An Economic and Thermodynamic Evaluation of the Conversion of Natural Gas to Liquid Fuels Using an Ion-Transport Membrane

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Abstract

A comparative analysis suggests that the conversion of natural gas to diesel fuel is more attractive thermodynamically and economically than construction of a pipeline, liquefaction, combustion and expansion through a turbine to produce electricity, or conversion of the natural gas to methanol or gasoline. The particular process examined consists of the conversion of methane and steam to H_2 and CO by partial oxidation using an ion-transport membrane, the reaction of these products by the Fischer-Tropsch process to produce a mixture of long-chain hydrocarbons (paraffinic wax) that is then converted to shorter and branched chains by hydrocracking, and finally the separation of that mixture into fuel gas, naphtha, kerosene, diesel fuel, and heavy oil by steam-distillation. The heavy-oil fraction is recycled to the hydrocracker. Some of the high-pressure steam, which is a byproduct of the Fischer-Tropsch process, is recycled to the ion-membrane reactor and the excess may be used to generate electricity. The diesel fuel, which is the primary product, is of premium grade and can be used for blending with poorer grades because of the absence of sulfur and aromatics. The unique characteristic of this process is the use of the ion-transport membrane, thereby avoiding the need for cryogenic separation of O_2 from air. It is superior to steam reforming or dry reforming by virtue of the production of the optimal 2/1 ratio of H_2 and CO for the Fischer-Tropsch reaction. The economic advantage of the process can be considered to be a consequence of a lesser loss of exergy than that for the alternatives.

Introduction

Most sources of natural gas are far from the primary markets for its direct use as a fuel or as a raw material for the manufacture of petrochemicals. The early method of coping with this impediment was by means of delivery of the gas through a pipeline, which has several obvious geographical, technical, and economic limitations.

Many alternatives have since been proposed. In particular, in 1941, a facility was designed and constructed in Cleveland, Ohio to liquefy and store natural gas with the objective of peak-shaving - that is utilizing the full capacity of a pipeline from Texas in the summer months when demand and usage are reduced. However, a failure of one of the storage tanks in 1944 resulted in a catastrophic fire with the loss of over a hundred lives and infliction of great damage to the nearby property. That event discouraged the use of liquefaction for some time, although a facility in Russia, similar to that in Cleveland continued to operate for many years without incident. In 1952 it was proposed to liquefy small, dispersed pockets of gas from spent oil wells in the bayou-region of Louisiana by using portable equipment for liquefaction and then transporting the liquefied natural gas (LNG) up the Mississippi river to Chicago in barges. This overall process proved uneconomical for reasons of scale, but the associated developmental studies, which focused on safe-handling and storage, suggested that the conditions that lead to the tank failure, namely the wrong choice of a metal, and the widespread damage, namely the failure to provide confinement in the form of earthen dykes, could be avoided by proper design. Accordingly, attention was shifted to storage in underground tanks and oceanic transport in large, specially designed tankers. The feasibility of this process was demonstrated in 1959 by a specially designed ship which carried LNG from Louisiana to England. Soon thereafter regular shipments from Algeria to France began on a commercial scale. Such shipments are now commonplace throughout the world. This development is cited in some length because it provides a warning that factors that are overlooked in the analysis of a new process such as the present one may have both short- and long-term consequences.

Many isolated sources of natural gas, either residual, such as those in Louisiana, or in stranded puddles remain unexploited because they are distant from an existing pipeline or waterway and/or too small to justify liquefaction or local usage. This manuscript is based on the analysis of one possible alternative for that limited situation but the results appear to have wider application.

Several patents (see, for example, 5,240,480 in 1993 by Thorogood, et al., and 2003/0039601A1 by Halvorson et al.) have suggested the use of an ion-transport membrane for the conversion natural gas to *syngas* ($CO + H_2$) by partial oxidation. The two particular advantages of such a membrane are that it avoids the need to separate oxygen from air cryogenically and produces a gas with nearly the optimal H_2/CO ratio of 2/1 for the Fischer-Tropsch process for the conversion of the syngas to long-chain hydrocarbons. The latter can in turn be hydrocracked and isomerized to produce primarily diesel fuel, which along with the other liquid products, is readily transportable in tank trucks or railroad tank cars.

