GAS, NATURAL

1. Introduction

Natural gas is a mixture of naturally occurring hydrocarbon and nonhydrocarbon gases found in porous geologic formations beneath the earth's surface (see HYDROCARBONS). Methane is a principal constituent and the mixture may contain higher hydrocarbons such as ethane, propane, butane, and pentane. Gases such as carbon dioxide (qv), nitrogen (qv), hydrogen sulfide, various mercaptans, and water vapor along with trace amounts of other inorganic and organic compounds can also be present. Natural gas is found in a variety of geological formations including sandstones, shales, and coals (see COAL; OIL SHALE).

Discussions of natural gas can involve the definitions listed in Table 1(1).

2. History

Natural gas and its combustion properties appear to have been known since early times (2). Some early temples of worship were located in areas where gas

Table 1. **Definitions Associated with Natural Gas**

Term	Definition
Associated gas	free natural gas in immediate contact, but not in solution, with crude oil in the reservoir.
Dissolved gas	natural gas in solution in crude oil in the reservoir.
Dry gas	gas where the water content has been reduced by a dehydration process or gas containing little or no hydrocarbons commercially recoverable as liquid product.
Liquefied natural gas (LNG)	natural gas that has been liquefied by reducing its temperature to 111 K at atmospheric pressure. It remains a liquid at 191 K and 4.64 MPa (673 psig).
Natural gas liquids (NGL)	a liquid hydrocarbon mixture which is gaseous at reservoir temperatures and pressures, but recover able by condensation or absorption (qv).
Nonassociated gas	free natural gas not in contact with, nor dissolved in, crude oil in the reservoir.
Sour gas	gas found in its natural state containing compounds of sulfur at concentrations exceeding levels for practical use because of corrosivity and toxicity.
Sweet gas	gas found in its natural state containing such small amounts of sulfur compounds that it can be used without purification with no deleterious effect on piping or equipment, and without the potential for health hazards.
Wet gas	unprocessed or partially processed natural gas produced from strata containing condensible hydrocarbons.

was seeping from the ground or from springs, and it is reported that Julius Caesar saw a phenomenon called the “burning spring” near Grenoble, France. Gas wells were drilled in Japan as early as 615 AD and in 900 AD the Chinese employed bamboo tubes to transport natural gas to their salt works, where the heat was used to evaporate water from salt brine. The existence of natural gas in the United States was reported by early settlers who observed gas seeps and columns of fire in the Ohio Valley and the Appalachian area in 1775 (3).

The serious, practical use of natural gas occurred in the United States in 1821 when residents in the village of Fredonia, New York drilled the first well and piped the gas through hollowed-out logs to nearby houses for lighting. The depth of the initial well was 8.2 m and its drilling followed the accidental ignition of a gas seepage at nearby Canadaway Creek. The Fredonia Gas, Light, and Waterworks Company was formed in 1865 as the first natural gas company in the United States. The first large-scale, industrial use of natural gas in the United States was in the steel (qv) and glass (qv) works of Pittsburgh, Pennsylvania, in 1883.

The early use of natural gas relied on its availability from small, local, shallow fields. This frequently created a chaotic cycle of events consisting of the discovery of a field, followed by the development of a local distribution system which, in turn, attracted new industries and other customers to the locale and often resulted in a rapid depletion of the reserves. After a few years, curtailment, followed by a total cessation of supplies, occurred.

Later, larger reservoirs of natural gas were located and produced. The development of long-distance pipeline systems was initiated (see PIPELINES), natural gas storage systems were established, and gas processing technology evolved which could separate water vapor, noxious constituents, inert gases, and condensible hydrocarbons from the raw natural gas flowing from the wells. This provided an integrated infrastructure that allowed effective marketing of the natural gas. Natural gas is now used throughout the industrialized world as a source of energy in residential, commercial, industrial, and electric utility generation applications. It also represents an important feedstock to many segments of the chemical industry. Because of its clean burning characteristics, availability, and competitive cost, the use of natural gas continues to increase on a worldwide basis.

3. Reserves

Since the mid-1970s world natural gas reserves have generally trended upward. As of January 1, 2003 proved world natural gas reserves were estimated at 5501 trillion cubic feet. This was 50 trillion cubic feet more than estimated for 2002. Most of the increase is attributed to developing countries where reserves increased by 37 trillion cubic feet. Natural gas reserves in industrialized countries also increased by 18 trillion cubic feet in the period 2002–2003 (4).

Most of the world’s natural gas reserves (71%) are located in the Middle East, Eastern Europe, and the former Soviet Union. Russia and Iran account for 45% of the world’s reserves. Table 2 gives world’s reserves by country as of January 2003 (5). The United States natural gas reserve summary is given in

Table 2. **World Natural Gas Reserves by Country as of January 1, 2003**[a]

Country	Reserves (trillion cubic feet)[b]	Percent of world total
World	*5,501*	*100.0*
Top 20 countries	*4,879*	*88.7*
Russia	1,680	30.5
Iran	812	14.8
Qatar	509	9.2
Saudi Arabia	224	4.1
United Arab Emirates	212	3.9
United States	183	3.3
Algeria	160	2.9
Venezuela	148	2.7
Nigeria	124	2.3
Iraq	110	2.0
Indonesia	93	1.7
Australia	90	1.6
Norway	77	1.4
Malaysia	75	1.4
Turkmenistan	71	1.3
Uzbekistan	66	1.2
Kazakhstan	65	1.2
Netherlands	62	1.1
Canada	60	1.1
Egypt	59	1.1
Rest of world	*622*	*11.3*

[a] Ref. 5.

[b] To convert ft^3 to m^3, multiply by 2.832×10^{-2}.

Table 3 (6). The largest expansion in 2002–2003 occurred in Western Europe, most attributed to Norway as a result of new gas finds.

United States proven reserves increased by 6 trillion cubic feet. Canada reported an increase of less than 1 trillion cubic feet and Mexico's reserves dropped by 21 trillion cubic feet due to a revision of estimates.

Table 3. **United States Natural Gas Reserves Summary, 10^9 ft^3**[a]

Data series	1998	1999	2000	2001	2002[b]
dry natural gas	164,041	167,406	177,427	183,460	186,940
natural gas, wet after lease separation	172,443	176,159	186,510	191,743	195,560
natural gas nonassociated, wet after lease separation	141,783	144,744	156,677	161,921	166,020
natural gas associated-dissolved, wet after lease separation	30,660	31,415	29,833	29,824	29,540
natural gas liquids, $\times 10^6$ barrels	7,524	7,906	8,345	7,993	7,990

[a] Ref. 6, as of December 31, updated Jan. 30, 2004.

