8. Gas Use in Transportation Fuels--Economic Analysis

In this section, the economics of processes for converting natural gas to transportation fuels will be analyzed. The processes for making transportation fuel from natural gas are broken into three categories: commercial, demonstrated, and under development.

A summary of the processes covered in this section is as follows:

Product	Process	Status	Section No.
Methanol	Liquid Phase Methanol	Commercial	8.1
MTBE		Commercial	8.5
CNG		Demonstrated	8.6
LNG		Demonstrated	8.7
Gasoline or Diesel	Fischer-Tropsch	Demonstrated	8.2
Higher Alcohols	IFP Process	Pilot Plant	8.4
DME (as Diesel Fuel)	Haldor Topsoe	Pilot Plant	8.5
Gasoline	Oxidative Coupling	Research	8.3
Gasoline	Oxyhydrochlorination	Research	8.3

A cost summary for six of the processes covered in this section is given in Exhibit 8-1. Cost for the six processes are also compared with the prices of the fuels against which these products must compete in the fuels market. A more detailed discussion of these products and their costs is presented in Section 11.1

Exhibit 8-1. Economic Comparison of Gas-to-Liquids Processes

Process	Liquid Phase Methanol (LPMEOH)	UOP-MTBE	IFP Higher Alcohol	Fischer-Tropsch	Oxidative Coupling	Delivered CNG
Product	Methanol	MTBE	C1-C6 Alcohol	Gasoline/Diesel	Gasoline	CNG
Costs: (cents per gallon product)						
Feed	24	51	36	52	52	48[2]
Other Operating	7	17	22	28	43	11
Capital	12	14	43	58	67	7
TOTAL	44	86	120	137	169	73
Gasoline Equivalent Gallon Cost	74	NA	NA	137	169	73
Competing Fuel	Gasoline	High Octane Blend Components	Gasoline Blend Components	Gasoline	Gasoline	Delivered Gasoline
Price of Competing Fuel	68	98	68-98	68	68	84[3]

[1] Delivered to consumer, not including fuel taxes

[2] Range for delivery to Middle Atlantic and Midwest locations

[3] Retail price excluding fuel taxes

8.1. Natural Gas to Methanol by the Liquid-phase Methanol Process

The liquid-phase methanol (LPMEOH) process was invented by Chem Systems Inc. In a report by Chem Systems it is compared to a version of the more conventional gas-phase processes [29]. The biggest difference between the two processes is in the method of removing the heat of reaction.

Due to its ability to absorb the methanol synthesis heat of reaction in an inert hydrocarbon liquid and transfer this heat to generate steam, the LPMEOH process is capable of achieving a high conv per pass. Thus, it has economic advantages when combined with larger single-train natural gas-based plants that utilize advanced technology for generating synthesis gas.

The following section will give details of this process. Other methods of converting natural gas to methanol will also be discussed briefly.

LPMEOH Process Description

Exhibit 8-2 shows the LPMEOH process flow diagram. The LPMEOH process converts synthesis gas produced from natural gas to methanol. Alternatively, the process could use syngas from coal. The usual design incorporates generation of synthesis gas (H_2, CO and CO_2) from natural gas by steam reforming.

An advanced synthesis gas generation process (not shown) includes both quench and convective trains to achieve maximum thermal efficiency in the methanol production. The synthesis gas is then fed to a three-stage LPMEOH system. The first reactor operates as "once-through" and the last two reactors in series with converted syngas recycled to the second stage reactor. The methanol reactor operates at 1600 psia and a 482°F exit temperature [29].

Major Reactions

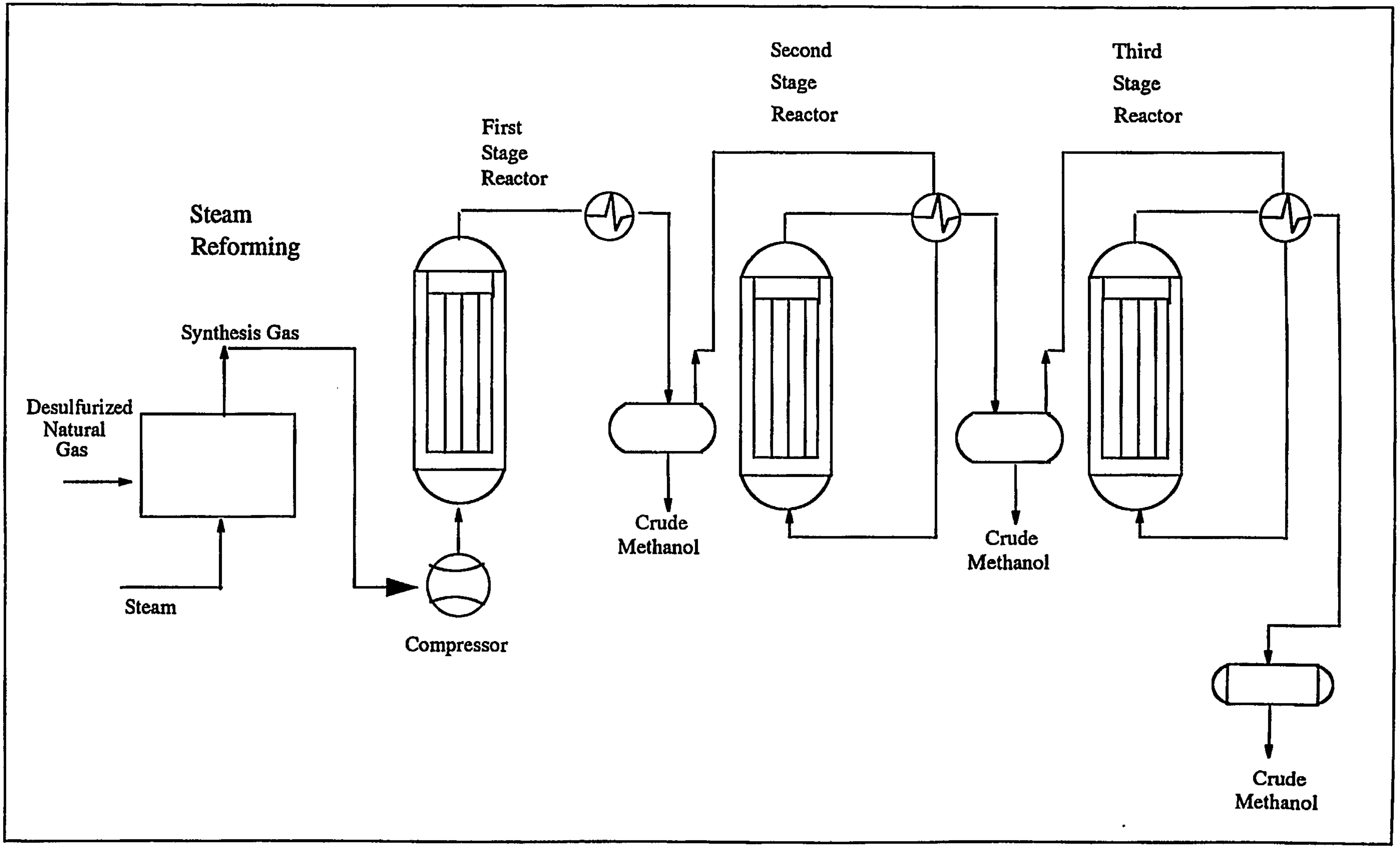
The synthesis gas contains, H_2, CO and CO_2 along with inert gases such as CH_4 and N_2. The key reactions which take place in the reactor are:

		ΔH, Btu/Lb Mole of CO or CO_2
(1)	$CO + 2 H_2 \rightarrow CH_3OH$	-39,100
(2)	$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$	-21,300
(3)	$CO + H_2O \rightarrow CO_2 + H_2$	-17,600

Material Balance

According to the report on LPMEOH [29] (page 69, Table III - B-3), when charging a feed consisting of 582,000 lb/hr of syngas to the LPMEOH section, the products consist of 525,000 lb/hr of crude methanol and 58,000 lb/hr of fuel gas. The syngas has the following composition in mol %: 30% carbon monoxide, 3% carbon dioxide, 65% hydrogen and 2% other gases. The fuel gas produced consists of 5% carbon monoxide, 11% carbon dioxide, 17% argon, 14% nitrogen, 50% hydrogen and 3% other gases.

EXHIBIT 8-2
LPMEOH PROCESS FLOW DIAGRAM



Economics

The following economics table for the liquid phase methanol process is based on the report proposed by Chem Systems [29]. The natural gas feed cost and the operating and maintenance cost shown below are for the initial year.

Plant Capacity, BPSD of Methanol	39,572
Total Capital, 10^6 US$ (USGC, December 1993)	451.4
	$/B Methanol Product
Natural Gas Feed, $2.43/$10^6$ Btu	10.08
Operating & Maintenance Costs	2.73
Capital Charges, 14.2% of Total Capital	4.91
Product Price:	
$/Barrel	18.65
$/Gallon	0.444

Other Methanol Process Routes

There are two major process steps in the production of methanol, i.e., production of syngas from natural gas and conversion of the syngas into methanol. Therefore, in developing new process routes, improvements can be made in either or both of these steps. The two major methods of producing syngas are steam reforming and partial oxidation. The partial oxidation can be carried out in three different ways: (1) autothermal reforming, (2) non-catalytic partial oxidation and (3) catalytic partial oxidation. These steps vary considerably in temperature. Haldor Topsoe claims advantages for an autothermal reforming process which has a special burner and a fixed catalyst bed in a brick lined reactor [30]. For commercial-scale plants Haldor Topsoe suggests a two-step combination of tubular and autothermal reforming processes. There are tradeoffs between using air or oxygen for manufacturing the syngas. Cryogenic oxygen plants are expensive but so is air compression. Oxygen addition through a membrane may be possible but the feasibility still has not been proven.

Bechtel identified three processes for methanol production as emerging technology [31]. These techniques substitute partial oxidation with 99.5% oxygen for reforming, in whole or in part, for stoichiometric or near stoichiometric synthesis gas production. They are:

- Catalytic partial oxidation (Davy McKee) plus ICI-licensed methanol reactor design using internal tubes for preheating inlet gas.

- Combined reforming (Lurgi) design using a small conventional primary and non-catalytic secondary reformer. The methanol synthesis step uses a copper-based catalyst which permits high activity at less than 300°C.

- Combined reforming and fluid bed synthesis (Mitsubishi) design using a fluid-bed methanol reactor which permits optimum heat recovery but adds to investment and catalyst makeup requirements.

Comparing the natural gas requirements of these technologies with the requirement for conventional technologies, the natural gas consumption from the greatest to the least is required for conventional technology, catalytic partial oxidation, combined reforming, and fluidized-bed synthesis.

