The ÉCLAIRS Process for Converting Natural Gas to Hydrocarbon Liquids

BY

Sean C. Gattis, P.E.,
Principal Process Engineer, S&B Engineers & Constructors, Ltd.
Edward R. Peterson, P.E.,
Senior Staff Process Engineer, S&B Engineers & Constructors, Ltd.
Marvin M. Johnson, P.E.,
Senior Fellow Emeritus of Phillips Petroleum

200 CRESCENT COURT, SUITE 1801
DALLAS, TEXAS 75201
TEL: (214) 855 8920
FAX: (214) 855 8955
E-MAIL: INFO@SYNFUELS.COM
INTERNET: WWW.SYNFUELS.COM

The ÉCLAIRS Process for Converting Natural Gas to Hydrocarbon Liquids

Sean C. Gattis, P.E., Principal Process Engineer, S&B Engineers & Constructors, Ltd.
Edward R. Peterson, P.E., Senior Staff Process Engineer, S&B Engineers & Constructors, Ltd.
Marvin M. Johnson, P.E., Senior Fellow Emeritus of Phillips Petroleum

ABSTRACT

Since shortly after crude was refined into petroleum fractions, governments and corporations have been searching for an economical method to convert natural gas, often stranded in remote locations or copiously associated with produced oil, into liquid products. Many routes have been discovered to transform this gas into a product that is liquid at atmospheric conditions, but few, if any, provide any economic incentive. All too often, the processes fail economically because they must handle great quantities of gas, only a small fraction of which is useful in making liquid product. Gas compression, enormous equipment, and reaction inefficiencies are usually responsible for crippling the value of the overall process. The SynFuels technology, developed by S&B Engineers and Constructors, converts gas to liquid product more economically by rejection of unwanted gases early in the process, formation of a novel liquids precursor, and highly selective conversion of the liquids precursor to a liquids intermediate that results in very high quality liquid product.

The Synfuels process is presented here, starting with natural gas through to the formation of liquid products. Where useful, streams, compositions, temperatures and pressures are discussed to show the clear benefits of this technology at key processing steps. Test data are presented where appropriate. An economic analysis shows that the process is profitable at much smaller scale than any potentially competitive processes.

GTL BACKGROUND and CURRENT DIRECTION

The conversion of natural gas into hydrocarbon liquids has been a technological goal for many years. In 1923, Germans Franz Fischer and Hans Tropsch developed a process to convert coal or natural gas to hydrocarbon liquids. Their namesake process has been the primary focus of gas-to-liquids (GTL) research and development work to date and remains the basis for almost all commercially proven or viable GTL processes.

The historical Fischer-Tropsch (F-T) process has three main steps. First, natural gas is combined with oxygen and steam in a catalytic reforming reaction to form a hydrogen and carbon oxide mixture, or syngas. Second, the syngas is reacted in a catalytic F-T reactor to form paraffinic hydrocarbons. Third, the paraffinic mix is hydrotreated and processed to convert, separate and purify the final synthetic petroleum products, including diesel fuel, kerosene, naphtha, and even waxes.

Germany used the F-T process to fuel its military during World War II. South Africa installed the first world-scale GTL unit in 1955 during apartheid. Only a few other commercial-scale GTL plants are currently in operation in the world, each started-up in the 1990's. In fact, most, if not all, GTL plants to date would not have been built if it were not for governmental subsidies or political restrictions or influences.

Enormous capital cost has always been the primary concern, necessitating huge plants to create the economy of scale needed for a venture to be economical. Of course, with a required capital investment of hundreds of millions of dollars for such a plant, controlling the technological risk becomes another major obstacle.

There are many incentives to continue to pursue an economical GTL process. Rising energy prices and the need for a new source of fuel to replace depleting oil reserves are often cited. Gas converted into liquids transportable to end markets would be a significant help. Over 75% of the world's known gas reserves are not currently accessible by pipeline, and the majority of those reserves exist in remote locations where gas pipelines cannot be economically justified. Approximately 15.5 trillion cubic feet of stranded natural gas is flared, vented, or reinjected each year.

