

CONTROL OF POLLUTION IN THE PETROLEUM INDUSTRY

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Summary

The present chapter discusses the main features of the petroleum industry and its overall impact on environmental pollution. Separate attention is paid to the identification and estimation of the main sources of air emission, waste water and solid waste generated by this industry.

Modern pollution control technologies applied by and developed for the petroleum industry constitute the hard-core of the chapter.

Petroleum industry is the industry, which unites anthropogenic activities to explore for, produce, transport world wide, and process around 3.5 billion tons of crude oil and 2.5 giga m³ of natural gas and their derivatives each year. More than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricants, and feed stocks for the petrochemical industry are the direct results of these activities. Bigger refineries integrated with petrochemical plants may produce

additionally different synthetic derivatives - from pure chemicals to additives for fuels and lubricants, synthetic polymers, elastomers, etc.

The petroleum industry is facing three major challenges - heavier crude oils, containing more sulfur and metals, stricter pollution control regulations and emerging of energy sources, which may eventually replace petroleum products in vital applications, such as in vehicles. The first two challenges have already influenced the petroleum industry. It responded by introducing new processes for upgrading of residuals before destructive processes, for production of new additives and reformulated gasoline, for increasing the amount of isomers and controlling arenes (aromatic hydrocarbons) in gasoline, for deep hydrogenation of gas oils to low sulfur diesel fuels and numerous new pollution control options, which are discussed in the present chapter.

The practical applications related to the third challenge (i. e. zero emission vehicles, wider use of solar energy and the unpredictable future of nuclear energy) may influence drastically the petroleum industry in the 21st century.

1. Introduction

Petroleum industry is the industry, which unites anthropogenic activities to explore for, produce, transport world wide, and process around 3.5 billion tons of crude oil and 2.5 giga m³ of natural gas and their derivatives each year. More than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricants, and feed stocks for the petrochemical industry are the direct results of these activities. Bigger refineries integrated with petrochemical plants may produce additionally different synthetic derivatives - from pure chemicals to additives for fuels and lubricants, synthetic polymers, rubber, etc. Figure 1 illustrates the main activities of the petroleum industry.

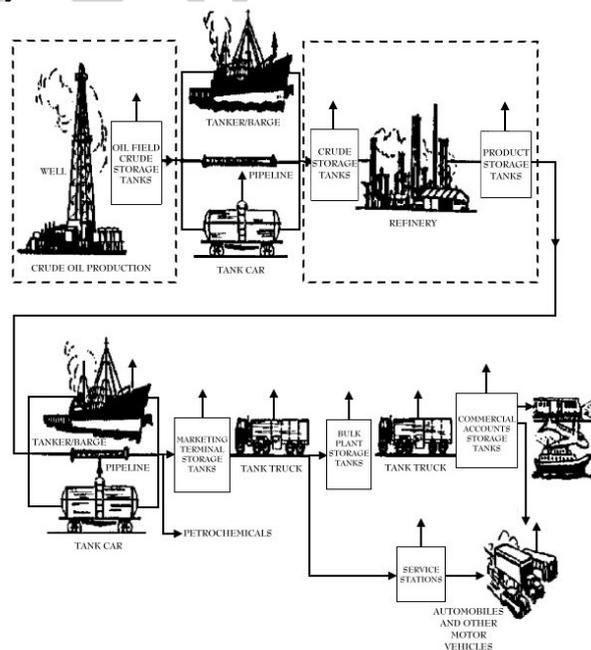


Figure 1: Flow sheet of petroleum production, refining, and distribution systems.

2. Overview of the environmental impact of the petroleum industry

The main purpose of the petroleum industry is to find and bring above ground natural gas and crude oil, to process it into products and to distribute petroleum derivatives to customers. A major factor, which determines the importance, ease of processing, quality of final products, and the environmental impact of the petroleum industry, is the composition of natural gas and especially - crude oils.