Additional details on Lurgi's combined reforming process shows that that process begins to have a cost advantage over the conventional process at about 1300 tons per day [32]. The advantage comes from small boiler feed water and steam systems and elimination of some utilities which are provided by the air separation unit. Lurgi and Foster Wheeler compare their reforming process to three other processes [33]. Some of the advantages of combined reforming according to Lurgi and Foster Wheeler are:

- 8% to 10% reduction in the consumption of natural gas
- Reduction in the size of the primary reformer
- Reduction of syngas compression requirement due to increased syngas pressure
- Reduced steam consumption
- Production of syngas with the stoichiometric composition required by methanol synthesis

Combined reforming has a lower total energy requirement than conventional reforming, catalytic autothermal reforming and noncatalytic partial oxidation. This confirms the findings of Bechtel mentioned previously. Investment requirements from highest to lowest are in this order: conventional steam reforming, noncatalytic partial oxidation, combined reforming and catalytic autothermal reforming. In terms of CO_2 and NO_x emissions, the lowest emissions are projected for catalytic autothermal reforming and noncatalytic partial oxidation with conventional steam reforming having the highest emissions.

ICI gives details of their process for methanol synthesis and shows how through improvements over the years overall efficiency has risen from 58% in early designs to 72% in a current design [34] and [35]. This has been accompanied by rising capital costs for heat recovery equipment. The design can be varied depending on whether a plant is located in a high or low cost energy area and whether fresh water is available.

Sud-Chemie AG proposes to increase methanol production from a given facility by adding more CO_2 from an outside source [36]. A catalyst was developed which showed greater stability in the CO_2-rich environment.

Effect of Cost Factors on Product Costs

As shown in the previous discussion there are newer syngas processes which have lower costs than conventional reforming. In addition, ICI has been moving in the direction of better thermal efficiency. Designs are available with savings in capital cost at the expense of higher rates of energy consumption. When lower energy consumption is needed, capital costs are increased to provide better heat recovery. The choice of these alternatives is a function of how rapidly energy costs are increasing. Some guidelines for achieving the best process designs are:

- Build new facilities to test the new improved technology in both syngas production and methanol synthesis. According to the USDOE it has been difficult to test new technology because very few methanol plants have been built in the past 15 years [37].
- Current and future developments should include larger size plants beyond the 3000 metric tons per day (MTPD) level. This would permit the testing of new technologies such as designed by Davy McKee and Mitsubishi. Bechtel has shown that multi-train designs have the advantage of scale in offplots and engineering savings in onplots [31]. While the increase in costs of the onplots is almost linear with the number of trains (capacity exponent is 0.97), the exponents for offplots, indirects and engineering are much lower, resulting in an overall capacity exponent of 0.69.
- According to Haldor Topsoe [30] 70% of the investments in a methanol plant is for syngas manufacture. Therefore, more effort is justified in improving syngas manufacture than in improving methanol synthesis.
- Two-step syngas production has an advantage over conventional reforming. Thermal efficiency is better, and it is easier to get the right composition of gas for methanol synthesis.
- In syngas production processes where oxygen is used, studies could determine whether to use air or enriched air instead. Membranes could be used for air enrichment. Results of studies comparing use of air, oxygen or enriched air for coal gasification could be applied to methanol production.
- Research could be done to study the feasibility of using a syngas process to supply gas for both methanol and ammonia production in a single plant. This has been done in a Terra International plant in Woodward, Oklahoma [38].

Bechtel [31] made a study of investment and operating costs in various locations in the world for methanol plants. Costs were estimated for six locations. These are as follows, listed in order of lowest to highest investment costs: Port Arthur in Texas, Point Lisas in Trinidad, Edmonton in Alberta, Jubail in Saudi Arabia, Dampier in Australia, and Prudhoe Bay in Alaska. Investment cost location factors are as high as 1.63 for Prudhoe Bay whereas Port Arthur had a factor of 1.00. Costs are higher for both investments and operating costs where fresh water is in limited supply and sea water has to be used for cooling. Other problems in remote locations involve labor supply and importing equipment.

Commercial Methanol Plants

According to the PACE Petrochemical Service [39] expected U.S. production of methanol in 199[illegible] will be 2,225 million gallons and the apparent consumption will be 2,700 million gallons with an estimated plant operating rate of 99%. Thus, U.S. plants are currently nearly at full capacity and are importing methanol. Any significant increase in methanol demand would require plant construction and greater use of natural gas.

Hydrocarbon Processing [40] shows three licensors of methanol plants. These are:

- Haldor Topsoe A/S. They use two-step reforming followed by low-pressure synthesis. Their newest plant is in Norway with a 2500 MTPD capacity and is scheduled for start -up in 1996. They claim a 10% reduction in cost compared to a conventional plant based on straight steam reforming when building large-scale plants.
- ICI Katalco. They have a low pressure methanol process. Synthesis gas is most commonly produced by steam reforming. They have built 47 plants and presently have four under construction.
- The M. W. Kellogg Co. They use high-pressure steam reforming. The methanol reactors use BASF low-pressure synthesis catalyst. There are approximately 180 M. W. Kellogg synthesis gas plants including methanol, ammonia and hydrogen production. The most recent methanol plant was a 2268 tpd plant in Chile.

Summary

The process description, major reactions, material balance and economics have been shown for the Liquid Phase Methanol (LPMEOH) process. The LPMEOH process has never been experimentally tested and there is a need for a demonstration plant similar to the tests of coal-based power plants carried out under the Clean Coal program. The LPMEOH process is economically competitive or somewhat better than commercial methanol plants. Commercial methanol plants are in a high state of development. Nevertheless, there is still room for small improvements in the methanol processes and a potential advantage for building larger, more economical plants.

8.2. Natural Gas to Liquid Products via Fischer-Tropsch

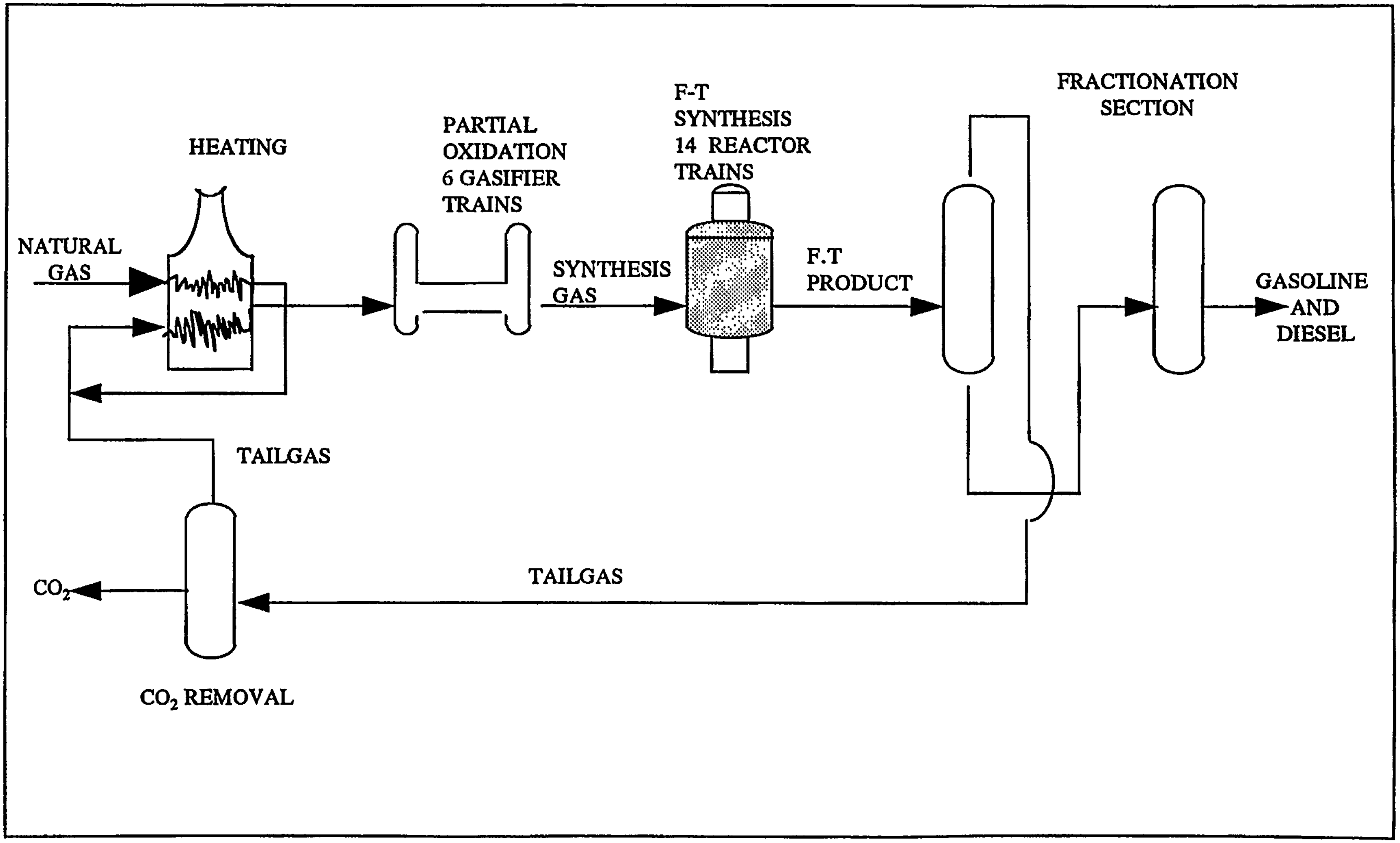
The Fischer-Tropsch process for conversion of synthesis gas to liquid fuels (primarily gasoline and diesel) was discovered in Germany in the 1920's and has been commercialized by SASOL Ltd. in South Africa [41]. The technology has been undergoing development over a period of many years. Three plants are in operation: Sasol I at Sasolburg and Sasol II and III at Secunda. The economics presented in this section are based on use of natural gas as a feedstock and combining some of the Fisher-Tropsch technologies from SASOL with a more modern method of synthesis gas production for the natural gas feed.

The SASOL plants are the only commercial plants using Fischer-Tropsch and they use coal to make synthesis gas to use as a feed to the Fischer-Tropsch process. However, natural gas as well as other hydrocarbons can also be used to generate synthesis gas for use in Fischer-Tropsch reactors. There is a difference in carbon-to-hydrogen ratio depending on the feedstock type. The design of the synthesis gas and the Fischer-Tropsch steps must take these differences into account.

Process Description

The flow diagram for the gas-to-liquids Fischer-Tropsch process, as developed by Bechtel [42] is shown in Exhibit 8-3. Synthesis gas is produced in a non-catalytic partial oxidation (POX) gasifier operating at 2600°F and at sufficient pressure that compression of synthesis gas is not required. After heat recovery and water removal, synthesis gas is admitted directly to the Fischer-Tropsch synthesis loop. Fourteen tubular fixed-bed reactors with steam generators in the shell are used . These reactors are patterned after the ARGE reactors at SASOL but have 3.3 times the capacity. Conditions are 400°F and 250 psig. CO conversion per pass is 60%, with an ultimate conversion of 89%. Selectivity to C_5 and heaver hydrocarbons is 84% and the Schulz-Flory parameter is 0.9. A stabilized waxy syncrude is produced for fractionation. Excess tail gas from the fractionation section, over and above that required for fuel balance, is recycled back to the POX converter. CO_2 removal on the recycle stream prevents buildup of CO_2 in the system.

EXHIBIT 8-3
FISCHER-TROPSCH PROCESS



Major Reactions

The F-T conversion to fuel products, primarily normal paraffins, proceeds according to the following equation:

	ΔH, Btu/Lb Mole of CO
$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$	-100,000

A concurrent reaction is the water-gas shift reaction:

$CO + H_2O \rightarrow CO_2 + H_2$	-17,600

Other reactions that may be found in the Fischer-Tropsch synthesis are those producing alcohols, olefins and carbon according to Burns and Roe and PETC [43].