[b] Rounded.

Despite high rates of increase in natural gas consumption, most regional reserves-to-production ratios have remained high. Worldwide reserves-to-production ratio is estimated at 61.9 years.

The U.S. Geological Survey has reported that a significant volume of natural gas remains to be discovered. Estimate of undiscovered gas in 4839 trillion cubic feet. Stranded reserves (too remote) are estimated at 3000 trillion cubic feet.

More than one-half of the mean undiscovered gas estimate is expected to come from the former Soviet Union, the Middle East and North Africa. One third is expected to come from North, Central, and South America.

The United States has produced more than 40% of its total estimate gas resource and carries less than 10% reserves. Outside the U.S., the world has produced less than 10% of its resources and carries more than 30% as remaining reserves.

The results of research and development programs now in progress should impact the future availability and use of natural gas. In all industrialized countries, programs have been underway to improve the cost effectiveness of activities associated with natural gas. These programs are supported financially by funds from individual governments, funds derived from corporate activities, or monies collected from users of natural gas. The International Gas Union and the Gas Research Institute (7) both provide forums for the development of coordinated programs. These programs cover activities associated with exploration, production, processing, transmission, stroage, and use of natural gas.

The development of new techniques and diagnostic tools has increased the probability of locating specific gas-rich formations. Innovations include (*1*) 3-D and 4-D seismic imaging. 4-D imaging shows how subsurface characteristics change over time. (*2*) Use of sand propants and liquid carbon dioxide to fracture formations so natural gas can flow more freely. (*3*) Coiled tubing is a long flexible coiled-pipe string that reduces cost and provides a smaller footprint. Less drilling is needed and a faster set up is possible. There is also less environmental impact. (*4*) New measurement techniques allow for collection of data from the bottom of the well as drilling is in progress. (*5*) Offshore deep water rigs with dynamic positioning devices and navigation systems are improvements (4).

The more effective delivery of natural gas is being realized by the use of computerized operation centers that allow rapid responses to the variations in gas demand. Automated valves, more precise measuring systems, and high speed communication networks make it possible to closely monitor and manage the transmission and delivery of natural gas. This translates into improved service and cost effectiveness.

In the United States, the development of high performance, gas-fueled cogeneration systems that simultaneously generate electricity and produce steam has impacted gas use in both the commercial and industrial sectors (see POWER GENERATION). The phosphoric acid, natural gas-based fuel cell, a cogeneration technology which produces both electricity and heat electrochemically, is in the early stages of commercialization, whereas advanced fuel cells based on the use of molten carbonates and solid oxides are in the later stages of development. These technologies are expected to have broad applications in the commercial, industrial, and electricity-generating sectors of the natural gas market.

Combined-cycle power generation systems using natural gas and advanced gas turbine technology offer the potential for increasing power generation cycle efficiencies from 33% with conventional boilers to 48%. Opportunities are projected to retrofit existing power plants and to use the technology in new plant construction. Natural gas can also be used in co-firing and reburn modes to help coal-based electric power generation plants achieve lower emissions of sulfur dioxide and nitrogen oxides while protecting the investments in the original coal units. Natural gas can also be co-fired with solid wastes, providing for the more effective destruction of these materials, easing potential pollution problems, and assisting in converting the energy content of solid wastes to a more useable form (see FUELS FROM WASTE).

Technologies are being evaluated which could expand the opportunities for the use of natural gas in the general area of space conditioning. A heat pump being developed for residential applications uses a natural gas-fueled engine to drive the compressor in the refrigeration unit (8). On a larger scale, an advanced natural gas-fired engine has been developed and integrated with a compressor to form the basis for engine-driven chillers. Engine-driven chillers having capacities of 150 t are being marketed. The use of natural gas to regenerate desiccant-based dehumidifiers which could be used in individual family dwellings is also being explored. Similar technology has been successfully developed for larger-scale applications in the commercial market (9).

The Natural Gas Vehicle Coalition has reported that as of May 2003 there were 130,000 natural gas vehicles on United States' roads and 2×10^6 worldwide. There are 1300 fueling stations in the United States. Fifty manufacturers produce 150 models and about 22% of bus orders are for natural gas vehicles (10).

4. Properties

The composition of natural gas at the wellhead depends on the characteristics of the reservoir and is highly variable with respect to both the constituents present and the concentrations of these constituents. Compositions of various natural gases are given in Table 4.

Argon, oxygen, helium, hydrogen, organic sulfides, organic mercaptans, and organic disulfides may also be present and, using highly sensitive analytical instrumentation, trace concentrations of a variety of other constituents are being detected (see TRACE AND RESIDUE ANALYSIS). Mercury has been found in some wellhead gases at concentrations based on weight ranging from 1 to 230 ppm and arsenic compounds (qv) have been detected at the ppb level in gases obtained from a formation in New Mexico (U.S.). Arsines have been found in gases from West Virginia (U.S.) and gases produced from offshore Louisiana (U.S.) wells (12).

The physical properties of the principal constituents of natural gas are listed in Table 5. These gases are odorless, but for safety reasons, natural gas is odorized before distribution to provide a distinct odor to warn users of possible gas leaks in equipment. Sulfur-containing compounds such as organic mercaptans, aliphatic sulfides, and cyclic sulfur compounds are effective odorants

Table 4. **Wellhead Compositions of North American Natural Gases**[a]

Parameter	Rio Arriba County, N. Mex.	Terrell County, Tex.	Stanton County, Kans.	San Juan County, N. Mex.	Olds Field, Alberta, Canada	Cliffside Field, Amarillo, Tex.[b]
component, mol%						
methane	96.91	45.64	67.56	77.28	52.34	65.8
ethane	1.33	0.21	6.23	11.18	0.41	3.8
propane	0.19		3.18	5.83	0.14	1.7
butanes	0.05		1.42	2.34	0.16	0.8
pentanes and heavier	0.02		0.04	1.18	0.41	0.5
carbon dioxide	0.82	53.93	0.07	0.80	8.22	0.0
hydrogen sulfide		0.01			35.79	0.0
nitrogen	0.68	0.21	21.14	1.39	2.53	25.6
total sulfur, mg/m^3	0	0.27	0	0	984	
classification						
wet				x		
lean	x	x	x		x	x
sweet	x		x	x		x
sour		x			x	
gross heating value,[c] MJ/m^3	37.6	17.3	34.9	46.8	30.0	30.7
specific gravity	0.574	1.077	0.733	0.741	0.882	0.711

[a] Ref. 11.

