

O.S. Kukurina, Ya.V. Rozanova



ENGLISH
FOR SPECIFIC PURPOSES.
OIL-REFINING

TOMSK POLYTECHNIC UNIVERSITY

O.S. Kukurina, Ya.V. Rozanova

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OIL-REFINING**

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ТОМСКИЙ ПОЛИТЕХНИЧЕСКИЙ УНИВЕРСИТЕТ»**

О.С. Кукурина, Я.В. Розанова

**ПРОФЕССИОНАЛЬНЫЙ АНГЛИЙСКИЙ ЯЗЫК.
НЕФТЕПЕРЕРАБОТКА**

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Пособие разработано для студентов старших курсов, изучающих курс «Химия и технология сырья и мономеров». Целью пособия является формирование профессионального англоязычного тезауруса в области нефтепереработки. Включает терминологический справочник, словарные статьи, рассматривающие основные стадии подготовки и переработки нефти на английском языке, а также содержит блок заданий для мониторинга лексических навыков в сфере нефтепереработки.

Предназначено для бакалавров, обучающихся по направлению 240100 «Химическая технология», профили подготовки «Химическая технология органических веществ» и «Технология и переработка полимеров».

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Рецензенты

Кандидат педагогических наук, доцент

Зав.каф. ИЯ международного факультета управления ТГУ

Е. Ю. Надеждина

Начальник производственно-технического отдела ООО «ЗапСиб НПЗ»

Р. Я. Масагутов

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CONTENTS

Introduction	7
Unit 1	8
1.1 Formation.....	8
1.2 Crude Oil Characteristics	12
1.3 Classification	18
Glossary	20
Review Questions and Exercises.....	22
Unit 2	26
2.1 Removal of oil gases (dissolved in oil) or oil stabilization.....	26
2.2 Oil distillation	28
2.3 The fractions from oil distillation.....	31
Glossary	33
Review Questions and Exercises.....	34
Unit 3	38
3.1 Refining Schemes	40
3.2 Cracking.....	42
3.3 Catalytic Cracking	44
3.4 Hydrocracking	48
3.5 Catalytic Reforming	51
3.6 Alkylation	53
Glossary	55
Review Questions and Exercises.....	57
Unit 4	62
4.1 Refined Products	62
4.2 Crude Oil Fractions	63
4.3 Sulfur Content	66

4.4 Octane Number.....	67
4.5 Distillates.....	69
4.6 Residuals.....	70
4.7 Petrochemicals.....	71
Glossary.....	80
Review Questions and Exercises.....	84
References.....	88
Appendix A.....	90
Appendix B.....	92
Appendix C.....	95
Appendix D.....	98

INTRODUCTION

Petroleum is found at great depths underground or below seabeds. It can exist as a gas, liquid, solid, or a combination of these three states, which is very common. Drilling efforts are used to reach and extract gaseous and liquid deposits. These products are brought to the surface via piping. Once found in a reservoir, gas usually flows under its own pressure. Conversely, discovered liquid hydrocarbons may flow on their own due to pressure from the reservoir or may be forced to the surface by submerged pumps. Also injection of fluids and gases provides a driving force to push liquid hydrocarbon through rock strata. Solid or semi-solid petroleum is brought to the surface through several methods: by digging with conventional mining techniques, by gasifying or liquefying with high-temperature steam, or by burning a portion of the material in the ground so that the remainder can flow to the surface.

There are several major oil producing regions around the globe. The Kuwait and Saudi Arabia's crude oil fields are the largest, although Middle East oil from other countries in the region such as Iran and Iraq also make up a significant part of world production figures.

The North Sea crude oil fields are still fairly full, and are arguably the second most influential oil field in economic terms. Texas, once the world's major oil region, is now almost completely dry.

In 1859 Edwin Drake sank the first known oil well, this was in Pennsylvania. Since this time oil and petroleum production figure grew exponentially.

Russia is the world's second largest producer of crude oil after Saudi Arabia and also one of the world's top oil exporters [1]. Russia's proven oil reserves were estimated at 72.3 billion barrels at the end of 2004, or approximately 6.1 % of the world's total proven reserves of oil estimated at 1,188.6 billion barrels according to the BP statistical Review of World Energy published in June 2005.

Following the rapid privatization drive in the mid-1990s, the Russian oil industry has evolved into a reasonably well defined sector, led by the large Russian oil companies (LUKOIL, Gazprom, Surgutneftegaz and TNK-BP). As these companies were generally created from the remains of the Soviet-controlled production associations that had asset concentrations for efficiency reasons, their operations are typically concentrated in certain regions. A number of other smaller Russian and Western oil companies also conduct operations in Russia. As a result, the industry is highly competitive. Current Russian oil production is predominantly based in Western Siberia.

UNIT 1

Oil is an important part of our everyday life. Millions of products are made from oil including plastics, life-saving medications, clothing, cosmetics, and many other items you may use daily.

Oil is called liquid fossil fuel which extended in sedimentary rock layers beneath the surface of the earth.

Petroleum (Lat. petroleum lit. "rock oil" was first used in 1556 in a treatise published by the German mineralogist Georg Bauer, known as Georgius Agricola.) is a naturally occurring, flammable liquid found in rock formations in the Earth consisting of a complex mixture of hydrocarbons of various molecular weights, plus other organic compounds. The proportion of hydrocarbons in the mixture is highly variable and ranges from as much as 97% by weight in the lighter oils to as little as 50% in the heavier oils and bitumens.

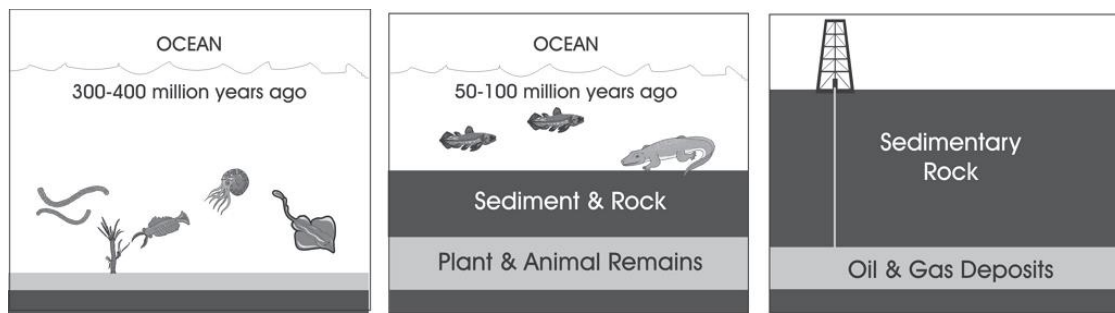
1.1 Formation

Formation of petroleum occurs from kerogen pyrolysis, in a variety of mostly endothermic reactions at high temperature and/or pressure.

Nowadays the *two theories* of oil birth are existing:

1. biogenic;
2. abiogenous.

On the one hand scientists believe that oil was formed from the remains of prehistoric plant and animals. Hundreds of years millions ago, prehistoric plant and animal remains settled into the seas along with sand, silt, and rocks. As the rocks and silt settled, layer upon layer piled up in rivers, along coastlines, and on the sea bottom. Geologic shifts resulted in some of these layers being buried deep in the earth. Over time, the layers of organic material were compressed under the weight of the sediments above them, and the increasing pressure and temperature changed the mud, sand, and silt into rock and the organic matter into petroleum.



Biogenic theory

Most geologists view crude oil and natural gas as the product of compression and heating of ancient organic materials over geological time. Oil is formed from the preserved *remains of prehistoric zooplankton and algae* which have been settled to the sea (or lake) bottom in large quantities under *anoxic conditions*. Terrestrial plants, on the other hand, tend to form coal. Over geological time this organic matter, mixed with mud, is buried under heavy layers of sediment. The resulting high levels of heat and pressure cause the organic matter to chemically change during diagenesis, first into a waxy material known as *kerogen which is found in various oil shales* around the world, and then with more heat into liquid and gaseous hydrocarbons in a process known as catagenesis.

Geologists often refer to an "oil window" which is the temperature range that oil forms in – below the minimum temperature oil remains trapped in the form of kerogen, and above the maximum temperature the oil is converted to natural gas through the process of thermal cracking. Though this happens at different depths in different locations around the world, a 'typical' depth for the oil window might be 4 ÷ 6 km.

The vast majority of oil that has been produced by the earth has long ago escaped to the surface and been biodegraded by *oil-eating bacteria*. Oil companies are looking for the small fraction that has been trapped by this rare combination of circumstances. Oil sands are reservoirs of partially biodegraded oil still in the process of escaping, but contain so much migrating oil that, although most of it has escaped, vast amounts are still present – more than can be found in conventional oil reservoirs. On the other hand, oil shales are source rocks that have never been buried deep enough to convert their trapped kerogen into oil.

The reactions that produce oil and natural gas are often modeled as first order breakdown reactions, where kerogen is broken down to oil and natural gas by a set of parallel reactions, and oil eventually breaks down to natural gas by another set of reactions. The first set was originally patented in 1694 under British Crown Patent No. 330 covering, "*a way to extract and make*

great quantities of pitch, tarr, and oyle out of a sort of stone.” The latter set is regularly used in petrochemical plants and oil refineries.

Abiogenic theory

On the over hand the number of investigations show that some oil compounds can form carbon dioxide and water under temperature and pressure like the conditions in upper Earth mantle.

The idea of abiogenic petroleum origin was championed in the Western world by astronomer *Thomas Gold* based on thoughts from Russia, mainly on studies of Nikolai Kudryavtsev in the 1800s. Gold's hypothesis was that hydrocarbons of purely inorganic origin exist on the planet Earth. Since most petroleum hydrocarbons are less dense than aqueous pore fluids, Gold proposed that they migrate upward into oil reservoirs through deep fracture networks. Although biomarkers are found in petroleum that most petroleum geologists interpret as indicating biological origin, Gold proposed that *thermophilic, rock-dwelling microbial life-forms* are responsible for their presence.

This hypothesis is accepted by only a small minority of geologists and petroleum engineers, and to date has not been particularly successful in predicting petroleum deposits on earth, so it is considered a fringe theory. Methods of making hydrocarbons from inorganic material have been known for some time, however no substantial proof exists that this is happening on any significant scale in the earth's crust for any hydrocarbon other than methane (natural gas).



Debates
“THE OIL ORIGIN THEORY”

Step 1	Read the rules of how to debate	
	Speaker of AT states the position taken by the team, introduces some vocabulary providing definitions for terms, brings up the “yes” side of the issue, and watches the flow of the arguments. At the end, the speaker will summarize, recap, and state which the points made can be salvaged support the team’s position.	Speaker of NT states the position taken by the team, introduces some vocabulary providing definitions for terms, brings up the “no” side of the issue, and watches the flow of the arguments. At the end, the speaker will summarize,

		recap, and state which the points made can be salvaged support the team's position.
	Attackers (another members of team) take their turns leading the arguments against the "No" team, providing examples and probing the opposite team for weaknesses in their arguments by asking questions.	Attackers (another members of team) take their turns leading the arguments against the "Yes" team, providing examples and probing the opposite team for weaknesses in their arguments by asking questions.
	Moderator – summarizes and recaps the main points of both teams and theories, and make the conclusion.	
Step 2	Discuss a biogenic theory of oil origin and then, taking turns debate an abiogenic theory following the debates rules.	
Step 3	Answer the question: "What kind of theory has the right to exist?"	