Other incentives to pursue an economical GTL process continue to appear and grow. Governmental restrictions on flaring and emissions are increasing. In some cases, production of oil from certain fields may stop or at least decrease due to lack of options for handling the associated gas. Environmental concerns are gaining support. Laws for cleaner fuels are being enacted and enforced. More often of late, a government may desire to monetize its country's resources that may have been considered worthless or even wasted (flared).

Mega-scale GTL plants have been garnering much attention and study. However, while there are over 15,000 natural gas fields outside North America, less than 200 of them are large enough to support mega-scale GTL plants. Liquefied natural gas (LNG) and methanol projects have also attracted attention as means of liquefying gas for transport and use. LNG has extremely high capital costs and requires long-term agreements to be profitable. On the other hand, LNG can be used on much smaller gas fields, even ones located offshore. Methanol-only plants have been around for decades, but their economics do not match those of GTL.

In recent years, companies have spent billions of dollars in research and development of gas-to-liquids (GTL) technology, almost all of which is based upon Fischer-Tropsch technology. Companies are planning to spend billions of dollars in the next few years to construct mega-scale GTL plants at the world's largest gas fields in Qatar. Several other projects have also been announced by various partnerships in locals such as Nigeria, Malaysia, and the Middle East. However, the costs and economics will likely keep most such GTL projects in the planning stages longer, and few of them will actually be constructed near term.

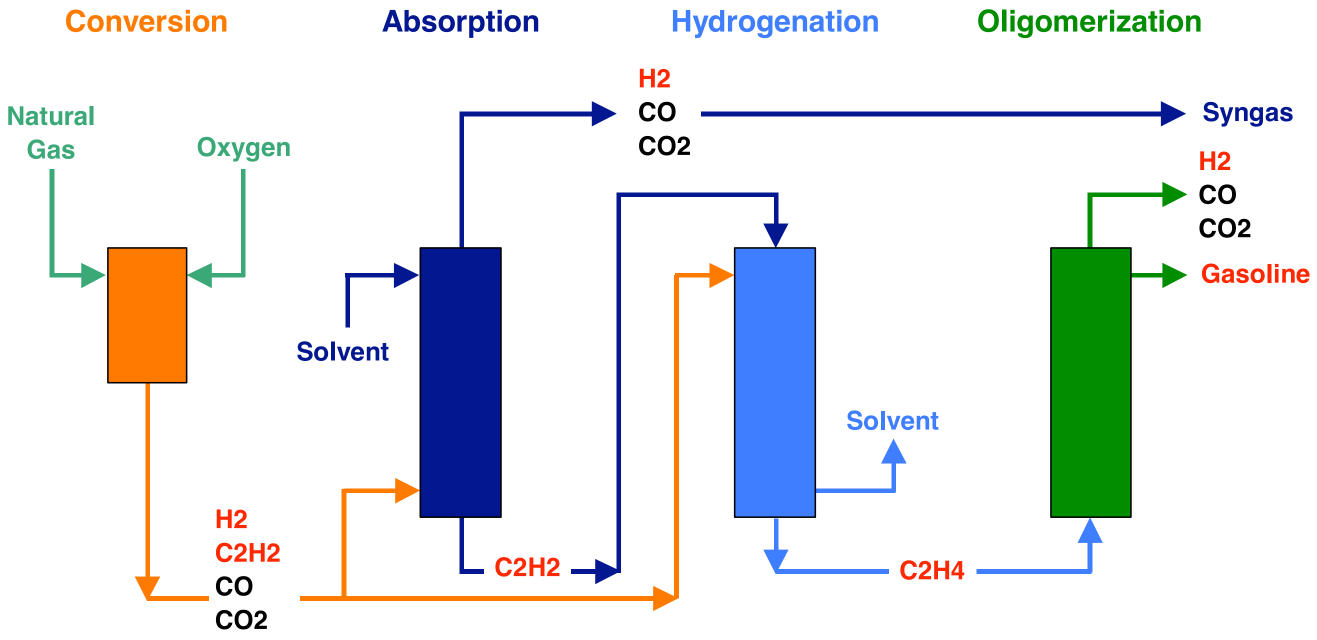
THE ÉCLAIRS PROCESS – SYNFUELS' GTL TECHNOLOGY

Refinements to existing Fischer-Tropsch processes are not likely to provide the order of magnitude change in economics needed to overcome the obstacles of inefficiency and high capital cost. GTL plants must be economical on a stand-alone basis at a much smaller scale than the existing and planned mega-plants in order to facilitate a broader and faster commercialization by making it possible for liquid fuel to be marketed from the great multitude of stranded and associated gas fields. Smaller fields need smaller plants that require much less capital.