The majority of the current national and world production of diesel fuel is from crude oil, most of which contains some sulfur, often as much as several percent. A significant fraction of that sulfur finds its way into the boiling range of the diesel fuel during refining. The Environmental Protection Agency has announced plans to reduce the upper limit of the allowable sulfur content in diesel fuel for highway vehicles by 97% (from the present 500 ppm to 15ppm). The virtual absence of sulfur in natural gas gives it a great advantage relative to crude oil as a source for diesel fuel.

In the work reported here, a preliminary process design was carried out to provide the basis for an economic and thermodynamic analysis for this process as compared to several alternatives. The design was arbitrarily based on a hypothetical natural gas well in Ohio that is capable of producing 1800 SCFH for 15 years or more. This choice of location and of the rate of production proved to be rather irrelevant, but that was not known in advance.

Many processes for the direct conversion of natural gas to liquids have been proposed in the past, including the production of methanol, but few of them have been commercialized because the reactions involve high energies of activation, and therefore high temperatures, and/or are difficult to control. At one time, gasoline was produced from natural gas in New Zealand but that facility has since been shut down as no longer economical.

Most processes for the conversion of gas to liquid have involved the intermediate production of syngas. The three most common routes are

steam reforming: $CH_4 + H_20 \rightarrow CO + 3H_2$ (1)

dry reforming : $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ (2)

partial oxidation: $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ (3)

Steam reforming, which is typically accomplished with a fired heater and a catalytic converter, is a strongly endothermic. Dry reforming is carried out in the presence of CO_2 rather than steam and is also an endothermic. On the other hand, partial oxidation is exothermic and has, as mentioned previously, the advantage of producing close to the optimal ratio of H_2/CO for the Fischer-Tropsch reaction.

One process that is currently in commercial use to produce syngas is autothermal reforming, which combines partial oxidation and steam reforming in a single reactor. Autothermal reformers require oxygen concentrations of greater than 95%, which typically is attained by cryogenic separation of air, an energy-intensive process. The U.S. Department of Energy (DOE) has, since 1998, been funding ion-membrane technology with the objective of reducing this particular usage of energy.

Oxygen Ion-Transport Membrane Technology

Ion-membrane technology utilizes conducting non-porous metal-oxide films supported by a porous ceramic structure. In the current application the chosen films are selective with respect to oxygen and oxygen ions, that is, these species are transported under a chemical potential difference whereas the transport of other elements and their ions is excluded.

The operation of a ceramic ion-transport membrane for the production of syngas from natural gas is shown conceptually in Fig. 1 The required chemical potential difference is created by maintaining a higher partial pressure of O_2 on the right (cathode) side than on the left (anode) side where the oxygen reacts with a mixture of methane and steam to produce H_2 and CO by a combination of partial oxidation and steam reforming.

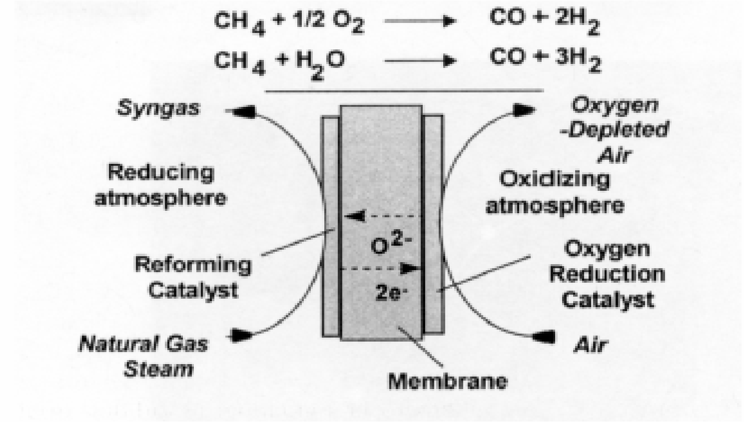


Figure 1. Conceptual Use of an Ion Membrane to Produce Syngas (courtesy of Air Products and Chemicals, Inc.

The ÉCLAIR$_{TM}$ process of Synfuels International, Inc. utilizes partial oxidation of natural gas with ion-membrane technology to produce C_2H_2 and CO_2 as well as CO and H_2 but thereby loses the advantage of the ideal CO/H_2 ratio produced by Reaction 3.

Although plans if not details for several mega-ventures involving ion-exchange membranes have recently been announced (see, for example, Parkinson^1), no commercial developments or economic analyses were known to the authors when they undertook this study.

