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Catalysis Today 106 (2005) 243–246
CATALYSIS TODAY
www.elsevier.com/locate/cattod

A new gas to liquids (GTL) or gas to ethylene (GTE) technology

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Abstract

Natural gas is a clean-burning and abundant energy resource, but much of it resides in locations remote from an economic means of transporting it to market. A logical solution for the problem would be to liquefy the natural gas, but this option requires very low temperatures and involves considerable costs. Another solution is to convert the natural gas into hydrocarbon liquids using chemical processing. Fischer-Tropsch technology converts the natural gas into ‘‘syngas’’ (a mixture of carbon monoxide and hydrogen) followed by reaction to liquid fuels. Unfortunately, Fischer-Tropsch technology is expensive.

At Texas A&M University, a research team has conceived a radically new process for converting natural gas into hydrocarbon liquids. It is a ‘‘direct’’ conversion method that does not require producing syngas. The process is essentially three reaction steps and two separation steps to produce hydrocarbon liquids. The process consists of two reaction steps and one separation step to produce ethylene. The process can operate economically with natural gas flows of as low as 300 kSCMD up to any desired capacity.

It is possible to use the GTL technology essentially anywhere natural gas exists from offshore platforms to relatively uninhabited onshore sites. This technology offers an alternative to flaring natural gas when pipelines do not exist. The liquids can be transported in liquid pipelines or in trucks or in tankers. Thus, it offers the opportunity to monetize a resource as well as to reduce undesirable emissions into the atmosphere. The GTE technology is more nearly suited to a location near an existing chemical industry that requires ethylene and/or hydrogen.

SynFuels International Inc. has licensed the technology to commercialize it, and the company has constructed a pilot plant capable of processing 3 kMCMD. The cost of a commercial 300 kSCMD plant should be in the US$ 50–75 million range. The cost of the liquids should be about US$ 25–28 per barrel. Of course, larger capacity plants would require a larger investment but produce a less expensive product.

Keywords: Natural gas; Hydrocarbon liquids; Fischer-Tropsch technology

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1. Introduction

Although natural gas has been, and in some cases still is, a nuisance in petroleum production, it is in the process of becoming a highly desirable commodity. When used as a fuel, it burns relatively cleanly, and it is relatively easy to remove sulfur (H_2S) from it. As a feedstock, it yields ethylene from its ethane content and forms the basis of a massive chemical industry. Large reserves exist in many regions of the world. However, it has a major drawback in transportation. Much of the natural gas appears in regions that are remote from markets or pipe lines, it is ‘‘stranded’’ gas. Moreover, the gas is at a relatively low density making pipe line construction expensive, hence, the drive to develop improved liquefaction technologies, compression technologies, and gas to liquid technologies.

Another technology that would meet with quick adoption is a means to ‘‘activate’’ the methane in natural gas. Producing ethylene from methane in addition to or instead of ethane would greatly increase the available feedstock. Producing hydrogen along with the ethylene could also be a benefit for the chemical industry.

This paper describes a new process that can convert natural gas economically into hydrocarbon liquids or into ethylene and hydrogen. Previous descriptions of this process appear in [1–5]. Of course, Fischer-Tropsch (FT) technology has existed for nearly a century, and it can convert natural

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doi:10.1016/j.cattod.2005.07.176