The new Synfuels' GTL technology, developed by S&B Engineers & Constructors, accomplishes these goals. It is a radically new GTL technology, not a F-T modification, that achieves better investment returns than the mega-plants at a fraction of their capacity and capital requirements. There are thousands of gas fields capable of supporting a Synfuels GTL plant.

A diagram of the new Synfuels GTL technology is presented in Figure 1. The process to produce a gasoline product from a natural gas feed consists of four main steps –conversion, absorption, hydrogenation, and oligomerization. The diagram shows the major constituents in the feeds and products of each step. Depending on plant operating conditions and specific equipment utilized, the relative amounts of the intermediate stream constituents will vary, as will the resultant products and by-products. For example, a syngas by-product is not produced in some configurations or modes of operation.

SYNFUELS INTERNATIONAL GTL TECHNOLOGY



S&B ENGINEERS AND CONSTRUCTORS, LTD.

FIGURE 1

The first processing step in the Synfuels process is the conversion of the hydrocarbons in a natural gas feed into useful amounts of acetylene. The cracking process is well known and documented, having been practiced by those in the acetylene industry for decades. There are several methods that have been used to crack methane, generally employing techniques of direct contact with hot combustion products, indirect heating (i.e. via furnace tubes), electric arc, and even catalytic reaction.

The most prevalent method used in industry is termed partial oxidation (PO), in which natural gas and oxygen are co-fed into a reactor in a sub-stoichiometric ratio. A portion of the gas is burned, primarily via incomplete combustion to carbon monoxide, to provide the heat necessary to crack the remaining gas. In addition to the intended olefins, the PO reactor outlet typically contains hydrogen and carbon oxides in such proportion that a standard, saleable syngas stream can easily be separated.

Another cracking method frequently used by industry has been termed by some as high temperature pyrolysis, in which a fuel stream and an oxygen source are co-fed into a reactor and burned, preferably completely to carbon dioxide and water. A natural gas feed stream is introduced into the reactor separately and is mixed with the hot combustion products to induce thermolytic cracking. Due to the proportion of hydrogen and carbon oxides in the reactor outlet, a syngas stream suitable for uses other than as fuel (i.e. such as conversion to methanol) is not readily generated.

Temperatures inside a cracking reactor can reach in excess of 4000^{o}F before the endothermic reaction and its subsequent quenching dramatically cool the gases to about 1000^{o}F or less. Pressures are low, usually less than 15 psig, though some designs operate closer to 50 psig.

The second processing step in the Synfuels process is absorption of the acetylene from the cracked gas using a solvent selective to acetylene. The absorption process has also been used in the acetylene industry for decades. The basic technique is a scrubber or contacting column in which the gas flows upward counter-current against the solvent flow. Acetylene-rich solvent exits the column bottom. The remaining gases comprise the column overhead, which, as mentioned previously, can be a near optimal syngas stream depending on the cracking method.

Variations of the absorption step abound within industry with each practitioner having its own solvent, operating conditions, and equipment configuration and design. Temperatures range widely and are dependent on the cooling media available. Many contactors operate between about 70^{o}F to about 120^{o}F. However, to maximize absorption efficiency, it is not an uncommon practice to use refrigeration to lower the operating temperature to the 40^{o}F to 60^{o}F range. Column pressures typically range from 100 psig to 250 psig.

The heart of the Synfuels technology lies in the third processing step – acetylene hydrogenation, or ÉCLAIRS (Ethylene from Concentrated Liquid phase Acetylene – Integrated, Rapid and Safe). Gas-phase hydrogenation of acetylene into ethylene is truly commonplace, particularly in ethylene production units. The novel invention used here is conducting the reaction in the liquid-phase.

In the liquid-phase process, acetylene-rich solvent from the absorption step is fed into a catalytic reactor along with a hydrogen source. With the right catalyst, the acetylene can be completely converted with 98% selectivity to ethylene. The reactor typically operates between 100 psig and 300 psig at temperatures between 200°F and 350°F. The liquid is easily separated from the product gases, cooled, and recycled to the absorption column. The resultant product gas comprises mostly ethylene with non-condensables and a small amount of higher olefins as the balance.