Useful phrases for debates

Opening phrases

Well, I'm going to be *talking to you about...*

telling/showing you...

reporting on...

talking a look at...

So, I'll start off by *giving you an overview of...*

making a few observations about...

outlining...

Giving opinions

In my opinion,...

As I see it,...

From my point of view...

It seems to me that...

I would say that...

I suppose...

As far as I'm able to judge...

It's quite clear that...

Generalizing and concluding

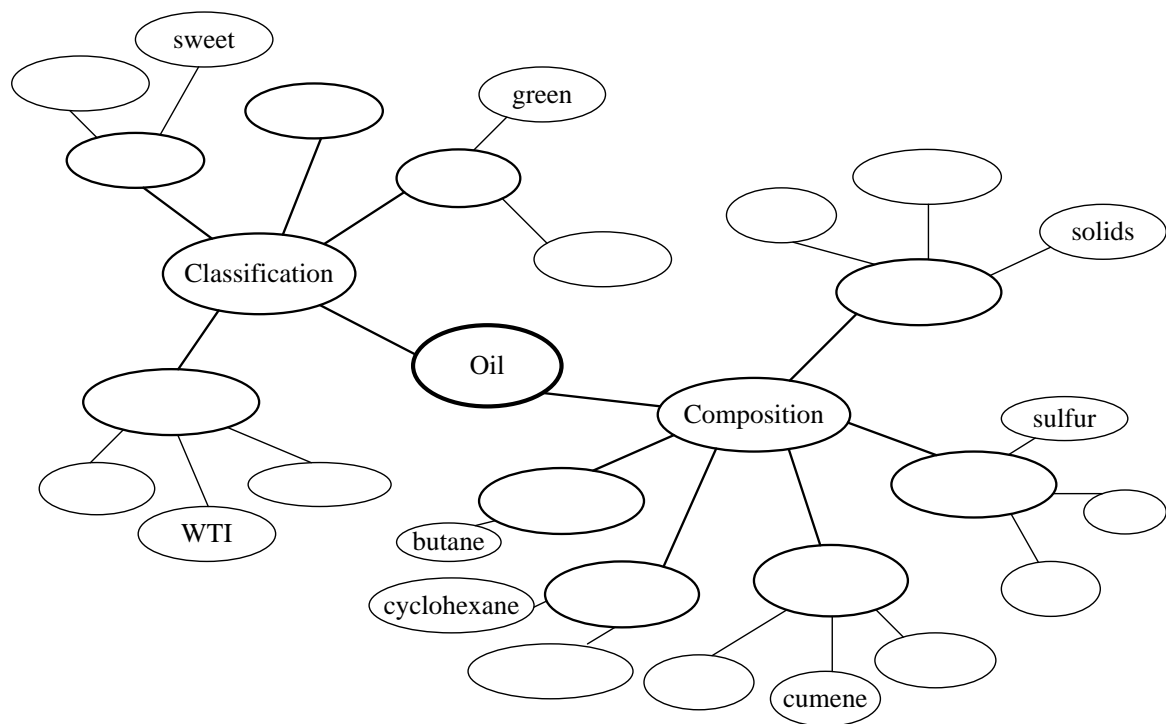
- | | |
|---------------------------|---|
| On the whole,... | Let me conclude by saying |
| In general,... | I'd like to conclude by stating that... |
| Generally speaking,... | Allow me to conclude by highlighting... |
| By and large,... | |
| All in all,... | |
| All things considered,... | |

Asking for an opinion

- What's your position on.../opinion of...
- What do you think of...
- I'd like to hear your views on...

1.2 Crude Oil Characteristics

Fill in the blanks in the spider graph below using the information from the text about oil classification and composition.



It is commonly thought that crude oil from conventional oil wells has the same composition and appearance regardless of the source. This is not true any longer. The physical characteristics and the composition of crude oil vary widely with the location of the oil field and the stage of production (new or mature).

Conventional crude oil ranges from *green to brown or black in color* depending on the petroleum type and the mineral matter present and is composed of a heterogeneous mixture of liquids, solids, and gases. Some components of the crude oil are dissolved and some are a separate phase. Water may occur with the petroleum produced as a readily separated phase or as an emulsion containing as much as 80–90 % water. The “*pour point*” is a measure of the low-temperature viscosity or flow characteristics of oil. It is defined as being 3 °C (or 5 °F) above the setting temperature (maximum temperature at which no observable flow occurs) of the oil. Pour points of some viscous conventional crudes can be above 5 °C, while the pour points of the less viscous, or lighter crudes can be less than –15 °C.

Composition

The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron (fer- rum), nickel, copper and vanadium, titanium, germanium [2]. The exact molecular composition varies widely from formation to formation but the proportion of chemical elements varies over fairly narrow limits as follows:

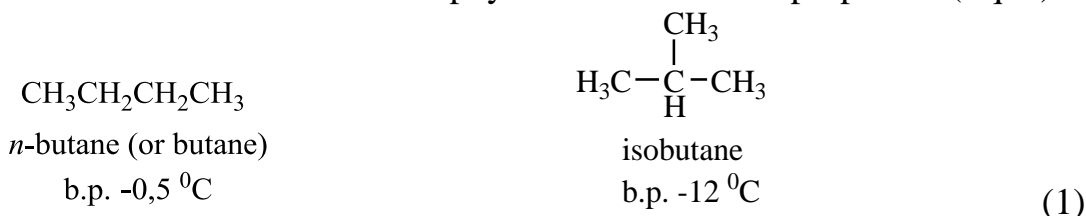
~	Carbon	83–87 %;
~	Hydrogen	10–14 %;
~	Nitrogen	0.1–2 %;
~	Oxygen	0.1–1.5 %;
~	Sulfur	0.5–6 %;
~	Metals	<1000 ppm.

Crude oil is a mixture of hydrocarbons. They are often chains of carbon atoms with hydrogens attached. The longer chains have higher boiling points, so they can be separated by distillation.

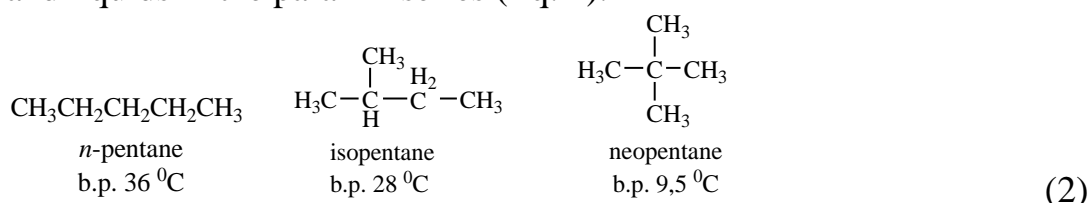
Paraffins

The petroleum itself consists of a mixture of straight hydrocarbons and hydrocarbons containing one or more heteroatoms. Even natural gas that is mostly methane also contains small amounts of four or five other low-molecular weight hydrocarbons. The paraffin hydrocarbon component of crude oil has the generic formula C_nH_{2n+2} , and may comprise gases, liquids, or solids depending on their molecular weight (or the value of n). The simplest example of this group is methane, CH_4 , the chief constituent of natural gas. It has a boiling point of –164 °C and a melting point of –183 °C. Propane and butane, C_3H_8 , and C_4H_{10} , both are gases under ordinary conditions, but with boiling points of –42 and –1 °C, respectively, are relatively easily

liquefied. Butane and the higher (larger carbon number) members of this series occur not only in the straight chain form, referred to as the normal or “*n*” form, but also in various branched chain structures of the same molecular formula but with different physical and chemical properties (Eq. 1).



Pentane isomers, C₅H₁₂, have boiling points in the range of normal ambient conditions, and represent the approximate borderline between gases and liquids in the paraffin series (Eq. 2).



Octane, a hydrocarbon found in petroleum, lines are single bonds, black spheres are carbon, and white spheres are hydrogen.

As the carbon number gets larger in the paraffin series the number of possible structural isomers also gets larger so that hexane (C₆H₁₄), for example, has five structural isomers and heptane (C₇H₁₆) has six. All 18 isomers of octane have been isolated or synthesized, as have the 35 isomers of nonane. Beyond this, however little is established about the natural occurrence of the 75 possible structural isomers of decane (C₁₀H₂₂) or the over 4,000 possible isomers with pentadecane (C₁₅H₃₂). Meanwhile many of the possible paraffin isomers have been found and isolated from exhaustive separations of natural petroleum.

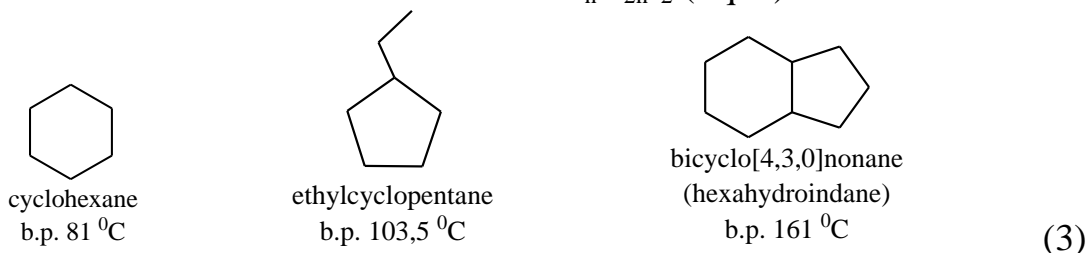
Normal octane, C₈H₁₈, with a melting point of -57 °C and boiling point of 126 °C, occurs near the upper end of the liquid paraffinic constituents of gasoline. *n*-Eicosane (C₂₀H₄₂; CH₃(CH₂)₁₈CH₃), with a melting point of 36 °C and a boiling point of >340 °C, is the first of the higher (longer carbon chain or larger molecular weight) paraffins, which is isolated in the solid state (a wax) under ordinary conditions. These larger saturated hydrocarbons occur dissolved in the lower molecular weight liquid hydrocarbons, which comprise the bulk of light natural petroleum.

The alkanes, also known as paraffins, are saturated hydrocarbons with straight or branched chains which contain only carbon and hydrogen and have the general formula C_{*n*}H_{2*n*+2}. They generally have from 5 to 40 carbon atoms per molecule, although trace amounts of shorter or longer molecules may be present in the mixture.

The alkanes from pentane (C_5H_{12}) to octane (C_8H_{18}) are refined into gasoline (petrol), the ones from nonane (C_9H_{20}) to hexadecane ($C_{16}H_{34}$) into diesel fuel and kerosene (primary component of many types of jet fuel), and the ones from hexadecane upwards into fuel oil and lubricating oil. At the heavier end of the range, paraffin wax is an alkane with approximately 25 carbon atoms, while asphalt has 35 and up, although these are usually cracked by modern refineries into more valuable products. Any shorter hydrocarbons are considered natural gas or natural gas liquids.