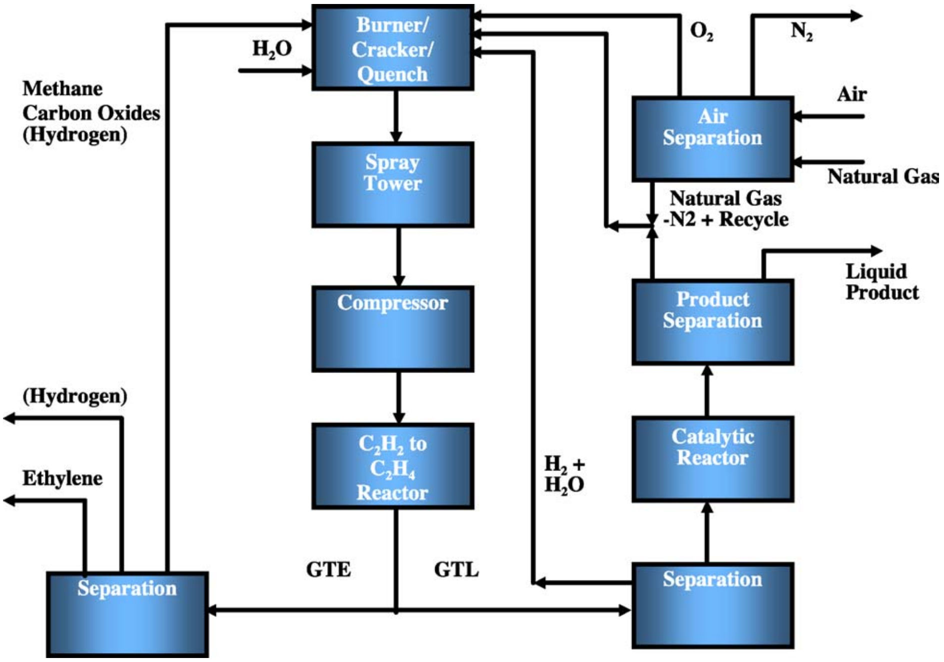
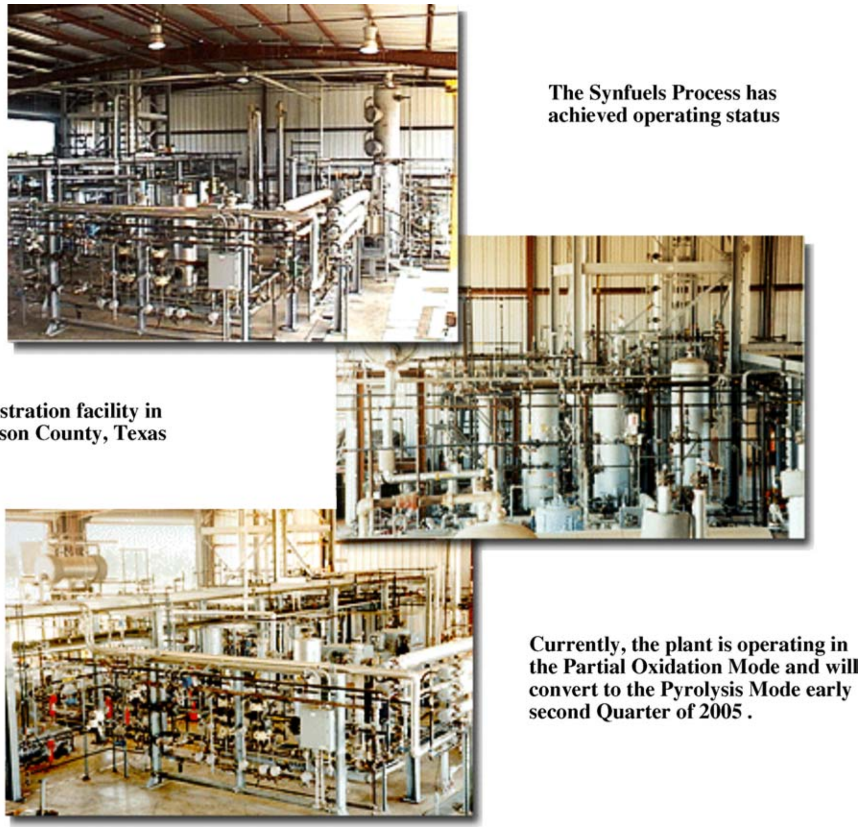


Fig. 1.

gas into hydrocarbon liquids. However, FT requires converting the gas first into syngas (a mixture of CO and H_2), and this is an expensive process. The new process avoids the syngas step and it does not produce wax.

Economics dictates that FT plants be large with capacities greater than 3 MSCMD (preferably on-the-order-of 30 MSCMD. However, the new process can be profitable at a capacity of 300 kSCMD. Plants with capacities less than



The Synfuels Process has achieved operating status

Demonstration facility in Robertson County, Texas

Currently, the plant is operating in the Partial Oxidation Mode and will convert to the Pyrolysis Mode early second Quarter of 2005 .

Fig. 2.

750 kSCMD can be skid mounted, while those with capacities less than 1.5 MSCMD can be barge mounted.

2. Process

Methane activation is a topic of considerable interest in the energy industry, of course it also is difficult to achieve. However, by subjecting methane to temperatures in the range of 2500 K, it is possible to crack it. Remarkably, acetylene is stable at these temperatures and, with careful attention to residence time, it is possible to design a cracker that produces acetylene and hydrogen. It is prudent to hydrogenate the acetylene to ethylene for safety reasons, and then the entire realm of ethylene chemistry becomes available.