Acetylene hydrogenation produces substantial heat. Typical gas phase hydrogenation:

1) must limit acetylene concentration in order to keep reaction and temperature under control;
2) requires processing a large volume of gas to yield a small amount of ethylene;
3) is operated at high temperatures that can lead to a “run-away” reaction; and
4) tends toward over conversion to ethane.

The Synfuels ÉCLAIRS process overcomes these and other difficulties by:

1) selectively absorbing the acetylene from the cracked gas product stream, thereby rejecting unwanted gases;
2) greatly reducing reaction volume leading to a smaller reactor and less catalyst;
3) operating at moderate conditions that are easily controlled and maintained; and
4) operating in a liquid phase so that the absorbent is the heat transfer and dispersion medium, eliminating the possibility of a thermal “run-away” reaction and allowing for much higher acetylene concentrations to be used.

The fourth and final processing step in the Synfuels GTL process is the oligomerization of ethylene to produce a gasoline product. This conversion reaction has been researched and developed since at least the early 1970’s, but it has not found notable commercial application. One likely reason is that those possessing ethylene are not interested in making gasoline. However, for a stranded gas field, making a transportable liquid is a prime goal.

The ethylene product gas from hydrogenation is fed to a catalytic reactor in which the ethylene is converted into primarily C6 to C11 hydrocarbons with a minor fraction of C4s and C5s also being produced. The reaction is highly exothermic. Fixed bed and fluidized bed reactors have been used. The final stabilized gasoline product is typically 95+% octane and contains 25-40% aromatics. The temperature, pressure, catalyst, reactor type and configuration, and residence time all affect the exact product composition. Each of these parameters can be either designed or adjusted to obtain a desired product. Reaction temperatures are typically 600°F to 800°F. Operating pressures can vary widely, from less than 25 psig to upwards of 500 psig.

The operation, equipment, or configuration of the Synfuels process can be altered to produce a variety of products or to maximize the production of a certain product. Portions of the gas streams exiting the absorption and oligomerization sections are used as fuel either for or in the process. Recycling the non-product gas in the process leads to increased gasoline production. As described earlier, switching cracker types can result in the absorber off-gas being a syngas stream suitable for further conversion, for example, into methanol. Methanol is itself a transportable and saleable liquid. Methanol can also be converted via known commercial technology into a wide range of products, including olefins, gasoline, or diesel fuel. As another example, a few minor changes to the oligomerization section, including increasing the reactor pressure to approximately the 500 psig range, would result in a predominantly diesel fuel product rather than gasoline. As yet another example, circumstances may arise in which the natural gas owner prefers to have an ethylene product (for further conversion locally) rather than a liquid fuel. In such a case, the oligomerization section can be eliminated, and the ethylene from the hydrogenation section purified to whatever specification desired (i.e. polymer grade).

The new Synfuels technology, developed by S&B Engineers & Constructors, Ltd., has led to four patents pending, both domestically and internationally. These cover hydrogenation in the liquid phase, the catalyst used in the liquid phase hydrogenation process, and the general and overall process for making products from natural gas employing hydrogenation technology.

LABORATORY and PILOT PLANT

The Synfuels liquid phase hydrogenation process has been proven at bench scale. Laboratory research and development confirmed the concept and theory. Extensive catalyst development and testing led to the discovery of the catalyst required. The process test results have been independently verified by another contracted catalyst testing laboratory. Subsequent and ongoing catalyst testing and refinement has enabled further conversion improvements.

Laboratory prepared, proprietary hydrogenation catalysts were originally used. Later, small batch, commercially prepared catalyst samples, with the same formulations as the lab catalysts, were obtained and tested. Performance of the commercial versions met or exceeded those of the lab.

An example of typical liquid-phase acetylene hydrogenation conversion and selectivity results are presented in Figure 2. An initial dip in catalyst selectivity is representative of the catalysts we have tested. We believe short term low selectivity is due to the presence of a few overactive hydrogenation sites in the fresh catalyst. The influence of these sites is consistently ephemeral.