Natural gas is mainly methane with small amounts of the next higher members of the n-alkane hydrocarbons. Natural gas is considered "sour" if it contains more than 5.7 mg m⁻³ hydrogen sulfide (H₂S). Carbon dioxide and water are the other major impurities.

Crude oils are usually dark and viscous, but may vary widely in color and viscosity. Typical element analysis of crude oils shows 79.5 - 87.3 per cent carbon, 10.4 - 14.8 per cent hydrogen, 0 - 8 per cent sulfur, 0 - 2 per cent oxygen, 0 - 0.1 per cent nitrogen, and 0 - 0.05 per cent metals (iron, vanadium, nickel, arsenic, etc.). The main crude oil constituents are hydrocarbons of different molecular mass and type, containing from 1 to 60 C atoms and including several thousands different compounds. The typical hydrocarbon groups in crude oils are normal and isoalkanes, cycloalkanes and arenes. A significant amount of hybrid hydrocarbons - i.e. cycloalkanes and arenes with side alkyl chains, combined cycloalkane-arene structures with side chains, etc. is present in heavier fractions. Normal boiling points of crude oil hydrocarbons range from 30 to above 500 ° C. Alkenes are not common in natural crude oil, but may be obtained by specific processes.

Sulfur is usually in the form of mercaptans (R-SH), hydrogen sulfide (H₂S), dissolved free sulfur, thiophene ((CH)₄S), sulfonic acids (RSO₃H), alkylsulfides (R-S-R) and disulfides (R-SS-R), sulfoxides (R-SO-R), alkylsulfates (R₂SO₄) and sulfones (RSO₂R), R being an organic radical.

Oxygen will be present appreciably in cycloalkanic (naphtenic) crudes as organic carboxylic acids (usually naphtenic), and to a limited extent as phenols. Nitrogen, found appreciably in naphtenic crude oils and heavy fractions, is in the form of alkylquinolines and pyridines, pyrroles, indoles and carbazoles. Organic metal complexes, containing pyrrole (CH₄)₄NH rings, might concentrate in heavier distillate fractions.

The world petroleum industry produces around 67 million tons of waste annually. Figure 1 above provided a bird eyes view of the major branches of the petroleum industry. Table 1 offers additional details of the activities related to this industry and their impact on air pollution in the USA.

INDUSTRY	Criteria pollutants ^a						
	CO, (% ^b)	NO _x , (% ^b)	Pb, (% ^b)	PM10, (% ^b)	PT, (% ^b)	SO ₂ , (% ^b)	VOC, (% ^b)

Crude Petroleum & Natural Gas	1.50	1.61	NA	0.53	0.12	0.79	2.72
Natural Gas Liquids	1.59	2.07	NA	0.12	0.03	0.43	2.26
Drilling Oil And Gas Wells	0.00	0.00	NA	NA	NA	NA	0.01
Oil And Gas Exploration Services	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Oil And Gas Field Services	0.01	0.01	NA	NA	NA	NA	0.03
Petroleum Refining	4.25	3.43	0.18	4.18	2.17	2.96	11.9
Crude Petroleum Pipe Lines	0.11	0.02	NA	0.01	0.00	0.00	0.59
Refined Petroleum Pipe Lines	0.01	0.05	NA	0.00	0.02	0.00	0.35
Pipe Lines, Nec	0.00	0.01	NA	NA	NA	0.00	0.01
Natural Gas Transmission	3.16	6.49	NA	0.28	0.13	0.01	3.52
Gas Transmission and Distribution	0.13	0.14	NA	0.01	0.00	0.01	0.08
Natural Gas Distribution	0.01	0.03	NA	0.00	0.00	0.00	0.02
Gas Production/Distribution	0.06	0.10	NA	0.04	0.03	0.00	0.06
Petroleum Bulk Stations & Terminals	0.04	0.06	NA	0.01	0.03	0.02	2.95
Petroleum Products, Nec	0.00	0.00	NA	NA	NA	NA	0.02
Gasoline Service Stations	NA	0.00	NA	NA	NA	NA	0.01
Fuel Oil Dealers	NA	NA	NA	NA	NA	NA	0.02
Petroleum industry total, %	10.87	13.93	0.18	5.18	2.53	4.22	24.56
Petroleum industry total, thousand tons per year	495.5	1306.8	36.193	29.975	37.145	729.561	47.7243

