Plasma Processing of Hydrocarbon

Electric Power 2007

Peter C. Kong
Brent A. Detering
Jon D. Grandy
Larry D. Zuck

May 2007

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

Idaho National
Laboratory

Plasma Processing Of Hydrocarbon

Peter C. Kong, Brent A. Detering, Jon D. Grandy, and Larry D. Zuck
Industrial Technology Department,
Idaho National Laboratory
P.O. Box, 1625 Idaho Falls, ID 83415-2210

Abstract

The Idaho National Laboratory (INL) developed several patented plasma technologies for hydrocarbon processing. The INL patents include nonthermal and thermal plasma technologies for direct natural gas to liquid conversion, upgrading low value heavy oil to synthetic light crude, and to convert refinery bottom heavy streams directly to transportation fuel products. Proof of concepts has been demonstrated with bench scale plasma processes and systems to convert heavy and light hydrocarbons to higher market value products. This paper provides an overview of three selected INL patented plasma technologies for hydrocarbon conversion or upgrade.

Introduction

There are two distinct categories of atmospheric-pressure plasmas, thermal and nonthermal. Thermal plasmas include those produced in high intensity arcs, plasma torches, or in high intensity, high frequency discharges. The electron and gas temperatures as well as the energy content for thermal plasma are very high. The plasma gas temperature ranges from 10^3 to 10^4 Kelvin. Thermal plasmas are equilibrium plasma because the electron and gas temperatures are approximately equal. However, the temperature drop for thermal plasmas is extremely fast, usually in the order of milliseconds. The unique properties of plasma make it attractive for materials processing. Although the bulk gas temperature for nonthermal plasmas is at room temperatures, however, the plasmas are extremely effective in producing reactive species, e.g., ions, particularly free radicals and excited state atoms. Thus, both thermal and nonthermal atmospheric-pressure plasmas are finding applications in a wide variety of industrial processes, e.g. waste destruction, material recovery, extractive metallurgy, powder synthesis, and energy conversion. For energy conversion, the INL has a rich portfolio of patented nonthermal and thermal plasma technologies for heavy and light hydrocarbon processing.

In light hydrocarbon processing, methane conversion to other high value products is the main focus. Two patented plasma technologies including both high temperature thermal plasma and low temperature nonthermal plasma had been developed for this specific application. In high temperature conversion of methane, thermal plasma combines with a rapid quench nozzle to produce acetylene, hydrogen, and carbon nanoparticles. In the low temperature process, nonthermal methane plasma combines with a solid oxide electrochemical cell for direct methane to liquid hydrocarbon conversion.

In the area of heavy hydrocarbon processing, the focus has been on heavy oil upgrade. Current state of the art for upgrading heavy oil is divided into two general approaches – hydrogen addition or carbon rejection. Hydrogen addition processes are often desirable because of high liquid

yield. However, these types of process are expensive, requiring high temperature and pressure equipment and a hydrogen source. Carbon rejection processes are also desirable because they are much cheaper to construct and operate. However, the carbon rejection processes produce large quantities of very low-grade materials, which are not always readily marketable or disposable, and with heavy oils, have high yield losses. The INL developed plasma technologies are aiming at solving the above bottlenecks for heavy oil upgrade and to produce more fuel products than current processes. The INL patents include thermal and nonthermal plasma technologies to upgrade low market value hydrocarbons such as heavy crude oil with natural gas to higher market value synthetic light crude, or to convert refinery bottom heavy streams directly to transportation fuel products.

Methane Conversion to Acetylene

Light olefins can be formed by very high temperature ($>1800^{o}C$) abstraction of hydrogen from methane, followed by coupling of hydrocarbon radicals. High temperature conversion of methane to acetylene by the reaction $\mathbf{2CH_4 \rightarrow C_2H_2 + 3H_2}$ has existed for a long time. Methane conversion to acetylene processes currently use cold liquid hydrocarbon quenchants to prevent back reactions. Perhaps the best known of these is the Huels process, which has been in commercial use in Germany for many years. The electric arc reactor of Huels transfers electrical energy by direct contact between the high temperature arc (15,000 – 20,000 K) and the methane feed stock. The product gas is quenched with water and liquefied propane to prevent back reactions. Single pass yield of acetylene is less than 40% and the overall yield of acetylene greater than 60% by recycling all the hydrocarbons except acetylene and ethylene. The Huels process produces a significant amount of carbon deposit on the electrodes, which requires periodic shut down of the conversion process and performs a steam reforming cleaning of the electrodes. Although in commercial use, the Huels process is only marginally economical because of the low single pass efficiencies and the need to separate the product gases from quench gases. Subsidies by the German government have helped to keep this process in production.

Westinghouse has employed a hydrogen plasma reactor for the cracking the natural gas to produce acetylene. In the plasma reactor, hydrogen is fed into the arc zone and heated to a plasma state. The exiting stream of hot H_2 plasma at temperature above 5000 K is mixed rapidly with the natural gas below the arc zone, and the electrical energy is indirectly transferred to the feedstock. The hot product gas is quenched with liquid propane and water, as in the Huels process, to prevent back reactions. However as with the Huels process separation of the product gas from the quench gas is needed. Recycling all of the hydrocarbons except acetylene and ethylene has reportedly increased the overall yield to 67%. The hydrogen plasma process for natural gas conversion has been extensively tested on a bench scale only, but further development and demonstration on a pilot scale is required.