Naphthenes

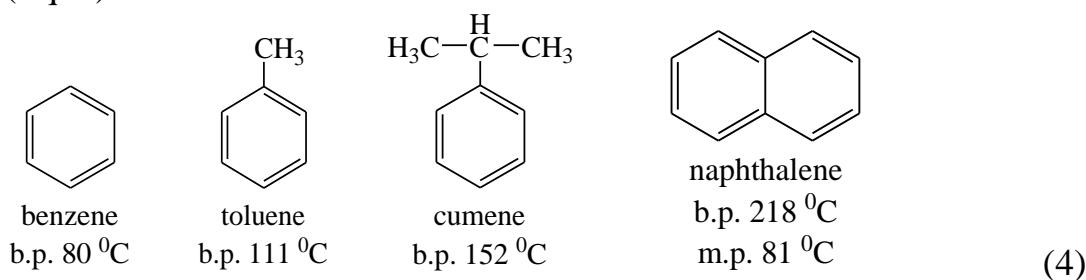
Saturated hydrocarbons also occur in petroleum in cyclic form, and will have generic molecular formulas of the form C_nH_{2n} (if monocyclic). These cycloparaffins are referred to as *naphthenes* in the petroleum industry and occur primarily as five, six, and seven-membered rings, with and without alkyl substituents. They also occasionally occur as various combinations of two of these ring systems linked or fused together, in which case their molecular formulas become of the form C_nH_{2n-2} (Eq. 3).



The cycloalkanes, also known as naphthenes, are saturated hydrocarbons which have one or more carbon rings to which hydrogen atoms are attached according to the formula C_nH_{2n} . Cycloalkanes have similar properties to alkanes but have higher boiling points.

Aromatic hydrocarbons

Aromatic hydrocarbons occur to a varying extent and have a higher ratio of carbon to hydrogen than any of the commonly occurring paraffins or naphthenes. They correspond to a molecular formula of C_nH_{2n-6} if they are mononuclear (single ring only). Benzene, toluene, and cumene are mononuclear examples of this series, and naphthalene is a dinuclear example (Eq. 4).



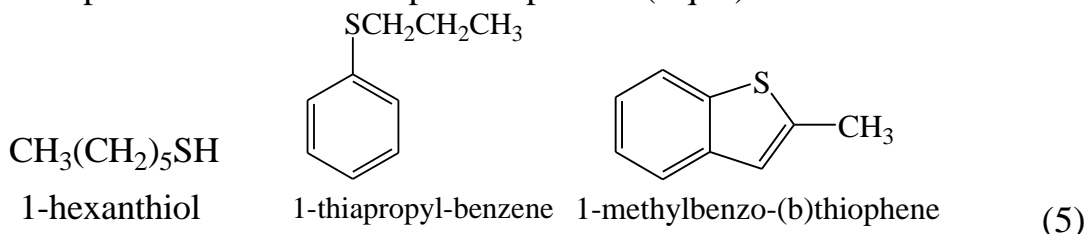
These and many other aromatics have been isolated from petroleum fractions. The aromatic content of crude oils can vary widely, but an aromatic content of a third or more of the total, as has been noted for some Borneo crudes, is not unusual. The density (or °API) of a crude oil is an indicator of the aromatic content since the high C:H ratio of aromatic components tends to make these the most dense constituents present. This is particularly true with polynuclear aromatic constituents since each additional ring further reduces the hydrogen count by two, increasing the already high C:H ratio and therefore also the density.

While the bulk of the hydrocarbon content of crude oils is represented by the paraffins, naphthenes, and aromatics, small percentages of several other types of compounds are also present. Olefinic hydrocarbons, unsaturated chain compounds having a carbon-carbon double bond and a type formula C_nH_{2n} , also occur in natural petroleum but only to a very small extent since they are relatively unstable. They are mentioned here, however, since substantial amounts of these are formed by some refinery processes, particularly those involving cracking.

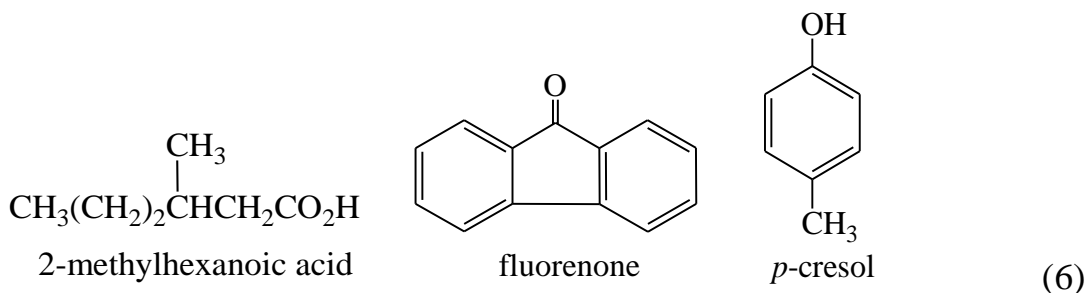
The aromatic hydrocarbons are unsaturated hydrocarbons which have one or more planar six-carbon rings called benzene rings, to which hydrogen atoms are attached with the formula C_nH_n . They tend to burn with a sooty flame, and many have a sweet aroma. Some are carcinogenic.

Sulfur compounds

A wide variety of compounds that contain a heteroatom as well as carbon and hydrogen also occur in petroleum but generally to a lesser extent. Hydrogen sulfide and a variety of thiols, sulfides, and thiophenes are some examples of the sulfur compounds present (Eq. 5).

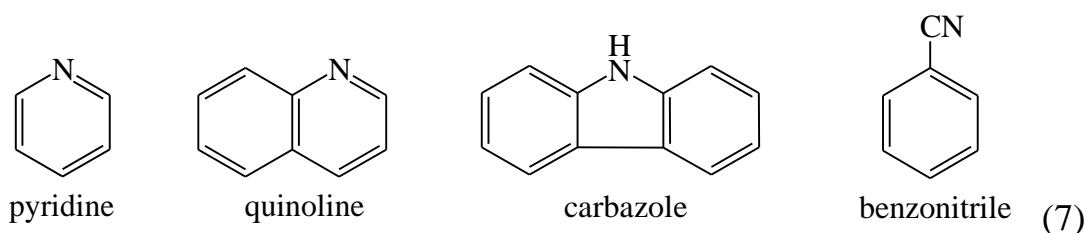


The sulfur content of petroleum containing these compounds is usually quite low but it can be as high as 6% of the total. The more stable oxygen derivatives of hydrocarbons, such as the paraffinic acids, ketones, and phenols (Eq. 6), also occur in crude oils.



Nitrogen compounds

And nitrogen compounds, either on their own or complexed to a transition metal, such as vanadium, also occur in petroleum to a small extent. Pyridine, quinoline, and many other heteroaromatics (Eq. 7) have also been found.



The first two of these compounds occur at sufficiently high concentrations in some crudes to enable production of them from petroleum. Benzonitrile has also been detected. Much of the trace metal content of petroleum, in particular vanadium and nickel, is present in association with porphyrins, which are polycyclic pyrroles closely related in structure to the hemes and chlorophylls. These materials are examples of the more complex nitrogen heterocycles to be found in petroleum. These particular heterocycles with their complexed metal atoms contribute much to our present knowledge of the original biogenesis of the petroleum hydrocarbons.

If the proportion of low-molecular weight hydrocarbons (low-carbon number, small molecules) to high-molecular weight hydrocarbons is high, then very fluid (low-viscosity and density) and light crude is obtained. If, however, high-molecular weight paraffins or polynuclear aromatics (asphaltenes) predominate then this will give a crude of high viscosity (and density), and pour-point, the so-called "heavy crudes". The composition of crude oil produced from a particular oil field will vary somewhat with the stage of production. The proportion of lighter (lower molecular weight) hydrocarbons will generally be higher in the early stages of production of a new oil field. The ratio of the percentage of paraffins to the proportion of naphthenes and aromatics present will be relatively consistent from the different producing wells of a particular oil field but can vary widely from one oil field to another. With all these variables in mind, refineries seldom rely on

crude oil from a single oil field for the whole of their production. A selection of different crudes will be employed, depending on price, availability, operational processing equipment, and the proportions of the various refined products that are desired.

1.3 Classification

The petroleum industry classifies “crude” by the location of its origin (e.g., “West Texas Intermediate, WTI” or “Brent”) and often by its relative weight or viscosity (“light”, “intermediate” or “heavy”); refiners may also refer to it as “sweet”, which means it contains relatively little sulfur, or as “sour”, which means it contains substantial amounts of sulfur and requires more refining in order to meet current product specifications. Each crude oil has unique molecular characteristics which are understood by the use of crude oil assay analysis in petroleum laboratories.

Barrels from an area in which the crude oil's molecular characteristics have been determined and the oil has been classified are used as pricing references throughout the world. These references are known as Crude oil benchmarks:

- ~ Brent Crude, comprising 15 oils from fields in the Brent and Ninian systems in the East Shetland Basin of the North Sea. The oil is landed at SullomVoe terminal in the Shetlands. Oil production from Europe, Africa and Middle Eastern oil flowing West tends to be priced off the price of this oil, which forms a benchmark.
- ~ West Texas Intermediate (WTI) for North American oil.
- ~ Dubai, used as benchmark for Middle East oil flowing to the Asia-Pacific region.
- ~ Tapis (from Malaysia, used as a reference for light Far East oil)
- ~ Minas (from Indonesia, used as a reference for heavy Far East oil)
- ~ The OPEC Reference Basket, a weighted average of oil blends from various OPEC (The Organization of the Petroleum Exporting Countries) countries.
- ~ Russian export blend crude oil (REBCO) is a medium gravity sour crude that accounts for exports of approximately 4 million barrels per day into the Atlantic Basin or to other nearby refining markets.

There are two main qualities of export oil in Russia: Urals Blend and Siberian Light. Siberian Light, produced in Siberia, has a lower sulphur content and lower viscosity than Urals Blend – a mixture of crude oils consisting of Siberian Light with high sulphur oils produced in Russia's European regions.

The industry standard for bulk measurement for both crude oil and liquid products was the petroleum industry barrel (abbreviated bbl) but now the metric tonne and the cubic meter are more commonly used, especially in international trade. The metric tonne may be converted to the barrel volume unit by dividing the mass unit by the density (specific gravity) of the particular oil being measured and multiplying by 6.2898. For example 1 tonne of Canadian crude, of density 0.85 g/cm^3 , equates to 7.4 bbl of oil (Eq. 8).

$$\frac{1 \text{ tonne} \times 6.2898 \text{ bbl/m}^3}{0.85 \text{ tonne/m}^3} = 7.4 \text{ bbl} \quad (8)$$

In all bulk measurements of petroleum and especially of crude oil it is necessary to specify the gross concentration of solids and nonpetroleum liquids present. This is normally stated as percent bottom sediment and water [% BS&W], and is determined by centrifuging of a representative sample.

Light petroleum gas is almost always present in solution in conventional crude oil and some wells are brought into production to produce solely natural gas. However, even when the objective is to produce oil this may contain as much as $50 \text{ m}^3/\text{m}^3$ (ca. $300 \text{ ft}^3/\text{bbl}$) of dissolved gas. High formation pressures help to dissolve the gas in the oil. Gas is usually separated at well gathering stations by the controlled release of gas from solution. Depending on the producing temperature and pressure of the oil, gas may be released from the oil in several stages and flared. Or it may be compressed for pipeline transport or for injection back into the formation when oil, rather than gas, is the product desired.

