

FEASIBILITY STUDY OF A NOVEL THERMAL PLASMA PROCESS FOR NATURAL GAS CONVERSION

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OBJECTIVE

The objective of this research was to conduct a feasibility study on a new process, called the plasma quench process, for the conversion of methane to acetylene. These efforts were focused on determining the economic viability of this process using bench scale experimental data previously generated.

INTRODUCTION

During the last decade most major oil companies have conducted internal studies on "remote gas" in efforts to capitalize on the large quantities of natural gas known to exist in various parts of the world. Such studies have typically been directed toward gas resources which are located too far away from population centers and end-use markets for conventional use, and cannot be economically liquefied for liquid natural gas carriers.

The Huels Company¹ in Germany has been using a plasma arc process to make light unsaturated hydrocarbons (acetylene and ethylene) from natural gas since the 1930's. These light hydrocarbons are subsequently converted to synthetic rubber and liquid hydrocarbons. The Huels process for arc plasma conversion of natural gas to acetylene requires quenching of the products by injection of cold liquefied hydrocarbons to prevent back reactions as the plasma is cooled. Quenching by this method is very energy intensive, inefficient, and the yield of the light olefin products is relatively low. The single pass yield of acetylene is less than 40% for the Huels process. Overall process yields are increased to 65% by recycling all of the hydrocarbons except acetylene and ethylene.

Patent protection for this novel process is being pursued by the inventors through the Idaho National Engineering Laboratory (INEL).² Initial work on this process demonstrated yields of acetylene as high as 70%. Further experiments have resulted in yields greater than 85% acetylene. Application of catalysts downstream of the quench reactor gaseous products can convert acetylene to higher molecular weight fractions such as liquid hydrocarbons.

The PFQR technology overcomes the limitations of other pyrolysis processes by adiabatic isentropic expansion of gases. Thermochemical modeling studies of the conversion of methane to acetylene were conducted to determine the equilibrium concentrations of acetylene and other reaction products between 500 to 3000 K. As expected, these studies determined that acetylene is a metastable compound that will decompose to carbon and other hydrocarbons if it is allowed to reach equilibrium at elevated temperatures (>800 K). The basic concept of the PFQR is that it will maximize the acetylene yield by "freezing" the product out of the reaction zone with extremely rapid decrease in temperature and pressure.

Successful development of the plasma quench technology (i.e., favorable product conversion and energy efficiencies) will result in an economic process for conversion of natural gas to high value hydrocarbons. This technology provide a means for the petroleum industry to capitalize on the vast quantities of natural gas which are known to exist (i.e., remote locations and shut-in gas wells) but are not in close proximity to population centers and thus end-use applications.

PROJECT DESCRIPTION

Historically, methane in non-fuel applications has been limited to feed stock for methanol, ammonia or hydrogen. With the discovery of natural gas in remote locations, such as, the North Slope of Alaska, the need for technologies to convert gas to transportable fuels has arisen. To this date, much of the research effort has been focused on the conversion of natural gas to methanol (Mobil case) or the oxidative coupling of methane (ARCO Chemical, ACC, case). LNG is not a viable option in many cases because of the limitations on access to shipping lanes due to seasonally closed ports or other logistical considerations.

The key variable in the profitability of both the ACC and Mobil technologies is the cost of the natural gas and the value of the gasoline produced. With the current crude/gasoline pricing, natural gas cost must be less than \$1 per thousand standard cubic feet (MSCF) for an after tax return on investment (ATROI) of greater than 10%.

RESULTS

METHANE TO GASOLINE ECONOMICS

In this analysis, an alternate route using acetylene from methane pyrolysis is considered. It has been demonstrated that acetylene can be produced from methane in high yields by high temperature, short residence time pyrolysis. Free energy favors the formation of acetylene at high temperatures. Methane pyrolysis has been practiced in the past with varying degrees of success. The major drawback is the inability to raise the temperature of the feed natural gas very rapidly and to quench the products to a non-reacting mixture in less than half of the reaction time.

To avoid the formation of non-selective byproducts via secondary reactions, the products must be quenched very rapidly. Historically, direct quench and direct reactive quench using LPG pyrolysis have been studied in this regard. Recently, the aerodynamic quench has been demonstrated by INEL to provide quenching in under two milliseconds. Acetylene yields have exceeded 90%.