[b] Also contains 1.8 mol% helium.

[c] To convert MJ/m^3 to Btu/ft^3, multiply by 26.86.

at low concentrations and are added to natural gas at levels ranging from 4 to 24 mg/m^3.

The pressure–volume–temperature (PVT) behavior of many natural gas mixtures can be represented over wide ranges of temperatures and pressures by the relationship

$$PV = ZnRT$$

where P is the absolute pressure; V, the volume; Z, the compressibility factor for the mixture; n, the number of moles of gas; R, the universal gas constant; and T, the temperature in Kelvin. When natural gas contains high concentrations of H_2S and CO_2, along with water vapor, the PVT behavior deviates from the conventional compressibility relationship. The PVT properties of these mixtures can be described using empirically determined pseudocritical temperature and pressure adjustment factors which are a function of the total acid gas concentration and the H_2S to CO_2 ratio of the acid gases (13). More complex relationships such as the Benedict-Webb-Rubin relationship (BWR), an eight-constant parameter equation, provide a good representation of both liquid and vapor properties for mixtures containing nonpolar gases and light hydrocarbons. Modifications of the BWR equation extend the basic BWR approach to more of the complex mixtures encountered during the production and processing of natural gas (14) (see ENGINEERING, CHEMICAL DATA CORRELATION).

Table 5. **Physical Constants of Natural Gas Constituents**

Compound	CAS Registry number	Formula	Mol wt	Boiling point, K[a]	Critical pressure, kPa[b]	Critical temperature, K	Specific gravity, liquid[c]	Gross heating value,[d] MJ/m^3
methane	[74-82-8]	CH_4	16.043	111.64	4595	190.56	(0.3)[e]	37.57
ethane	[74-84-0]	C_2H_6	30.070	184.55	4871	305.34	0.3562[f]	65.83
propane	[74-98-6]	C_3H_8	44.097	231.08	4247	369.86	0.5070[f]	93.60
2-butane	[75-28-5]	C_4H_{10}	58.123	261.37	3640	407.86	0.5629[f]	120.98
n-butane	[106-97-8]	C_4H_{10}	58.123	272.65	3796	425.17	0.5840[f]	121.37
2-pentane	[78-78-4]	C_5H_{12}	72.150	301.00	3381	460.44	0.6247	148.84
n-pentane	[109-66-0]	C_5H_{12}	72.150	309.23	3369	469.71	0.6311	149.14
n-hexane	[110-54-3]	C_6H_{14}	86.177	341.89	3012	507.38	0.6638	176.93
n-heptane	[142-82-5]	C_7H_{16}	100.204	371.58	2736	540.21	0.6682	204.71
n-octane	[111-65-9]	C_8H_{18}	114.231	398.83	2487	568.83	0.7070	232.47
n-decane	[124-18-5]	$C_{10}H_{22}$	142.285	447.32	2104	617.60	0.7342	288.05
nitrogen	[7727-37-9]	N_2	28.013	77.35	3400	126.21	0.8094[g]	
oxygen	[7782-44-7]	O_2	31.999	90.20	5043	154.59	1.1421[g]	
carbon dioxide	[124-38-9]	CO_2	44.010	194.68[h]	7384	304.22	0.8180[f]	
hydrogen sulfide	[7783-06-4]	H_2S	34.076	212.88	8963	373.41	0.8014[f]	23.70
water	[7732-18-5]	H_2O	18.015	373.16	22055	647.14	1.0000	
air			28.963	78.83	3771	132.43	0.8748[g]	

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[a] At atmospheric pressure, 101.3 kPa (1 atm).

[b] To convert kPa to psi, multiply by 0.145.

[c] At 288.72 K.

[d] At 288.72 K, 101.325 kPa (1 atm).

[e] Above critical point, estimated or extrapolated.

[f] At saturation pressure, 288.72 K.

[g] At normal boiling point.

[h] Denotes sublimation temperature.

5. Production

Natural gas is produced from reservoirs containing both oil and gas (associated gas) and from nonassociated reservoirs holding only gas. These reservoirs may be relatively shallow and require wells drilled to depths of a few hundred meters. However, production is also being realized from reservoirs located at substantial depths requiring wells drilled to depths in excess of 6100 m. Production takes place both at onshore installations and on offshore platforms which service wells drilled to provide access to reservoirs located below the floor of the ocean. Offshore facilities are operating in the continental shelf regions and shallow coastal waters of many parts of the world including the United States, Canada, Australia, Brazil, Norway, the North Sea, and the Persian Gulf. A gas field located in the Norwegian North Sea having recoverable reserves of 8000 m^3 had a water depth of 100 m.

Production data indicate that dry gas production increased 3.7% in 2000. Production data and import data for Canada and Mexico are given in Table 6.

U.S. production of natural gas is expected to increase more slowly than consumption over the period 2001–2025 from 19.3 trillion cubic feet (TCF) in 2000 to 29.0 TCF in 2020. To produce 29.0 TCF in 2020, the number of U.S. lower 48 states wells drilled will have to increase from 10,500 in 1999 to 24,000 in 2020.

Uncertainty with regard to U.S. natural gas reserves have always been an issue in projecting production. The U.S. Geological Survey tends to be cautious because it is difficult to estimate reserves not actually measured. Natural Gas Organizations have stated that perhaps with all the new innovations reported that fewer wells will be needed. Drilling wastes have decreased by 148×10^6 barrels. Drilling footprints have decreased by 70%, which is good for sensitive areas. Modular rigs and slimhole drilling have reduced the size and weight of rigs by 78% (4).

Natural gas production is affected by prices and price controls. Consumption fell in 1997–1998 because of warm winters. In 1999 gas rig activity dropped to 362 units from 657 in 1997. After April 1999, gas rig activity strengthened to yield 854 units in 2000. In early 2001, 900 units were in operation. Gas rig activity is assumed to increase with underlying strength in demand. Price incentives for higher competition rates are expected.