Formation water is produced along with the crude oil at rates that average about 10 % by volume. Much higher volumes are obtained from oil fields, which are using water flooding for enhanced recovery. The water and any dissolved salts are separated from the oil by gravity settling in field tank batteries after degassing, which leaves the crude oil ready for delivery. Shipped oil usually contains less than 0.5 % by volume sediment and water. Sediment and salts, mainly sodium chloride, can occur either dissolved in the aqueous phase of the oil, or as a fine particulate suspension in the oil phase. Other entrained insoluble mineral matter, such as sands and silts may also be present the extent of 15–30 g/tonne oil (5–10 lb/1,000 bbl), although the salt content alone can run as high as 300–1,500 g/tonne (100–500 lb/1,000 bbl). If this mineral matter is not removed before distillation, it can concentrate and accumulate on heat transfer surfaces during distillation and decrease thermal efficiency of the distillation. Thus, removal of nondissolved material has to be considered in the design of refinery process sequences.



Glossary

Alkane [al'keɪn] (n) – any saturated aliphatic hydrocarbon with the general formula C_nH_{2n+2} . Alkanes belong to organic compounds in which elements differ by a constant relative atomic mass 14. These organic hydrocarbon compounds have only single chemical bond in their chemical structure.

Aromatic hydrocarbons [æərəu'mætɪk 'haɪdrə(u)'kɑ:bən] – are those which contain one or more benzene rings. The name of the class came from the fact that many of them have strong, pungent aromas.

Barrel ['bær(ə)l] (abbreviated *bbl*) – the industry standard for bulk measurement for both crude oil and liquid products.

Crude oil [kru:d oɪl] (n) – a mixture of hydrocarbons.

Cycloalkane ['saɪkləu al'keɪn] (n) – (also called naphthenes, especially from petroleum sources) the type of alkanes which has one or more rings of carbon atoms in the chemical structure of their elements. It consists of only carbon (C) and hydrogen (H) atoms. Cycloalkane is saturated because there are no multiple C–C bonds to add more hydrogen to. General chemical formula $-C_nH_{2(n+1-g)}$ where **n** = number of C atoms and **g** = number of rings in the molecule.

Heavy crude oil ['hevi kru:d oɪl] or **Extra Heavy Crude oil** – is any type of crude oil which does not flow easily.

Heteroatom ['het(ə)rəu'ætəm] (n) – (from Ancient Greek *heteros* ≈ different + *atomos*) it is any atom that is not carbon or hydrogen. It is typically, but not exclusively, nitrogen, oxygen, sulfur, phosphorus, boron, chlorine, bromine, or iodine.

Homologue ['hɒmələʒ] (n) – the term homologue is used to describe a compound belonging to a series of compounds differing from each other by a repeating unit, such as a methylene group, a peptide residue, etc.

Hydrocarbon ['haɪdrə(u)'kɑ:bən] (n) – organic compounds consisting entirely of hydrogen and carbon.

Isoparaffin ['aɪsəu'pærəfɪn] (n) – branched-chain alkanes.

Kerogen ['kærədʒen] – is a mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks. It is insoluble in normal organic solvents because of the huge molecular weight of its component compounds. The soluble portion is known as bitumen.

When heated to the right temperatures in the Earth's crust, some types of kerogen release crude oil or natural gas, collectively known as hydrocarbons (fossil fuels).

Light crude oil [laɪt kru:d oɪl] – is crude oil with a low wax content.

Naphthalene [ˈnæftə, ɔɪ:n] (n) – also called cycloalkane has one or more rings of carbon atoms in the chemical structure of their elements.

Oil shale [ˈoɪl ʃeɪl] (n) – fine-grained shale containing oil, which can be extracted by heating. The chemical process of pyrolysis can convert the kerogen in oil shale into synthetic crude oil.

Organonitrogen compounds [o:ˈgænəuˈnaɪtrəʊdʒən ˈkɒmpaʊndz] – organic compounds having a C–N bond.

Organooxygen compounds [o:ˈgænəʊoˈɒksɪdʒən ˈkɒmpaʊndz] – are organic compounds that contain oxygen are (where “R” is an organic group): alcohols (R–OH); ethers (R–O–R); ketones (R–CO–R); aldehydes (R–CO–H); carboxylic acids (R–COOH); esters (R–COO–R); acid anhydrides (R–CO–O–CO–R); and amides (R–C(O)–NR₂).

Organosulfur compounds [o:ˈgænəʊsʌlfə ˈkɒmpaʊndz] – are organic compounds that contain sulfur (sulphur). They are often associated with foul odours, but ironically many of the sweetest compounds known are organosulfur derivatives. Nature abounds with organosulfur compounds – sulfur is essential for life. Two of the 20 common amino acids are organosulfur compounds.

Paraffin [ˈpærəfɪn] (n) – a common name for the alkane hydrocarbons.

Petrochemistry [ˌpetrəˈkemɪstri] (n) – the chemistry of petroleum and its derivatives; the branch of chemistry concerned with the chemical composition of rocks.

Petroleum [pəˈtrəʊlɪəm] (n) – (from Greek *petra* – rock and *elaion* – oil or Latin *oleum* – oil) a black, dark brown or greenish liquid found in porous rock formations in the earth.

Sour crude oil [ˈsauə kru:d oɪl] is crude oil containing the impurity sulfur. It is common to find crude oil containing some impurities. When the total sulfur level in the oil is >0.5 % the oil is called “sour”.

Sweet crude oil [swi:t kru:d oɪl] – is a type of petroleum. Petroleum is considered "sweet" if it contains less than 0.5 % sulfur, compared to a higher level of sulfur in sour crude oil. Sweet crude oil contains small amounts of hydrogen sulfide and carbon dioxide.

The American Petroleum Institute (API) gravity ['grævɪtɪ] – or API gravity, is a measure of how heavy or light a petroleum liquid is compared to water. If its API gravity is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks. API gravity is thus a measure of the relative density of a petroleum liquid and the density of water, but it is used to compare the relative densities of petroleum liquids.

Review Questions and Exercises



Exercise 1.1.

Answer the questions

1. Compare the structures and properties of the material in place for conventional petroleum, “heavy oil”, tar sands, and oil shale deposits.
2. How do the recovery methods and the recovery rates (as a proportion of the resource in place) compare for the hydrocarbon sources of question 1?
3. What postproduction measures are necessary for the reclamation of exhausted production areas for the hydrocarbon sources of sources of question 1?
4. Define the meaning of °API and explain how it is evaluated.
5. What general composition information does this quantity convey with respect to petroleum fractions?
6. What range of °API values could be expected for crude oils, for gasolines, and for lubricating oils?
7. Fully define the petroleum industry volume units: the barrel (bbl) and, in relation to natural gas, the “standard cubic foot”.

Exercise 1.2.



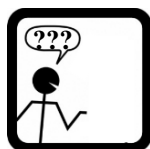
Choose two or three terms from the glossary and explain the meaning of these words to your partner, so let him/her guess what word you've chosen.



Exercise 1.3.

Match the substances with their characteristics.

1. Alkanes	a) Saturated cycloalkanes
2. Naphthenes	b) Organosulfur compounds
3. Arenes	c) Branched-chain alkanes
4. Thiols, sulfides, thiophenes	d) Organooxygen compounds
5. Piridine, quinoline, carbazole	e) Compounds have only single chemical bond
6. Isoparaffines	f) Organonitrogen compounds
7. Paraffinic acids, ketones, phenoles	g) Compounds contain one or more benzene rings



Exercise 1.4.

Find the substances out, which are not contained in oil.

1. Alkanes
2. Arenes
3. Naphthenes
4. Alkynes
5. Paraffines
6. Phenoles
7. Hydrogen sulfide



Exercise 1.5.

- *Watch video episode for the first time and choose a title for it.*

- A) Composition of crude oil.
- B) Equipment used for crude oil distillation.
- C) Crude oil distillation process.
- D) Condition needed for crude oil distillation.

- *Watch video episode for the second time and for A – E decide whether the statement is true or false according to the video. Give reasons.*

- A. Crude oil consists of small atoms joining together.
- B. When heated in a hot water pot, hydrocarbons with low boiling point are evaporated immediately.
- C. A white liquid is formed during the first fraction.
- D. The second fraction occurs at the temperature about 75⁰C.
- E. Fractional distillation occurs by means of electric heater, fractionating column, condenser and conical flask.



Exercise 1.6.

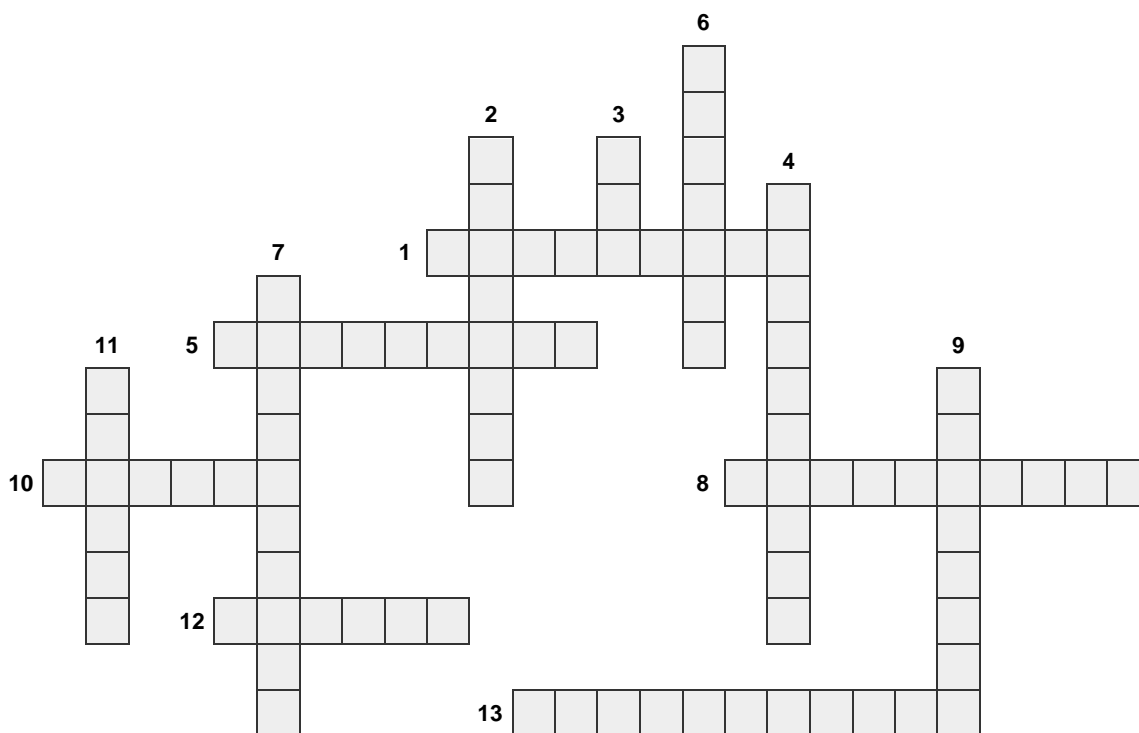
Discuss these questions with your partner.

- A) Why is fractional distillation used by technologists?
- B) Could you explain, why do diverse hydrocarbons need separating?
- C) What are the functions of electric heater, fractionating column, condenser and conical flask in fractional distillation?
- D) Why are different hydrocarbons condensed at divers temperatures?
- E) What do you know about boiling points of long and short molecules?
- F) What fractions and their products/derivatives do you know?