The Overall Process

As shown as a block diagram in Fig. 2 and schematically in Fig. 3, the overall gas to liquids (GTL) process considered herein can be divided into four main parts, namely, (1) conversion of the CH_4 into syngas (CO_2 and H_2) in an ion-transport membrane (ITM) reactor, (2) conversion of the syngas to long-chain (waxy) hydrocarbons in a Fischer-Tropsch reactor, (3) reduction of the products of the Fischer-Tropsch process by hydrocracking, and (4) separation of the products of hydrocracking by distillation. As indicated in Fig. 1, fuel gas and heavy gas oil are recycled to the hydrocracker for reaction with excess H_2 from the Fischer-Tropsch reactor, and electricity can be generated from high-pressure steam. These four steps are described only briefly for two reasons. First, except for the ion-transport membrane reactor, the technologies are well-developed and well-known. Second, the details of the equipment and costs prove not to be critical to the objectives of the preliminary thermodynamic and economic analysis

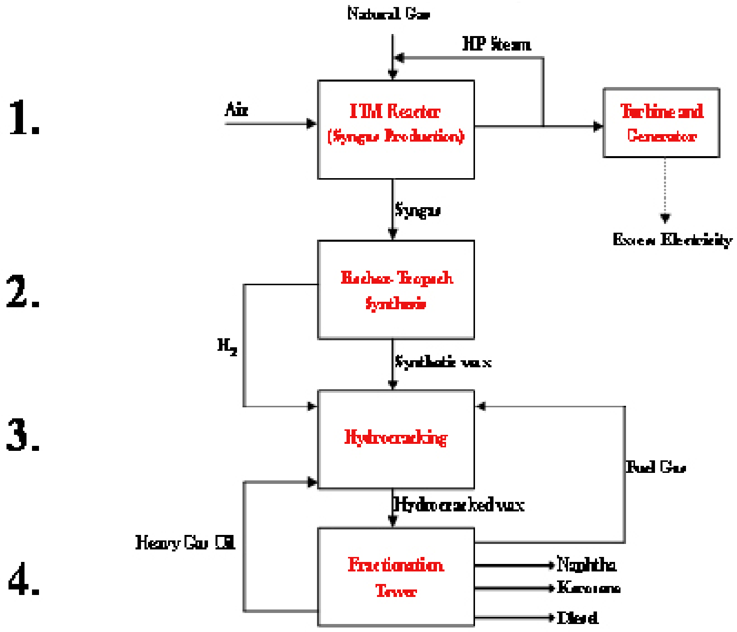


Figure 2. Block Diagram for Overall Process

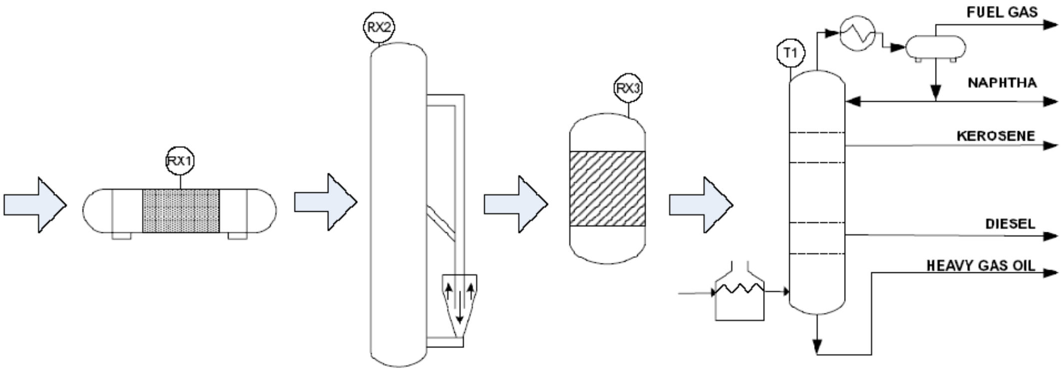
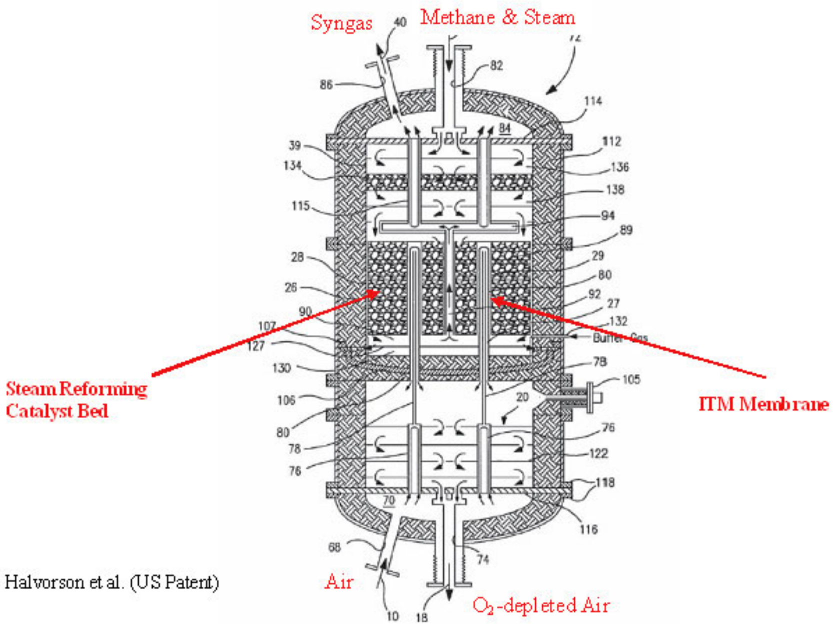


