Electrically Mediated Hydrocarbon Conversion Processes
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Theme: Conversion of saturated \( C_1, C_2 \& C_3 \) HC’s to chemicals by any means that involves electricity.

1. Limiting economics.
2. Direct hydrocarbon fuel cells (DHCFC’s): Chemicals from FC’s?
4. Methane to \( C_2 \) HC’s via electrical plasma processes.
1. Limiting Economics

Natural gas (NG) @ $2.67 / MMBtu (2015 ave. price)
Ideally Electricity @ 0.9 cents/KWh
Electricity cost: 8-12 cents/KWh (Pa 2015)
Currently NG, lowest cost fuel for electric power generation.
But electricity is a relatively costly reagent if it’s required for endothermic hydrocarbon (HC) conversion processes (eg CH₄ to C₂ HC’s or syn gas via plasma).
Consider first an (exothermic) selective anodic oxidation of HC’s that provides both electricity and chemicals- in a ‘tailored’ direct hydrocarbon fuel cell (DHCFC)*

Fuel Cell Fundamentals: The H$_2$-O$_2$ FC

H$_2$ + ½ O$_2$ = H$_2$O(g)  $E_{\text{rev}} = 1.17$ V  at 80°C

Rev. Efficiency ($\eta_r$) = ($\Delta H - T\Delta S$)/$\Delta H$

Gasteiger, Wagner et al, Appl. Cat. B 56 (2005), 9

Xianguo Li “Principles of FC’s” Taylor &Francis Publ. 1962

Polarization Curve (E Cell vs Current)
Losses from: mass transp. res.( $\eta_{tx}$), Ohmic.res. ,but mainly slow O$_2$ redn. kinetics($\eta_{\text{ORR}}$).

Figure from p 62 of Li’s book

Figure 1 on p 14 of Gasteiger
Thermodynamically feasible FC’s for chemicals and energy cogeneration

1. Ethane to ethylene.
   \[ \text{C}_2\text{H}_6 + \frac{1}{2}\text{O}_2 = \text{C}_2\text{H}_4 + \text{H}_2\text{O}(g) \]
   \[ E = 0.693 \text{ V at } (80 \, ^\circ\text{C}) ; \ 0.855 \text{ V (500} \, ^\circ\text{C}) \]

2. Methane coupling to ethane.
   \[ 2\text{CH}_4 + \text{O}_2 = \text{C}_2\text{H}_6 + \text{H}_2\text{O}(g) \]
   \[ E = 0.815 \text{ V at } 80 \, ^\circ\text{C} ; \ 0.695 \text{ V (500} \, ^\circ\text{C}) \]

   \[ 2\text{CH}_4 + \text{O}_2 = \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}(g) \]
   \[ E = 0.748 \text{ V at } 80 \, ^\circ\text{C} ; \ 0.755 \text{ V (500} \, ^\circ\text{C}) \]

4. Methane to methanol.
   \[ \text{CH}_4 + \frac{1}{2} \text{O}_2 = \text{CH}_3\text{OH}(g) \]
   \[ E = 0.565 \text{ V at } 80 \, ^\circ\text{C} ; \ 0.453 \text{ V (500} \, ^\circ\text{C}) \]

Hydrogen/Oxygen FC.

\[ \text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O} (g) \]
\[ E = 1.17 \text{ V at } (80 \, ^\circ\text{C}) ; \ 1.062 \text{ V (500} \, ^\circ\text{C}) \]

Methane/Oxygen FC

\[ \text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}(g) \]
\[ E = 1.033 \text{ V at } (80 \, ^\circ\text{C}) ; \ 1.037 \text{ V (500} \, ^\circ\text{C}) \]
Ethane to Ethylene FC: \( C_2H_6 + \frac{1}{2}O_2 = C_2H_4 + H_2O \)

See Figure from Abstract, for the overall cell design.