Imports are expected to grow by 17% in 2020. Most of the imports will come from Canada. The average natural gas wellhead price in 2000–2001 was estimated to be 144% higher than the previous year. Dynamics show that wellhead prices will not be returning to $\$2/10^6$ Btu. Ninety percent of all additions to the electric power sector will use natural gas as a primary fuel.

6. Processing

Because of the wide variation in the composition of natural gas as it is recovered at the wellhead and because natural gas can be used over a wide range of hydrocarbon contents, any specification for natural gas is usually broadly defined. However, the natural gas obtained at the wellhead usually undergoes some

Table 6. **Natural Gas Production and Imports, Trillion Cubic Feet/year**[a]

	2001	2002	2003	2004	2005	2006	2010	2015	2020	2025	2002–2025
Production											
dry gas	19.70	19.05	19.57	19.51	19.58	19.66	20.50	21.62	23.79	23.99	1.0%
production[b]	0.09	0.08	0.08	0.08	0.10	0.10	0.10	0.10	0.10	0.10	0.8%
supplemental natural gas[c]											
Net Imports	3.60	3.49	3.51	3.60	3.87	4.28	5.50	6.24	6.47	7.24	3.2%
Canada	3.56	3.59	3.40	3.50	3.46	3.42	3.68	3.17	2.51	2.56	−1.4%
Mexico	−0.13	−0.26	−0.31	−0.42	−0.43	−0.45	−0.34	−0.15	−0.18	−0.12	−3.2%
liquefied natural gas	0.17	0.17	0.43	0.52	0.84	1.31	2.16	3.22	30.36	4.80	15.8%
Total supply	23.39	22.62	23.15	23.19	23.54	24.04	26.09	27.95	30.36	31.33	1.4%

[a] Ref. 6.

[b] Marketed production (wet) minus extraction losses.

[c] Synthetic natural gas, propane air, coke oven gas, refinery gas, biomass gas, air injected for Btu stabilization, and manufactured gas commingled and distributed with natural gas.

Table 7. **United States Total Natural Gas Plant Processing**[a]

Data series	1998	1999	2000	2001	2002
natural gas processed, 10^6 ft^3	16,557,779	16,662,873	16,998,687	16,511,427	
total liquids extracted, 10^3 barrels	668,011	686,862	721,895	682,873	
extraction loss, 10^6 ft^3	937,784	972,616	1,015,531	953,984	956,990

[a] Ref. 6, last update March 8, 2004.

type of treatment or processing prior to its use for safety, economic, or system and material compatibility reasons.

Table 7 gives U.S. total natural gas processing for 1998–2002 (6).

6.1. Dehydration. Produced gas is usually saturated with water vapor at the wellhead temperature and pressure. Generally, these water-vapor levels are reduced to concentrations no greater than 112 mg/m^3 (7 lbs/10^6 ft^3) gas to prevent condensation during transmission in high pressure pipelines and to reduce the possibility of corrosion. If the gas undergoes additional processing in a cryogenic plant to remove inert gases such as nitrogen or helium, the water-vapor levels must be reduced to a dew point corresponding to 172 K.

Usually the process selected for dehydration involves either liquid or solid desiccants (qv). Whereas solid desiccants, such as alumina, silica gel, or molecular sieves (qv), offer advantages of lower dew points and less susceptibility to corrosion, liquid systems based on glycols are frequently selected because of lower construction costs, lower operating costs, and greater economic effectiveness at larger scales. Glycol units can dehydrate natural gas to moisture contents of 8 mg/m^3 and, with the addition of other units, can achieve dehydration to a level of 4 mg/m^3. Triethylene glycol is frequently the liquid desiccant of choice. Tetraethylene glycol is also used.

Dehydration may also be accomplished by expansion refrigeration which utilizes the Joule-Thompson effect. This technique is normally used when the prime objective is hydrocarbon recovery.

Anhydrous calcium chloride absorbs water to a capacity of 3.5 kg/kg of calcium chloride and forms a nonreuseable brine. This technique is best suited for remote applications where modest dew point depressions are required and gas processing volumes are small.

The lower molecular weight hydrocarbon constituents of natural gas can react with liquid or free water to form crystalline solids called hydrates (12). These reactions can take place under many of the conditions associated with the recovery and movement of water-saturated natural gas. In solid hydrates, water and the hydrocarbon molecules interact through hydrogen bonding to form a stable cage-like structure known as a clathrate. These clathrates typically consist of 90 wt% water, the remaining 10 wt% being made up of methane, ethane, propane, isobutane, *n*-butane, nitrogen, carbon dioxide, and hydrogen sulfide. Hydrates involving only water and *n*-butane do not form; however, *n*-butane participates in hydrate formation in a mixture of other gases. Hydrate formation is prevented by reducing the water content of the gas below concentrations where hydrates form, by heating flow lines, or by the use of chemical additives such as ethylene glycol, diethylene glycol, or methanol (qv) to depress the temperature at which the hydrates or ice forms (see GLYCOLS; INCLUSION COMPOUNDS).

6.2. Natural Gas Liquids. Natural gases containing high concentrations of the higher hydrocarbons are processed both to reduce the potential for condensation of these higher molecular-weight compounds during transmission and subsequent use, and to recover the natural gas liquid (NGL) products which can be marketed in both the fuel and petrochemical feedstock market (see FEEDSTOCKS, PETROCHEMICAL). Natural gases are characterized with respect to the higher (ethane and above) hydrocarbon content as lean, moderately rich, or very rich. Lean gases have higher hydrocarbon contents that are less than 334 mL/m^3; very rich gases have hydrocarbon liquid contents greater than 668 mL/m^3. In 2000, 5.62×10^8 L of natural gas liquids were produced. It is expected, however, that gas processing will increase and the production of NGLs will increase also (15).

The market value of natural gas liquids is highly volatile and historically has been weakly related to the world price of crude oil. During the 1980s, the market value of natural gas liquids ranged from approximately 60% of the price of crude to 73% (16). In a 10-year interval, several fluctuations occurred in the natural gas liquid market. Because of the variability of the natural gas liquid market, the NGL recovery plants need to have flexibility. Natural gas liquid products compete in the following markets: ethane; propane; a liquefied petroleum gas (LPG); a C-3/C-4 mix; and *n*-butane all compete as petrochemical feedstocks. Propane and LPG are also used as industrial and domestic fuels, whereas 2-butane and natural gasoline, consisting of C-5 and heavier hydrocarbons, are used as refinery feedstocks.