The Scientific and Industrial Research Foundation of Norway has developed a reactor consisting of concentric, resistance-heated graphite tubes. Reaction cracking of the methane occurs in the narrow annular space between the tubes where the temperature is 1900 – 2100 K. In operation, carbon formation in the annulus led to significant operational problems. Again, liquefied quenchant is used to quench the reaction product to prevent back reactions. As with the previous two acetylene production processes, separation of the product gas from quench gas is needed. The

overall multi-pass acetylene yield from the resistance-heated reactor is about 80% and the process has been tested to the pilot plant levels. The Huels, Westinghouse, and Norway processes all require liquefied hydrocarbon quenching and the separation of product and quench gases. Solid carbon fouling of the reactor is a common problem.

Leutner[1] synthesized acetylene from methane in an argon plasma jet and observed greater than 70% acetylene yield and solid carbon byproduct. No liquid quenchant was used in this process. The argon plasma jet process as well as the Huels, the Westinghouse hydrogen plasma, and the Norway resistance-heated process, whether using liquid quenchant or not, all reported an acetylene yield greater than 60%. However, these results contradict the system free energy minimization calculation, reported by Chang and Pfender[2], which showed a maximum acetylene theoretical yield of 38% for the methane endothermic conversion reaction, $2CH_4 \rightarrow C_2H_2 + 3H_2$. Chang's result is shown in figure 1, which plots the equilibrium compositions as a function of the reaction temperature.
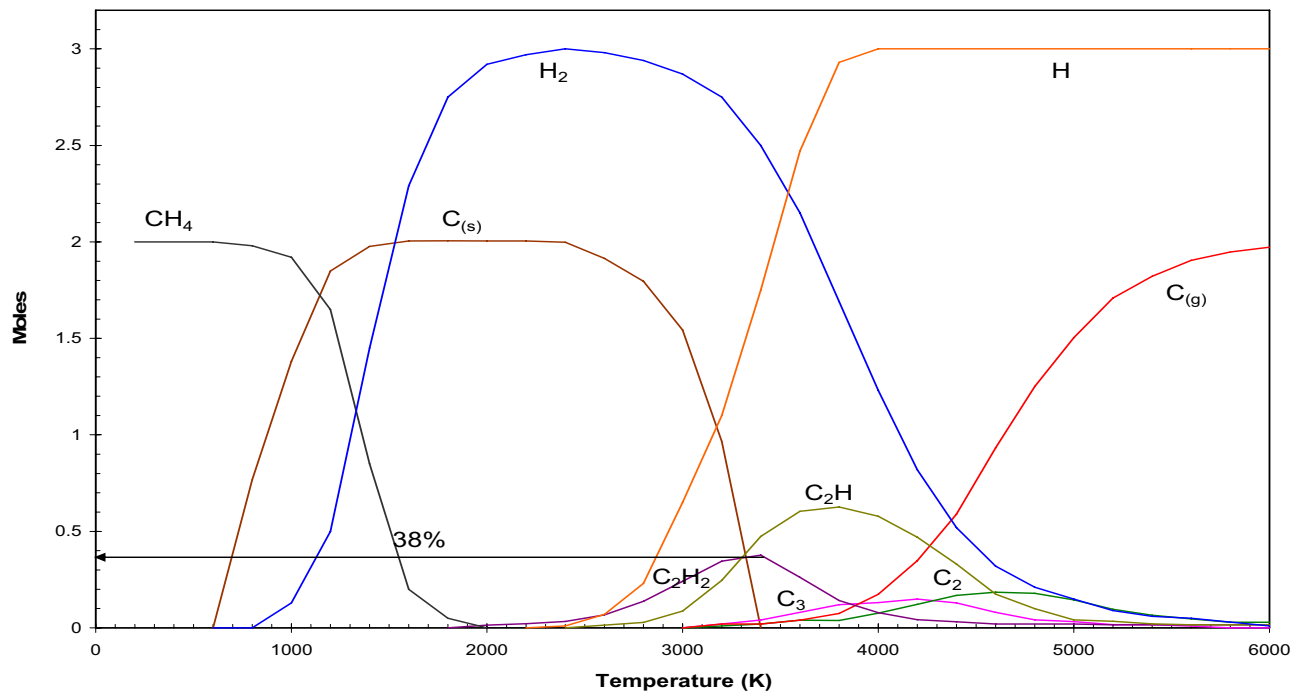

Figure 1. Maximum acetylene yield is 38% and decomposed to solid carbon at slow cooling

The calculation shows that acetylene is a metastable compound and only exists at high temperatures. The maximum yield for acetylene occurs just under 3500 K. Slightly below that temperature, acetylene is lost to solid carbon formation as soon as the temperature drops. When the system is allowed to reach equilibrium at low temperatures slowly all the acetylene would decompose to carbon black and hydrogen. To preserve the metastable product solid carbon nucleation at high temperatures must be reduced or eliminated. Lowering the gas temperatures rapidly from high temperature equilibrium will preserve the majority of the acetylene product. This is the reason for the Huels, Westinghouse, and Norway processes to use liquefied hydrocarbon to

[1]   H. W. Leutner, Ind. Eng. Chem. Process Des. Dev. 1, p166(1962).
[2]   Yl Change and E. Pfender, Plasma Chemistry and Plasma Processing, vol. 7, No. 3, p275(1987).