Figure 3. Schematic Diagram for Overall Process

The Ion-Transport-Membrane Reactor

An ion-transport-membrane reactor for the production of syngas as described by Halvorson et al (U.S. Patent Application 2003/0039601 A1) is shown in Figure 4. It consists of a horizontal, countercurrent, shell-and-tube reaction- vessel. Because this technology is the most critical element of the analysis, a few details are given.



Halvorson et al. (US Patent)

Figure 4. Praxair ITM Reactor Model (2003)

In order to operate the reactor isothermally, the exothermic partial-oxidation of methane to synthesis gas is balanced by the highly endothermic steam- reforming reaction of methane to synthesis gas. At 1650^{o}F, approximately 90% of the methane is estimated to undergoes partial oxidation. For the previously stated rate of processing 1800 SCFH of natural gas, 2,500 lb-mol/hr of O_2 are required for the partial oxidation. Based on an O_2-flux of 20 SCFH/ft^2, the required area of ceramic membrane area was estimated to be 45,000 ft^2. Because the oxygen ion transport membranes are only 100 microns in thickness, they must be supported on a porous tube. Halvorson et al. recommended by Inconel 200 tubes with an OD of 2 in and a length of 30 ft. The corresponding number of internal reaction tubes in our design was estimated to be 2,900. Postulating that 50% of the cross-sectional area of the vessel is occupied by the tubes, the reactor would be 30 ft in length and 12 ft in diameter. Postulating that at least 1/5 of the reactor void space is available for the catalyst, and that 5%-nickel-on-alumina is used for the steam reforming of methane, 39,300 lbs are required.

An excess of air in the amount of 23,800 lb-mol/hr is compressed to 15 psig and 265 ºF and then heated to 752 ºF in a countercurrent, shell-and-tube heat exchanger before being fed in to the reactor. The air is passed through the shell side, and the hot, O_2-depleted, air stream from the ITM reactor is fed to the tube side of the exchanger. Natural gas mixed with steam is fed in to the ITM reactor at a 354 ºF and 300 psig

The Fischer-Tropsch Process

The syngas may be converted into straight-chained hydrocarbons by means of the well-known Fischer-Tropsch process, in this instance carried out in a slurry-bubble reactor containing a cobalt-ruthenium catalyst. The main reaction is:

$$nCO + 2nH_2 \rightarrow (-CH_2-)_n + nH_2O \tag{4}$$

The mixture of carbon monoxide and hydrogen is bubbled through a slurry of the solid catalyst particles and reacts on the surface of their surface. The hydrocarbon products of this reaction are primarily straight-chained. According to the Anderson-Flory-Schulz (AFS) probability distribution they are predominantly in the range from C_1 to C_{70} as shown in Fig. 5.

The Co/Ru catalyst was chosen for its selectivity with respect to chains of C_{5+} and its reduced selectivity with respect to methane. Byproducts include water, $CO_{2,}$ and unreacted syngas. The effluent product still contains catalyst particles that must be separated and returned to the reactor slurry. This is accomplished using a large dynamic settler. The wax is injected slowly into the settler so as to allow the solid particles to fall to the bottom while the wax rises upward. The solid particles reach the bottom and are returned to the slurry, and the clarified wax is sent to a decanter. The reactor is operated isothermally at 392^{o}F and 400 psig, requiring process water to be vaporized in the cooling coils. The resulting steam at 125 psig is sent to a steam turbine for the generation of electricity.