Composition of Product Stream

The Bechtel study [42] used for the economics of natural gas conversion to Fischer-Tropsch liquids shows that the CO conversion is 89% and the selectivity is 84% to C_5 and heavier. The product is waxy (i.e., highly paraffinic).

In a literature reference on the coal-based Sasol plant in South Africa, M.E. Dry [44] gave breakdowns of products from the SASOL reactors on a % carbon atom basis. The breakdowns are shown in Exhibit 8-4.

Exhibit 8.4. SASOL Reactor Product Composition (% Carbon Atom)

Product	Fixed bed (220°C)	Synthol (325°C)
CH_4	2.0	10
C_2H_4	0.1	4
C_2H_6	1.8	4
C_3H_6	2.7	12
C_3H_8	1.7	2
C_4H_8	3.1	9
C_4H_{10}	1.9	2
C_5 to C_{11} (gasoline)	18	40
C_{12} to C_{18} (diesel)	14	7
C_{19} to C_{23}	7	
C_{24} to C_{35} (medium wax)	20	4
$>C_{35}$ (hard wax)	25	
Water-soluble, non-acid chemicals	3.0	5
Water-soluble acids	0.2	1

SASOL hydrocracks the wax and oligomerizes the C_3-C_4. They use the naphtha as feed for making ethylene and the diesel is of good quality without further treating. In addition, the oil work-up for Sasol II includes fractionation, catalytic polymerization, C_4 isomerization and alkylation, C_5/C_6 isomerization and naphtha hydrotreatment and reforming [45].

Economics

The following economics table for the Fischer-Tropsch process used data from the report prepared by Bechtel [40].

Plant Capacity, BPSD of Fischer-Tropsch Liquid	14,500
Total Capital, 10^6 U.S.$ (USGC, December 1993)	813.9

	$/B Fischer-Tropsch Product
Natural Gas Feed, $2.43/$10^6$ Btu	21.68
Operating and Maintenance Costs	11.90
Capital Charges, 14.2% of Total Capital	24.53
Product Price:	
$/Barrel	57.46
$/Gallon	1.37

Other Fischer-Tropsch Routes

Variations in the Fischer-Tropsch process consist of differences in reactor designs and differences in catalysts used in the reactors. The SASOL operations employ two different reactor systems, the ARGE fixed bed reactor and the Synthol entrained bed reactor. Other reactor designs have been proposed. In order to provide guidance for further development efforts the U.S. Department of Energy did a comparative study of four reactor systems for Fischer-Tropsch technology [46]. They are as follows:

- Entrained bed reactor, designed by Kellogg and used at SASOL.
- The tube-wall reactor developed by Pittsburgh Energy Technology Center (PETC).
- The slurry reactor, designed in Germany by H. Koelbel and operated semi-commercially in Germany.
- The ebullating bed reactor, developed by the U.S. Bureau of Mines and utilized by Chem Systems, Inc.

These designs vary from 530 to 640°F in the outlet temperature and from 0.7 to 2.4 in H_2/CO ratio in the feed. The relative investment costs are: entrained bed 100, tube-wall 208, slurry 45 and ebullating bed 65. In terms of product yields there are wide variations with the slurry reactor having twice the gasoline yield as the entrained bed reactor. This study is based on conversion of 793 x 10^3 std m^3/h of $CO + H_2$, and it is not dependent on whether the synthesis gas was made from natural gas or coal. The overall conclusion is that the slurry reactor is the best design. It has the lowest investment and catalyst costs of the four reactors. A comparison of the slurry versus fixed-bed reactors [47] by Bechtel shows that both the investment costs and operating costs are lower for the slurry reactor than for the fixed-bed reactor.

The Shell Middle Distillate Synthesis Process [48] combines reforming of natural gas, a Fischer-Tropsch step and conversion to middle distillates by hydroisomerization and hydrocracking of the waxy product. The Fischer-Tropsch step uses a tubular fixed-bed reactor. It is chosen because it is simple and the technology is proven.

A review of Fischer-Tropsch processes by Burns and Roe and PETC [43] emphasizes iron-based catalysts for Fischer-Tropsch particularly for slurry phase reactors. There are recommendations for further work on catalyst and engineering development and catalyst characterization. The Fischer-Tropsch catalyst development work is continuing under the sponsorship of the U.S. Department of Energy. Following are highlights of some of the work reported at 1993 and 1994 Contractors Review Conferences:

- Energy International [49, 50] formulated Fischer-Tropsch cobalt catalysts and tested them in a fixed-bed reactor and in a slurry bubble column reactor.
- University of Kentucky [51, 52] attempted to formulate iron-based Fischer-Tropsch catalysts with the highest possible activity and life and the highest selectivity to desired products. A 100 lb batch of Si and K promoted catalyst was prepared for PETC.
- UOP [53] is developing the means of preparing 100 lb/day batches of Fischer-Tropsch catalyst for slurry processing.
- Texas A&M [54] has done Fischer-Tropsch catalyst development with emphasis on the effect of pretreatment procedures, promoters and binders. The work was done using iron/silica catalysts. Indications are that the targets set for them would be met in a bubble column slurry reactor.
- Bechtel, Amoco and Burns and Roe [55] have developed economics for 3 cases of indirect liquefaction using advanced Fischer-Tropsch technology using coal as a feedstock. They also developed ASPEN simulation models for the plants represented in these cases.
- Brookhaven National Laboratory [56] investigated ultrafine particle iron catalysts in slurry-phase Fischer-Tropsch synthesis. They developed 2 catalysts which were effective catalysts for Fischer-Tropsch synthesis.

- The MITRE Corporation [57] has updated their coal liquefaction simulation model to make it compatible with a Bechtel case. They carried out simulations which showed that (1) considerable savings can be obtained in a Fischer-Tropsch synthesis by adding the coproduction of electricity; (2) the break-even cost of natural gas was estimated to be about $3 per million Btus to give the same Fischer-Tropsch products as coal at $1 per million Btus; (3) the cobalt catalyst system is preferred over iron catalyst; and (4) when using $0.50 per million Btus natural gas the Fischer-Tropsch products are competitive with a spot price of gasoline of about $23 per barrel.

- PETC, Gilbert/Commonwealth and University of Kentucky [58] are testing catalysts called "low-alpha" catalysts which produce hydrocarbons mainly in the gasoline range. These Fischer-Tropsch catalysts consisting of iron, copper and potassium in oxide form were given steady conversions and selectivities over 15 days.

- USDOE, University of Kentucky and Texas A&M [59] have shown that the nature of binders, promoters and pretreatment affects iron phases formed during pretreatment and Fischer-Tropsch synthesis.

Cost Factors

Nearly all of the work done to evaluate Fischer-Tropsch processes has been done using coal as the original feed. However, the work can also be applied to natural gas-based processing by adjusting the CO/H_2 ratio through the design of the synthesis gas production plant.

Although SASOL in South Africa has operated coal-based Fischer-Tropsch plants, no natural gas-based Fischer-Tropsch plants have been built. A study was made by Bechtel, Amoco and Burns and Roe [60] for a plant including coal gasification, slurry Fischer-Tropsch and upgrading processes. The study by Bechtel shows that coal-based Fischer-Tropsch processing and coal-liquid upgrading would be competitive with crude oil production and refining at a crude cost of 30.7$/bbl. This indicates that a considerable increase in crude price would be needed before the Fischer-Tropsch process, using coal-gas, could compete with petroleum refining for production of transportation fuels. Use of natural gas and elimination of coal-gasification could improve the economics of Fischer-Tropsch processing.

As indicated earlier, the slurry reactor has the most economical design for Fischer-Tropsch. Further work on optimizing and characterizing catalysts is needed to ensure that catalyst conversion, life and selectivity can be sufficiently good to give a catalyst which can be used commercially.

UOP [61] has obtained economics for the upgrading of Fischer-Tropsch liquids from an ARGE reactor. UOP assumed that 38,860 Bbl/d of upgraded liquids were obtained by processing various fractions of product by use of units for (1) producing C_6-C_7 aromatics from LPG, (2) converting benzene to alkyl aromatics, (3) converting naphtha to high octane gasoline, (4) converting C_5-C_6 normal paraffins to isoparaffins and (5) hydrocracking heavy waxy materials to lighter products. The capital cost in 1993 dollars would be 259 million dollars. The total upgrading cost including capital charge factor and operating and maintenance but excluding feedstock costs is $5.78/Bbl of liquid product.

The work by UOP is an example of what can be done to determine upgrading costs and methodology and was done on UOP processes. To get the optimum method of upgrading Fischer-Tropsch liquids depending on product distribution and quality further work is needed. This work could be done using a refinery model or by a series of economic studies on various combinations of upgrading units. When determining the cost of transportation fuels from Fischer-Tropsch processing, the cost of upgrading needs to be added to the cost of producing raw Fischer-Tropsch liquids.

Burns and Roe and PETC [43] have provided a good overview of the development work needed to make Fischer-Tropsch competitive with other methods of making transportation fuels from natural gas. The work they propose includes catalyst development, catalyst characterization and engineering development.

A large part of the production of Fischer-Tropsch liquids consists of the production of synthesis gas to use as feed to the Fischer-Tropsch reactor. It is important to choose the right process for producing the synthesis gas to have the synthesis gas in the proper hydrogen to carbon monoxide ratio. The various ways for producing synthesis gas were discussed under the section on methanol production.

Summary

The process description, major reactions, material balance, product composition and economics have been shown for a process for producing Fischer-Tropsch liquids from natural gas. This process has never been tested but much of the process design and economics are based on the commercial coal-based Fischer-Tropsch process at SASOL in South Africa using the ARGE reactor. The economics could be improved somewhat by using the slurry reactor design. In addition, other methods of producing the synthesis gas may be preferred. Although further design and catalyst development and commercial testing would probably improve the Fischer-Tropsch process, it does not appear that the natural gas-based Fischer-Tropsch process would be an economical method for producing transportation fuels in the foreseeable future using lower 48 U.S. gas. This is true primarily because of current gas prices and the expectation that natural gas prices will increase faster than crude oil prices in the future. The Fischer-Tropsch process may be an economic process using low value gas in remote locations.

8.3. Gasoline by Oxidative Coupling of Methane and Oligomerization

There have been extensive research efforts undertaken during the 1980's and 1990's to find a process for the direct conversion of natural gas to gasoline to avoid the necessity of producing synthesis gas as an intermediate. In 1988 Bechtel [62] did a study to choose three direct conversion processes for further study. Partial oxidation, oxidative coupling and oxyhydrochlorination were selected from a list of nineteen processes.

When comparing the three processes, i.e., partial oxidation, oxidative coupling and oxyhydrochlorination it was found that a) partial oxidation had a higher production cost due to its higher capital cost and b) oxyhydrochlorination though more favorable from a cost standpoint had corrosion problems to overcome. Therefore, the oxidative coupling and oligomerization process was chosen for detailed examination in this section. Following is a process description for this process.

