

PETROLEUM: CHEMISTRY, REFINING, FUELS AND PETROCHEMICALS - PETROLEUM PRODUCTS

James G. Speight

2476 Overland Road, Laramie, WY 82070-4808, USA

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Summary

Petroleum products (in contrast to *petrochemicals*) are those bulk fractions that are derived from petroleum and have commercial value as a bulk product. In the strictest sense, *petrochemicals* are also petroleum products but they are individual chemicals that are used as the basic building blocks of the chemical industry.

The fuels derived from petroleum contribute approximately one-third to one-half of the total world energy supply and are used not only for transportation fuels (i.e., gasoline, diesel fuel, and aviation fuel, among others), lubricants and asphalt - a once-maligned by-product – which is now a premium value product for highway surfaces, roofing materials, and miscellaneous waterproofing uses.

1. Introduction

Petroleum products (in contrast to *petrochemicals*) are those bulk fractions that are derived from petroleum and have commercial value as a bulk product. In the strictest sense, *petrochemicals* are also petroleum products but they are individual chemicals that are used as the basic building blocks of the chemical industry.

The demand for petroleum products (Table 1) – particularly transportation fuels (gasoline and diesel) and petrochemical feedstocks (such as aromatics and olefins) – is increasing throughout the world. Traditional markets such as North America and Europe are experiencing moderate increase in demand, whereas emerging Asian markets such as India and China are witnessing a rapid surge. This has resulted in a ‘squeeze’ on existing refineries, prompting a fresh technological approach to optimize efficiency and throughput. Major oil companies and technology suppliers/licensors are investing heavily to revamp their refining technologies in an effort to cater to the growing needs of customers.

Product	Lower Carbon Limit	Upper Carbon Limit	Lower Boiling Point °C	Upper Boiling Point °C	Lower Boiling Point °F	Upper Boiling Point °F
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Refinery gas	C ₁	C ₄	-161	-1	-259	31
Liquefied petroleum gas	C ₃	C ₄	-42	-1	-44	31
Naphtha	C ₅	C ₁₇	36	302	97	575
Gasoline	C ₄	C ₁₂	-1	216	31	421
Kerosene/diesel fuel	C ₈	C ₁₈	126	258	302	575
Aviation turbine fuel	C ₈	C ₁₆	126	287	302	548
Fuel oil	C ₁₂	>C ₂₀	216	421	>343	>649
Lubricating oil	>C ₂₀		>343		>649	
Wax	C ₁₇	>C ₂₀	302	>343	575	>649
Asphalt	>C ₂₀		>343		>649	
Coke	>C ₅₀ *		>1000*		>1832*	

* Carbon number and boiling point difficult to assess; inserted for illustrative purposes only.

Table 1. Petroleum products.

An infinite variety of processes are involved in the manufacture of these miscellaneous products because of variations in the specifications which must be met, in the type of the original crude oil and additives, and in local conditions. Since the demand for any one product is usually limited, batches of these substances are prepared from time to time according to special procedures. Variations and improvements are made as changes occur in the customers' demands, the crude-oil stocks available, and chemical or industrial developments. As a result, considerable flexibility is possible, although local conditions may make it impractical to manufacture small quantities of these specialty petroleum products at large petroleum installations.

2. Gaseous Fuels

Natural gas, which is predominantly methane, occurs in underground reservoirs separately or in association with crude oil. The principal types of gaseous fuels are oil (distillation) gas, reformed natural gas, and reformed propane or liquefied petroleum gas (LPG).

Liquefied petroleum gas (LPG) is the term applied to certain specific hydrocarbons and their mixtures, which exist in the gaseous state under atmospheric ambient conditions but can be converted to the liquid state under conditions of moderate pressure at ambient temperature. These are the light hydrocarbons fraction of the paraffin series, derived from refinery processes, crude oil stabilization plants and natural gas processing plants comprising propane ($\text{CH}_3\text{CH}_2\text{CH}_3$), butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$), *iso*-butane [$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$] and to a lesser extent propylene ($\text{CH}_3\text{CH}=\text{CH}_2$), or butylene ($\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$). The most common commercial products are propane, butane, or some mixture of the two (Table 2) and are generally extracted from natural gas or crude petroleum. Propylene and butylenes result from cracking other hydrocarbons in a petroleum refinery and are two important chemical feedstocks.