Exercise 1.7.

Crossword



1. A series of compounds with a similar general formula, usually varying by a single parameter such as the length of a carbon chain.
2. One of the two theories of oil birth.
3. ...-refining.
4. Any atom that is not carbon or hydrogen.
5. A black dark brown or greenish liquid found in porous rock formations in the Earth.
6. A mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks.
- 7.
8. Cycloalkane.
9. Approximately 4/5 of the Earth's atmosphere is made up of this gas
10. Aliphatic hydrocarbons with the general formula C_nH_{2n+2} .
11. On the periodic table of elements. This element has an atomic number of 16.
12. The industry standard for bulk measurement for both crude oil and liquid products.
13. Branched-chain alkanes.

UNIT 2

The *petroleum industry* includes the global processes of exploration, extraction, refining, transporting (often by oil tankers and pipelines), and marketing petroleum products. The largest volume products of the industry are fuel oil and gasoline (petrol). Petroleum is also the raw material for many chemical products, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics. The industry is usually divided into three major components: *upstream* (exploration, development and production of crude oil or natural gas), *midstream* and *downstream* (oil tankers, refiners, retailers, and consumers). Midstream operations are usually included in the downstream category.

Extracted crude oil has *oil gases* (50–100 m³/t), *reservoir water* (200–300 kg/t) and *mineral salts* dissolved in water (10–15 kg/t) which have negatively influence on transportation, storing and subsequent treatment. Hence, oil preparation to treatment includes some stages:

- ~ Oil stabilization
- ~ Oil desalting and dehydration
- ~ Oil distillation

2.1 Removal of oil gases (dissolved in oil) or oil stabilization.

Casinghead Gas

Crude oil has high degree of light hydrocarbons dissolved in it, so while transporting and storing they may be emitted and result changes in oil structure. In order to avoid gas loss, light benzene fraction and prevent pollution, it is necessary to extract these products from oil before its treatment.

Depending on conditions, oil stabilization is carried out by separation on the oil-field itself or gas processing plant. Oil gas is separated from oil by many-staged separation in *canks* (a gas separator device), where pressure and velocity of oil flow decreases. As the result, gas desorption occurs and light volatile hydrocarbons are removed and then condensed, forming “gas condensate”. Separation method of stabilization leaves up to 2 % of hydrocarbons C₁-C₄ in oil.

Gas produced with oil from an oil well as distinguished from gas from a gas well. The casing-head gas is taken off at the top of the well or at the separator. Over the years condensate has gone by many names: casing-head gas, casing-head gasoline, white gas, and drip gas.

Oil desalting and dehydration.

Crude oils delivered to the refinery frequently contain substantial quantities of water, silts, sand, extraneous salts, etc. “Desalting” involves removal of most of these impurities before further processing. If not removed they can increase scaling rates (buildup of deposits) or cause blockages of refinery equipment, such as heat exchangers, and increase corrosion. Two desalting methods are in common use, each using several processing units operating in series.

Chemical desalting is accomplished by addition of about 10 % water to the oil to be treated, plus sulfuric acid or sodium hydroxide as necessary for crude pH adjustment. Reagents are added just before the oil enters the desalting system charging pump to obtain good mixing (Fig. 1).

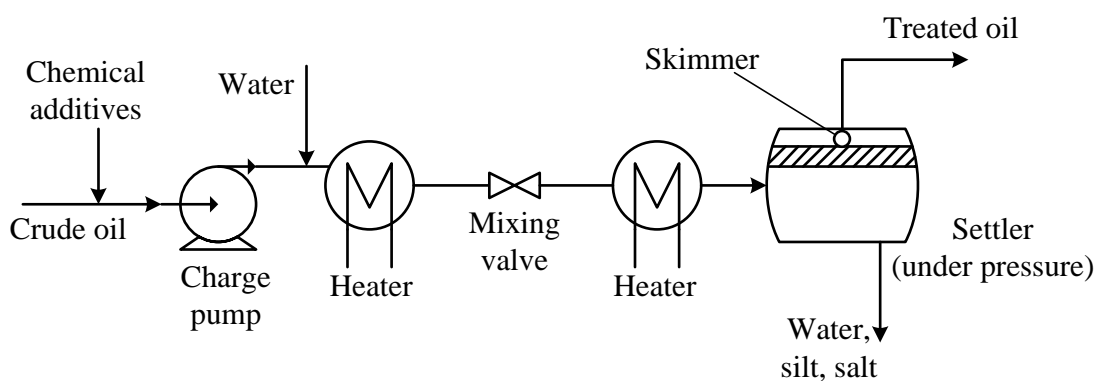


Fig. 1. Flow-sheet for the main steps involved in chemical desalting

The acid or base addition may be sufficient by itself to cause rapid demulsification after mixing, or a small concentration of a proprietary demulsifier, such as Tretolite (a polyethylenimine) may have to be added with the water to assist the process. The mixture is then heated to 65–180 °C (depending on oil viscosity and boiling point) and mixing is assured by passage through a mixing valve. It is then held for a time to allow separation of the oil and aqueous phases. Cleaned oil is drawn from the top of the vessel and the aqueous phase containing the salts, sand, silt, and other extraneous material is drawn from the bottom.

Electrostatic desalting is also common. As in chemical desalting, water is added to the oil stream (to dissolve any suspended salts) and the stream passed through a mixing valve into the desalter. Here oil–water separation is mainly accomplished with a high-potential electrostatic field instead of with demulsifying chemicals. The electrostatic field induces rapid coalescence and settling of water droplets together with any other water-associated impurities and “creaming” of the oil phase. The water phase is drawn continuously from the bottom of the desalter vessel and passed to the refinery effluent-

treatment plant. The oil phase is skimmed from the top for further processing. Desalting by one or the other or both of these two procedures is now a routine for the refining of most crudes. It is also sometimes used as a secondary clean-up to remove excess salt still remaining in distilled atmospheric gas oil before it is further processed. Desalting techniques have recently been reexamined experimentally.

2.2 Oil distillation

An oil refinery changes crude oil into many useful products. The refinery products can be taken away by sea, by pipeline or go to the chemical plant to be made into synthetic materials.

The first step is always primary distillation. The crude oil is a complicated mixture of compounds – most of them hydrocarbons. This mixture is split up into different fractions in the distillation tower. The fractions come out of the column at different levels.

The two major types of classical distillation include *continuous* distillation and *batch* distillation. Continuous distillation, as the name says, continuously takes a feed and separates it into two or more products. Batch distillation takes on lot (or batch) at a time of feed and splits it into products by selectively removing the more volatile fractions over time.

System refers to the chemical components present in the mixture being distilled. The two main groups are *binary* distillation and *multicomponent* distillation.

Binary distillation is a separation of only two chemicals. A good example is separating ethyl alcohol (ethanol) from water.

Multicomponent distillation is the separation of a mixture of chemicals. A good example is petroleum refining. Crude oil is a very complex mixture of hydrocarbons with literally thousands of different molecules. Nearly all commercial distillation is multicomponent distillation.

Distillation of crude oil accomplishes a rough sorting of the main components on the basis of boiling point differences. This was originally carried out on a batch basis, where the crude oil to be distilled was entirely in place in the distilling vessel at the start of heating. With a batch still the components of the crude are obtained in vapor form in sequence as the heat is applied, the lighter (lower boiling point) components first. Midrange and heavier, less volatile constituents are distilled later in the sequence, eventually leaving behind a viscous, high boiling point asphaltic residue in the distilling vessel.

Batch distillations are inefficient because of the need for separate steps for filling, heating, stopping, pumping out the residue, and refilling of the

distilling vessel again. For this reason, they tend to be economic only for distillations on a scale of less than 300 bbl/day (or 45 m³/day). This scale of production was only appropriate for local, very small distillate requirements from a simple refinery, which also happened to be close to a petroleum producing area, not a common situation today.

Processing Sequence

The major processing objectives set the system type and the equipment configuration needed. The common objectives include removing a light component from a heavy product, removing a heavy component from a light product, making two products, or making more than two products. All these major categories are called stripping, rectification, fractionation, and complex fractionation.

Stripping systems remove light material from a heavy product. *Rectification* systems remove heavy material from a light product. *Fractionation* systems remove a light material from a heavy product and a heavy material from a light product at the same time. *Complex fractionation* makes multiple products from either a single tower or a complex of towers combined with recycle streams between them.

Equipment Type

Industrial distillation is typically performed in large, vertical cylindrical columns known as distillation towers or distillation columns (are often called a *still*) with diameters ranging from about 65 centimeters to 16 meters and heights ranging from about 6 meters to 90 meters or more. When the process feed has a diverse composition, as in distilling crude oil, liquid outlets at intervals up the column allow for the withdrawal of different fractions or products having different boiling points or boiling ranges. The "lightest" products (those with the lowest boiling point) exit from the top of the columns and the "heaviest" products (those with the highest boiling point) exit from the bottom of the column and are often called the bottoms.

Distillation equipment includes two major categories, trays and packing. *Trays* force a rising vapor to bubble through a pool of descending liquid. *Packing* creates a surface for liquid to spread on.

For continuous distillation the crude oil is first heated to 400–550 °C while it is continuously flowing through a pipe still, using natural gas, "lightends" (miscellaneous low boiling point hydrocarbons), or fuel oil for fuel. The heated crude is then passed into a fractionating tower near the bottom, the hotter end of the tower. In the fractionating tower, a unit 2–3 m in diameter and 30–40 m high for a large modern refinery, the lower boiling components move up as vapors. As the vapor moves upward past each plate of the column it is forced, via the bubble caps ("bell caps") of that level, to

pass through and come to thermal equilibrium with the liquid on that plate or tray (see Fig. 2).