Natural gas liquids are recovered from natural gas using condensation processes, absorption (qv) processes employing hydrocarbon liquids similar to gasoline or kerosene as the absorber oil, or solid-bed adsorption (qv) processes using adsorbants such as silica, molecular sieves, or activated charcoal. For condensation processes, cooling can be provided by refrigeration units which frequently use vapor-compression cycles with propane as the refrigerant or by using the Joule-Thompson expansion to lower the temperature of the feed gas, or through the use of expansion turbines which both reduce the temperature of the gas and derive work for use at other points in the recovery and separation process.

The condensation processes are generally favored for recovering natural gas liquids. If the feed gas is very rich in liquids, plants based on simple refrigeration cycles may be used. When the liquid content of the feed gas is relatively low, use of the expansion turbine may be favored. For conditions providing a very high inlet pressure, the Joule-Thompson expansion may be more economical. Low inlet pressures generally favor an expander plant or straight-refrigeration. Very low flow rates require a relatively simple process and may favor an automatically operated Joule-Thompson unit.

Absorber oil units offer the advantage that liquids can be removed at the expense of only a small (34–69 kPa (4.9–10.0 psi)) pressure loss in the absorption column. If the feed gas is available at pipeline pressure, then little if any recompression is required to introduce the processed natural gas into the transmission system. However, the absorption and subsequent absorber-oil regeneration process tends to be complex, favoring the simpler, more efficient expander plants. Separations using solid desiccants are energy-intensive because of the bed regeneration requirements. This process option is generally considered only in special situations such as hydrocarbon dew point control in remote locations.

6.3. Acid Gas Constituents. Hydrogen sulfide is both highly toxic and acidic enough to precipitate corrosion. Natural gases containing hydrogen sulfide are subjected to processing to reduce H_2S concentrations to less than 4 ppmv, or approximately 5.7 mg/m^3. Carbon dioxide, like hydrogen sulfide, forms acidic solutions in the presence of water and is also referred to as an acid gas. However, it is not toxic, and processing requirements to reduce CO_2 levels are less severe than those for H_2S. Carbon dioxide concentrations of 1 to 2% are usually tolerated. At these concentrations, the expenditure of energy to transport the inert constituent through pipelines is minimal, and the extent of the corrosion of materials used in transmission systems is acceptable (see CORROSION AND CORROSION CONTROL).

There are more than 30 processes available for removing the acid gas constituents such as hydrogen sulfide, carbon dioxide, and other organic sulfur compounds, ie, carbonyl sulfide, organic mercaptans, and disulfides (12,13). Because of the toxicity of hydrogen sulfide, requirements for removal are severe. In the United States, natural gas is almost always processed to provide hydrogen sulfide levels not greater than 4 mg/m^3 and the specification can be as low as 1 mg/m^3 in some countries. Carbon dioxide levels of 2 to 3% are usually acceptable and in many instances it may be necessary to treat the gas for other sulfur-containing molecules. When the CO_2 content exceeds specifications, or when cryogenic processing follows, removal of carbon dioxide to levels of 100 ppmv can be achieved.

The process options reflect the broad range of compositions and gas volumes that must be processed. Both batch processes and continuous processes are used. Batch processes are used when the daily production of sulfur is small and of the order of 10 kg. When the daily sulfur production is higher, of the order of 45 kg, continuous processes are usually more economical. Using batch processes, regeneration of the absorbant or adsorbant is carried out in the primary reactor. Using continuous processes, absorption of the acid gases occurs in one vessel and acid gas recovery and solvent regeneration occur in a separate reactor.

Iron sponge is the oldest and most widely used batch process for removing sulfur compounds from natural gas. Iron sponge consists of wood chips or shavings impregnated with ferric oxide and sodium hydroxide. The chips are placed in a vertical contact tower where the hydrogen sulfide in the natural gas reacts with the iron oxide, forming ferric sulfide. Mercaptans also react with the iron oxide to form ferric mercaptides. When the chips are saturated, ie, no longer able to react with hydrogen sulfide, the addition of oxygen to the spent bed converts the iron sulfide back to iron oxide and elemental sulfur. The mercaptides are converted to iron oxide and a disulfide. These beds eventually deteriorate and must be replaced. The spent chips are considered toxic and disposal must be done in an environmentally acceptable manner. Other batch processes involve the use of an iron oxide slurry, zinc oxide particles suspended in a water solution of zinc acetate, or aqueous solutions of sodium nitrite.

There are numerous chemical and physical solvents available for use in continuous acid gas removal processes (12). The chemical absorbants include aqueous solutions of organic amines such as monoethanolamine, diethanolamine, triethanolamine, diglycolamine, or methyldiethanolamine. These solutions, which can be regenerated, react chemically with the acid gases and can be used to remove large quantities of hydrogen sulfide and carbon dioxide. Physical solvents are organic liquids that absorb carbon dioxide and hydrogen sulfide into solution at high pressures and ambient or low temperature. When physical solvents are used, the acid gases are recovered and the solvents regenerated by flashing at low pressures. The energy required to regenerate physical solvents is less than the regeneration requirements for chemical solvents. Physical solvents include methanol, mixtures of dimethylethers of polyethylene glycols, propylene carbonate, sulfolane, 1-acetylmorpholine, and other complex organic molecules. Solvent systems can include solutions of physical solvents and more chemically reactive materials. Solutions of potassium carbonate have been employed, and solutions involving metal–organic complexes are now being used in some small-scale applications. These metal–organic-complex-based solvents result in the direct oxidation of hydrogen sulfide to elemental sulfur as part of the regeneration process.

Adsorption systems employing molecular sieves are available for feed gases having low acid gas concentrations. Another option is based on the use of polymeric, semipermeable membranes which rely on the higher solubilities and diffusion rates of carbon dioxide and hydrogen sulfide in the polymeric material relative to methane for membrane selectivity and separation of the various constituents. Membrane units have been designed that are effective at small and medium flow rates for the bulk removal of carbon dioxide.

Whereas the list of process options for gas sweetening is extensive, the batch processes and the amine processes are used for over 90% of the wellhead applications. The early amine processes were based on monoethanolamine [141-43-5] (MEA) as the absorbant. In many applications, the use of diethanolamine [111-42-2] (DEA) is frequently favored because of its lower heats of reaction, reduced corrosivity, and ability to be used at higher concentrations. These characteristics translate into process advantages which include higher acid gas loadings in the solvent, lower energy requirements for solvent regeneration, and lower solvent recirculation rates.