	Propane	Butane
Formula	C ₃ H ₈	C ₄ H ₁₀
Boiling point F.	-44°	32°
Specific gravity - gas (air = 1.00)	1.53	2.00
Specific gravity - liquid (water = 1.00)	0.51	0.58
lb/gallon - liquid @ 60°F.	4.24	4.81
BTU/gallon - gas @ 60°F.	91690	102032
BTU/lb. - gas	21591	21221
BTU/ft. ³ - gas @ 60°F.	2516	3280
Flash point, F.	-156	-96
Ignition temperature in air, F.	920-1020	900-1000
Maximum flame temperature in air, F.	3595	3615
Octane number (ISO-octane=100)	100+	92

Table 2. Properties of propane and butane.

Mixed gas is a gas prepared by adding natural gas or liquefied petroleum gas to a manufactured gas, giving a product of better utility and higher heat content or Btu value.

2.1. Composition

The principal constituent of natural gas is methane (CH₄). Other constituents are paraffinic hydrocarbons such as ethane (CH₃CH₃), propane (CH₃CH₂CH₃), and the butanes [CH₃CH₂CH₂CH₃ and/or (CH₃)₃CH]. Many natural gases contain nitrogen (N₂) as well as carbon dioxide (CO₂) and hydrogen sulfide (H₂S). Trace quantities of argon, hydrogen, and helium may also be present. Generally, the hydrocarbons having a higher molecular weight than methane, carbon dioxide, and hydrogen sulfide are removed from natural gas prior to its use as a fuel. Gases produced in a refinery contain methane, ethane, ethylene, propylene, hydrogen, carbon monoxide, carbon dioxide, and nitrogen, with low concentrations of water vapor, oxygen, and other gases.

2.2. Manufacture

Natural gas is processed in natural gasoline plants, cycling plants, and petrochemical plants to extract hydrocarbons heavier than ethane by compression, adsorption, or absorption. The extracted hydrocarbons are then separated by fractionation. The propane and/or butane fractions, after treatment to remove undesirable constituents (such as hydrogen sulfide, mercaptans, sulfur, and water), constitute the commercial grades of liquefied petroleum gas.

Natural gas which is not associated with crude oil in the producing formation (*dry gas*) usually contains only minor quantities of easily liquefiable hydrocarbons. Therefore, the production of liquefied petroleum gas from dry gas is sometimes restricted by the necessity of maintaining a thermal content sufficient to meet natural-gas pipeline requirements.

The gas streams from thermal and catalytic cracking, reforming, and coking units

contain appreciable quantities of propane, propylene, butanes, and butylenes. These are extracted by conventional oil absorption, distillation, condensation, and fractionation processes.

The propane and propylene recovered are usually charged to a polymerization unit, which reduces the propylene content from 2 to 5 per cent in the effluent propane stream. The propylene polymer is used in the petrochemical industry or blended in premium motor fuel. In some cases, a portion of the propane is cracked to produce hydrogen for refinery hydrogenation or desulfurization processes. It can also be cracked to produce ethylene or propylene for other refining or petrochemical processes.

The butanes and butylenes recovered are usually charged to a hydrofluoric or sulfuric acid alkylation plant. The butylenes and isobutane form an alkylate which is used as an aviation gasoline or premium motor fuel component. As a rule, the feed stream is deficient in isobutane, which must be supplemented by outside supplies or by isobutane produced by isomerization of excess refinery normal butane.

The butylenes can also be converted into petrochemicals or dehydrogenated to butadiene, which is used in the manufacture of synthetic rubber. In the absence of an alkylation plant, where the removal of butylenes is practically 100 per cent, the butanes-butylene can be charged to a polymerization unit either with the propane-propylene stream or separately if advantage of its higher octane polymer is economically desirable.

2.3. Properties and Uses

The *specific gravity* of product gases, including liquefied petroleum gas, may be determined conveniently by a number of methods and a variety of instruments (ASTM 2007, Test Methods D1070 and D4891).

The *heat value* of gases is generally determined at constant pressure in a flow calorimeter in which the heat released by the combustion of a definite quantity of gas is absorbed by a measured quantity of water or air. A continuous recording calorimeter is available for measuring heat values of natural gases (ASTM 2007, Test Method D1826).

The lower and upper limits of *flammability* of organic compounds (Table 3) indicate the percentage of combustible gas in air below which and above which flame will not propagate. When flame is initiated in mixtures having compositions within these limits, it will propagate and therefore the mixtures are flammable. Knowledge of flammable limits and their use in establishing safe practices in handling gaseous fuels is important, e.g., when purging equipment used in gas service, in controlling factory or mine atmospheres, or in handling liquefied gases.