Fig. 1 presents a schematic diagram of a possible arrangement for the process(es), while Fig. 2 is a current photo of the demonstration plant. We assume sweet natural gas enters the process (sour gas is easy to sweeten). A portion, less than 10%, fuels an internal combustion thermal cracker into which the remainder of the gas flows. The combustion products reach temperatures sufficient to crack much of the methane, and all other hydrocarbons in the gas, to hydrogen and acetylene. Of course, subjecting hydrocarbons to these temperatures causes coke formation in the cracker. We add some steam to reduce this effect, and the overall coke formation is very low, approximately 5% of the inlet carbon. We then catalytically hydrogenate the acetylene to ethylene using some of the hydrogen produced in the cracker. At this point, we must decide if we want ethylene (and possibly hydrogen) as products or liquids.

Assuming we select the GTE path, we would run the stream into a separation unit that would split out the ethylene and hydrogen (if desired). The remaining components of the stream would consist of methane, carbon monoxide, possibly hydrogen, and nitrogen compounds. The nitrogen compounds are removed and the remainder flows back to the cracker as fuel. The ethylene and hydrogen could feed a chemical process.

Table 1
Catalytic reactor outlet composition

Component	Mol %
Ethane	0.180
Propane	3.143
Isobutane	4.511
n-Butane	6.440
2,2 Dimethylpropane	0.016
Isopentane	9.703
n-Pentane	5.817
2,2 Dimethylbutane	0.204
2,3 Dimethylbutane	0.479
2-Methylpentane	5.945
3-Methylpentane	2.254
n-Hexane	2.577
Methylcyclopentane	1.655
Benzene	0.755
Cyclohexane	2.844
Dimethylpentanes	2.539
2-Methylhexane	0.987
3-Methylhexane	0.687
Dimethylcyclopentanes	1.230
n-Heptane	0.771
Methylcyclohexane	1.161
Ethylcyclopentane	0.488
Dimethylhexanes	0.439
Trimethylpentanes	0.641
Trimethylcyclopentanes	0.060
Toluene	6.164
Methylheptanes	2.130
Dimethylcyclohexanes	0.465
Methylethylcyclopentanes	1.384
Ethylbenzene	2.708
Xylenes	9.597
n-Octane	0.276
Nonane paraffins	1.394
Nonane naphthenes	1.012
Nonane aromatics	3.143
n-Nonane	0.082
Decane paraffins	6.871
Decane naphthenes	0.593
n-Decane	1.291
Undecanes	2.685
Dodecanes	1.232
Tridecanes	1.130
Tetradecanes +	2.317
Total	100.000

Assuming we select the GTL path, the stream would pass to a catalytic reactor in which the ethylene, and possibly a small amount of the methane, would oligimerize into heavier hydrocarbons. The stream then passes to a stabilizer that produces the liquid product and a recycle stream of light hydrocarbons for the cracker. Table 1 presents a typical low molecular weight stream from the reactor that resembles an aviation fuel. This product results when the reactor operates at low pressure. High-pressure operation would result in a diesel fuel. The product that results after stabilizing the stream represented by Table 1 is a 95 octane, C_8 average "fuel." It is approximately 50% aromatics (but low in benzene), 30% isoalkanes, and 20% cycloalkanes. Rather than using it as a fuel, a higher profit use would be to separate the aromatics from the alkanes. The aromatics would be a good feedstock for a chemical industry, while the alkanes would be a good alkylation stock for gasoline refineries.

3. Chemistry

While the actual kinetic mechanism is undoubtedly complex, the overall effect of the cracker is:

$$2CH_4 \xrightarrow[\text{``fast''}]{} C_2H_6 + H_2 \xrightarrow[\text{``fast''}]{} C_2H_4 + H_2 \xrightarrow[\text{``slow''}]{} C_2H_2 + H_2 \xrightarrow[\text{``slow''}]{} 2C + H_2$$

We quench the reaction before the final step resulting in the overall reaction:

$$2CH_4 \rightarrow C_2H_2 + 3H_2$$

Another reaction that appears to occur to a significant extent within the residence time of the process is:

$$C_2H_2 + 2H_2O \rightarrow 2CO + 3H_2$$

4. Economics

We arrive at our cost per barrel by assuming remote gas at US\$ 0.018/m^3, 10-year straight-line amortization, 25% fixed costs, and US\$ 1–3 per barrel operating costs. For a 1.4 MSCMD plant, this results in US\$ 25 per barrel of liquid product.

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