For performance data see Fig 4A on p 764

Fig 5, on p765

Anode: \((Pr_{0.4}Sr_{0.6})_3(Fe_{0.85}Mo_{0.15})_2O_7/Co-Fe\) alloy nanoparticles

\[ C_2H_6 \rightarrow C_2H_4 + 2H^+ + 2e^- \]

H\(^+\) Electrolyte: \(BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}\)

Cathode: \((La_{0.6}Sr_{0.4})_{0.95}Co_{0.20}Fe_{0.80}O_{3-\delta}\)

\[ O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \]

“Button” cell, 0.2 cm\(^2\),

A replacement for steam-ethane cracking?

S. Liu, K.T. Chuang and J-L. Luo (Univ. of Alberta), ACS Catal. 2016, 6, 760

By-Products:

\(CH_4, CO(\text{trace}), no CO_2\)
Methane to Ethane-Ethylene FC

CH$_4$ Conversion and Products Selectivity vs Temperature. (Max. 91% Selectivity for C$_2$’s, at 23.7% Conversion of CH$_4$ at 1273K). Note: C$_2$H$_4$>> C$_2$H$_6$

Anode Cat.: La$_{1.8}$Al$_{0.2}$O$_3$ O$^{2-}$ ion conducting YSZ tube electrolyte
Cathode Cat: La$_{0.85}$Sr$_{0.15}$MnO$_3$

Electrolytically induced catalytic methane to methanol conversion.

No reports of a direct methane + ½ O₂ to methanol FC (E= 0.565 V at 80 °C). However,

**A.** \[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \ (+ \text{Power}) \rightarrow \text{CH}_3\text{OH} \ (\pm \text{CO}_2) \]

Cathode: \[ \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]

\[ \text{H}^+ \uparrow \text{H}_2\text{O} \downarrow \]

Anode: \[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + 2\text{H}^+ + 2\text{e}^- \ (\pm \text{CO}_2) \]

(V2O5/SnO2)

Fig 3 (c) on p237 of Lee Hibino

**B.** \[ \text{CH}_4 + \text{H}_2\text{O} \ (+ \text{Power}) \rightarrow \text{CH}_3\text{OH} + \text{H}_2 \ (\pm \text{CO}_2) \]

Cathode: \[ 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \]; Pt cat.

\[ \text{OH}^- \downarrow \text{H}_2\text{O} \uparrow \]

Anode: \[ \text{CH}_4 + 2\text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} + \text{e}^- \ (\pm \text{CO}_2) \]; Ni(OH) cat.

Methanol conc. vs anode (applied) potential using V2O5/SnO2 anode for wt% V2O5, at 100 C. Max: 61% current efficiency and 88% selectivity for CH3OH. B. Lee, T. Hibino, J. Catal. 2011, 279, 233


Feed CH₄ (top curve), and Products: CH₃OH, CO₂ and O₂ at anode. Qinbai Fan, US Pat. Appl. 2015/0129430
Electrode catalyst design: The Direct Methane FC

**Key Novelty:** Pt complex, ‘molecular’ CH\(_4\) activation catalyst, tethered to an ordered mesoporous carbon (OMC) support.

\[
\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \quad 2\text{O}_2 + 8\text{H}^+ + 8\text{e}^- = 4\text{H}_2\text{O}
\]

**Net:** \(\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O(g)}\), \(E = 1.033\) V at 80 C


Voltage-Current Polarization Curve for OMC tethered catalysts.

Figure: Schematic of cell design from Abstract

Figures 3 D & E
Electrochemical Promotion of Catalysis (EPOC) or Non-Faradaic electrochemical modification of catalytic activity (NEMCA)

(a) Faradaic: Stoichiometric use of electron as a reactant, 
Eg \( n = \frac{12e}{\text{mole } C_2H_4 \text{ reacted}} \).

(b) Non-Faradaic: Non-stoichiometric use of electron, with \( n \) potentially much larger. \( (\Lambda > 1) \), often \( \Lambda > > 1 \)

Oxide ion conducting YSZ disc, Pt catalyst-electrode coating.

Following \( C_2H_4 \) Oxidation rate as a function of applied potential.  

Faraday Efficiency, \( \Lambda = \frac{\Delta r}{r_e} = 74,000 \quad \Delta r/r_0 = 25 \)

Mechanism: (as for CO, CO\(_2\) reactants on Pt / YSZ solid el.)