Subsequent to separating and recovering the acid gases from the raw natural gases, additional processing is undertaken to convert the hydrogen sulfide to elemental sulfur. A number of processes have been developed to accomplish this conversion, the process known as the Claus process being the most widely used in the natural gas industry. This process provides the basis for producing sulfur from acid gas streams having hydrogen sulfide concentrations ranging from approximately 20 to 100%. Economic considerations generally limit its application to plants that have a production capacity of sulfur greater than 30 t/d. Whereas there are several variations of the Claus process to accommodate specific feed stream conditions, the fundamental element is a reaction furnace operating at temperatures of approximately 1273 K where one-third of the hydrogen sulfide is burned with air (or oxygen-enriched air) to produce sulfur dioxide and water. A shift reaction then takes place between the remaining hydrogen sulfide and the sulfur dioxide to produce additional water and elemental sulfur which can be recovered. The reactor furnace is reported to achieve sulfur yields as high as 90% directly. Conversion of the remaining hydrogen sulfide to sulfur is accomplished in lower temperature catalytic reactors (see SULFUR REMOVAL AND RECOVERY).

6.4. Nitrogen. Natural gases containing nitrogen are processed to reduce the nitrogen levels to concentrations that do not detract significantly from the energy level of the gas and do not require the expenditure of excessive amounts of energy during transmission of the gas.

The separation of nitrogen from natural gas relies on the differences between the boiling points of nitrogen (77.4 K) and methane (91.7 K) and involves the cryogenic distillation of a feed stream that has been preconditioned to very low levels of carbon dioxide, water vapor, and other constituents that would form solids at the low processing temperatures.

7. Specifications

Whereas there is no universally accepted specification for marketed natural gas, standards addressed in the United States are listed in Table 8 (12). In addition to these specifications, the combustion behavior of natural gases is frequently characterized by several parameters that aid in assessing the influence of compositional variations on the performance of a gas burner or burner configuration. The parameters of flash-back and blow-off limits help to define the operational limits of a burner with respect to flow rates. The yellow-tip index helps to define the conditions under which components of the natural gas do not undergo complete combustion, and the characteristic blue flame of natural gas burners begins to show yellow at the flame tip. These three parameters are determined experimentally using standardized test methods. An index referred to as the Wobbe Number is indicative of the combustion energy being delivered to a burner at a constant pressure drop across the burner. The Wobbe Number, defined as the square root of the ratio of the volumetric heat of combustion of the gas to the specific gravity of the gas, can be calculated directly from a knowledge of the gas composition.

Table 8. **Natural Gas Pipeline Specifications**[a]

Characteristic	Specification	Test method[b]
water content, mg/m^3	64–112	ASTM (1986) D1142
hydrogen sulfide, mg/m^3	5.7	GPA (1968) Std. 2265
gross heating value,[c] MJ/m^3	35.4	GPA (1986) Std. 2172
hydrocarbon dew point at 5.5 MPa,[d] K	264.9	ASTM (1986) D1142
mercaptan content, mg/m^3	4.6	GPA (1968) Std. 2265
total sulfur, mg/m^3	23–114	ASTM (1980) D1072
carbon dioxide, mol%	1–3	GPA (1990) Std. 2261
oxygen, mol%	0–0.4	GPA (1990) Std. 2261

[a] Gas must be commercially free of sand, dust, gums, and free liquid. Delivery temperature, 322.16 K; delivery pressure, 4.83 MPa. Ref. 12.

[b] ASTM = American Society for Testing Materials; GPA = Gas Processors' Association.

[c] To convert MJ/m^3, multiply by 26.86.

[d] To convert MPa to psi, multiply by 145.

Two gases characterized by the same Wobbe Number deliver approximately the same amount of chemical energy to the combustion zone of a burner without the need for adjustments in the pressure drop or orifice size of the burner even though the volumetric heating values and the specific gravities of the gases are different. For existing burners having fixed piping and dimensions, these performance indexes become important as variations in the composition of the gas being delivered are encountered. These parameters must also be considered during the development of new burner hardware.

8. Transmission and Storage

As exploration and production activities have expanded both the natural gas resource base and the worldwide proven reserves, long-distance gas transmission pipelines have been constructed to link these resources to the industrialized areas and population centers of the world. The availability of high tensile-strength steel pipe and the development of techniques to construct, weld, and lay large diameter high pressure pipelines make it possible to economically transport natural gas to the marketplace. These transmission systems, coupled with localized, lower pressure distribution networks, bring gas to large segments of the world. Long-distance pipelines transport gas from the large fields in Siberia and the Ural Mountains of the Confederation of Independent States to both eastern and central Europe. Pipelines across the Mediterranean Sea connect the gas fields of North Africa with the European market. The European market is also served by long-distance pipelines transporting gas from the gas fields in the Middle East. Depending on the availability of the resource and the anticipated market volume, these long-distance transmission lines have used pipes having diameters ranging from approximately 36 to 142 cm (2,12).

The U.S. natural gas pipeline network has grown since 1990 with more than 20 billion cubic feet in 2000 (an increase of 27%). The networks have become more interconnected and routings more complex. New market centers, such as storage facilities, have become further integrated into the pipeline grid. System reliability has improved. Except for extreme weather or isolated outages, there has been no sustained interruption since the 1970s.

Increased use in the U.S. has resulted in pressure to produce more pipelines. More than 60 natural gas pipelines have been completed and placed into service during 1999–2000. Since 1996 new pipeline capacities have grown by 5 billion cubic feet/day annually. Annual expenditures have exceeded $1.4 billion in most years. In 1999, the largest share of expenditures ($1.1 billion) was for projects terminating in the U.S. Northeast. In 2000, the Midwest accounted for expenditures of $1.8 billion.

A major growth expansion of pipelines is in the import/export area. Much of the pipeline construction has been focused on Canadian imports in the last few years.

A large factor in much of the recent installations of natural gas pipelines has been the construction of many new gas-fired electric power plants and cogeneration of electricity by industrial and other large users of natural gas.

Table 9. **United States Total Natural Gas Stroage Activity, 10^6 ft^{3a}**

Data series	07/03	08/03	09/03	10/03	11/03[b]
gas in underground storage	6,451,370	6,759,583	7,170,904	7,456,965	7,343,060
base gas	4,322,630	4,324,366	4,327,988	4,326,753	4,304,640
working gas	2,128,740	2,435,218	2,842,916	3,130,212	3,038,420
injections	425,619	370,695	441,204	343,370	141,570
withdrawals	64,130	61,860	30,638	59,400	228,060
net withdrawals	−361,489	−308,835	−410,566	−283,970	86,490

[a] Ref. 6, last update March 8, 2004.
[b] Rounded.