An example of extended duration conversion and selectivity results are presented in Figure 3. The box on the graph lists the product analysis of the last data point for the test run shown. For this particular test, the conversion was intentionally not driven to 100% so that influences of certain parameters could be observed more clearly. However, complete conversion of acetylene with 98% selectivity to ethylene was and can be readily achieved. Liquid phase hydrogenation tests exceeding 100 hours show no perceptible depletion in selectivity or activity of the catalyst.

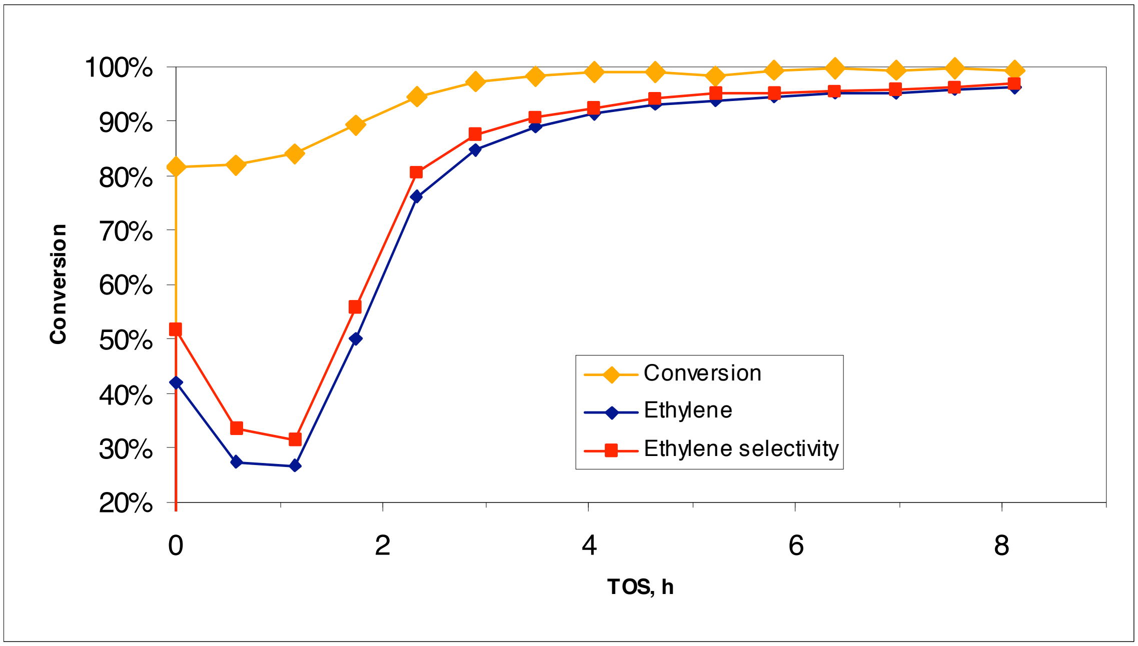
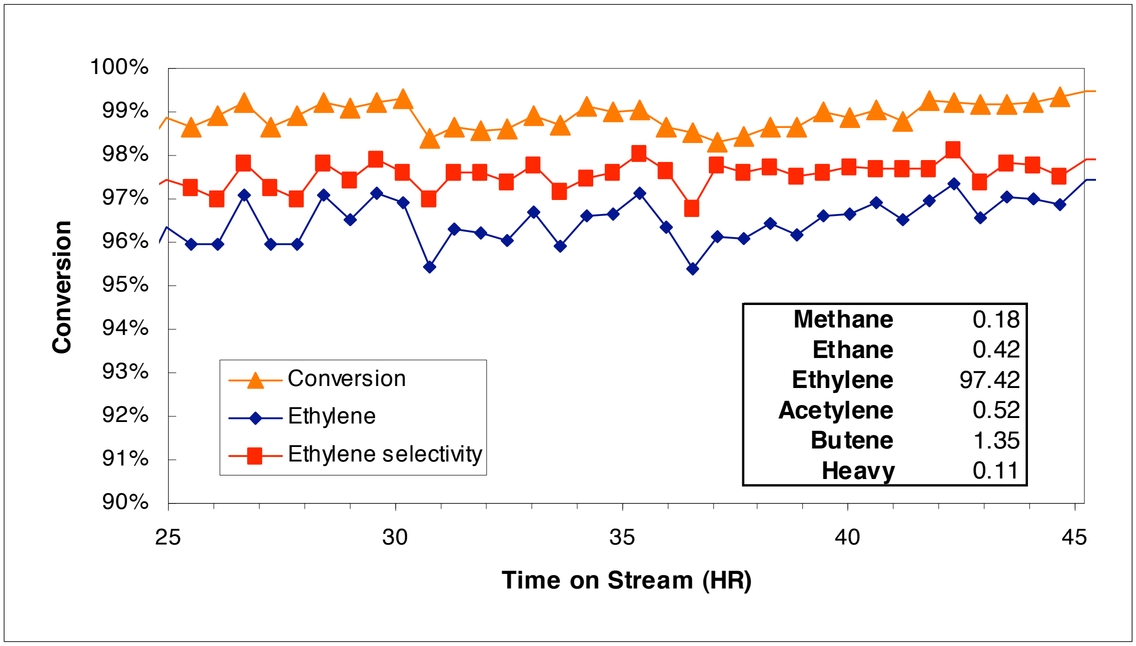