Fig 1 p866 of Katsaounis


Ethylene Oxidation rate increases of up to 25 \( \times (\Delta r) \) with applied potential of ca. 0.6 V (375 C)
Non-Faradaic "Electroreforming" of methane to syn. gas and H₂

Steam-methane reforming (SMR), current practice:

\[ 	ext{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 + \text{H}_2\text{O} \]

Ni cat., then WGS to 4H₂+CO₂

Endothermic React. Heat from external methane combustion.

Tubular metal alloy reactors, at ca. 30 atm. Pressure and ca. 800 °C.

Electroreforming:

CH₄ Conv. vs T(K) for Pt/metal oxide cats. Open: Conv. SMR : Dark: Electroreforming.

Dramatic decrease in reaction temperature

Products yield vs T(K) for conventional (left), and electroreforming (right), for which the yield exceeds the calc. thermo. equilibrium.

Electroreforming Apparatus. E = 500 V - 800 V for I= 3mA of “Dark current”; Elect. Eff. 15-25 %

NEMCA Effect. Faradaic Efficiency, \( \Lambda \) (reacted CH₄/mole-electron)= 84 for Pt/Ce₀.₅Zr₀.₅O₂ cat.

Electrical Discharges/Plasma for Methane Conversion

Methane to $C_2H_2$ in spark discharge

Reactor: +/- 30 kV, 0-10 mA, 0-400 Hz
Feed: $CH_4$, 10 ccm, ambient T, P.
Products: $C_2H_2$ (90% sel.); $C_2H_6$, $C_2H_4$ (4% Sel)

El. Efficiency ~ 10% (ie 10X of energy needed for react. endotherm.)


Methane oxidative coupling in corona discharge, +/- catalyst

Feed: $CH_4/O_2 = 4$ @ 100 sccm
Catalyst: $Sr/La_2O_3$, $T= 823K$
Products: $C_2H_4$, $C_2H_6$ Yields (%): Cat. Alone. 0.4%
Corona alone. 3.6% (6% conv.)
Corona + cat. 5.6% (14% conv)

El. Efficiency At 5.6 W input, ~ Heat value of conv. $CH_4$
A. Marafee, C. Liu, G. Xu, R. Mallison, L. Lobban

From Kado Fig 1 p1378

Fig 2 Corona Schematic
**Electrolyte:** Polymer (PEM)  
**Carrier Ion:** $H^+$, $CO_3^{2-}$  
**Temperature:** RT-200°C  
**Features:** Commercial ($H^+$)  
**Key Issues:** ORR  

**Electrolyte:** Phosphoric Acid  
**Carrier Ion:** $H^+$  
**Temperature:** 150-200°C  
**Features:** Commercial  
**Key Issues:** Acid loss, ORR  

**Electrolyte:** Solid Oxide, ceramic (SOFC)  
**Carrier Ion:** $O^-$, $H^+$  
**Temperature:** 200-500°C  
**Features:** Commercial  
**Key Issues:** High Temps., Materials  

**Electrolyte:** Molten Carbonate  
**Carrier Ion:** $CO_3^{2-}$/$CO_2$  
**Temperature:** 500-1000°C  

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**Hydrocarbon/Air Fuel Cell Systems. Reports for chem. products (currently) only from SOFC’s**

(Faradaic processes)  
With Electric Power Co-Generation (All exothermic conversions)

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**Potential for: Hydrocarbons $\rightarrow$ Chemicals via Electrocatalysis**

(Non-Faradaic processes)  
With Electric Power Consumption (Exothermic or endothermic conv.)

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**Electrochemical Promotion of Catalysis (EPC):** Dramatic rate enhancement in reduction, oxidation & isomerization reactions. “Triode” operation in SOFC’s. Potentially lowest power consumption. Issue: Practical reactor design

**Electroreforming** for endothermic CH$_4$ to syn gas & H$_2$. Large rate increases and improved conversion equilibria, at lower temps. Electricity use efficiency, only 15-25%

**Plasma processes** for methane to syn gas. Key issue: High power usage.
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