The quickest and least expensive way of providing additional gas transportation capacity is to increase compression in the system. Looping (integrating a parallel pipelines with all or portion of the system) or a combination of looping and compression would be the least expensive alternatives.

U.S. companies have announced 88 new pipeline project covering the next few years. It is expected that an additional 20.8 billion cubic feet/day of capacity will be added to the network.

Underground storage is a vital part of natural gas infrastructure. The ability to store natural gas ensures supply in low and high usage periods. Storage supplements pipelines and provides an alternative source of gas in case of interruptions. Storage also allows daily balancing in the pipelines. Storage is also being used to take advantage of expected price movements and future market trades.

Natural gas can be stored in many ways. The most common is in underground geologic formations. These locations are largely former producing fields now considered depleted. Two types of underground storage facilities are aquifer reservoirs and salt caverns. Storage and withdrawal rates can change for different geologic formations. Salt domes can be emptied in 2–4 weeks and can be refilled in 4–8 weeks. Depleted fields usually have more storage capacity than salt deposits. Most depleted fields are designed to provide for withdrawals during the heating season (151 days) and for refilling in the non-heating period (214 days). Table 9 give U.S. storage activity for a five-month period in 2003 as an example.

Liquefied natural gas (LNG) also plays a large role in both the transportation and storage of natural gas. At a pressure of 101.3 kPa (1 atm), methane can be liquefied by reducing the temperature to about −161°C. When in the liquid form, methane occupies approximately 1/600 of the space occupied by gaseous methane at normal temperature and pressure. In spite of the very low temperature of the liquid, LNG offers advantages for both shipping and storing natural gas.

9. Economic Aspects

Natural gas is expected to be the fastest growing component of world primary energy. Consumption of natural gas is expected to increase by the rate of 2.8%

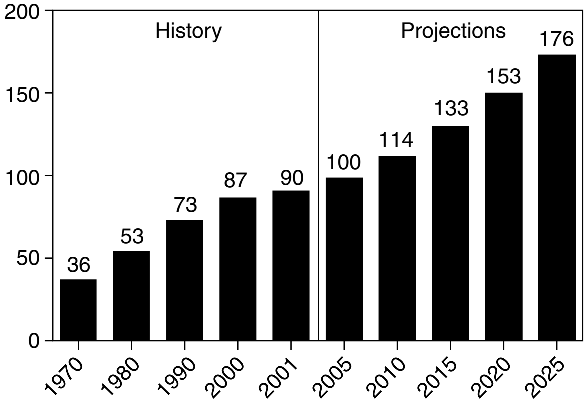

Fig. 1. World natural gas consumption, 1970–2025, in trillion cubic feet (17).

annually through the year 2025. This is compared to the expected growth rate of oil at 1.8% and coal at 1.5%. The developing world will show the largest growth and is expected demand will increase by 3.9%. Industrialized nations are also projected to increase their reliance on natural gas (see Figures 1 and 2) (17).

The United States consumed about 1531 trillion cubic feet of natural gas for the period January to October 2003. The United States accounts for 66% of total North American increment in gas consumption.

Table 6 gives United States gas imports for the period starting 2001 and estimations through the year 2005. For the U.S., international trade means trade with Canada and Mexico.

In the near term, natural gas prices are likely to be higher than projected in 2001. Prices for natural gas reflect the impact of weather systems on the heating/cooling seasons. An expected surge in drilling for natural gas should result in a lowering of prices. Gas-generating technologies should be the preferred choice

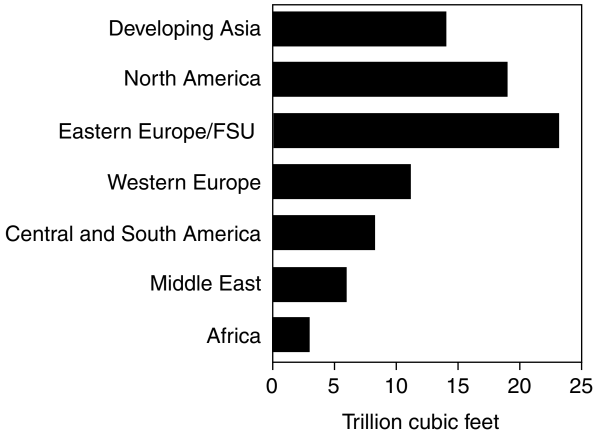

Fig. 2. Increase in natural gas consumption by region, 2001–2025 (17). FSU = Former Soviet Union.

Table 10. **U.S. Total Natural Gas Prices, \$$10^3$ ft^{3a}**

Data series	06/03	07/03	08/03	09/03[b]
wellhead price	5.35	4.91	4.72	4.58
imports price	5.76	5.13	4.13	5.01
exports price	5.94	5.31	4.9	5
city gate price	6.4	5.82	5.44	5.57
residential price	11.8	12.57	12.76	12.19
commercial price	8.87	8.75	8.29	8.33
percentage of total commercial deliveries	72.8	70.8	72.6	72.7
industrial price	6.37	5.64	5.23	5.31
percentage of total industrial deliveries	19.9	25.4	23.1	22.7
electric utility price	6.38	5.75	5.4	NA

[a] Ref. 6, last update Jan. 30, 2004.
[b] NA = not available.

after the year 2010. U.S. total natural gas prices for several months in 2003 are given as a sample in Table 10 (6).

10. Uses

10.1. Fuel.

Natural gas is used as a primary fuel and source of heat energy throughout the industrialized countries for a broad range of residential, commercial, and industrial applications. The methane and other hydrocarbons react readily with oxygen to release heat by forming carbon dioxide and water through a series of kinetic steps that results in the overall reaction,

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O\ (g)$$

This exothermic reaction has an energy release of 50 kJ/g (12 kcal/g) of methane reacted. This energy can be released by raising the temperature of a methane–air mixture to its ignition temperature where the reaction becomes self-sustaining, producing high temperature reaction products. At atmospheric pressure, the combustion reactions can be sustained in methane–air mixtures for methane concentrations ranging from approximately 5.4 to 14 vol%. A methane–air mixture containing approximately 9.5% methane would be stoichiometrically balanced for CO_2 and H_2O (18). The adiabatic combustion temperatures for combustible methane–air mixtures are in the range of 1950 to 2325 K depending on the specific conditions. The overall reaction of methane and oxygen can also be promoted at lower temperature through a series of steps using catalysts and electrolytic cells that result in the direct conversion of the chemical energy to electrical energy without the use of an intermediate heat engine and generator. Heat energy is also derived from fuel-cell reactions and the overall energy utilization efficiencies of these units can exceed 80% (19) (see COMBUSTION SCIENCE AND TECHNOLOGY; FUEL CELLS).