quench the reaction to preserve the yield. For the argon plasma jet process, the natural high intrinsic quench rate in the plasma jet helps freezing the product without the use of liquid quenchant. Based on the conversion yield, these processes have not reached maximum quench of the reaction to preserve 100% yield of acetylene. Further calculation by Chang and Pfender also demonstrated that if solid carbon nucleation is suppressed in the gas phase at high temperatures acetylene yield would achieve 100%. Therefore, rapid quenching of the reaction from high temperature equilibrium is necessary to suppress acetylene decomposition to nucleate carbon black. Figure 2 shows the calculated result of 100% acetylene yield when solid carbon nucleation is suppressed.
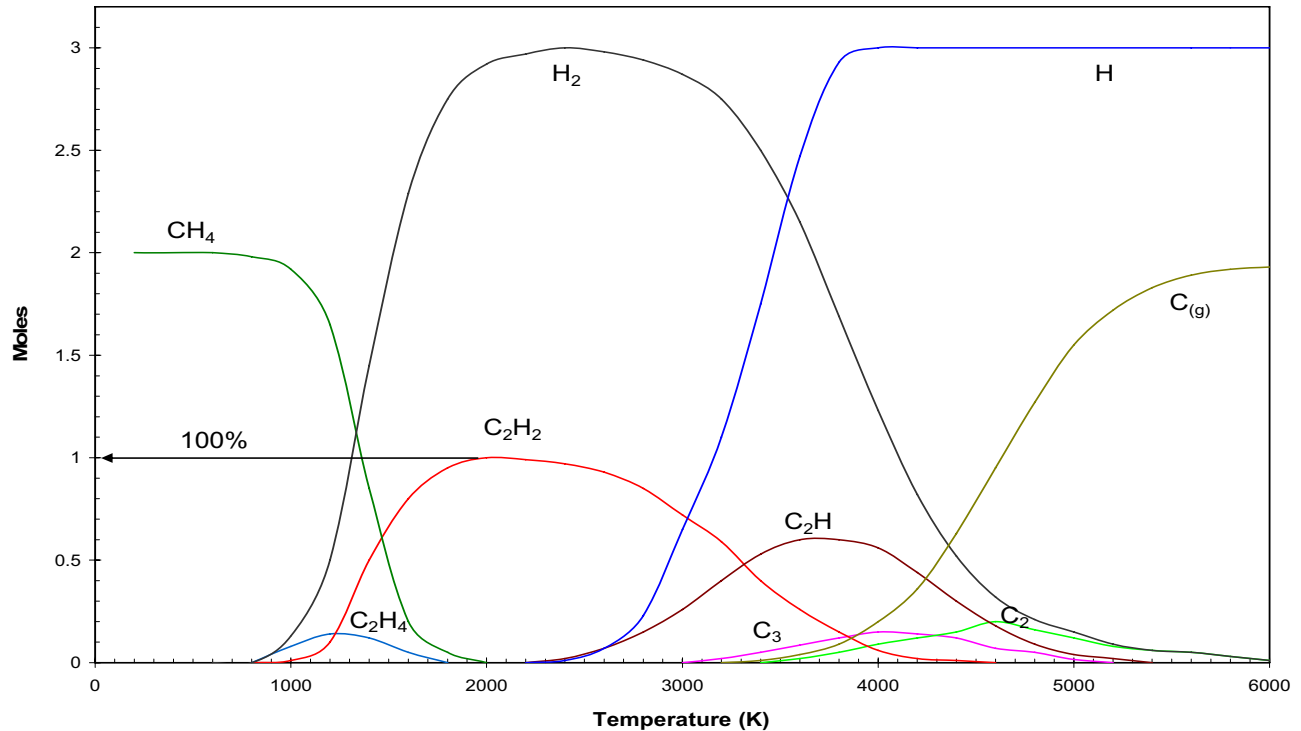

Figure 2. Maximum acetylene yield with solid carbon nucleation suppressed under fast quenching

The methane to acetylene conversion result intrigued the plasma research team at the Idaho National Laboratory. The INL plasma research team developed a plasma fast quench technology to verify Chang's calculation and to address the common solid carbon precipitation problem plaguing the processes discussed above. The plasma fast quench process developed include methane conversion to acetylene[3,4,5], synthesis gas (carbon monoxide and hydrogen) production[6], and hydrogen and solid carbon production from natural gas and other hydrocarbons[7,8].

3   U.S. Patent 5,749,937, (1998), "Plasma Fast Quench Reactor and Method".
4   U.S. Patent 5,935,293 (cont. in part), (1999), "Plasma Fast Quench Reactor and Method".
5   U.S. Patent RE37,853, (2002), "Fast Quench Reactor and Method"
6   U.S. Patent 6,187,226, (2001), "Thermal Device and Method for Production of Carbon Monoxide and Hydrogen by Thermal Dissociation of Hydrocarbon Gases".
7   U.S. Patent 6,395,197, (2002), "Hydrogen and Elemental Carbon Production from Natural Gas and Other Hydrocarbons".
8   U.S Patent 7,097,675, (2006), **"Fast-quench reactor for hydrogen and elemental carbon production from natural gas and other hydrocarbons"**

Plasma Fast Quench Reactor and Process

The plasma fast quench reactor and process are intended for high temperature reactions that require rapid cooling to freeze the reaction products to prevent decompositions or back reactions to undesirable products. The fast quench phenomenon is achieved by rapidly converting thermal energy in the plasma gas to kinetic energy via a modified adiabatic and isentropic expansion through a converging-diverging nozzle. In the process, the high gas temperature and pressure drop extremely fast and the gas reaches supersonic velocity. It is important to first raise the temperature of the reactants in the reactor to a level at which the desired end product is the only stable phase that exists. This is normally a consequence of the fact that the desired end product has the lowest overall system free energy at the selected elevated temperatures among all other possible reactions. However, this window of opportunity is generally very short-lived ($<<10^{-3}$ sec) in a high temperature reactor. To stabilize maximum conversion of the reaction product, it is necessary to rapidly cool the gas compositions at high temperature instantaneously to very low temperatures to force it to bypass all back reactions or decomposition of the end product. This condition is achievable by means of a modified adiabatic and isentropic expansion of the super hot plasma gas. This modified adiabatic and isentropic expansion can result in cooling rates as high as 10^{10} K/s, thus preserving reaction products that are in equilibrium only at high temperatures. The schematic of the plasma fast quench reactor is shown figure 3 below.