A considerable unconverted hydrogen exits through the top of the Fischer-Tropsch reactor. Other components in this stream include water, CO, CO_2, and a variety of light hydrocarbons. All these components can be fed to the hydrocracker, except water which may be removed in a water-cooled condenser.

Hydrocracking

The final chemical step in the production of diesel fuel from natural gas is hydrocracking. A fixed-trickle-bed reactor with a catalyst of 0.6% platinum on silica was designed to convert the long paraffin chains into middle distillates in the range from C_9 to $C_{1.}$ A H_2-enriched stream is fed at the bottom of the reactor and the hydrocarbon wax at the top. A kinetic model developed by Pellegrini et al.[1] was adapted to determine the product distribution, as shown in Figs. 6 and 7, as well as the required quantity of catalyst.

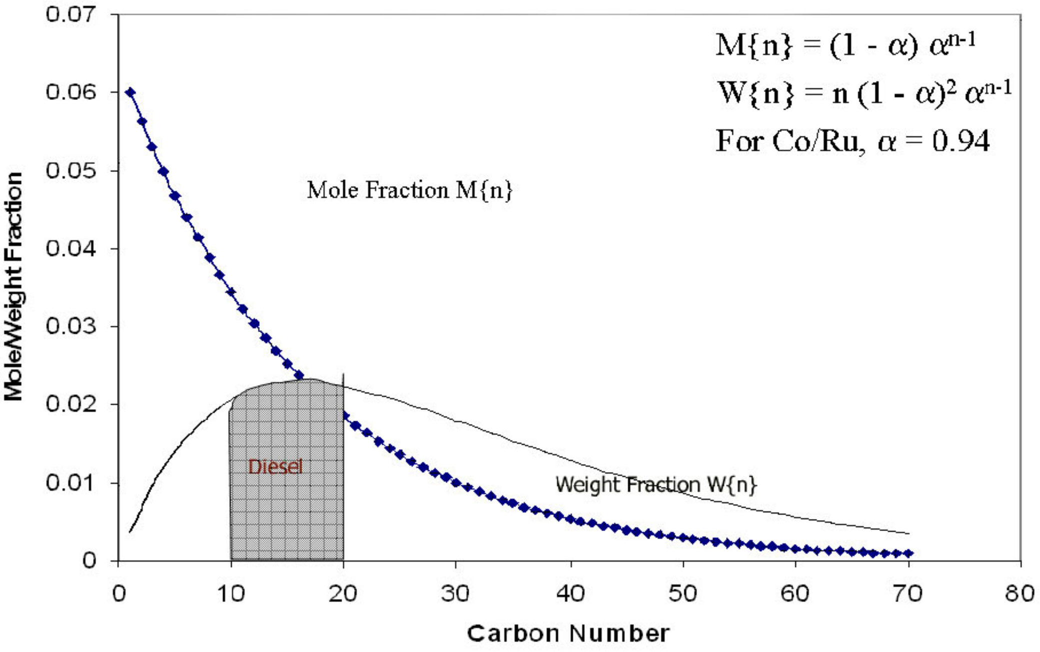


Figure 5. Anderson-Schulz-Flory Distribution of Fischer-Tropsch Products

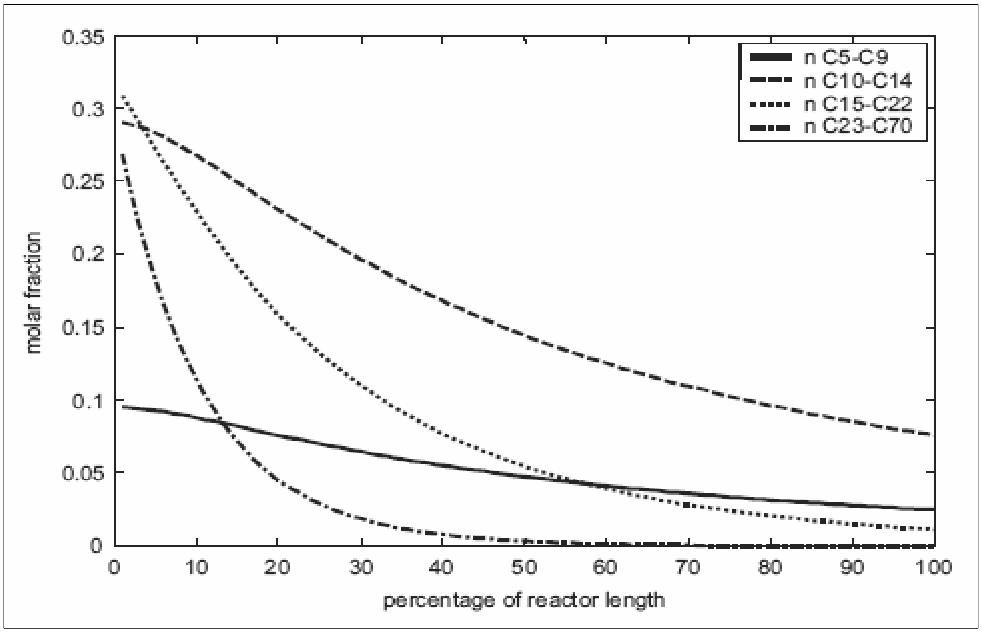


Figure 6. Molar Fractions of Lumped Isomers and Lumped C_1-C_4 (from Pellegrini et al.[1])