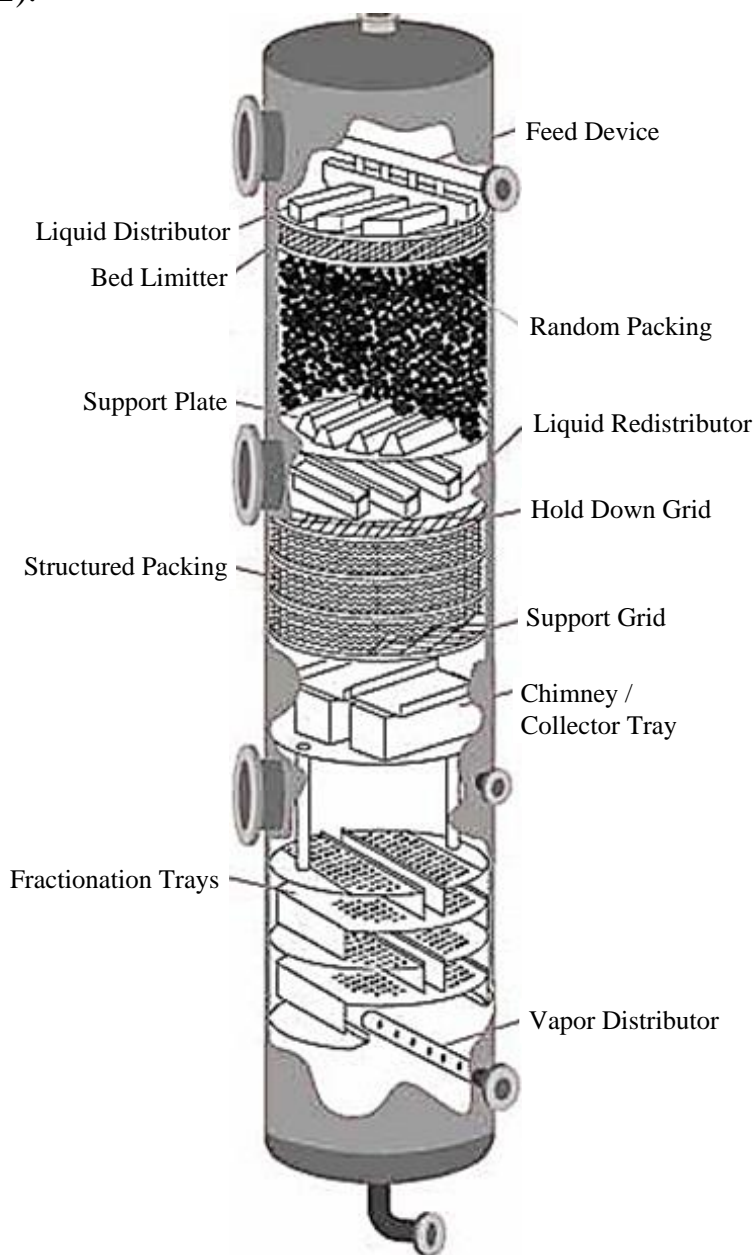


Fig. 2. Graphic and cutaway of a still

Hydrocarbons having a boiling point lower than the temperature of the liquid on the plate will continue to move up the column in vapor form. Components of the heated crude having a boiling point higher or the same as the temperature of the liquid on the plate will tend to condense in the liquid on the plate. As liquids of similar boiling points accumulate on the plate they either overflow into the projecting end of a “downcomer” pipe to the next lower plate, or they are drawn off the plate and the column as one of the product streams of the crude distillation. The lower end of each down-

comer is of sufficient length that it dips some distance into the liquid on the lower tray to prevent vapor movement up the downcomer.

2.3 The fractions from oil distillation

Follows after the crude oil has been cleaned and any remnants of brine removed. Distillation is the primary refining process. Distillation involves the separation of the different hydrocarbon compounds that occur naturally in a crude oil into a number of different fractions. In the atmospheric distillation process (Fig. 3), heated crude oil is separated in a distillation column (distillation tower, fractionating tower, atmospheric pipe still) into streams that are then purified, transformed, adapted, and treated in a number of subsequent refining processes, into products for the refinery's market. The lighter, more volatile, products separate out higher up the column, whereas the heavier, less volatile, products settle out toward the bottom of the distillation column. The fractions produced in this manner are known as straight run fractions ranging from (atmospheric tower) gas, gasoline, and naphtha, to kerosene, gas oils, and light diesel, and to (vacuum tower) lubricating oil and residuum.

The picture shows the familiar diagram of the names of the fractions and the levels at which they come out of the distillation tower.

In reality, a single tower could not cover the full range of temperatures needed to split up the heavier fractions.

The bottom three fractions have to be split up in a separate vacuum still.

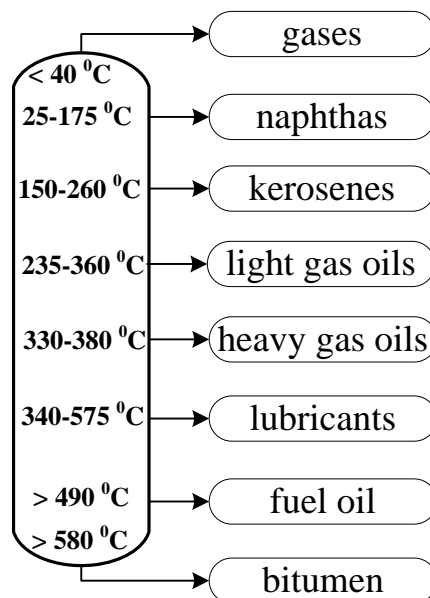


Fig. 3. Fractions of the atmospheric and vacuum distillations

The table 1 below shows the names and uses of the fractions that come from the distillation process. It also shows the ranges of hydrocarbons in each fraction.

Table 1

The fractions from distillation

Fraction	Carbons	BP °C	Uses
Gases	1 to 4	<40	~ Fuel in refinery ~ Bottled and sold as LPG
Naphthas	5 to 10	25–175	~ Blended into petrols ~ Feedstock for making chemicals
Kerosenes	10 to 16	150–260	~ Aviation fuel
Light gas oils	14 to 50	235–360	~ Diesel fuel production
Heavy gas oils	20 to 70	330–380	~ Feedstock for catalytic cracker
Lubricants	>60	340–575	~ Grease for lubrication ~ Fuel additives ~ Feedstock for catalytic cracker
Fuel oil	>70	>490	~ Fuel oil (power stations and ships)
Bitumen	>80	>580	~ Road and roof surfaces

Each fraction is a mix of hydrocarbons and each fraction has its own range of boiling points and comes off at a different level in the tower.

Notice that the ranges overlap. This is because the distillation process is not exact – some C-30 hydrocarbons will condense at the level for light gas oil and some will condense lower down.

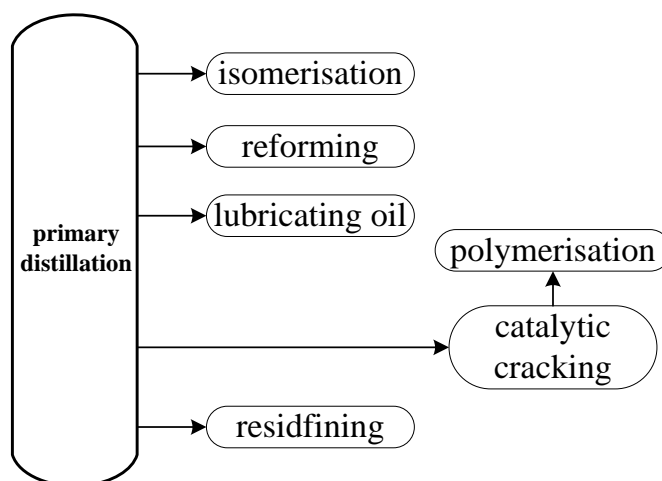


Fig. 4. An overview of some of the refinery processes

This overlap isn't very important for the heavier fractions. However, the lighter fractions, like LPG, are usually separated more tightly in another fractionating tower.

Some of the fractions are nearly ready to use. However, other fractions need more treatment.

Some treatments, like cracking, split the hydrocarbons into smaller groups. Others, like reforming and polymerisation, change the structure of the molecules.

Some of the lighter molecules are used as feedstock for the isomeriser and reformer.

Heavier molecules are often fed to the catalytic cracker (to be broken into smaller hydrocarbons) or are cleaned up in the residfiner before being used as fuel oil.



Glossary

Chimney [ˈtʃɪmni] – a vertical channel or pipe which conducts smoke and combustion gases up from a fire or furnace and typically through the roof of a building.

Grid [grɪd] – a framework of spaced bars that are parallel to or cross each other; a grating. The support grid is the physical support of the packing and the liquid hold up. In addition, the support grids must permit both the downward liquid as well as the upward gas to pass through to the limit of the capacity of the tower packing itself.

Oil dehydration and desalting [oɪl ˈdiːhɑːdreɪʃ(ə)n ənd ˈdiːˈsoːltɪŋ] – the process of preparation of oil for refining by elimination of water from it, mineral salt and mechanical impurities.

Oil-field water [oɪlfiːld ˈwoːtə] – it is water that accompanies oil when it is extracted from the earth. When dispersed in oil, it forms emulsions “water in oil” (dispersive phase – oil, disperse phase – water).

Oil pipeline [oɪl ˈpaɪplajn] (n) – some construction for transportation of oil and mineral oil.

Oil stabilization [oɪl ˈsteɪb(ə)laɪˈzeɪʃ(ə)n] – the process of removal of flying hydrocarbons. It is carried out on oil-fields or main pump stations. Dissolved gases content in stable petroleum is not higher than 1 – 2 %. Hydrocarbon gases are directed to gas processing plants. Stable petroleum is directed to refineries.

Primary distillation of oil [ˈpraɪm(ə)rɪ ˌdɪstrɪˈleɪʃ(ə)n əv oɪl] – the process of oil refining based on the hydrocarbon mix division making it by a method of fractional distillation, on separate distillates with certain in-

tervals of boiling temperature. Preliminary oil refinery is a physical process and doesn't affect chemical structure and nature of substances contained in oil. Straight-run of oil is the major primary process.

Skimmer ['skɪmə] – is a machine that separates a liquid from particles floating on it or from another liquid. A common application is removing oil floating on water.

Surface equipment ['sɜːfɪs ɪ'kwɪpmənt] – special equipment for surface mining fulfillment.

The upstream oil sector [ʌp'stri:m oil 'sektə] – is a term commonly used to refer to the searching for and the recovery and production of crude oil and natural gas. The upstream oil sector is also known as the exploration and production (E&P) sector.

The downstream oil sector [ˌdaʊn'stri:m oil 'sektə] – is a term commonly used to refer to the refining of crude oil, and the selling and distribution of natural gas and products derived from crude oil. Such products include liquified petroleum gas (LPG), gasoline or petrol, jet fuel, diesel oil, other fuel oils, asphalt and petroleum coke.

Tray [treɪ] – one of still components used for liquid distribution in rectification.

Vacuum distillation ['vækjuəm ˌdɪstrɪ'leɪʃ(ə)n] – a secondary distillation process which uses a partial vacuum to decrease the boiling point of residues from primary distillation and extract further blending components.



Review Questions and Exercises

1. Why is 520 °C approximately the upper limit for atmospheric pressure distillation of crude oil? How does this factor relate to the need to use reduced pressure for the refinement of lubricating oils by distillation?



Exercise 2.1.

Choose two or three terms from the glossary and explain the meaning of these words to your partner, so let him/her guess what word you've chosen.



Exercise 2.2.

Match the numbers with the letters to find out the meaning of the word.

- | | |
|-----------------------|---|
| 1. crude oil | a) деминерализация |
| 2. petroleum coke | b) пластовая вода |
| 3. naphathene | c) обезвоживание |
| 4. dehydration | d) бензин-растворитель |
| 5. desalting | e) нефтепровод |
| 6. naphtha | f) циклоалкан |
| 7. fuel oil | g) жидкое топливо |
| 8. oil shale | h) наземное оборудование
(буровой установки) |
| 9. oil refinery | i) нефтяной кокс |
| 10. alkylation | ж) нефтеносный сланец |
| 11. residue refining | к) октановое число (бензина) |
| 12. oil pipeline | л) сырая нефть |
| 13. oil-field water | м) нефтеперегонный завод |
| 14. surface equipment | н) переработка остатка |
| 15. octane number | o) алкилирование |



Exercise 2.3

Match the fraction and its boiling point interval

1. Gases	a) 330–380 °C
2. Naphtha	b) >490 °C
3. Kerosene	c) 150–260 °C
4. Light Gas Oil	d) <40 °C
5. Heavy Gas Oil	e) >580 °C
6. Lubricant	f) 25–175 °C
7. Fuel Oil	g) 340–575 °C
8. Bitumen	h) 235–360 °C



Exercise 2.4.