Process Description

Exhibit 8-5 shows an oxidative coupling process flow diagram. Desulfurized methane-rich gas is contacted at 1,472°F (800°C) and 55 psia with a reducible metal oxide catalysts in a circulating fluid-bed riser reactor. The catalyst is reoxidized in a separate oxidizer using air. Methane and other light paraffins undergo oxidative dehydrogenation with the reactor catalyst to produce free radicals and water. The radicals combine to form light olefins which are oligomerized to gasoline in a second reaction step over ZSM-5 catalyst in fixed-bed reactors. Byproduct CO_2 and water are removed between the two reaction steps. Conversion in the first step is limited to 25 percent to maintain 78% selectivity, thus unconverted gases are recycled between reactors. Heat recovery produces steam to drive the recycle compressor. The large amount of recycle moderates the temperature rise in the second step permitting the use of fixed-bed reactors. The design is based primarily on ARCO data [62].

Major Reactions

The overall reaction is as follows:

	ΔH, Btu/Lb Mole of CH_4
$CH_4 + \frac{1}{2} O_2 \rightarrow \frac{1}{2} C_2H_4 + H_2$	-59,400

The mechanism for the oxidative coupling step in which methane is converted to ethane and ethylene over a metal oxide catalyst involves abstraction of hydrogen from methane to produce methyl radicals and surface hydroxyls on the catalyst, followed by release of the methyl radicals into the gas phase where they couple to form ethane

$\text{Catalyst-O}^* + CH_4 \rightarrow CH_3\bullet + \text{Catalyst-OH}$

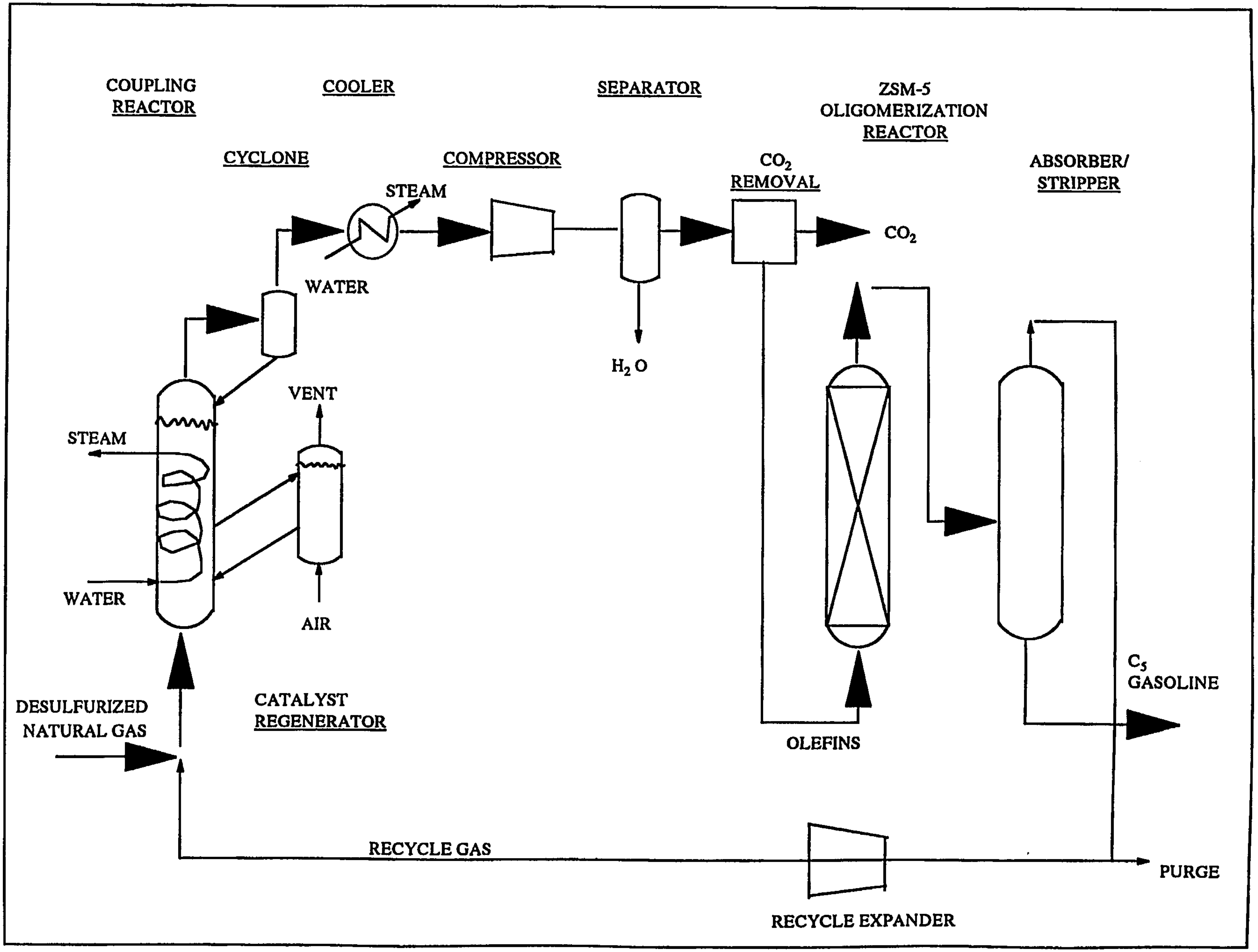
$CH_3\bullet \text{ (adsorbed)} \rightarrow CH_3\bullet \text{ (gas phase)}$

$2\ CH_3\bullet \rightarrow C_2H_6$

$C_2H_6 \rightarrow C_2H_4 + H_2$

The conversion of ethane to ethylene occurs in the gas phase and is largely independent of the catalyst, but dependent on temperature and other operating conditions.

EXHIBIT 8-5
METHANE TO GASOLINE/OXIDATIVE COUPLING PROCESS



In the second step the ethylene oligomerizes (i.e., forms large chain paraffins and aromatics) in the presence of a zeolitic shape selective catalyst (Mobil ZSM5) to give higher molecular weight olefins which then to convert to aromatics, cycloparaffins and paraffins.

$C_2H_4 \rightarrow C^+_5$ olefins → paraffins + cycloparaffins + aromatics

Composition of Product Stream

Bechtel's study assumes a methane conversion of 25% per pass [42]. This study assumes that in a recycle situation the ethane and higher paraffins will react completely to produce 90% olefins and 10% carbon dioxide. It is further assumed that 90.5% of the olefins are converted to C_5+ material with formation of 5% iC_4 and nC_4 and 4% C_3. The liquid product would have a specific gravity of 0.73.

Economics

The following economics table for oxidative coupling is based on the report prepared by Bechtel [42].

Plant Capacity, BPSD of Gasoline	14,500
Total Capital, 10^6 U.S. \$ (USGC, December 1993)	937.7
	\$/B Gasoline
Natural Gas Feed, \$2.43/10^6 Btu	21.77
Operating and Maintenance Costs	8.12
Capital Charges, 14.2% of Total Capital	28.25
Product Price:	
\$/Barrel	71.12
\$/Gallon	1.69

Other Direct Conversion Processes

In addition to oxidative coupling plus oligomerization Bechtel [42] chose the following two direct conversion processes for detailed study:

- Oxyhydrochlorination plus oligomerization
- Partial oxidation plus oligomerization

The primary reservations for the oxychlorination step have to do with the extreme corrosiveness of the process and the tendency to lose selectivity as the conversion increases. The partial oxidation step has also had limited success in obtaining good selectivity at a reasonable conversion level. The Bechtel economics study ranks the six cases they evaluated in the following order from most expensive production costs to least expensive production costs: partial oxidation, oxidative coupling, oxyhydrochlorination, Fischer-Tropsch, Fixed-Bed MTG and Fluid-Bed MTG. There is possible improvement in the direct conversion process costs, if conversion and selectivity can be improved. The study also compares thermal efficiency for the six processes and finds them to be in the range of 45 to 53%.

The oxyhydrochlorination process is based on research conducted by the Department of Energy's Pittsburgh Energy Technology Center (PETC) [63]. In this process, natural gas is reacted with oxygen and hydrogen chloride over a catalyst made of CuCl, KCl and $LaCl_2$. The products are primarily chloromethane and dichloromethane in a 4 to 1 ratio. The chlorinated hydrocarbons are fed to a fixed bed reactor and are oligomerized to gasoline. The HCl and water are separated and recycled.

The following economics table for oxyhydrochlorination is based on a report by Bechtel [42]. The economics from Bechtel were based on 25% conversion of methane. Arun Bose of PETC indicated that experimental results showed an 18% conversion. Therefore, the economics were adjusted to a basis of 18% conversion.

Plant Capacity, BPSD of Gasoline	14,500
Total Capital, 10^6 US$ (USGC, December 1993)	956.4
	$/B Gasoline
Natural Gas Feed, $2.43/$10^6$ Btu	19.96
Operating and Maintenance Costs	24.89
Capital Charges, 14.2% of Total Capital	29.69
Product Price:	
$/Barrel	76.53
$/Gallon	1.82

These economics show that the cost of producing gasoline by oxyhydrochlorination is about 8% higher than the cost by oxidative coupling. The oxyhydrochlorination process can be stopped part way through to take off methyl chloride as a chemical rather than making gasoline. The production of methyl chloride from natural gas is discussed in Section 9.6.

Considerable research on direct conversion processes has been sponsored by the U.S. Department of Energy in recent years. None of these processes has yet shown evidence of competitive economics but they have attempted to use innovative materials, catalysis and technology in their research. Following are brief highlights of this research based on proceedings of the 1993 and 1994 Contractor Review Meeting.

- Sandia [64, 65] is using biometric computer-aided molecular design to develop a process for the direct conversion of methane and other light hydrocarbons to liquid fuels. They have tested a series of halogenated iron dodecaphenylporphyrin catalysts and plan to develop and test new, more active iron based catalysts. They hope to have W. R. Grace as an industrial partner.

- Amax [66] is attempting to develop a catalyst which facilitates methane oxidation to methanol at high conversion and selectivity. Vanadium phosphate catalysts have been selected for this study. The catalyst tested was 90% selective to carbon monoxide but gave no methanol. They are exploring the effects of variables and use of promoters.

- Argonne National Laboratory and Amoco Research Center [67] are developing mixed-conductivity oxides for use as oxygen-permeating membranes that can operate without electrodes. These can be used in converting methane or other hydrocarbons using air for the oxidant rather than oxygen. Membrane tubes have been developed with 99% conversion to syngas but have not produced hydrocarbons by direct conversion.

- Worcester Polytechnic Institute [68, 69] is developing membrane reactors for use in oxidative coupling of methane. The aim is to have control over reaction conversions and selectivity. The work to date has concentrated on fabricating membranes and doing modeling.

- SRI International [70, 71] is preparing fullerene-based catalysts or soots for conversion of methane to ethane and ethylene. The effect of adding hydrogen or other gases will be examined. Results so far show that activated carbon and fullerene soot activate the C-H bond of methane and convert it into higher hydrocarbons. No condensable products are formed.

- The University of Colorado [72] is studying the direct partial oxidation of methane to methanol using a catalytic membrane system. A cooling tube gives a rapid quench to inhibit further oxidation of the methanol. With a conversion of 4 to 7%, methanol selectivity is 40 to 50% with quenching. Work is being done to test use of air-like mixtures and to better understand reactor mechanisms.