Compound	Limits of Flammability	
	Lower	Upper
	volume %	volume %

Acetaldehyde	3.97	57.00
Acetic acid	5.40	20.00
Acetone	2.55	12.80
Acetylene	2.50	80.00
Allyl alcohol	2.50	18.00
Allyl bromide	4.36	7.25
Allyl chloride	3.28	11.15
n-Amyl acetate	1.10	7.50
n-Amyl alcohol	1.19	10.00
iso-Amyl alcohol	1.20	9.00
n-Amyl chloride	1.60	8.63
n-Amylene	1.42	8.70
Benzene	1.40	7.10
n-Butane	1.86	8.41
iso-Butane	1.80	8.44
Butene-1	1.65	9.95
Butene-2	1.75	9.70
n-Butyl acetate	1.39	7.55
n-Butyl alcohol	1.45	11.25
iso-Butyl alcohol	1.68	9.80
n-Butyl chloride	1.85	10.10
iso-Butyl chloride	2.05	8.75
Carbon disulfide	1.25	50.00
Crotonic aldehyde	2.12	15.50
Cyclohexane	1.26	7.75
Cyclopropane	2.40	10.40
n-Decane	0.77	5.35
Diethylamine	1.77	10.10
Diethyl ether	1.85	36.50
Diethyl peroxide	2.34	
Dimethylamine	2.80	14.40
2,3-Dimethylpentane	1.12	6.75
2,2-Dimethylpropane	1.38	7.50
1,4-Dioxane	1.97	22.25
Divinyl ether	1.70	27.00
Ethane	3.00	12.50

Ethyl acetate	2.18	11.40
Ethyl alcohol	3.28	18.95
Ethylamine	3.55	13.95
Ethyl bromide	6.75	11.25
Ethyl chloride	4.00	14.80
Ethylene	2.75	28.60
Ethylene dichloride	6.20	15.90
Ethylene oxide	3.00	80.00
Ethyl formate	2.75	16.40
Ethyl nitrate	3.80	
Ethyl nitrite	3.01	50.00
Furfural	2.10	19.30
n-Heptane	1.10	6.70
n-Hexane	1.18	7.40
Methane	5.00	15.00
Methyl acetate	3.15	15.60
Methyl alcohol	6.72	36.50
Methylamine	4.95	20.75
Methyl bromide	13.50	14.50
Methyl iso-butyl ketone	1.35	7.60
Methyl chloride	8.25	18.70
Methylcyclohexane	1.15	6.70
Methyl ethyl ether	2.00	10.00
Methyl ethyl ketone	1.81	9.50
Methyl formate	5.05	22.70
Methyl iso-propyl ketone	1.55	8.15
n-Nonane	0.83	2.90
n-Octane	0.95	6.50
Paraldehyde	1.30	
n-Pentane	1.40	7.80
iso-Pentane (2-Methylbutane)	1.32	7.60
Propane	2.12	9.35
n-Propyl acetate	1.77	8.00
iso-Propyl acetate	1.78	7.80

n-Propyl alcohol	2.15	13.50
iso-Propyl alcohol	2.02	11.80
Propylamine	2.01	10.35
n-Propyl chloride	2.60	11.10
Propylene	2.00	11.20
Propylene dichloride	3.40	14.50
Propylene oxide	2.00	22.00
Pyridine	1.81	12.40
Toluene	1.27	6.75
Triethylamine	1.25	7.90
Trimethylamine	2.00	11.60
Turpentine	0.80	
Vinyl chloride	4.00	21.70
o-Xylene	1.00	6.00
m-Xylene	1.10	7.00
p-Xylene	1.10	7.00

Table 3. Flammability limits of selected organic compounds.

3. Gasoline

Gasoline, also called *gas* (United States and Canada), or *petrol* (Great Britain) or *benzine* (Europe) is a mixture of hydrocarbons that usually boil below 180°C (355°F) or, at most, below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have four to twelve carbon atoms in their molecular structure and fall into three general types: paraffins (including the cycloparaffins and branched materials), olefins, and aromatics.

Gasoline is still in great demand as a major product from petroleum. The network of interstate highways that links towns and cities in the United States is dotted with frequent service centers where motorists can obtain refreshment not only for themselves but also for their vehicles.

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Biographical Sketch

Dr. Speight has more than thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research and development in refining heavy oil and coal, and related environmental issues. He has well over four hundred publications, reports, and presentations detailing these research activities and has taught more than forty related courses.

Dr. Speight is currently editor of the journal *Petroleum Science and Technology* (formerly *Fuel Science and Technology International*) and editor of the journal *Energy Sources*. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemical and Fuels Engineering at the University of Utah.

Dr. Speight is the author/editor/compiler of more than twenty books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, for Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996 for his Contributions to Coal Research. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia for Exceptional Work in Petroleum Science in 1997. In 2001, Dr. Speight was also awarded the Einstein Medal of the Russian Academy of Sciences (Natural) in recognition of Outstanding Contributions and Service in the field of Geologic Sciences.