Using this technology and "conventional" hydrogenation and oligomerization catalysts, an economic evaluation was performed. Given the current state of process development, the INEL technology is clearly the low raw material cost and the low cost capital option relative to ACC and Mobil. The estimated capital cost is about 80 % of the nearest competitor, ACC. The leveraging economic variable for the INEL reactor, however, is the amount of power consumed in the pyrolysis reactor and the cost of that power. In the INEL case, the power contribution to required netback can be 50%, easily the largest contributor and over twice the contribution of the cost of the natural gas feed.

The overall economics for the instantaneous construction/operation case indicate that the ACC Redox case is the most attractive for the conversion of natural gas to gasoline. Assuming a 4.5 ¢/kWH power cost and a consumption of 3.6 kWh/lb gasoline for the INEL case, the required netback is 30% greater than the ACC Redox case. With lower cost power, less than 3 ¢/kWH, INEL technology becomes the most attractive of the conversion technologies.

However, the current and forecasted economic situation does not favor using natural gas conversion to make gasoline in any of the processes. Historical data indicate that the refinery gate price of gasoline reaches about \$1/gal only when crude rises to \$35/bbl. Currently, gasoline and crude oil are much lower, about 60% of these figures. As a target, natural gas would have to be free, when crude is \$ 35/bbl in order for the ACC case at 12,500 barrels per standard day (BPSD) to approach a 12% ATROI. There are significant economies of scale that tend to improve the economics substantially, when dealing with large gas fields. The North Slope of Alaska, has a gas supply that would require up to 20 plants of the size evaluated in this report. With these volumes, the ACC technology attains a 12% ATROI when the natural gas price is a maximum of \$1/MSCF at \$35/bbl crude oil.

With \$ 35/bbl crude and a 2 MMMSCFD field, the INEL technology shows break-even economics (12% ATROI, capital USGC basis) at a gas price of \$ 1/MSCF, a power cost of 2.5 ¢/kwh and a consumption of 2.5 kWh/lb gasoline. If crude oil prices remain flat on average, as in the 1980's, then the target numbers get more severe.

ALTERNATIVE METHANE CONVERSION TECHNOLOGY

Even given the gloomy economic picture for gas conversion technologies caused by the low crude oil cost, the INEL technology shows significant promise due to low capital cost and high yields. The key process questions that must be addressed are the scalability of the pyrolysis-quench, the reduction in the required power, and the reactor design for the acetylene hydrogenation to insure selective conversion to ethylene rather than ethane.

Developments in the cyclotrimerization of acetylene to benzene provide the possibility of additional improvement in the economics by reducing the capital and operating costs. The downside is the likely inability to use benzene directly as a motor fuel due to environmental and toxicity issues. Since benzene has a higher value than gasoline, the economics could be greatly improved if this market could be exploited. Technologies such as the direct coupled pyrolysis and oligomerization developed at NREL should be investigated. There may be operating conditions in the Plasma- Quench process where the NREL technology may be applicable.

Along the same lines as the benzene argument, the INEL technology may provide an attractive route to ethylene. Rough calculations indicate that the INEL technology is nearly competitive with Ethane/Propane steam pyrolysis. Although much of the US olefin capacity is already in place, there may be another, aggressive round of olefin plant construction in the next two decades, some of which will be based on non-conventional technology. This should be studied in further detail. In order to properly assess the INEL technology in an ethylene case, it is suggested that an entire petrochemical facility be considered based on

natural gas. Products should include acetylene, ethylene, hydrogen, benzene, ethylbenzene and styrene. All of these products are potentially recoverable in controllable, high yields and with high purity.

CONCLUSION

The major conclusion of this analysis is that the INEL technology could be competitive with existing natural gas conversion technologies given the proper power consumption and pricing. However, none of the technologies will be economical if the predicted long term crude pricing is correct. The INEL technology does have the advantage of providing high yields of valuable chemicals (ethylene and acetylene) at low cost. Downgrading these to gasoline value, although taking advantage of the market demand, reduces the product value significantly and the margins are insufficient to carry the project.

REFERENCES

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