Plasma flow in

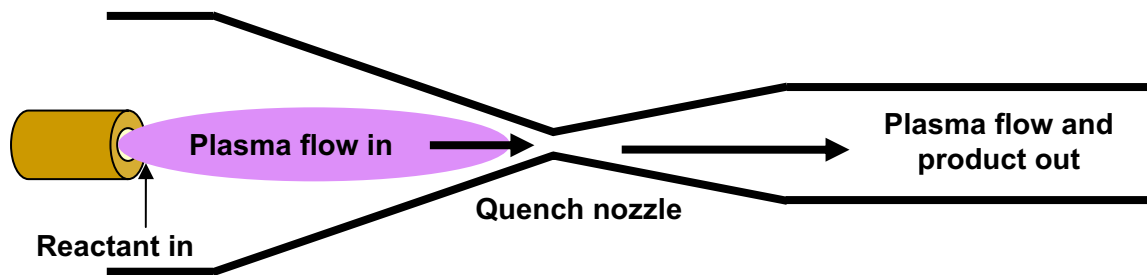**Plasma flow and product out**

Quench nozzle

Reactant in

Figure 3. Schematic of the Idaho National Laboratory plasma fast quench reactor

The technology concept is simple and centers on a converging-diverging reactor chamber. The converging part of the chamber is the high temperature reaction chamber where the feed material is heated to several thousand degrees Kelvin. The converging chamber is necked down to a very small cross-section quench nozzle. In the converging-diverging nozzle, the gas flows from a high pressure, P_o, to a lower pressure, P. The gas enters the converging section at a much lower velocity and during passage of the gas through the nozzle there will be a rapid transformation of thermal energy to kinetic energy. This kinetic energy will give rise to a very high gas velocity after discharging from the nozzle. The velocity of the gas in the throat of the nozzle, assuming adiabatic expansion, will achieve supersonic values. When the gas accelerates through the nozzle throat, the temperature of the gas will simultaneously drop rapidly. As a result of high velocity
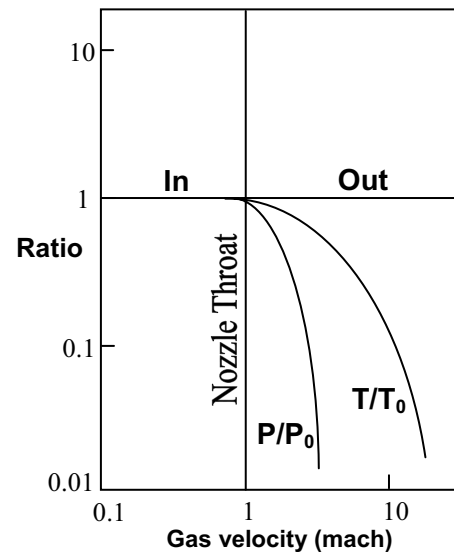

Figure 4. Pressure-temperature drop through the nozzle

cooling, the initial gas temperature, T_o, will drop to a much lower temperature, T, upon exiting from the nozzle. This rapid temperature quenching through a nozzle freezes the equilibrium products of a high temperature gas phase reaction thus preserving the maximum product yield. Figure 4 is a plot of the ratio of pressure and temperature drop as a function of the gas velocity in mach numbers. The plots show the gas velocity achieves supersonic values when the pressure and temperature drop are high. In testing Chang's result the INL plasma team constructed several quench nozzle reactors for methane conversion to acetylene. The analytical results showed 100% methane conversion in a single pass with acetylene yield greater than 98%. The by products include a small amount of solid carbon, ethane, ethene, and a significant amount of hydrogen. The experimental result confirms Chang's calculation that if solid carbon nucleation is suppressed acetylene yield should approach 100%. The INL plasma quench technology has shown a much higher conversion of methane to acetylene in a single pass than the Huels, Westinghouse, and the Norway processes without needing liquid hydrocarbon quenchant. The INL process had been demonstrated on bench scale and a small pilot scale. Large pilot scale development is necessary to assess the full economic implication for acetylene production with this technology.

Nonthermal Plasma Conversion of Methane and Heavy Hydrocarbon Upgrade

Besides thermal plasma, INL also engages in nonthermal plasma technology research and development for energy conversion. Two important areas of research are direct conversion of natural gas to a liquid and heavy hydrocarbon and natural gas co-conversion. Several patents cover the novel technologies[9,10,11]

Nonthermal Plasma Direct Conversion of Methane to Liquid

The patented technology for direct natural gas to liquid conversion combines a solid oxide electrochemical cell and dielectric barrier discharge plasma to convert natural gas to hydrocarbon liquids in a single step. The solid oxide electrochemical cell is an oxygen anion diffusion pump that provides activated oxygen atoms for reaction. The solid oxide electrochemical cell consists of a closed-one-end mixed conducting (both oxide and electronic conducting) thin ceramic oxide membrane tube, an interior porous cathode layer, and an exterior porous anode layer. A conductor connecting the anode and cathode completes the circuit. The mixed conducting ceramic oxide is internally short-circuited and the rate of oxide diffusion is controlled by electron diffusion at elevated temperatures (>600°C) in the opposite direction. To enhance the oxide diffusion, the cell is external short-circuited by a conductor to provide a fast electron path. During operation, the oxygen molecules dissociate and ionize at the porous cathode to form anions. The oxide anions diffuse through the thin membrane and discharge at the anode, forming oxygen atoms. The electrons conduct through the metallic conductor and return to the cathode at a much faster rate. This solid oxide electrochemical cell produces a low grade of power when functioning. The oxygen atoms combine with hydrogen and hydrocarbon radicals at the surface of the porous anode. Depletion of oxygen atoms on the surface of the anode sets up a chemical gradient to enhance the oxide anion diffusion through the membrane. The dielectric barrier discharge plasma activates the