- Sun Company, Inc. [73] is trying to find new materials to catalyze the direct reaction of light alkanes with molecular oxygen to form alcohols and to develop practical processes for the direct oxidative conversion of natural gas to alcohol-rich liquid oxygenates. Work is concentrating on synthesizing, characterizing and testing porphyrin macrocycles as hosts for oxidation active transition metal centers including iron, manganese, chromium, ruthenium, cobalt and others. Proof-of-concept work consists of converting propane and isobutane to alcohols because this is much more readily done than conversion of methane.

- Lehigh University [74] is investigating catalytic processes for the selective oxidation of methane to C_2 hydrocarbons and methanol under relatively mild reaction conditions. The use of acid promoted Sr/La_2O_3 has been shown to be very selective for the conversion of methane to C_2 hydrocarbons. Further work will be directed toward conversion to oxygenates. Study of new catalysts will continue.

- Dow Corning Corporation [75] has been working on the design and construction of a process demonstration unit for converting light alkane gases to methyl chloride via oxyhydrochlorination. They also will try to develop a stable, highly selective catalyst.

- The Institute of Gas Technology [76] is developing a process for converting natural gas to gasoline using carbon disulfide as an intermediate. This eliminates the necessity of sulfur removal as part of the process. Results so far show carbon disulfide produced in yields up to 98%.

- Lawrence Berkeley Laboratory [77] is converting methane using catalytic materials in membrane reactors. They have used Ca-Ni-K oxides for oxidative coupling and plan to study Li/MgO catalysts as well. They have a CRADA between LBL, Orion ACT and DOE.

In the 1980's research was done on direct conversion of methane by oxidative coupling by Union Carbide, Phillips Petroleum, ARCO Chemical, METC, Texas A&M, University of Pittsburgh, and Lawrence Livermore Laboratories. This work included catalyst development, mechanistic studies, and experimental studies. Information and literature surveys of direct conversion by oxidative coupling and other processes to obtain liquid fuels is available in the literature. References of particular interest are referred to in a report by A. D. Little [78] and the previously cited report by Bechtel [42]. An overview of the current work sponsored by PETC, much of which was highlighted earlier, was given by PETC and Burns and Roe. Parkyns et al of British Gas plc [79] has reviewed the literature for the direct conversion of methane to oxygenates and higher hydrocarbons. They conclude that they are not ready to challenge syngas-based processes.

Process Status and Potential

Arthur D. Little [78] states that researchers have shown that single-pass conversion and C_2+ selectivity sum to 100% for oxidative coupling. A rule of thumb used by active researchers in oxidative coupling is that the overall yield of C_2+ must be greater than 30% for the process to become economically attractive.

According to J. Lyons [80], Sun is not interested in oxidative coupling because the product, ethylene, is a gas and Sun wants to obtain a liquid fuel which can be easily transported. He said a process with better than 80% selectivity and 30% conversion of methane is needed to be worth considering. Bechtel [42] says that if selectivity could be increased to 100% the total plant costs reduction for oxidative coupling would be 10.5%. This improvement in selectivity would have the following effects:

- A reduction in catalyst circulation.

- A reduction in regenerator size and air compressor horsepower.

- A reduction in cooling water duty.

Arthur D. Little gives the following as goals and considerations for improving the oxidative coupling process:

- Achieve better than 35% single-pass conversion and 90% selectivity.
- Maintain high ratios of ethylene to ethane and of carbon monoxide to carbon dioxide.
- Reduce the reaction temperature to between 450-700°C.
- The re-oxidization of metal oxide catalysts from their reduced states using air in a fluidized-bed is preferred over the use of oxygen from an engineering standpoint.
- A system at pressures of 8 to 28 atmospheres is needed from an economic standpoint.
- Design catalysts which can be reactivated and have long catalyst lives if operated under proper conditions.

Commercialization

The oxidative coupling process has not been commercialized. None of the processes developed up to this time have had sufficiently good selectivity and conversion to compete with other natural gas to liquids processes.

The process description, major reactions, material balance, product composition and economics have been shown for the oxidative coupling and oligomerization process. This is a method for the direct conversion of natural gas to gasoline and thus is a means of bypassing the production of synthesis gas as an intermediate step. This process is based on considerable experimental work but has never been commercialized. The process has poor economics because the selectivity and conversion factors are low. Significant improvements in this process selectivity and conversion must be made to make this process viable. To date, the results of an extensive research has been discouraging and has diminished the likelihood of achieving that significant improvement in process selectivity, conversion, and economics. A comparison of economics for oxidative coupling and oxyhydrochlorination shows that the cost of product from oxyhydrochlorination is higher.

8.4. Natural Gas to Higher Alcohols by the IFP Process

Processes for the synthesis of higher alcohols using natural gas for a feedstock have been developed in Europe. In addition, the U.S. Department of Energy has sponsored research in this area. The economics to be presented in the following section will use the conversion of natural gas to higher alcohols by the Institute Francais du Petrole (IFP) process. The IFP process was developed in France and has been tested in Japan by the Idemitsu Kosan Company under a program sponsored by the Japanese government. The process was tested in a mini-pilot scale of 800 metric tons/year in Chiba, Japan. It has not been commercialized. [81]

Process Description

Details of the IFP process descriptions are given both by the MITRE Corporation [81] and IFP [82]. Synthesis gas is produced by high temperature partial oxidation of natural gas to minimize residual methane and carbon dioxide and to avoid unwanted CO_2 removal. By CO_2 recycle and removal the H_2/CO ratio is adjusted to be in the range of 2 to 2.5.

The alcohol synthesis reaction takes place in two adiabatic multibed quench reactors in series to get good temperature control. The reaction temperature ranges from 260-320°C, the pressure range is 6-10 MPa and the space velocity range is 3000-6000 per hour. A copper-cobalt catalyst is used. After leaving the reactors, the product goes through a series of separation steps to separate gas, methanol and water from the C_2 and heavier alcohol. A simplified flow diagram for this process is shown in Exhibit 8-6.

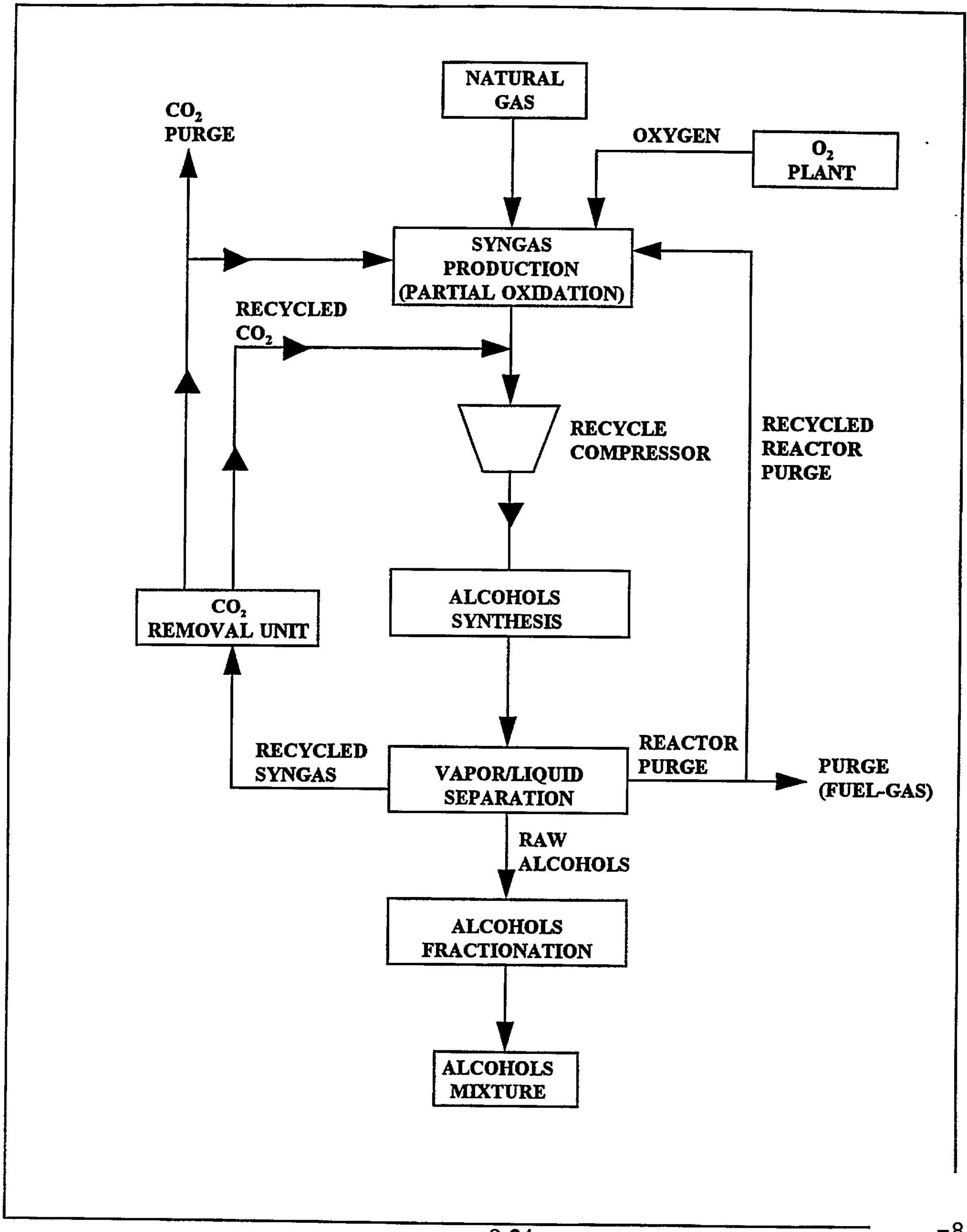
Major Reactions

The stoichiometry of mixed alcohol synthesis is based mainly on the following generalized reactions:

$$nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$
$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$$

The first equation represents the primary alcohol synthesis reaction. The next equation represents the water-gas shift activity of the alcohol synthesis catalyst, and the last two reactions represent the Fischer-Tropsch activity of the catalyst to form paraffinic and olefinic hydrocarbons.

EXHIBIT 8-6
SIMPLIFIED BLOCK DIAGRAM OF THE IFP PROCESS



According to the first equation, the synthesis of mixed alcohols requires two moles (volumes) of hydrogen for each mole (volume) of carbon monoxide. On the other hand, the formation of paraffinic and olefinic hydrocarbons results in a molar H_2/CO consumption (usage) ratio equal to or greater than two. However, the overall stoichiometric usage ratio in the mixed alcohol synthesis reaction system can become less than 2 if the catalyst used has a strong water-gas shift activity. The low H_2/CO ratio means a carbon-monoxide rich syngas that favors the formation of higher alcohols.

The heat of formation of higher alcohols is greater than that for methanol. The combined synthesis of alcohols and hydrocarbons entails the release of large amounts of heat. The heat of reaction for a typical 50/50 methanol/higher alcohol mix, for example, is estimated to be about 25 percent higher per mole of carbon monoxide (CO) converted than for methanol alone. This indicates that efficient heat removal is an important aspect of higher alcohol production.