^a - Abbreviations correspond to the chemical formula or the typical codes of the pollutant, as used in the AIRS database – CO is carbon monoxide; NO_x – total nitrogen oxides, PM10 – particulate matter below 10 µm; PT – particulate matter total; SO₂ – sulfur dioxide, VOC – volatile organic compounds, NA – not applicable.

^b – Per cent of total measured contribution of the particular pollutant to US air pollution.

Table 1: Annual relative contribution to air pollution from activities related to the petroleum industry in the USA.

The total contribution of methane (CH₄), carbon dioxide (CO₂) and non methane volatile organic compounds (NMVOCs) from the natural gas and petroleum systems in the USA for 1997 has been estimated at: CH₄ – 6 118 000 Gg; CO₂ – 15 235 000 Gg; NMVOCs – 488 000 Gg.

The petroleum industry consumes huge amounts of water, especially in the production and processing sector, but modern refineries work with a nearly closed water cycle, compensating with fresh water only for evaporation losses. Their main contribution to water pollution comes from uncontrolled leaks and spills, and during transportation of crude oil and products. The contribution of the latter to marine pollution is the object of a separate chapter in this presentation.

A 1996 US study identified 29 refinery solid wastes, some of which are typical for other sectors of the petroleum industry as well. It should be noted also that despite the significant contribution of the petroleum industry to pollution, relatively few specific effluents directly associated with that industry have been classified as hazardous.

3. Sources of Environmental Pollution from the Petroleum Industry

Air emissions from the petroleum industry can be classified as combustion emissions, process emissions, fugitive emissions, emissions from storage and handling of petroleum liquids and secondary emissions.

Combustion emissions are produced with the onsite burning of fuels usually for energy production and transportation purposes. Flaring is a specific source of combustion emissions in the petroleum industry. It is used to control pressure and remove gas, which can not be otherwise used. *Fugitive emissions* (equipment leak emissions) are released through leaking valves, pumps, or other process devices. *Process emissions* are generated in the process units and released from process vents. *Storage and handling emissions* are contributed from the storage and manipulation of natural gas and crude oil, as well as their intermediate and finished derivatives. The water systems of a production or processing site (tanks, ponds, sewer system drains, etc.) are the main source of secondary emissions.

Polluted water in the petroleum industry is usually generated in the various production or processing operations. Leaks of liquids from the production, process, storage equipment or pipelines to the ground can also contribute to pollution of underground water.

Solid wastes containing varying amounts of different pollutants are generated from particular processes or as sludge in storage tanks.

3.1. Pollution from Exploration and Production of Crude oil and Natural Gas.

Production of oil and gas is a major operation of the petroleum industry. Nearly 100 countries are involved in it world wide, and a considerable amount of oil and gas is produced off shore. In the USA only, there are more than 575 000 crude oil wells, 252 000 gas wells and 724 gas plants.

Major activities in this branch of the petroleum industry include exploration and well site preparation; drilling; crude oil and gas production, enhanced (secondary) recovery and eventually some on-site processing.

Exploration for outlining of oil and gas reservoirs includes geological surveys, space, ground and sea mapping based on magnetic, gravity or seismic geophysical methods. Seismic methods if improperly applied might damage environmental species, especially in marine exploration.

Drilling employs usually rotary drilling rigs, driven by diesel fuel or natural gas internal combustion engines. Ground penetration is facilitated by drilling muds, which are gel-like (non-Newtonian) water-based, oil-based or water-in-oil emulsion based clay suspensions with additives. They may include polymers, caustic soda, different ionic or nonionic emulsifiers, etc. Recultivation of soils after drilling is a major requirement for environmental compatibility.