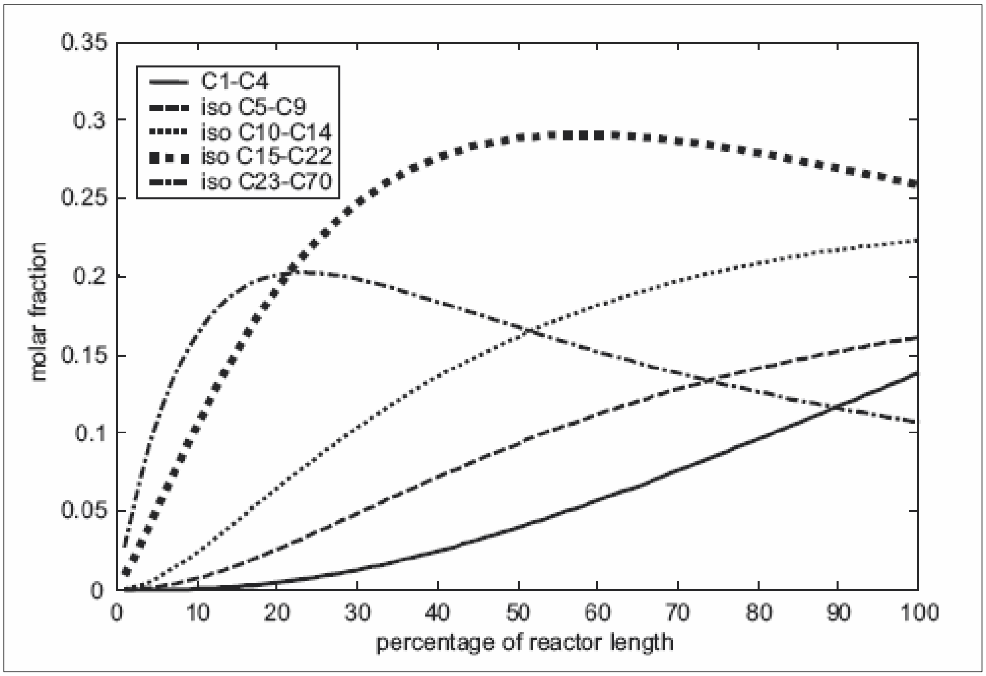


Figure 7. Mole Fractions of Normal Lumps versus Reactor Length (from Pellegrini et al.[1])

Separation

The final step in the process is to separate the hydrocracker effluent from the hydrocracker into useful fractions. This may be accomplished in a single distillation column similar to that for the crude oil in a refinery. The hydrocracker effluent is mixed with steam, and that mixture is preheated to 723^{o}F and fed to the bottom stage of the tower. Eighteen equilibrium stages, 16 of which are Koch Flexitrays, were found to be sufficient. As indicated in Fig. 2, a partial condenser produces fuel gas and naphtha, with the latter serving as recycle at a molar ratio of 2.3. Kerosene is drawn off from equilibrium-stage 8 and diesel fuel from equilibrium-stage 12. The tower operates at slightly above atmospheric except for a small purge pressure (5-15 psig). Except for a small purge to prevent the buildup of wastes, the heavy gas oil is recycled to the hydrocracker. The fuel gas is utilized in the preheater for the fractionating column.