- *Watch video episode and underline the words you will hear.*

- 1) refinery
- 2) by land
- 3) consumer
- 4) computer
- 5) pipeline
- 6) chemicals
- 7) plant
- 8) airplane
- 9) economy

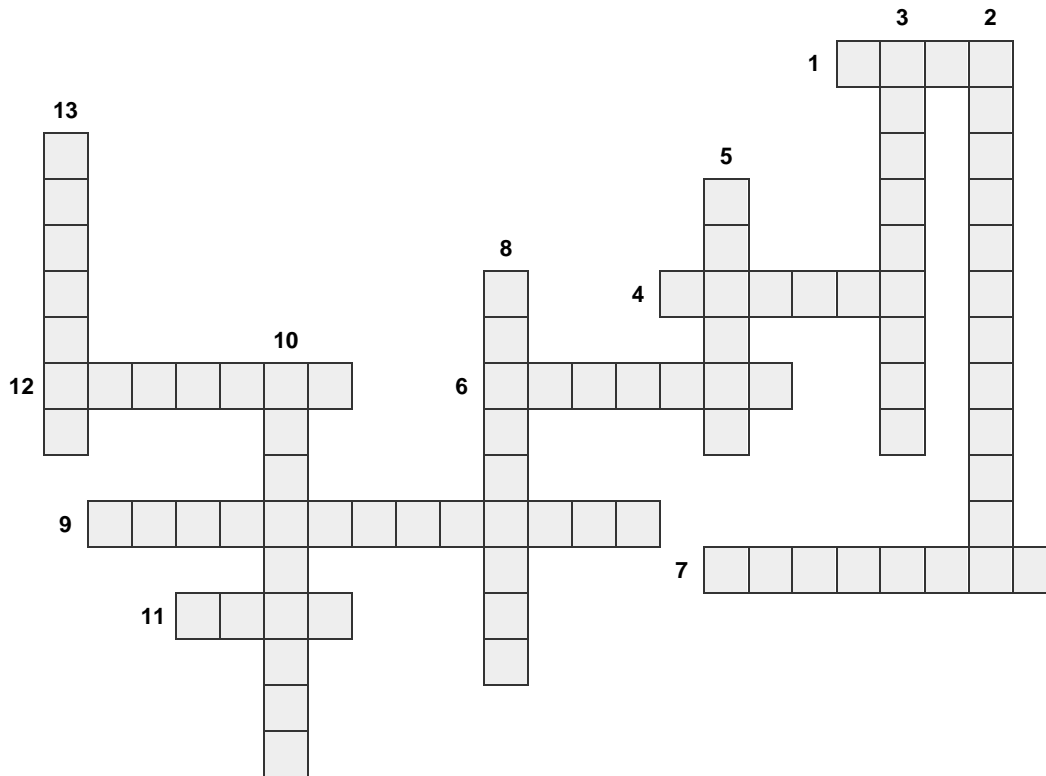
- *Watch video episode and for questions A-F, complete the gaps according to what you hear. You can use 1-3 words or a number or a combination of a number and words.*

Refinery it's a place where crude oil A into many petroleum products we need. The oil comes in through the B . When you look at the refinery most of the distilling towers are tall. C is based on a simple fact: the hydrocarbon compounds that make up a crude oil have D . Chemists know that it is needed E to evaporate solid carbon residues in the oil. Some of the fractions of crude oil result in many products we need today based on oil: F .



Exercise 2.5.

Crossword



1. A framework of spaced bars that are parallel to or cross each other; a grating.
2. Method for separating mixtures based on differences in the boiling points.
3. The process of cracking low-octane petroleum fractions in order to increase the octane number.
4. It is space that is empty of matter.
5. Is the equipment for increasing temperature.
6. Is a machine that separates a liquid from particles floating on it or from another liquid.
7. Some construction for oil transportation.
8. Is a process unit on an oil refinery that removes salt from the crude oil.
9. Is the process of removal of flying hydrocarbons. It is carried out on oil-fields or main pump stations.
10. Aggregate of mechanisms, machines, devices, and instruments necessary for the production
11. A machine or device for raising, compressing, or transferring fluids
12. A vertical channel or pipe, which conducts smoke and combustion, gases up from a fire or furnace and typically through the roof of a building.
13. The outer or the topmost boundary of an object.

UNIT 3

Oil is perhaps the most critical source of energy worldwide. Overall consumption is on the rise as more and more of the world industrialize and start utilizing modern machines.

Crude oil production for various countries is shown in table 2. The Middle Eastern countries produce more oil than they consume; the extra production is gated for export. Conversely, the United States and Western Europe consume much more crude oil than they produce. This condition demonstrates the great importance of worldwide petroleum movements. The difference between production and consumption for any one period is balanced by oil being added to or removed from extensive areas around the world.

Table 2
Top World Oil Producers, Exporters, Consumers, and Importers, 2006 [10]
(millions of barrels per day)

№	Producers	Total oil production	Exporters	Net oil exports	Consumers	Total oil consumption	Importers	Net oil imports
1	Saudi Arabia	10.72	Saudi Arabia	8.65	United States	20.59	United States	12.22
2	Russia	9.67	Russia	6.57	China	7.27	Japan	5.10
3	United States	8.37	Norway	2.54	Japan	5.22	China	3.44
4	Iran	4.12	Iran	2.52	Russia	3.10	Germany	2.48
5	Mexico	3.71	United Arab Emirates	2.52	Germany	2.63	South Korea	2.15
6	China	3.84	Venezuela	2.20	India	2.53	France	1.89
7	Canada	3.23	Kuwait	2.15	Canada	2.22	India	1.69
8	United Arab Emirates	2.94	Nigeria	2.15	Brazil	2.12	Italy	1.56
9	Venezuela	2.81	Algeria	1.85	South Korea	2.12	Spain	1.56
10	Norway	2.79	Mexico	1.68	Saudi Arabia	2.07	Taiwan	0.94

In 2010 total world crude oil production was 69.7 million bpd (barrels per day) it decreased by 1.9 million bpd compared to 2006. Russia is the major producer of crude oil and acquired no. 1 position. It shared 9.8 million bpd followed by Saudi Arabia 8.16 bpd and United States 5.5 million bpd. As Organization of the Petroleum Exporting Country (OPEC) has highest crude reserves but it produces only 42 % of total world production, whereas

Organization for Economic Co-operation and Development (OECD) has just 4 % crude oil reserves and produces 19 % of total crude production.

The growth of world refining capacity attempts to keep pace with rising demand for petroleum-based products. Curiously, refining capacity has surged ahead in some regions, notably the Middle East and the Asia–Pacific region. Last decades, the refinery throughput was almost flat in the developed markets. Thus, new and larger state-of-the-art refining facilities were more energy efficient and had lower operating costs per barrel of refined products. Consequently, smaller refiners could not compete against new facilities and subsequently had to shut down operations. Another factor in refining growth is the time to construct processing units. In highly industrialized countries such as the United States, Japan, and Western European countries, mounting environmental regulations and stiff emission and performance laws have all but stifled the construction of new grassroots refineries. Construction of new refining capacity must overcome a long list of federal, state, and local governmental requirements. New governmental regulations are focused on strict reductions on emissions (air, water, and solids) to improve air quality for high-density populated areas and high-density industrial regions. Consequently, construction of new facilities in developed markets is negligible.

In industrialized nations, new refining capacity will be realized by the expansion of existing facilities that are permitted by the local regulatory agencies. Even expanding existing facilities is exempted from environmental constraints. With new construction and capacity expansion, operating companies must cut emissions below present permitted levels. Thus, operating companies must install more intrusive emission reduction/control technologies and equipment to eliminate release from new and existing plant equipment.

Refiners have become particularly adept in using technology to find incremental capacity from existing processing equipment. Thus, the refining industry can process more crude oil with present equipment. In spite of this, the number of refineries is decreasing; yet, capacity increases incrementally.

Advancements and innovations in processing methods and catalyst systems have enabled construction of large, highly integrated and complex refining complexes. New materials of construction have aided in building larger facilities; thus, smaller, older refineries cannot compete with newer, larger facilities. The number of operating facilities continues to decrease; yet capacity rises. Less efficient facilities shut down their operations since they are handicapped in producing refined products. Technological advancements in processing methods and catalyst systems have enabled refiners to increase the capacity of existing units incrementally. Newer processing units are

larger than the earlier versions. Refiners are applying economies-of-scale to disperse the product costs of refineries.

3.1 Refining Schemes

A refinery is a complex processing methodology involving a massive network of vessels, reactors, distillation columns, rotating/compression equipment, heat exchangers, and piping. The total scheme can be subdivided into a number of unit processes. In what follows, only the major flow streams will be shown, and each unit will be depicted by a simple block in the flow diagram.

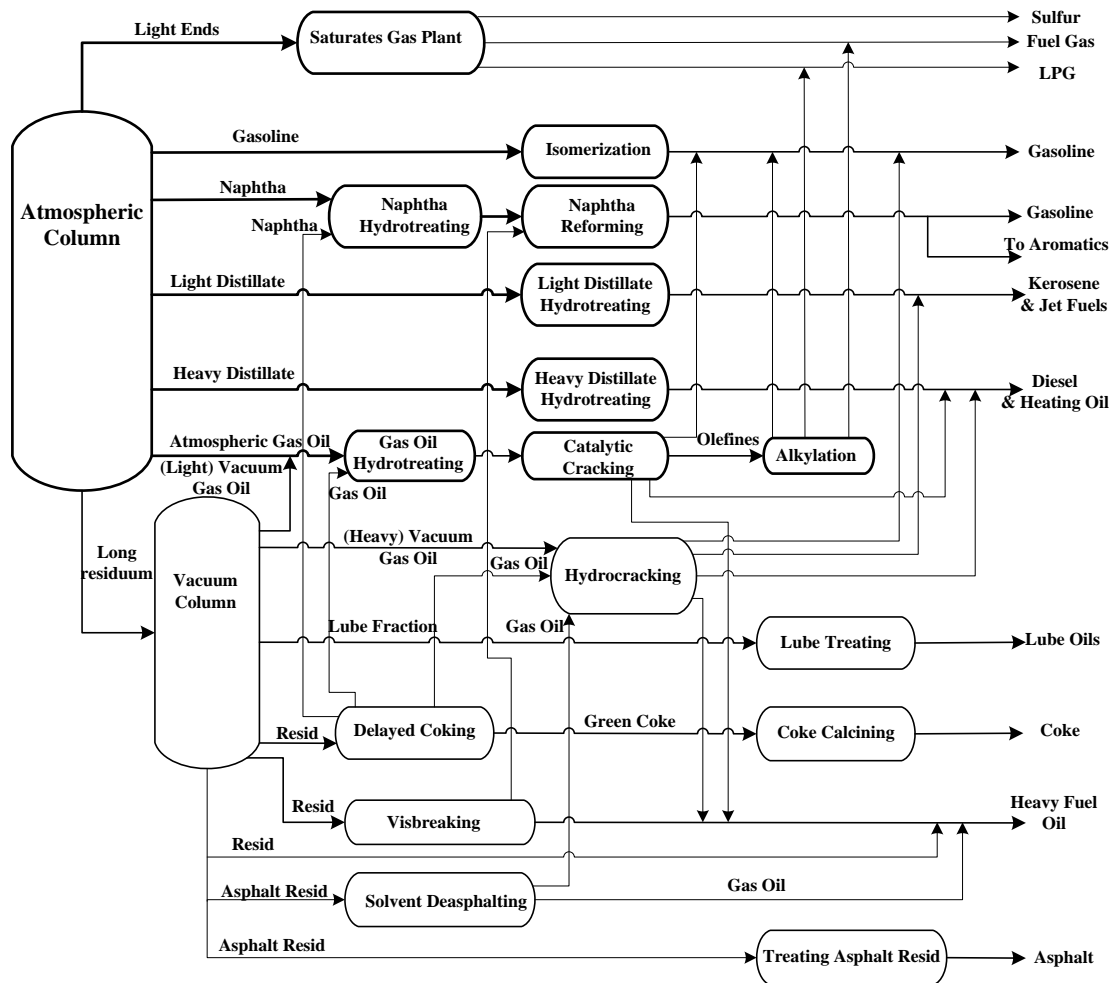


Fig. 5. Process flow diagram for a modern integrated refinery [3]

Refined products establish the order in which each refining unit will be introduced. Only one or two key product(s) specifications are used to explain the purpose of each unit. Nevertheless, the reader is reminded that the choices between several types of units and size of these units are complicat-

ed economic decisions. The trade-offs among product types, quantity, and quality will be mentioned only to the extent that they influence the choice of one type of processing technology over another.