Composition of Product Stream

When maintaining a H_2/CO ratio of 2-2.5, a temperature range of 260-320°C and a pressure range of 6-10 MPa, conversion per pass is 12-18% with a total conversion of 90+% [82]. The selectivity to alcohols is 70-75%. The composition of the gaseous products after hydrogen and carbon monoxide removal is 70-72% methane, 13-16% ethane and 8-12% C_3-C_5. The alcohol product consists of 50-70% methanol, 16-23% ethanol, 8-14% propanol and 7-13% C_4+ alcohols.

Economics

The following economics table for the C_1-C_6 alcohols used data from a report by the MITRE Corporation [81].

Plant Capacity, BPSD of C_1-C_6 alcohols	15,060
Total Capital, 10^6 U.S.\$ (USGC, December 1993)	638.1
	\$/B C_1-C_6 Alcohol Product
Natural Gas Feed, \$2.43/10_6 Btu	14.91
Operating and Maintenance Costs	9.10
Capital Charges, 14.2% of Total Capital	18.26
Product Price:	
\$/Barrel	50.37
\$/Gallon	1.20

Other C_1-C_6 Alcohol Routes

In addition to the IFP process there are several other processes which have been or are being developed along the path toward commercialization. These include the following according to the MITRE Corporation report [81]:

- Snamprogetti's MAS process has been developed in cooperation with Enichem and Haldor Topsoe A/S. This process has been implemented on an industrial demonstration scale of 15000 t/year in southern Italy. A syngas is produced and fed to the reactor at a temperature of 350 to 420°C. The reactor pressure is at 90 to 160 atmospheres. Separation of the product consists of taking methanol and ethanol as overhead products, and water is separated from the C_3+ alcohol.

- The Octamix process is claimed by Lurgi to be an extension of their low pressure methanol process. Lurgi believes the Octamix process is ready to be used commercially because it uses well proven elements of their methanol process. The reactor feed consists of a syngas stream with a H_2/CO ratio of 1.0 to 1.2 joined by a recycle gas stream . In the reactor the syngas mixture which has been compressed to 70 atmospheres is converted to alcohols at a temperature of 250° to 300°C over a Cu/ZnO catalyst. The product C_1 to C_8 alcohols are separated from the gases in a condensate drum. A unique feature of the Octamix process is the low level of water in the product. The product contains 17 to 42 weight percent C_2 to C_8 alcohols.

The U.S. Department of Energy has supported several programs for developing catalysts for the manufacture of higher alcohols [81]. Union Carbide Corporation did work to develop ruthenium-based catalytic systems for the synthesis of mixed alcohols. Lehigh University has done work to improve on molybdenum disulfide catalysts originally developed by the Dow Chemical Company.

Work was done at North Carolina State [83] to find a catalyst or catalysts for use in obtaining C_1-C_6 alcohols. The catalyst development work which involved Rh-based catalysts with various promoters was abandoned because they could not reach the established targets. Future work includes the use of a screening reactor to demonstrate the feasibility of "one step" synthesis of C_2+ alcohols from methanol or dimethyl ether.

Cost Factors

The economics of adding C_1-C_6 alcohol to a gasoline blend are determined by such factors as how much it contributes to increasing the octane number and what kind of tax subsidies are applicable. Also, butanes must be backed out to maintain Reid Vapor Pressure to account for the addition of the oxygenates which have relatively high vapor pressures. The key to developing a good C_1-C_6 alcohols process is finding a good catalyst and using a reactor design that matches the catalyst properties. In the U.S. further research and development work on the catalysts developed by Union Carbide Corporation and Lehigh University may be worthwhile. These could be tested in a slurry phase reactor system.

A large part of the cost of the production of C_1-C_6 liquids consists of the cost of production of synthesis gas to use as feed to the higher alcohols reactor. It is important to choose the right reactor to produce a synthesis gas with the proper hydrogen-to-carbon monoxide ratio. The various ways for producing synthesis gas were discussed under the section for methanol production.

Commercialization

Three processes are at an advanced state of development [81]. These are IFP, Lurgi's Octamix and the Snamprogetti MAS process. All of these have been tested on a pilot plant but none of them has been operated on a commercial scale. Of these, the Octamix process is the simplest configuration. Lurgi has eliminated the isotropic distillation which has given Octamix an economic advantage over the other competitive processes. IFP and Snamprogetti have more complex reactor arrangements and may have temperature excursions. Octamix does not have these problems. Lurgi has arranged for a license authorizing U.S. Texas Methanol Corporation to manufacture and sell Octamix plants. An EPA waiver for Octamix to be used as a gasoline octane booster was granted in 1988. In granting this waiver, EPA considered exhaust emissions, evaporative emissions, driveability and materials compatibility of the new fuel.

Therefore the Octamix process is the most economical and nearest to commercial reality of all of the processes to make higher alcohols. The IFP process was chosen for the presentation of economics and process description in this section because this information was available for IFP but not for the other processes.

Summary

The process description, major reactions, product composition and economics have been shown for the IFP process for the production of C_1-C_6 alcohols. This process was developed in France and tested in a mini pilot scale plant in Japan. The economics for this process are poor and the prospects for improving this process significantly are not good. There are other ways of producing higher alcohols that are better than processes based on natural gas. Furthermore, the product from processes such as the IFP process predominantly consist of methanol and ethanol, and these alcohols are less desirable for use in gasolines. Further development of processes for converting natural gas to C_1-C_6 alcohols may not be recommended unless there is evidence of improved prospects for selectivity to higher alcohols.

8.5. Natural Gas and Butane to MTBE

Over the past decade the addition of methyl tertiary butyl ether (MTBE) to gasoline has increased rapidly. First MTBE was used as a high octane blending component which was substituted for tetraethyl lead which had to be phased out because of EPA requirements. Then, CAAA of 1990 required that gasoline sold in some areas have a minimum oxygen content. The use of ethers and MTBE in particular became an important part of the refinery strategy to produce oxygenated and reformulated gasoline. UOP has developed a three-step method for converting mixed butanes and methanol to MTBE [84]. The three process steps are the Butamer, Oleflex and MTBE units. The following process description is for the UOP technology [84].

Process Description

In the first step butane is converted to isobutane. The mixed butane feed is routed to a deisobutanizer column which recovers isobutane as an overhead product. The normal butane side cut is isomerized to isobutane in the UOP Butamer unit. The product from the Butamer unit is sent back to the deisobutanizer. The Butamer unit uses a dual-function, chloride-promoted catalyst in the presence of hydrogen.

In the second step, isobutane-rich overhead from the deisobutanizer is routed to the Oleflex unit which dehydrogenates isobutane to isobutylene at an overall selectivity of 91 to 93 mol%. The Oleflex unit consists of a reactor section, continuous catalyst regenerator and a product recovery section.

Liquid product from the Oleflex unit is routed to the Huels MTBE process unit. MTBE is produced by reacting isobutylene with methanol. An ion-exchange resin catalyst is used. The reaction is essentially 100% selective.

Seven Butamer units were in design and construction and 16 Huels MTBE units were on line by 1991. The Oleflex unit regenerator is modeled after the CCR platforming unit regenerator with 91 units in operation by 1991. The flow diagram for this process is shown in Exhibit 8-7.

Major Reactions

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow (CH_3)_3CH$
nButane Isobutane

$(CH_3)_3\text{-}CH \rightarrow (CH_3)_2C{=}CH_2+H_2$
Isobutane Isobutylene

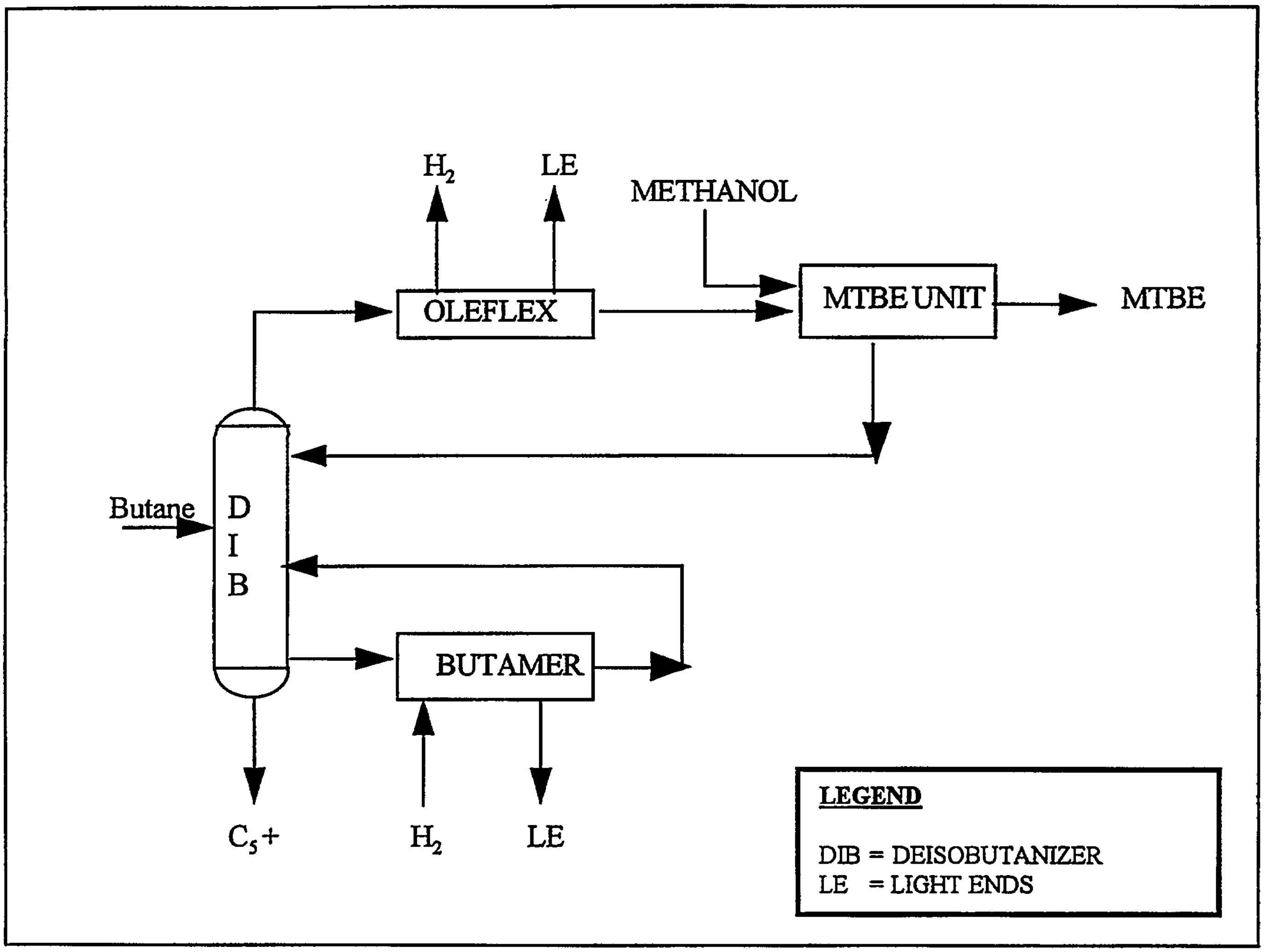
$(CH_3)_2C{=}CH_2+CH_3OH \rightarrow (CH_3)_3C\text{-}O\text{-}CH_3$
Isobutylene Methanol MTBE

Composition of Product Stream

The final product is essentially 100% MTBE coming from the Huels MTBE unit. The overall mass balance from a UOP-designed unit [84] is as follows:

EXHIBIT 8-7

MTBE PROCESS FLOW DIAGRAM



Feed	Flow Rate
Butanes (30 wt-%iC_4), BPSD	12,011
Methanol, BPSD	4,250
Products	
MTBE, BPSD	12,500
C_5 in butanes, BPSD	225
Hydrogen (88 mol-%), lb/hr	6,290
Light ends, lb/hr	8,880

Typical properties for MTBE are: gravity, °API, 57.9; RONC, 118; MONC, 101; Rvp, psi, 7.4. Typical blending octane numbers are 122 RONC and 100 MONC [85].