Environmental Considerations

Any water discharged from the process into nearby natural water sources must be treated to remove hydrocarbons and cooled to remove excess heat, but this is a minimal problem because essentially all of the water produced in the process is recycled to other units. The Fischer-Tropsch cobalt catalyst was selected to minimize the amount of light gaseous hydrocarbons produced in the process. Because of the isolated location that small amount of gas must be burned to drive a turbine and generate electricity or else sent to a flare, either way resulting in the exhaust of some CO_2 to the atmosphere.

Traces of the cobalt-based catalyst used in the Fischer-Tropsch process may appear in the decanted water and further treatment may be necessary. This catalyst is is very toxic and care must be taken to avoid human contact

Controllability

Close control of the temperature of the ITM reactor is very important to prevent acceleration of the exothermic partial-oxidation. The Fischer-Tropsch reaction temperature is readily controlled with cooling water in coils. The hydrocracking reaction is controllable by adjusting the temperature and rate of flow of the hydrocarbon wax.

Economic Evaluation

An economic analysis ordinarily begins with a process design and perhaps an optimization in some respects. This information is then utilized to estimate fixed and variable costs and thereby the potential profitability. Optimization may again be utilized at this stage. If the process is to be compared with alternative ones a complete economic analysis must be carried out for each of them as well.

The initial economic analysis was based on the quantities in Table 1. The economic analysis is strongly dependent upon the relative prices of natural gas and the products. These prices have been quite variable in the past and are anticipated to become even more volatile in the near future. In an attempt to reduce the sensitivity of the analysis in this respect, the relationship between the market values of natural gas and the several

Table 1. Raw Materials and Products

Raw Material		Products	
Natural Gas	$1.95X10^6$ SCFH	Diesel Fuel	2,700 bbl/day
		Kerosene	1,800 bbl/day
		Naphtha	200 bbl/day
		Heavy Gas Oil	90 bbl/day
		Electricity	10.5 MW

products, and in particular, diesel fuel, was investigated Timelines for the price of natural gas in $/MSCF and for diesel fuel in $/gal are shown in Fig. 8 and a correlation between the two prices in Fig. 9. A regression analysis revealed that these two prices have a statistical correlation coefficient of 0.85 and that for every $1 change in the price of natural gas, the price of diesel fuel changes by 16¢. A similar relationship is presumed to exist between the price of natural gas and each of the other products. A second special consideration is that the diesel fuel produced by this process is virtually sulfur-free and has an exceptionally high *cetane* number (above 60) and can be used as a blending agent to bring off-spec diesel fuel from crude oil up to the minimum of 40 required by law. It is therefore expected that the diesel fuel will bring a premium price of as much as 15% but it is obviously impossible to make a firm estimate at this stage.

The overriding factor in the process design is O_2-flux-density of the ion-transport membrane and its durability. It is essential that these aspects be determined before proceeding with a detailed design. Likewise, the economic analysis depends critically on the cost of the membranes, which cannot be determined with any certainty because they are not yet available commercially. In order to proceed with the analysis in the face of this lack of essential information, the break-even point for the process was determined as a function of the cost of the membrane. On this basis it was determined that the process would be quite profitable for any reasonable price for the membranes and much more so than such alternatives as burning the natural gas to drive a turbine and generate electricity.