---

9   U.S. Patent 5,427,747 (1995), "Methods and Apparatus for Producing Oxygenates from Hydrocarbons".
10   U.S. Patent 7,008,970 (2006), "Method for Direct Conversion of Gaseous Hydrocarbons to Liquids".
11   U.S. patent 7,033,551, (2006), "Apparatus and Methods for Direct Conversion of Gaseous Hydrocarbons to Liquids".

methane to produce high concentrations of reactive hydrogen and hydrocarbon radicals at high rates. Water is one of the main byproducts of this process; CO and CO_2 were not detected in the trapped products. This indicates that excess hydrogen radicals are eliminated by oxygen radicals, through water molecule formation, to promote hydrocarbon radical polymerization to form heavier hydrocarbons. This seems logical since the light hydrogen radicals diffuse through the reactor much faster than the much heavier hydrocarbon radicals. If hydrogen concentration builds up significantly faster than hydrocarbon radicals on the porous anode, then water formation would dominate. Depletion of hydrogen radicals in the reactor also encourages the polymerization of the light hydrocarbon radicals to heavier hydrocarbons. Analysis of the vacuum cold trap products (complete product preservation) by gas chromatography (GC) and GC-mass spectrometry (GC-MS) revealed C_1-C_5 alcohols, light hydrocarbon gases, hydrogen, gasoline and diesel range hydrocarbon liquids, no CO or CO_2, and H_2O byproduct. Figure 5 shows the schematic of the plasma system.
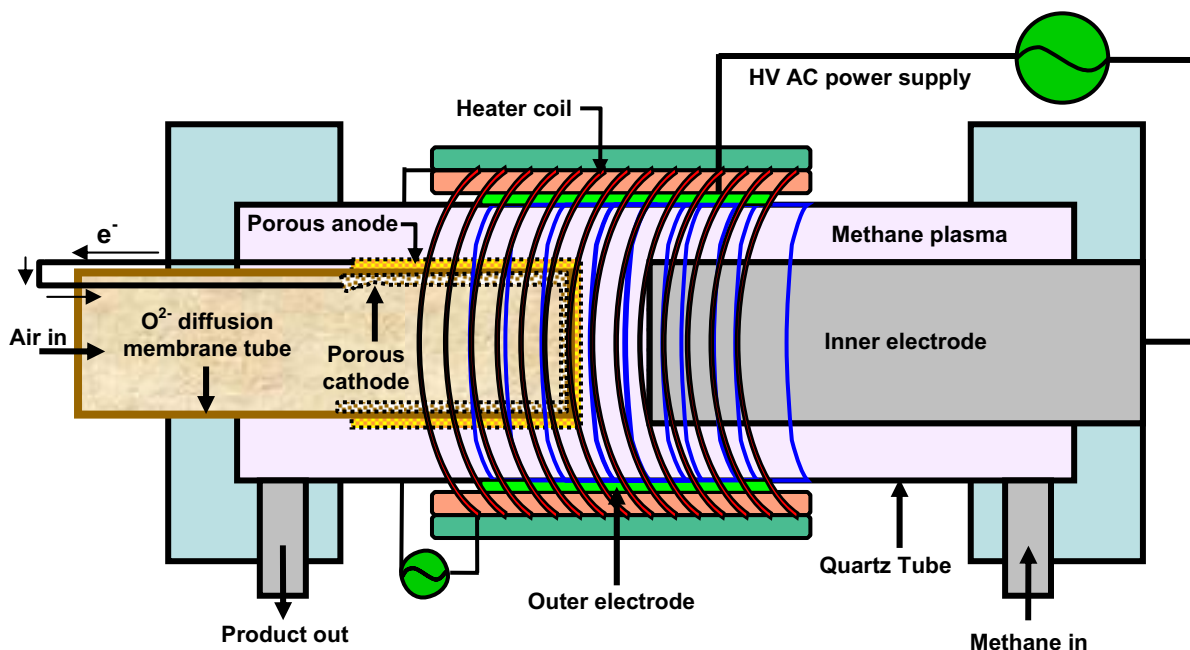

Figure 5. Plasma electrochemical reactor for direct methane to liquid conversion

In this plasma electrochemical conversion technology, CO and CO_2 are not observed byproducts. Water was the only byproduct beside hydrocarbon products. There are several possible mechanisms that lead to the formation of the products. In the electrochemical cell, the structure consists of a thin porous cathode, a dense thin layer of mixed conducting solid oxide electrolyte, and a thin porous anode. The electrochemical cell is a functioning oxygen pump at elevated temperatures. Oxygen molecules dissociate and pick up
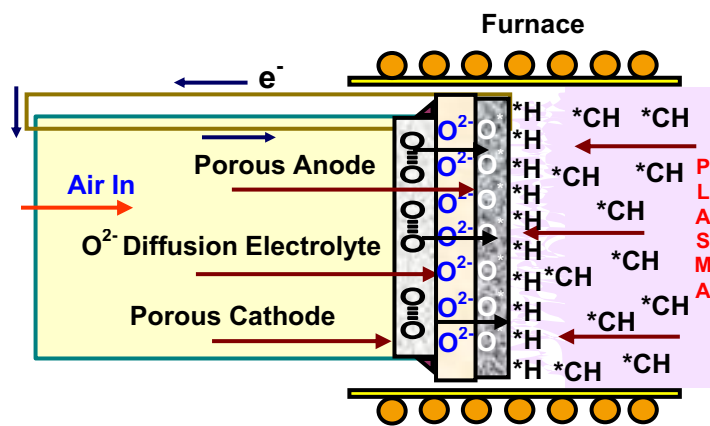