Gas burner technology has been developed that permits natural gas to be used effectively as a primary fuel in both small and large applications. Small applications include furnaces, hot water heaters, clothes dryers, and cooking stoves for residential installations. A high performance, natural gas fueled furnace using a pulse-combustion process and operating at conditions resulting in the condensation of the water vapor in the combustion products has an overall energy efficiency exceeding 90%. This technology has been successfully incorporated into many of the residential or small-scale applications (20). Large-scale applications include the use of natural gas to supply process heat in the production of steel (qv), glass (qv), ceramics (qv), cement (qv), paper (qv), chemicals, aluminum, processed foods, fabricated metal products, etc. Natural gas fueled, indirect-fired metallic radiant tubes and ceramic radiant-tube burners have facilitated the expanded use of natural gas for heat-treating applications (7). Natural gas is also used as a primary fuel for the production of electrical energy.

Because of its clean burning characteristics, natural gas is being strongly considered as a viable fuel for a larger segment of the transportation market throughout the world. Automobile manufacturers have produced more than 150 natural gas model vehicles (see GASOLINE AND OTHER MOTOR FUELS).

Natural gas is attractive as a fuel in many applications because of its relatively clean burning characteristics and low air pollution (qv) potential compared to other fossil fuels. Combustion of natural gas involves mixing with air or oxygen and igniting the mixture. The overall combustion process does not involve particulate combustion or the vaporization of liquid droplets. With proper burner design and operation, the combustion of natural gas is essentially complete. No unburned hydrocarbon or carbon monoxide is present in the products of combustion.

Natural gas combustion produces neither particulates nor significant quantities of SO_2. Natural gas, as delivered, usually contains only small amounts of sulfur (of the order of 0.3 mg/MJ) resulting from either residual H_2S or sulfur-containing odorants. In contrast, fuel oils contain between 50 and 500 mg/MJ and coal between 100 and 1500 mg/MJ (21). In addition, the individual constituents of natural gas do not contain nitrogen. Formation of nitrogen oxides, NO_x, through reactions involving the nitrogen in the air can be minimized by staging the mixing, ignition, and combustion processes. Burners specifically designed to be low NO_x burners have been developed.

Of all the fossil fuels, the use of natural gas results in the formation of the least amount of CO_2 per unit of heat energy produced. On a constant energy basis, natural gas combustion produces approximately 30% less CO_2 than liquid petroleum fuels and approximately 45% less CO_2 than coal and other solid fossil fuels.

10.2. Chemical Use. Both natural gas and natural gas liquids are used as feedstocks in the chemical industry. The largest chemical use of methane is through its reactions with steam to produce mixtures of carbon monoxide and hydrogen (qv). This overall endothermic reaction is represented as

$$CH_4 + H_2O \longrightarrow CO + 3\,H_2$$

In the presence of catalysts, the CO reacts with steam through the shift reaction to produce additional hydrogen and CO_2 as represented by

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Table 11. **Natural Gas Supply and Dispostion, 10^{12} ft^3/yr**[a]

Consumption by sector	2001	2002	2003	2004	2005	2006	2010	2015	2020	2025	2002–2025
residential	4.78	4.92	5.07	5.18	5.21	5.29	5.53	5.68	5.92	6.09	0.9%
commercial	3.24	3.12	3.17	3.11	3.17	3.25	3.48	3.62	3.83	4.04	1.1%
industrial[b]	7.35	7.23	7.21	7.55	7.72	7.83	8.39	8.87	9.57	10.29	1.5%
electric generators[c]	5.38	5.55	4.97	5.67	5.70	5.87	6.66	7.64	8.61	8.39	1.8%
transportation[d]	0.01	0.01	0.02	0.03	0.03	0.04	0.06	0.08	0.10	0.11	9.5%
pipeline fuel	0.62	0.63	0.66	0.65	0.65	0.65	0.67	0.70	0.81	0.84	1.2%
lease and plant fuel[e]	1.09	1.32	1.00	0.99	1.06	1.11	1.36	1.44	1.61	1.65	1.0%
Total	*22.48*	*22.78*	*22.09*	*23.17*	*23.53*	*24.04*	*26.15*	*28.03*	*30.44*	*31.41*	*1.4%*
gas to liquids	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N/A
discrepancy[f]	0.92	−0.16	1.06	0.02	0.01	−0.01	−0.06	−0.07	−0.08	−0.09	N/A

[a] Ref. 6.

[b] Includes consumption for combined heat and power, which produces electricity and other useful thermal energy.

[c] Includes consumption of energy by electricity-only and combined heat and power (CHP) plants whose primary business is to sell electricity, or electricity and heat.

[d] Compressed natural gas used as vehicle fuel.

[e] Represents natural gas used in the field gathering and processing plant machinery.

[f] Balancing item. Natural gas lost as a result of converting flow data measured at varying temperatures and pressures to a standard temperature and pressure and the merger of different data reporting systems which vary in scope, format, definition, and respondent type. In addition, 2001 and 2002 values include net storage injections.

Hydrogen is used mainly in ammonia synthesis, methanol synthesis, and petroleum refining. Carbon monoxide, in addition to being used in the manufacture of methanol, is also used in the manufacture of many other products, including paints, plastics, pesticides, and adhesives.

Natural gas liquids represent a significant source of feedstocks for the production of important chemical building blocks that form the basis for many commercial and industrial products. Ethylene (qv) is produced by steam-cracking the ethane and propane fractions obtained from natural gas, and the butane fraction can be catalytically dehydrogenated to yield 1,3-butadiene, a compound used in the preparation of many polymers (see BUTADIENE). The *n*-butane fraction can also be used as a feedstock in the manufacture of MTBE.

Table 11 gives United States consumption of natural gas by sector for the years starting 2001 and projecting to the year 2025.

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