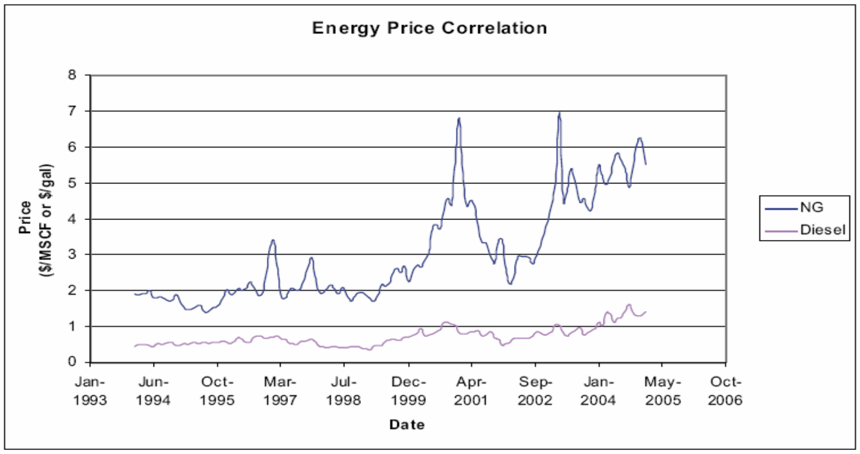


Figure 8. Timelines of Prices for Natural Gas and Diesel Fuel

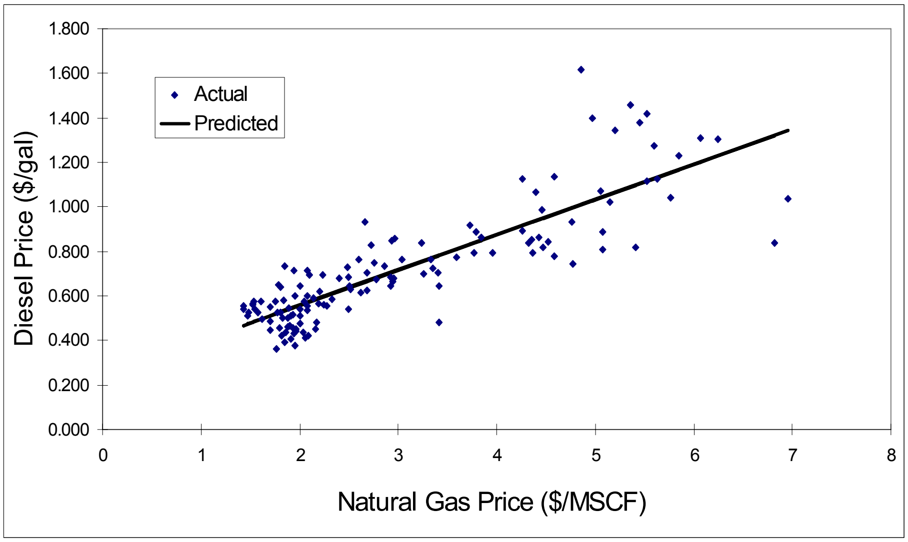


Figure 9. Correlation between Prices of Natural Gas and Diesel Fuel

An obvious conclusion is that if this process is feasible in this particular isolated location and at such a limited rate of feed that it may be even more profitable near some large natural gas field and perhaps at some location where natural gas is piped or LNG is shipped.

An Explanation for the Relative Profitability of the Ion-Transport Membrane Process

From the economic analyses it is evident that the advantage of this process relative to direct combustion to produce electricity is associated with the avoidance of high temperatures and extensive heat exchange. The advantage relative to other chemical paths may be attributed to the avoidance of the need for refrigeration. Even in more favorable locations, an advantage ensues relative to direct liquefaction due to the avoidance of the need for refrigeration.

The overall loss of exergy in each of these processes for the conversion of natural gas to liquid was found to bear a one to one correspondence with the profitability. The calculations of exergy were based on the external inputs and outputs of energy and the quantities and thermodynamic state of the products and as determined from the process designs. However, it may be possible to estimate these particular quantities with sufficient accuracy for this narrow purpose without carrying out a detailed process design.

An exergy analysis is not a substitute for an economic one, even in a comparative sense because it is not only independent of scale, but omits all details of both fixed and variable costs, which do not necessarily balance out between processes, for example, in this instance, the cost of the ion-transport membrane and the high quality of the diesel fuel.

However, because an exergy analysis provides insight as well a quantitative criterion of merit and requires a minimal effort, it is recommended as a preliminary screening device

Conclusions

The conversion of natural gas primarily to diesel fuel using an ion-transport membrane, the Fischer-Tropsch process, and hydrocracking appears to be advantageous relative to current alternatives both economically and technically. The diesel fuel that is produced is of premium grade.

Although this analysis was carried out for an isolated puddle of natural gas in Ohio, the advantages of the process would appear to carry over, and indeed be enhanced in every respect by a larger source of natural gas located anywhere in the world.

The greatest uncertainty arises from the specific capacity and the cost of the ion-transport membrane, which is apparently not yet available commercially. However, these factors are unlikely to overbalance the gain from avoiding a cryogenic separation of oxygen from air or the high temperatures associated with direct combustion.

A thermodynamic analysis in terms of exergy was found to insightful in this instance, and is recommended as a useful screening device in the preliminary comparison of different processes in general.

Acknowledgement

The advice and criticisms of Leonard Fabiano and the assistance of Baron Lipschutz-Perry in preparing the graphical work are greatly appreciated.

Reference

1. Pellegrini, L., Rasella, S., Bonomi, S., Calamma, V., Modeling Fischer-Tropsch Products Hydrocracking, *Chem. Eng. Sci.* **59** (2004) 4781-4787.