Figure 6. Possible plasma electrochemical reaction mechanisms for direct methane to liquid conversion

electrons at the cathode and become anions. The oxide anions diffuse through the oxide conducting membrane electrolyte. The anions discharge at the anode and form the oxygen radicals at the surface. The nonthermal plasma is generated within a dielectric barrier discharge cell. Pure methane is fed into the dielectric barrier discharge cell and under a high applied voltage nonthermal methane plasma is produced. The nonthermal methane plasma generates high concentrations of hydrogen and hydrocarbon radicals at ambient temperatures. Hydrogen radicals are much lighter and move with much higher drift velocities than the heavy hydrocarbon radicals. A significant hydrogen radical concentration builds up at the anode of the electrochemical cell. The hydrogen and oxygen radicals combine to form the hydroxyl radicals. The hydroxyl radicals further combine with hydrogen radicals to form water. This reaction reduces the concentration of hydrogen in the system by water elimination. A lower hydrogen radical concentration reduces the probability of radical termination reactions. This would promote the polymerization of the hydrocarbon radicals to form higher molecular weight fragments. A fast hydrogen radical concentration reduction in the system by water elimination reaction would enhance the formation of high molecular weight hydrocarbon compounds. The GC analysis (figure 7) of the trap products reveals primary products of non oxygenated hydrocarbons up to 20 carbons. Lower molecular weight oxygenated hydrocarbons, such as alcohols, make up insignificant products. The result seems logical since the concentration of the hydroxyl radical is depleted by water elimination reaction and it will not be available for radical termination reactions with the hydrocarbon radicals. The evidence for direct liquid hydrocarbon formation from methane with the plasma electrochemical technology points to a very different reaction mechanisms than the conventional oxidative coupling process. This technology has been tested on a bench scale. However, significant research is still needed to bring the technology to the next level of development.
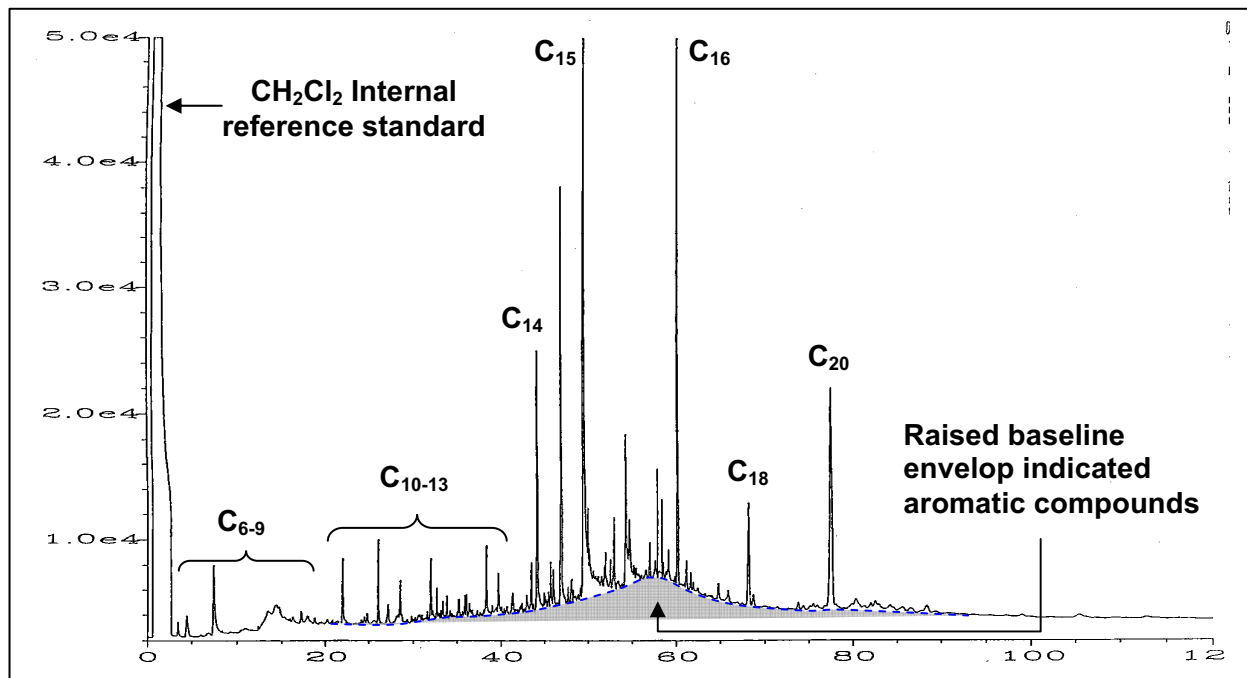

Figure 7. GC analysis of the cold trap products from the plasma electrochemical reaction showing fuel range liquid hydrocarbons.