Economics

The following economics table for the production of MTBE from methanol and butanes used data from the report prepared by UOP [84].

Plant Capacity, BPSD of MTBE	12,500
Total Capital, 10^6 U.S. \$ (USGC, December 1993)	174.3

	\$/B MTBE
Methanol Feed, \$0.42/gal	6.00
Butanes Feed, \$0.38/gal	15.34
Operating & Maintenance Costs	7.13
Capital Charges, 14.2% of Total Capital	5.87
Product Price:	
\$/Barrel	36.06
\$/Gallon	0.86

Other MTBE Process Routes

ABB Lummus Crest offers a technology for producing MTBE from mixed field butanes and methanol [86]. A single train can produce up to 32,000 BPSD of MTBE. The ABB Lummus Crest process uses TOTAL or AKZO technology for butane isomerization, Houdry CATOFIN for isobutane dehydrogeneration, and CDTECH process for MTBE production. Two butane isomerization units are in the engineering stage. For isobutane dehydrogenation the Houdry CATOFIN dehydrogenation process is developed by United Catalysts. Currently, four units are in production. The CDTECH MTBE process is available through a joint venture between ABB Lummus and Chemical Research and

Licensing Company. Fifty-four CDTECH MTBE plants are in operation, design, or construction stages. ABB Lummus Crest technology has a number of advantages, including lower butane demand (0.73 lb of butane needed to make 1 lb of MTBE) and no need to treat MTBE unit recycle isobutane raffinate.

Lyondell and Rohm and Haas [87] recommend using Amberlyst 35 Wet Polymeric catalyst to increase production of MTBE. Snamprogetti/ANIC [88] was one of the early designers of MTBE units. Their unit uses an ion exchange resin. Water is used for temperature control of the reactor. The product is greater than 98% MTBE.

In addition to using butanes and methanol as a starting point for the production of MTBE, mixed butylenes or isobutylene may be used in place of mixed butanes thus skipping the C_4 dehydration step. The unsaturated C_4's are available from refinery FCC or steam cracking units. IFP has developed new technology to isomerize normal butanes to isobutylene [89]. It is called ISO-4 and uses continuous regeneration technology and minimizes side reactions of oligomerization and cracking.

Other routes to obtain isobutylene to feed to an MTBE unit are available. Kinetics Technology [90] suggests steam cracking isobutane to obtain a 70% yield of isobutylene and propylene. Texaco [91] proposes the dehydration of tertiary butyl alcohol to isobutylene in an isothermal fixed bed reactor using aluminum catalyst.

John Brown has written a 2-part series on the etherification of field butanes which gives a good overview of the work going on in this field [92, 93]. In the first part they review the fundamentals of butane isomerization, isobutane dehydrogenation and etherification. In butane isomerization the biggest concern is the deleterious effect of contaminants on the catalyst. In isobutane dehydrogenation they discussed the need for an isothermal reactor, the desirability of using a catalyst which is also a heat carrier, other methods of providing heat, maintaining a low partial pressure and the problems of coking during regeneration. In MTBE conversion it is important to run in the liquid phase near the thermodynamic limit in order to get near 99% conversion. In the second part of the series the various commercial designs were discussed. Butane isomerization technology dates back to the 1940's. A variety of processes are available for the dehydrogenation of isobutane. These processes differ primarily in the characteristics of the reaction section. The MTBE process consists of (1) reaction, (2) recovery of the methanol and hydrocarbon raffinate stream and (3) recovery of excess methanol and its recycle to the reactor. The design of the reaction section differs mainly by the philosophy of heat of reaction removal. The three principal methods available are (1) fixed bed with recycle, (2) fixed bed tubular reaction and (3) catalytic distillation. Advantages of each system can be seen as a tradeoff between cost and feed efficiency. The higher production and capital costs are accompanied by higher conversion of the isobutylene.

Lehigh University [94, 95] have been developing catalysts and technology for the synthesis of oxygenated fuels and high value chemicals from natural gas. The concept of employing a dual reactor (SO_4^{2-}/ZrO_2 followed by Amberlyst - 15) for the formation of MTBE was verified. The productivity was an order of magnitude better than using Amberlyst-15 alone. The feedstock is a methanol/isobutanol mix. Work will continue on catalyst development and development of process steps for converting methane to MTBE in an optimal way.

Air Products and Chemicals, Inc. [96, 97] are developing one-and-two-stage processes to methanol plus isobutanol from synthesis gas. The isobutanol is converted to isobutylene and is combined with methanol to produce MTBE. A slurry reactor process for converting methane to methanol and isobutanol at 280-320°C uses a cesium-promoted $Cu/ZnO/Al_2O_3$ catalyst. Current efforts are concentrating on improvement in selectivity for the two-step process. The direct synthesis of mixed alcohols has been demonstrated on a pilot scale at LaPorte, Texas.

Cost Factors

Much work has been done to develop the MTBE process as well as the processes for producing feed for the MTBE process. One of the principal decisions in choosing a process route is the cost and availability of C_4 hydrocarbons. A 1988 study by ARCO printed in an American Petroleum Institute (API) publication [98] compares the cost of producing MTBE when using various feedstocks. The total cost of MTBE in cents per gallon was 71.3 when isobutane was the feedstock, 74.7 when mixed butanes was the feedstock, 53.4 when steam cracker butylenes was the feedstock and 57.6 when fluid cracker butylenes was the feedstock. Thus it is most economical to make MTBE from steam cracker or FCC butylenes. However, these feedstocks are in limited supply and therefore isobutane and mixed butane feedstocks must be used as the demand for MTBE continues to increase. Potentially all gasoline sold in ozone nonattainment areas will need to contain 2.0 wt % oxygen but production of MTBE from the available isobutylene would only result in an oxygen concentration in the gasoline of 0.3 wt %. Therefore, using all the isobutylene from the FCC, coker and steam cracker units would not provide nearly enough MTBE to meet the gasoline specification [84]. Thus, there is a definite need for MTBE processes starting with mixed butanes or isobutane.

The capital costs for an MTBE complex break down as follows [93]:

Isomerization	15% to 20%
Dehydrogenation	35% to 50%
Etherification	10% to 15%
Offsites	30% of TIC

Therefore, there is a better payoff to lower costs on the dehydrogenation section than on the isomerization and etherification sections. Some of the areas where improvement is still possible are in catalyst development, reaction design and utilization of byproducts. Eliminating or minimizing the recycle stream by improving conversion and selectivity rates is advantageous. There is an advantage in developing catalysts which are tolerant to contaminants.

Comparisons of Ethers Produced from Natural Gas

The processes which make MTBE can easily be adapted to make other ethers such as tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE). Manufacture of TAME is limited by the relatively small supply of isoamylenes from FCC refinery units, and ETBE is less economical than MTBE and depends on government economic support being available for ethanol.

ETBE normally is produced from agricultural products so the only two ethers normally used in transportation fuels and which are produced starting with natural gas are MTBE and TAME. According to a 1981 study by Gulf Canada [99], TAME can be made for 24 cents/gallon. These costs exclude the cost of isoamylene for TAME and isobutylene for MTBE but they show that production costs is not a deciding factor when choosing between TAME and MTBE for use in transportation fuels.

According to ARCO [100], MTBE is the most versatile ether. It requires the least amount of ether to achieve the required oxygen level. In making high octane premium gasolines, it provides the maximum distillation benefit in lowering the 50% point. Sources for isobutylene are growing.

TAME provides the most environmental benefit. It reduces tailpipe emissions and converts volatile and highly reactive olefins into a low RVP and clean burning ether. The low RVP is particularly helpful in summer when butanes are removed at an economic penalty to the refiner.

Production of both TAME and MTBE will be needed and will be driven by the need to include them in gasoline to meet environmental requirements. Usually they use isobutylene and isoamylenes from fluid catalytic cracking and steam cracking as sources of feedstock. MTBE can also be made starting with mixed butanes. As previously mentioned [98], these sources will ultimately prove inadequate. It is important to continue to develop processes such as those proposed by Lehigh University [94, 95] and Air Products and Chemicals [96, 97] because they can make MTBE entirely from natural gas and do not have to rely on the refineries for part of their feedstocks.

Dimethyl Ether as Diesel Fuel

Recently Amoco Corporation, Haldor Topsoe A/S, AVL LIST Gmbh and Navistar International Transportation Corporation have developed a new, alternative fuel for diesel engines that has ultra-low emissions. The fuel, predominantly Dimethyl Ether (DME), can be made from natural gas or other feedstocks such as coal or biomass. Details of diesel equipment development and diesel engine test results using DME were presented at a 1995 meeting [101-103]. Unlike other alternative fuels, DME has a high cetane number, which makes it ideal for use in diesel engines. It can be used in diesel engines with minor engine modifications.

DME today is only used as an aerosol propellant and is produced in small quantities, about 150,000 tons annually. For fuel use, large DME plants would be necessary and they would take 3 to 5 years to build. There are two ways to make DME both available through Haldor Topsoe. For the natural gas to DME process [104], the following process steps are required: Natural gas desulfurization and reforming, CO_2 removal, DME and methanol synthesis and purification. For methanol to DME, methanol is dehydrated and recycle methanol, water and DME are obtained in several separation steps. Initially, DME could be obtained by the methanol to DME process. Haldor Topsoe says that DME can be made more economically by the natural gas to DME process and that DME costs could be similar to Compressed Natural Gas or Liquified Natural Gas, when DME is manufactured in large quantities. Continuing research is needed to improve the DME manufacturing process and reduce its cost, optimize diesel engines for DME and find ways to market the fuel.

Commercial Applications

The dehydrogenation of isobutane to make isobutylene is available using any of the following four commercial technologies [105]:

Process Name	Licensor	Catalyst
Oleflex	UOP	Noble-metal based
CATOFIN	ABB Lummus Crest	Chromia-alumina
STAR	Phillips Petroleum	Noble-metal based
FBD-4	Snamprogetti SpA	Chromia-alumina

These processes have much in common with differences being primarily in the characteristics of the reaction section.