FIGURE 2
Typical Liquid-phase Acetylene Hydrogenation Conversion and Selectivity



Methane	0.18
Ethane	0.42
Ethylene	97.42
Acetylene	0.52
Butene	1.35
Heavy	0.11

FIGURE 3
Example of Extended Duration Conversion and Selectivity

Two primary oligomerization catalysts have been identified and tested, one for a fixed bed reactor and another for a fluidized bed reactor. Additional work is ongoing to refine the selections to optimize the reaction results for the expected feed from the Synfuels process.

Synfuels has a 50 MSCFD pilot plant of the entire process with the exception of the oligomerization section. Figure 4 is a photograph of part of the plant. The gas cracking facilities have been in operation and testing for more than a year. Hydrogenation section equipment has been installed and, as of early September 2004, is being started-up to demonstrate the technology. Oligomerization equipment will be installed soon so that the complete GTL process can be exhibited.

FIGURE 4
Section of the Synfuels Pilot Plant

ECONOMIC ANALYSIS

Competition in the GTL area is very intense. The stakes are extraordinary given the nine-figure research and development budgets and even higher capital investments as well as the enormous return and market potential for commercializing the technology. Most of the companies developing GTL technology are doing so primarily for their own use and have not been inclined to release details of their economics, though there are individualized numbers scattered through the literature. Getting a complete picture of the economics of one company's technology is very difficult at best, and making economic comparisons between companies all the more uncertain. To add further complication, technology development continues to progress to improve efficiencies and economics, making comparisons a moving target.

An article[3] was published in the *Oil & Gas Journal* in March of 2001 in which data from a study comparing six Fischer-Tropsch technologies was presented. The author of the study recommended that the technologies be re-evaluated for the larger plant sizes "…given the rapid rate of evolution in current designs." Nevertheless, the study is "…one of the better comparisons of competing technologies…" Some of the economic data from the article is presented in Table 1. The new Synfuels GTL technology did not exist at the time of the study or article. Some Synfuels numbers are included at the bottom of the table for comparison.

TABLE 1
Economics Comparison

Company	% IRR	Products BPD
Exxon	12.9	n/a
	14.3	n/a
Shell	12.5	n/a
	13.2	n/a
Sasol	14.5	15,300
	16.7	50,900
Syntroleum	11.2	12,000
	10.7	40,000
Rentech	13.9	16,450
	15.4	54,900
Intevep	16.6	15,300

Source: Oil & Gas Journal, March 2001

Synfuels	22.8	1800 & 5800
	16.3	4,350

As can be seen in Table 1, the new Synfuels GTL technology achieves equivalent or higher returns than any of the others at a fraction of their size. Furthermore, the Synfuels plant size evaluated has not been optimized to try to reap the benefits of economies of scale, but rather was chosen to show that GTL was viable to the multitude of natural gas fields too small to support the mega-plants of the F-T technologies.

SUMMARY

The new Synfuels GTL process, developed by S&B Engineers and Constructors, Ltd., overcomes the obstacles of inefficiency and high capital cost necessary to make it possible for liquid fuels to be produced and marketed from the majority of stranded and associated gas fields around the world. Rather than another version or refinement of the F-T process as others have produced, Synfuels presents a unique new technology that combines well-established, industrial practices with novel inventions to create a GTL process that is quite profitable, even at production scales below which F-T processes are not.