Nonthermal Plasma for Heavy Hydrocarbon Upgrade

The patented technology[12] for heavy hydrocarbon and natural gas co-conversion using nonthermal plasma at moderately elevated temperatures (<300°C) uses a dielectric barrier discharge plasma to activate methane to produce a high concentration of reactive light hydrocarbon and hydrogen radicals. At the same time, the heavy hydrocarbon is activated by the methane plasma. Most heavy hydrocarbons with significant hydrogen budget deficit are grease like solids at room temperatures. Processing a heavy and viscous hydrocarbon stream the reactor is necessary to maintain at elevated temperatures (<300°C) to keep the heavy material flowing through the reactor. For liquid phase heavy hydrocarbon the reactor is maintained at room temperatures. Figure 8 is a schematic for the nonthermal plasma reactor for heavy hydrocarbon upgrade.
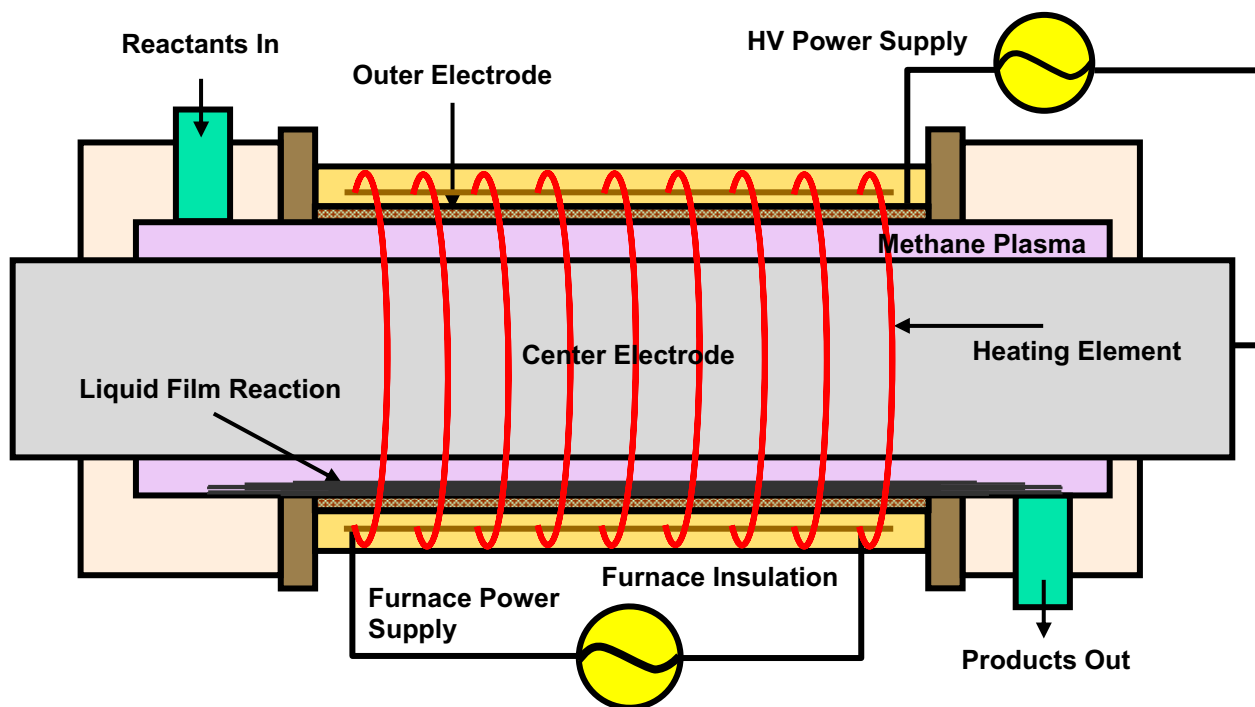

Figure 8. Nonthermal plasma reactor for heavy hydrocarbon and methane co-conversion.

In the process, the light hydrocarbon radicals crack the heavy molecules into multiple lighter fragments. Hydrogen radicals collide with these fragments and terminate the reaction by attachment, thus forming lighter molecules. The results of process development studies that used cetane, a n-alkane with 16 carbons, as a model compound, were quite amazing. Over 30% of the cetane was converted to a range of light hydrocarbon liquids and gases in a single pass. The converted product contains normal olefins and aliphatics, branched compounds, and aromatics. No heavy hydrocarbons higher than the original material were founded in the product. In another process development test, a refinery heavy stream, vacuum gas oil (VGO), was treated in the methane nonthermal plasma in a single pass. The results were just as encouraging as the model compound study. The heavy aliphatic and heavy aromatic compositions in the VGO were reduced and no compounds heavier than the original material were formed.   The GC results of plasma

---

12   U.S. Patent 6,896,854 (2005), "Non-Thermal Plasma Systems and Methods for Natural Gas and Heavy Hydrocarbon Co-Conversion".