The MTBE licensors and primary reactor technologies are as follows [105]:

	Fixed Bed		
Conventional	Boiling Point	Expanded Bed	Tubular
ARCO	CDTECH	IFP	Snamprogetti
Huels/UOP			Huels/UOP
Phillips			
RWE-DEA/Edeleanu			
E C Erdolchemie			

Summary descriptions of four of these processes are contained in Hydrocarbon Processing [106]. The Phillips process has licensed seven installations plus a plant at a Phillips refinery. The ARCO chemical process provides total ether capacity of 140,000 bpsd. ARCO has four plants in the U.S. and two plants worldwide and 27 additional licensed plants. CDTECH, a partnership between ABB Lummus Crest and Chemical Research & Licensing has approximately 35 units in operation using a catalytic distillation method to produce MTBE or TAME. UOP has sixteen Huels MTBE units in operation and six more in design or construction. HPI/IRI and ARCO list each of the facilities and their capacity making MTBE [107]. The total U.S. operating capacity is 232,000 B/SD. In contrast, TAME has only 20,000 B/SD of U.S. operating capacity. The Energy Information Administration [108] breaks the MTBE production down by PAD districts. PAD District III which includes Texas and Louisiana has 87% of the MTBE operating capacity.

Summary

The process description, major reactions, product stream composition and economics have been shown for the UOP method of producing MTBE. Specifically the process steps included are (a) isomerization of butane to isobutane, (b) dehydrogenation of isobutane to isobutylene and (c) conversion of isobutylene and methanol to MTBE. The processes are commercialized and are economically competitive with similar processes licensed by CDTECH, Snamprogetti spA and Phillips. All of these process packages are commercial and are highly developed and efficient. Further studies would show the best designs and catalysts and thus show which are the optimum processes. However, it does not appear that there is much room for significant improvement in them. The production rate of MTBE is expected to grow rapidly as the need for its use as a gasoline additive expands, and so there will be a greater demand for an optimized method of producing MTBE. MTBE can also be made using isobutylene from the FCC and steam cracker processes but this method of getting isobutylene will not be sufficient to meet the isobutylene demand. Therefore, there will be more emphasis on producing MTBE starting with butanes and converting them to isobutylene in the future. There will also be more emphasis on using TAME in gasoline in addition to MTBE. In addition, there is a need to continue to develop processes which can make both the methanol and isobutylene needed to make MTBE entirely from natural gas.

8.6. Compressed Natural Gas (CNG) for Transportation Fuel

Compressed Natural Gas (CNG) has been used as a fuel in commercial fleets particularly for transit fleets. Development is under way for engines to handle this fuel and demonstrations of these engines using CNG have been carried out in businesses in various parts of the country.

The following section will give the economics and some of the advantages and disadvantages of using CNG as a transportation fuel.

Economics

The following economics table is for the production of CNG including the compressor, gas storage and gas line connection when converting a gasoline service station to fast-fill CNG refueling [109]. There is no universal pressure used in CNG but 3000 psig is typical. The product price is calculated using a delivered natural gas cost typical of Midwest and Middle Atlantic locations.

Plant Capacity, 10^6 Btu/Yr CNG	108274
Total Capital, 10^6 US\$ (USGC, December 1993)	0.372
	$\$/10^6$ Btu
Natural Gas Feed, $\$4.14/10^6$ Btu	4.14
Operating and Maintenance Costs	0.95
Capital Charges, 14.2% of Total Capital	0.61
CNG Product Price, $\$10^6$ Btu	6.25
CNG Product Price, \$/geg* (delivered)	0.73

*geg = gasoline equivalent gallons

Some Advantages and Disadvantages of CNG as a Transportation Fuel

There are both advantages and disadvantages of CNG as a transportation fuel [110]. The disadvantages include slightly higher vehicle cost, greater vehicle weight and higher refueling costs. However, the relatively low cost in terms of gasoline equivalent gallons (geg) will give lower operating costs. There is an advantage where transit loadings are moderate and where there is not a long operating range so that fuel capacity can be reduced.

CNG refueling stations are of two types, i.e., fast-fill and slow-fill. In the fast-fill approach, vehicles are filled in 2 to 5 minutes. With slow-fill the refueling requires up to 14 hours. The slow-fill method is less costly in terms of storage and compression.

8.7. Liquefied Natural Gas (LNG) for Transportation Fuel

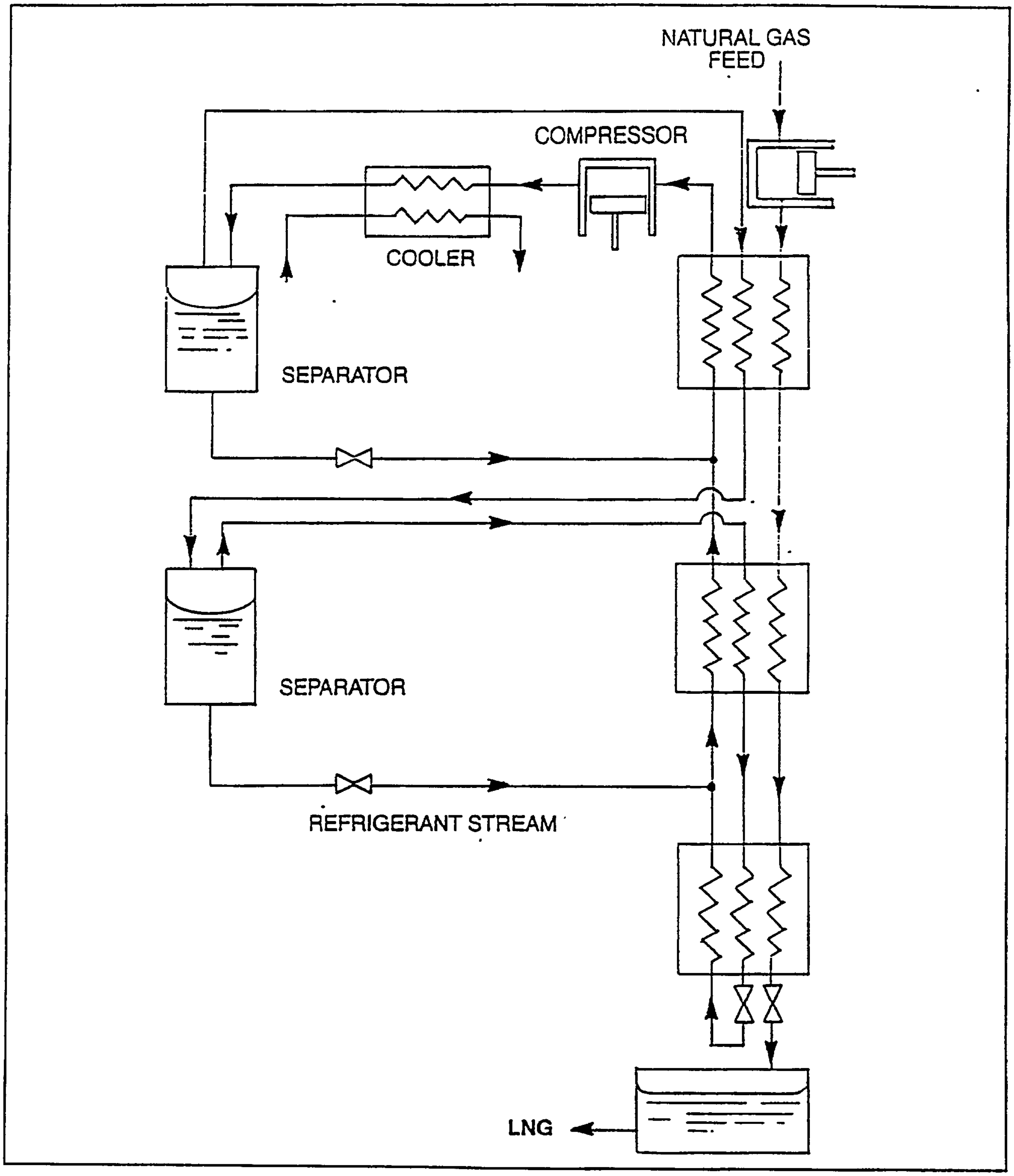
Liquefied Natural Gas (LNG) has been used as a form of import natural gas and for peak shaving in utility plants. It is now beginning to emerge as an alternative to CNG for buses, trucks and locomotives. Numerous LNG vehicle demonstration projects have been planned or are being carried out [110].

The following section will give a brief description of the process for producing LNG. In addition, a discussion of the commercialization of natural gas liquefaction will be provided.

Process Description

Natural gas is pretreated and is then send to liquefier equipment. The liquefied natural gas is stored and dispensed as needed. A flow diagram for the liquefaction of natural gas using technology licensed by Air Products and Chemicals, Incorporated is shown in Exhibit 8-8.

EXHIBIT 8-8
MIXED REFRIGERANT CASCADE SYSTEM USED FOR LIQUEFACTION OF NATURAL GAS



Economics

The following economics table is for the liquefaction of transportation fuels. The basis for this table is a report by Acurex for the Gas Research Institute on the use of liquefied natural gas (LNG) by railroads [111]. The product price is calculated using a delivered natural gas cost typical of Midwest and Middle Atlantic locations.

Plant Capacity, 10^6 Gallons/Yr CNG	168
Total Capital, 10^6 US$ (USGC, December 1993)	83.3
	$/Gallon LNG
Natural Gas Feed, $4.14/$10^6$ Btu	0.387
Operating and Maintenance Costs	0.020
Capital Charges, 14.2% of Total Capital	0.072
LNG Product Price, $/Gallon	0.537
LNG Product Price, $/geg*	0.85

*geg = gasoline equivalent gallons

Commercialization of Liquefied Natural Gas

Natural gas can be stored as high pressure gas (compressed natural gas, CNG), as a cryogenic liquid (liquefied natural gas, LNG) or through the absorption of methane on molecular sieves and activated carbon. The last method is in the research stage [111]. A primary advantage of LNG compared to CNG is the higher number of BTUs of LNG that can be put into a tank. Although both CNG and LNG have 21,500 Btu/lb, CNG has 30,000 Btu/gallon while LNG has 73,000 Btu/gallon. This is particularly advantageous for transportation of the gas over long distances. LNG could be supplied from a large liquefaction plant at a gas field or imported LNG could be trucked to a refueling facility. Imported LNG would have an advantage over domestic LNG if it could be liquefied in large facilities overseas from fields with relatively low wellhead gas prices. The Interagency Commission on Alternative Motor Fuels [112] believes that in the year 2000 remote gas prices from locations such as Trinidad, Australia and the Middle East could range from $0.79 to $1.65/MMBtu. This is considerably less than the $2.43/MMBTU which this report has been assuming for domestic natural gas.

HydrocarbonProcessing [112] shows that the following are licensors for LNG processes.

- Costain Oil, Gas & Process Ltd. has one installation.
- Air Products and Chemicals, Inc. has ten installations throughout the world.
- Technip and Snamprogetti SpA has fourteen plants operating.

The plants are designed for use in utilities for base load requirements from field gas or for peak shaving from pipeline gas. However, these same plant designs can be used for transportation fuels.

Summary

The process description and economics for the liquefaction of natural gas have been shown. The economics show that LNG is potentially competitive with other fuels for use in buses, locomotives and trucks both because of its relatively low cost, its environmental acceptability, its uniformity of composition and its amount of energy per unit volume. The technology for liquefaction is mature and is available from a variety of licensors. Facilities for refueling and vehicles adapted to use the fuels are not available except in a few places. Thus much capital expenditure is needed before this transportation fuel can be used. Even though LNG appears to have a number of advantages compared to CNG, CNG has the advantage of wider use and acceptance, and slightly better unit cost.