The key to the Synfuels process are the innovative steps that isolate and convert the reactive constituents apart from the main gas flow, reducing recycle and compression of non-participating gases as well as system and equipment volumes. Acetylene hydrogenation in the liquid-phase, or ÉCLAIRS, is the cornerstone of the technology. In fact, with all its advantages as described, liquid-phase hydrogenation may be applicable to other hydrogenation processes outside GTL.

REFERENCES

1. Synfuels International, Inc., 200 Crescent Court, Suite 1801, Dallas, TX 75201.
2. www.fischer-tropsch.org
3. Weeden, S.L., "Special Report, GTL: Progress and Prospects", Oil & Gas Journal, March 12, 2001.
4. "Gas-to-Liquid Projects Get the Green Light", Chemical Engineering, May 2004.
5. "GTL Projects: Finally Moving Forward?", Hydrocarbon Processing, July 2004.
6. Cook, L.J., "Turning Flames into Fuels", Houston Chronicle, August 8, 2004.
7. www.g-t-l.biz

AUTOBIOGRAPHICAL DETAILS FOR THE AUTHORS

Sean C. Gattis, P.E., Principal Process Engineer, S&B Engineers & Constructors, Ltd.

Mr. Sean Gattis holds a B.S.Ch.E. from the University of Arkansas and is a Licensed Professional Engineer. He has fifteen years experience in the petrochemical, polymer, and refining industries, ranging from process development, pilot plant design, and feasibility studies to revamps, expansions, and large grassroots facilities. Mr. Gattis is the co-inventor of four international patents (currently pending) covering the new Synfuels technologies. He has been responsible for creating and modeling various processing schemes; developing heat and material balances; assisting with plant operations, planning and testing; sizing and design of equipment; and generating cost estimates and economic evaluations for commercial scale units. Mr. Gattis has been the Process lead for development and commercialization of the Synfuels technology since S&B's involvement began.

Dr. Edward R. Peterson, P.E., Senior Staff Process Engineer, S&B Engineers & Constructors, Ltd.

Dr. Ed Peterson received his PhD from Oklahoma State University, is a Licensed Professional Engineer, and has 22 years experience. His work ranges from basic research to major chemical and petroleum plant upgrades, including design and operation of pilot plants and implementation of new technology. Dr. Peterson is a co-inventor of four international patents (currently pending) covering the new Synfuels technologies. He has been responsible for coordinating and directing laboratory catalyst work, managing external consultant agreements and interactions, and assisting with pilot plant operations, planning and testing.

Dr. Marvin M. Johnson, P.E., Senior Fellow Emeritus of Phillips Petroleum.

Dr. Marvin Johnson is a member of the National Academy of Engineering; a recipient of the National Medal of Technology which was presented by President Regan; winner of the IRI Achievement Award; the American Society of Curate Inventors' Distinguished Corporate Inventor Award; the Phillips Distinguished Inventor Award; the American Chemical Society Oklahoma Chemist Award; the American Chemical Society Southwest Region Award for Chemical Research; the Oklahoma Bar Association Inventor of the Year Award; the IR-100 Award for PROP oil recycling along with Drs. Nowack and Tabler, and twice awarded by the Oklahoma Society of Professional Engineers with the Outstanding Engineer of the Year award. He was inducted into the OSU Engineering Hall of Fame and given the "Hero" award by the American Chemical Society.

Dr. Johnson's areas of expertise include kinetics and catalysts, reactor design and refining processes and products. He is an active member of the ACS, a Fellow of the AIChE and a member of Sigma Xi. He is responsible for a number of catalysts and processes in use at Conoco Phillips and in the industry. He has over 225 U.S. patents. Of these patents, more than half relate to hydrogenation processes and catalysts. Dr. Johnson is also the co-inventor of two international patents (currently pending) for Synfuels' liquid-phase hydrogenation process and catalyst.

SYNFUELS
INTERNATIONAL, INC.

200 CRESCENT COURT, SUITE 1801
DALLAS, TEXAS 75201
WWW.SYNFUELS.COM