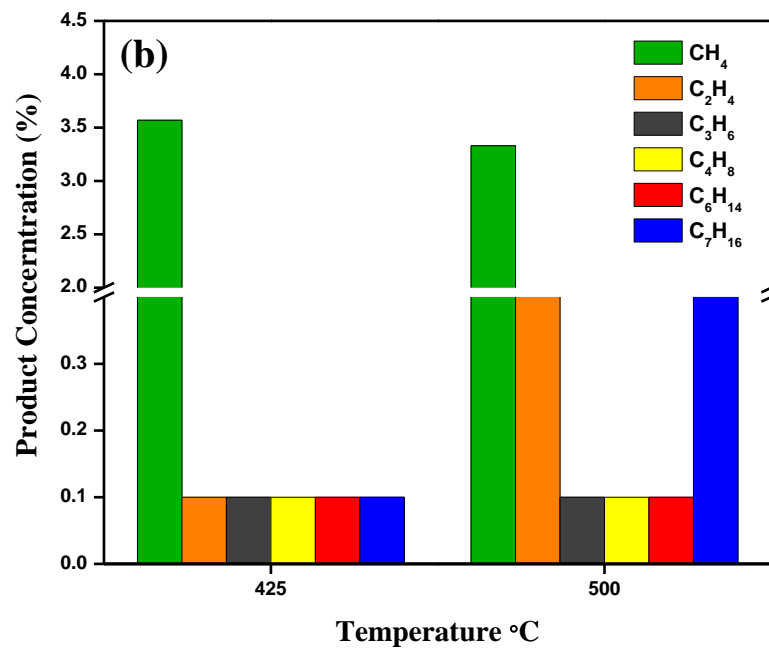
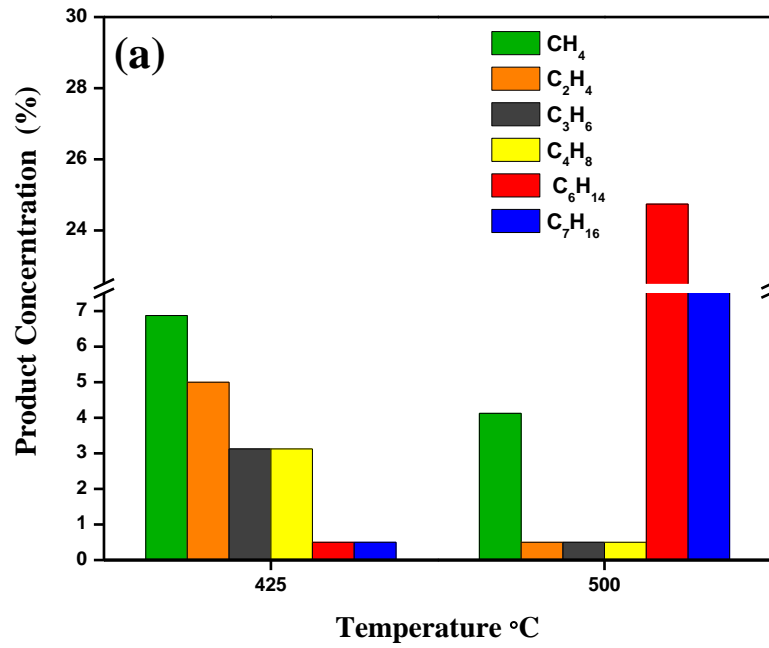




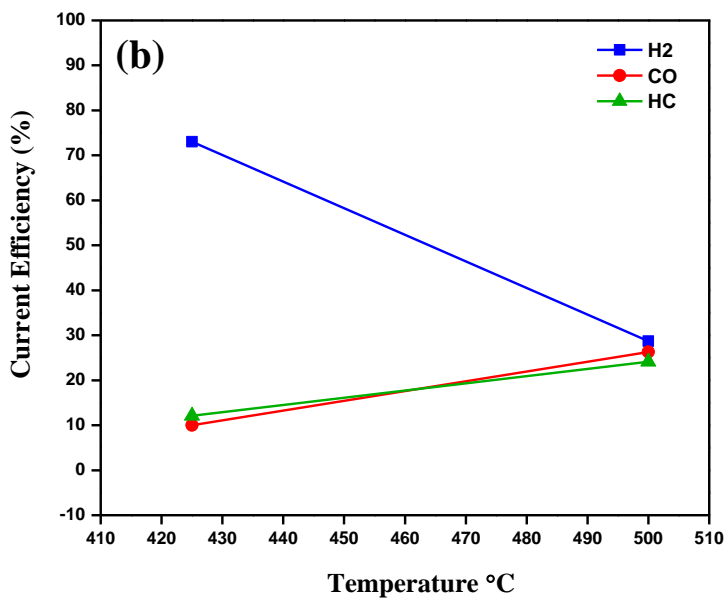
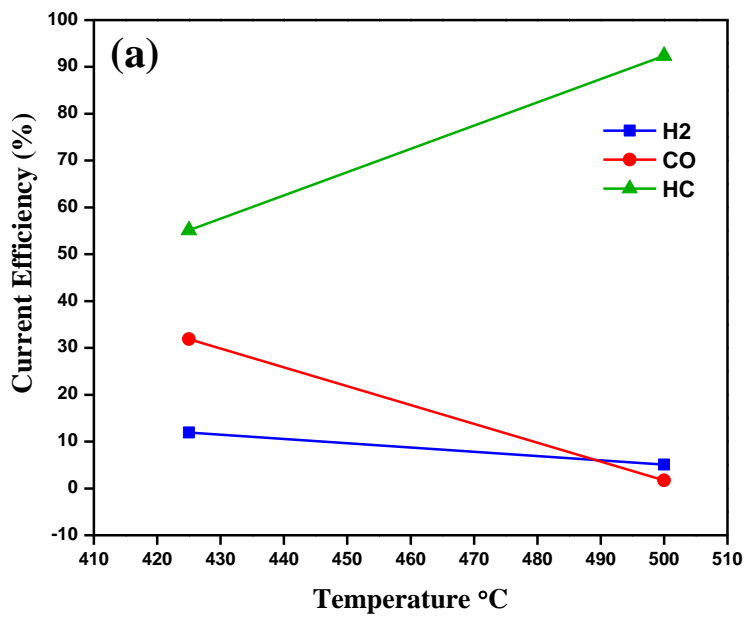
**Fig. 6.** FID detector analysis of gas sample during the electrolysis of molten carbonate using different cathode materials; (a) Mild steel and (b) Titanium foil.



**Fig. 7.** Production rates and current efficiencies of CO, H<sub>2</sub> and hydrocarbons at two different temperatures obtained by electrolysis in ternary molten carbonates at 1.5 V and different CO<sub>2</sub>/H<sub>2</sub>O feed gas ratio; (a)15.6 and (b) 9.2.



**Fig. 8.** Different hydrocarbon products obtained by electrolysis in ternary molten carbonates at 425 and 500 °C with different CO<sub>2</sub>/H<sub>2</sub>O feed gas ratio; (a) 15.6 and (b) 9.2.



**Fig. 9.** Current efficiencies of CO, H<sub>2</sub> and hydrocarbon species at different temperature and constant applied voltage of 1.5V with different CO<sub>2</sub>/H<sub>2</sub>O feed gas ratio for molten ternary carbonates; (a) 15.6 and (b) 9.2.

## For Table of Contents Use Only

### Graphical Abstract

Electrochemical reduction of carbon dioxide and water was performed to generate hydrocarbon fuels using three types of molten eutectic-salt electrolytes.