treatment of cetane and VGO are shown in Figures 9 and 10. Particularly, the large reduction in the GC baseline envelop for the starting VGO is a strong evidence of breaking up the high molecular weight poly-aromatic-ring compounds by the plasma. This technology has been tested on a bench scale; significant research is needed to bring the technology to the next level of development.
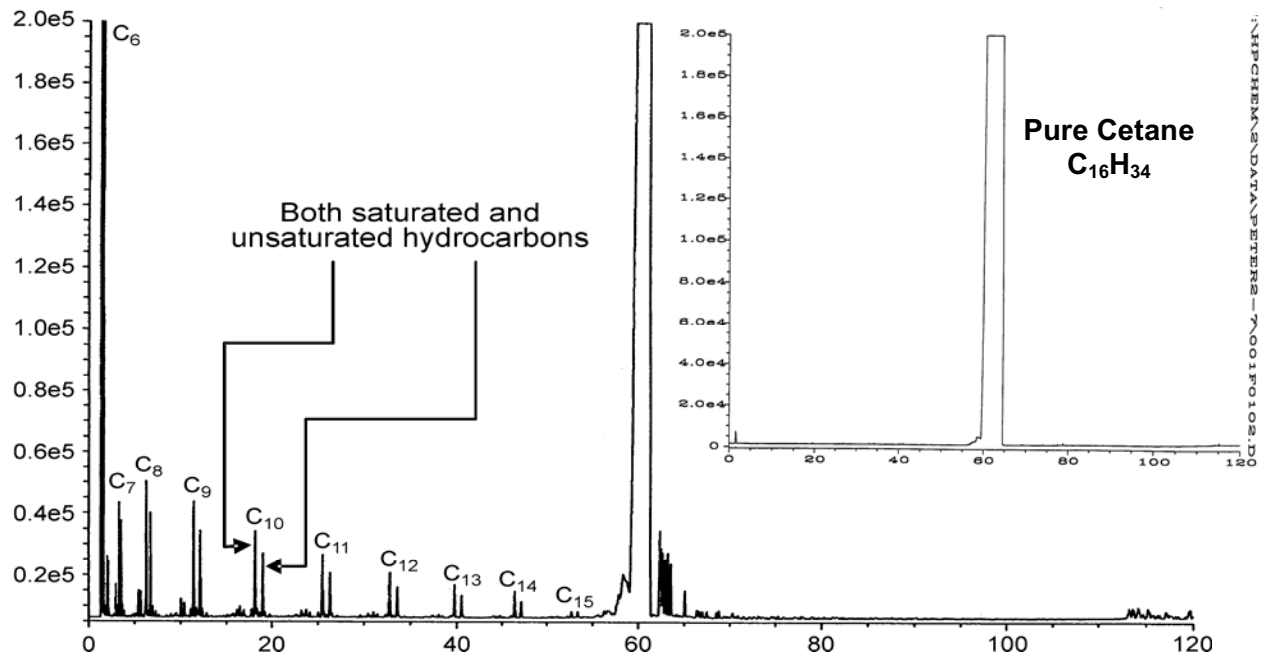

Figure 9. Result of the cetane model compound test in the nonthermal methane plasma.
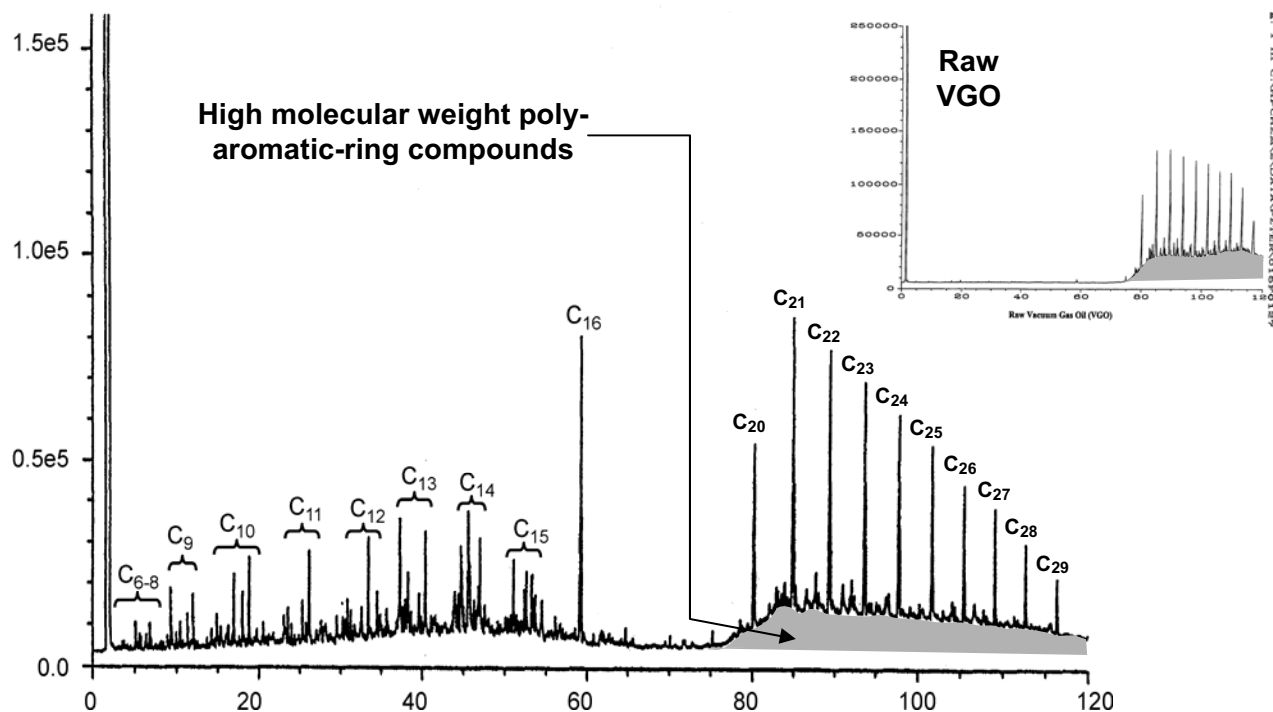

Figure 10. Result of the vacuum gas oil processed in the nonthermal methane plasma.

Summary

The Idaho National Laboratory (INL) developed several patented plasma technologies for hydrocarbon processing. This paper provides an overview of INL patented plasma technologies for hydrocarbon processing. The patents include nonthermal and thermal plasma technologies for direct natural gas to liquid conversion, upgrading low value heavy oil to synthetic light crude, and to convert refinery bottom heavy streams directly to transportation fuel products. Bench scale concepts have been validated for heavy or light hydrocarbons processing. The results were quite amazing and demonstrated that plasma has the capability to upgrade low value hydrocarbons to high value products. Plasma technology for hydrocarbon processing is attractive and promising however, significant research and development work are necessary to assess the economic potential for this technology.

Acknowledgements