Oil and gas production is done from wells, which are essentially pipelines with screwed joints reaching from the top of the ground to the producing formation. The pipe through which the oil is produced is called tubing and its diameter is between 31 and 115 mm.

Production is controlled by bottom-hole chokes, pressure gauges and down-hole safety valves mainly for prevention of "blow-outs", which usually are followed by ignition of the light fractions.

Enhanced (secondary) recovery methods are used to increase the amount of recovered crude oil to about 30 – 40 per cent of the amount in the reservoir since only 20 – 25 per cent of oil come out on its own. These include flooding with salt containing water, high-pressure gas injection (hydrocarbon gas, CO₂, N₂, etc. being used), heating with hot gas or steam or by burning part of the oil.

On-site processing of natural gas may include acid gas removal with amines and de-watering with glycols. On-site processing of crude oil usually includes gravitational separation of water and salts and recovery of condensable hydrocarbons. Sulfur recovery and fractionation of light hydrocarbons may be done if there is a near-by refinery or another available facility.

Air pollution from the production of oil and gas is with volatile hydrocarbons in fugitive emissions (mainly methane), as well as emissions from storage and manipulation. Employment of gases in enhanced oil recovery usually leads to increased process emissions, which also come from process vents of production equipment and eventually – from removing of acid gases. Exhaust combustion emissions are generated from compressors, pumps, drill engines and engines of servicing vehicles. Gas flaring is the major source of combustion emissions. The major source of secondary emissions is the water separated from the natural gas and crude oil.

Underground water pollution is usually associated with enhanced recovery and desalting of crude oils. The water from the desalting at a production facility, however, can be reused in the production well. Solid wastes are mainly sludge from the desalting of the crude oil and storage vessels, spent mud, etc.

3.2. Pollution from Storage, Manipulation, and Transportation of Petroleum Liquids

Storage, manipulation and transportation are operations, which are inherent to all branches of the petroleum industry. Considerable amounts of crude oil and/or natural gas are stored at the production site and transportation terminals. Processing facilities keep considerable amounts of crude oil and gas, as well as finished products.

Storage of liquid petroleum products may be done in above ground or underground steel or concrete tanks or in underground salt domes, mined caverns or abandoned mines. Above ground storage in tanks may require between 16 000 and 121 500 m² of land. Storage site in a salt dome, a former salt mine usually, may be up to 10 km in diameter. Small amounts of petroleum products might be kept for a shorter period in barrels. The normal practice for petroleum products is storage in specifically designed steel tanks, such as those at the gasoline stations.

Natural gas may be stored in pressurized tanks, depleted oil and gas wells, aquifers, salt domes and cavities, etc. Water sealed gasholders may contain 700 - 285 000 m³ of gas. For domestic purposes much smaller pressurized vessels (bottles) are used.

Above ground or underground steel tanks are the most widely used vessels in the petroleum industry for storage of petroleum derivatives (pure chemicals and petroleum products from crude oil fractions). Underground tanks are most common for military bases, gasoline stations and wholesale bulk storage terminals.

Six basic tank designs are used for organic liquid storage vessels: fixed roof (vertical and horizontal), external floating roof, domed external (or covered) floating roof, internal floating roof, variable vapor space, and pressure (low and high).

Transportation of crude oil and natural gas can be with pipelines, tanker ships, rail or road transport, or inland waterway barges. Tankers are a fifth of the total world merchant tonnage of marine transport, tanker-ships with up to 300 000 tons capacity or more being in use. Pipelines can provide the link between the oil field and the refinery or the sea-loading terminal.

They have intermediate boost compressor or pumping stations powered by electric motors, internal combustion engines or gas turbines. Natural gas is transported by high-pressure pipelines with a diameter up to 1.5 m. The crude oil and natural gas pipelines may be several thousands of kilometers long, crossing different countries, mountains and even the oceans.

Rail and road transport is usually used for petroleum derivatives, though lower pressure product pipelines are common in most industrialized countries. The total length of transportation natural gas pipelines of the USA in 1996 were a little above four hundred thousand kilometers while the gas distribution pipelines were more than 2.25 million kilometers.

Air emissions from storage and transportation are mainly evaporative hydrocarbon emissions from manipulation - loading/unloading, and transit (“breathing”) losses from the storage tanks and the tanks of transporting vehicle. When the volume of the liquid phase in a tank is changing, the volume of the gas phase is also increasing or

decreasing. This leads to emission of vapors in the atmosphere or sucking in of air during loading/unloading. Breathing, which occurs also in transit, is the result of changing of temperature and pressure outside of the tank. Fugitive emissions from different leaks of relevant equipment include those from pressurized pipelines as well.

Ballast water from transporting vessels and especially tankers is the major source of secondary emissions, but also a major source of marine water pollution (see *Pollution Control in Transportation*). The other source polluting underground water is leaking liquids from tanks and pipelines. Solid waste generated in storage and transportation is mainly sludge from the storage and transportation tanks.

3.3. Pollution from processing of natural gas and crude oil

Processing of natural gas is usually limited to de-watering and removing of acid components like hydrogen sulfide and eventually carbon dioxide.

The throughput of a crude oil refinery may be from between 2000 and 10 000 tons per day (1.8 to 9.0 million tons per year) for a small refinery, to 20 000 – 60 000 tons per day (18.0 to 54.0 million tons per year) - for a large one.

In 1995 the world petroleum processing industry produced around 3.3 billion tons of refined petroleum products, 23.4 per cent of which were manufactured in the USA, and nearly the same quantities – in Western Europe (20.7 per cent) and Far East and Oceania (22.4 per cent). In the course of refining energy equivalent to the energy value of 3 – 8 per cent of the processed crude oil is used.

The exact amount for a particular refinery depends mainly on the assortment of products being produced, but also on energy efficiency. One of the most advanced refinery industries – that of the USA in 1994 has used 6500 trillion BTUs of energy (Conversion factor: one British Thermal Unit, BTU=1.054 kJ).

Petroleum processing uses also huge amounts of water. In 1992, the total amount of water used in US refineries is estimated to average 1.5 – 2.2 m³ of water per one cubic meter of crude oil processed. Polluted water is treated inside the refinery and most of it is recycled.

The amount discharged to public water treatment facilities or returned to natural water sources is estimated to be in the range of 0.3 – 0.6 m³ of water per one cubic meter of crude. For old refineries in other parts of the world, the above parameters would be much higher.

Petroleum processing involves also large quantities of chemicals, which are utilized in different technologies – water treatment, processing of fractions, as additives to finished products, etc. Many of these are listed as toxic chemicals. Toxic chemicals managed by US refineries in 1995 were around 0.6 million tons.

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Biographical Sketch

Georgi St. Cholakov is Associate Professor at the University of Chemical Technology and Metallurgy in Sofia. He received his first hands-on experience of ecological problems during compulsory his military service as the Head of the Fuels and Lubricants Unit of an airbase. His PhD dissertation was on development of replacements for lubricant additives synthesized from the sperm oil, obtained from blue whales. He did a post doc specialization in tribology at the University of Birmingham, U.K. Later he specialized in effective and ecological processing and use of petroleum derivatives at Imperial College, London, the French Institute of Petroleum, and other leading universities. The scientific and research interests of G. St. Cholakov are centered around petroleum processing and petroleum derivatives – environmentally compatible processes and products, process and product design for the petroleum industry, chemistry of combustion and ecology, etc. He is teaching advanced courses in related academic disciplines – alternative fuels and lubricants, air pollution management, chemistry of combustion and

ecology, additives for fuels and lubricants, technological computation in petroleum processing, etc. He has contributed more than 50 papers in refereed international journals and co-edited the Bulgarian edition of Miall's Dictionary of Chemistry. G. St. Cholakov is member and has served in elective positions in different Bulgarian and Balkan professional organizations. He has been member of the editorial boards of two journals, published in Bulgaria in the English language.

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