The refining scheme shown in Fig. 5 is a simplified view of an integrated refinery. More processing steps can be added and are dependent upon the product slate of the refinery and the cracking slate anticipated for its design. If the refinery is a gasoline refinery, the cracking process will be directed toward producing light products – gasoline at the expense of diesel and heating oil. Conversely, if diesel is the desired end-product, gasoline product is sacrificed to produce more distillate streams. The U.S. refineries are predominately gasoline-oriented. Conversely, Western European refineries are diesel-fuel oriented. In Western Europe, the demand for gasoline is projected to decline over the next 10 years, while demand for middle distillates increases. Therefore, Western European refiners must adapt operations not only to produce more diesel but also to minimize gasoline production.

For industrial areas, where the principal demand is for transportation fuels or high-quality heating oils, the simplified refining scheme is shown in Fig. 5.

In the case of a U.S. refinery, the emphasis is directed into converting more of the crude oil into lighter products, namely gasoline. If this refinery processed a Light Arabian crude, nearly 80–85 vol. percent of the products would be lighter than the boiling temperature of 650 °F (340 °C) compared with the 55 vol. percent existing in the feed crude oil (Fig. 6). More than half of all U.S. products are gasoline and lighter distillates (boiling temperatures below 400°F (200 °C)) compared with 29 vol. percent in the crude oil.

	Cut	BP, °F (≈°C)		Product	BP, °F (≈°C)
8	LT Naph	50 – 200 (10 – 90)	5	Gases	-40 – 100 (-23 – 40)
21	NV Naph	200 – 400 (90 – 200)	45	Gasoline	100 – 400 (40 – 200)
11	Kerosine	400 – 500 (200 – 260)			
15	Gas oil	500 – 650 (260 – 340)	5	Jet fuel & Kerosine	300 – 500 (150 – 340)
45	Residue	650 (340)	25	Fuel oil	400 – 600 (200 – 320)
			5	Lube/etc	600 (320)
			15	Residue	600 (320)

Fig. 6. Light Arabian crude oil compared with U.S. product deliveries [3]

This comparison is unique for these circumstances. Refining technologies and catalysts have advanced from the earlier days. Notably, refiners can process a variety of crudes into valued end-products. Crudes that require more intense processing, that is, high-severity hydrocracking and hydrotreating, fetch a lower price on the market and are often referred to as *opportunity crudes*. Refiners processing lower-cost, sour, heavy crude must make more capital investment in processing capability. However, these refiners pay less for their feedstocks and risk attaining payback on capital investments through volume processing of lower-cost feedstocks. The design of an integrated refinery constantly balances the future price of oil against the return on investment for refining capacity. Thus, the decision on what types of crude to process will impact the design and operation of a refinery.

3.2 Cracking

As mentioned earlier, the refining process involves adding hydrogen to carbon molecules. Notably, the desired hydrocarbons are much lighter products; thus, the refining process strives to break the large, complex hydrocarbon molecules into smaller molecules and add hydrogen to the open bonds. Cracking processes typically break hydrocarbon molecules into two or more smaller molecules. Thermal cracking uses high-temperature (above 650 °F (340 °C)) and a long residence time to sever hydrocarbon bonds. Higher pressure facilitates the cracking process; however, the capital investment for a high-pressure reactor is greater than the expense for low- or medium-pressure reactors.

In *thermal cracking*, the formation and deposition of coke on piping and equipment walls is an unwanted side reaction. Another option to crack crude oil into desired products at lower pressures and temperatures is *catalytic cracking*. Catalytic cracking splits the molecules quicker and at lower temperatures. Catalysts are used to promote the desired reaction rate for the process.

Catalytic cracking involves large reactors with large fluidized catalyst beds. As in the case of thermal cracking, coke is also formed during the catalytic process, which can deposit on the catalyst and hinder its activity. Thus, this process uses reactor-separators and regenerators to remove the catalyst and regenerate it and return the catalyst back to process. The fluidized bed mixes the feed with the catalyst to optimize contact time. The catalyst is separated from the hydrocarbon products. A portion is regenerated; the remainder is returned to the catalytic cracker reactor.

Table 3

Comparison of products of thermal and catalytic cracking

Hydrocarbon Type	Thermal Cracking	Catalytic Cracking
<i>n</i> -Paraffins	C ₂ is major product, with much C ₁ and C ₃ , and C ₄ to C ₁₆ olefines; little branching	C ₃ to C ₆ is major product; few <i>n</i> -olefins above C ₄ ; much branching
Olefines	Slow double-bond shifts and little skeletal isomerization; H-transfer is minor and nonselective for tertiary olefins; only small amounts of aromatics formed from aliphatics at 932 °F (500 °C)	Rapid double-bond shifts, extensive skeletal isomerization, H-transfer is major and selective for tertiary olefins; large amounts of aromatics formed from aliphatics at 932 °F (500 °C)
Naphthenes	Crack at slower rate than paraffins	If structural groups are equivalent, crack at about the same rate as paraffins
Alkyl-aromatics	Cracked within side chain	Crack next to ring

Catalytic cracking is very effective in upgrading heavy refining streams, such as gas oils, into motor gasoline stocks thereby increasing the octane number for product streams. This process produces less gas and coke as compared with thermal cracking operations. Catalytic cracking also yields more liquid products, which can be tailored toward gasoline or diesel fuel and home heating oil products. Different operating conditions and catalysts will define the product mix from a catalytic cracker.

Several factors determine the best feeds for catalytic crackers. Heavy feeds are preferred; thus, the lower boiling point is about 650°F (340 °C). The feed should not be so heavy that it contains an undue amount of metal-bearing compounds or carbon-forming material. Deposition of metals and coke can quickly deactivate the catalyst.

The product distribution from thermal cracking is different from catalytic cracking, as shown in Table 3. The shift in product distribution confirms the fact that these two processes proceed via different mechanism.

Visbreaking is a mild, once-through thermal cracking process. It is used to crack resid products into fuel-oil specifications. Although some light products such as naphtha and gasoline are produced, this is not the purpose of the visbreaker.

Coking is another matter. It is a severe form of thermal cracking in which coke formation is tolerated to attain additional lighter liquids from the heavier, dirtier fractions of crude oil. In this process the metals that would foul catalysts are laid down with the coke. The coke settles out in large coke drums that are removed from service frequently (about once a day) to have

the coke removed by hydraulic methods. Several coke drums are used to make the process continuous; thus, one drum is online while the other is being emptied and readied for the next cycle.

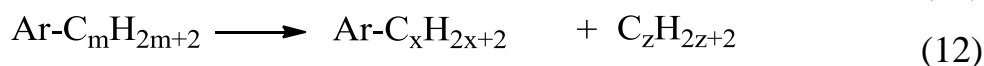
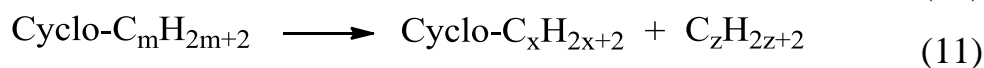
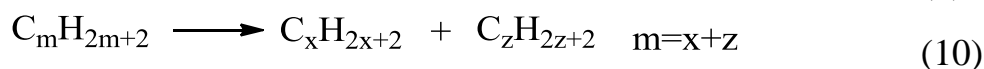
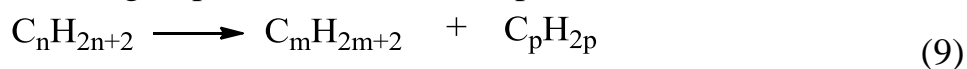
Hydrocracking converts a wide variety of heavy refining product streams into light products – fuels and distillates. A robust catalyst system is used to desulfurize, denitrify, and hydrocrack the feed. The process combines hydrotreating and catalytic cracking goals. However, hydrocracking is a more capital-intensive and operating-intensive step. The operating pressure is higher (up to 3000 psi (20.68 MPa)); consequently, thick-wall vessels are used as reactors (up to 9 in. (228.6 mm) thick). Products from a hydrocracker are very clean (desulfurized, denitrified, and demetalized) and will contain isomerized hydrocarbons in greater quantity than from conventional catalytic cracking. This process consumes a large quantity of hydrogen, which adds considerably to its operating costs.

3.3 Catalytic Cracking

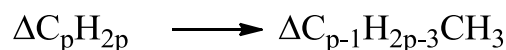
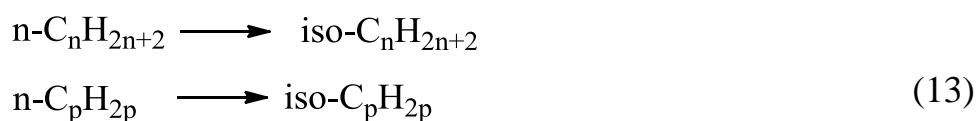
This process upgrades heavier products into lighter products. Catalyst systems are used to catalytically crack the large, heavy hydrocarbons into smaller compounds. The products contain a higher hydrogen to carbon ratio than the feed. Consequently, excess carbon is produced, which can deposit on the catalyst and piping and equipment walls; both effects are undesirable. The first commercial fluidized cracking catalyst was acid-treated natural clay. Later, synthetic silica-alumina materials containing 10 to 15 percent alumina replaced the natural clay catalysts. The synthetic silica-alumina catalysts were more stable and yielded superior products.

A complex series of reactions take place when a large gas-oil molecule comes in contact with a 1200 °F to 1400 °F (650 °C to 760 °C) FCC catalyst.

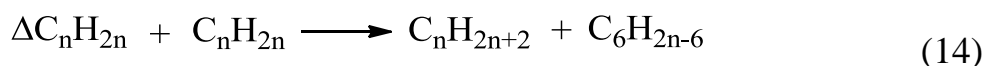
1. Cracking of paraffines, olefins, naphthenes and aromatic:



2. Isomerization:



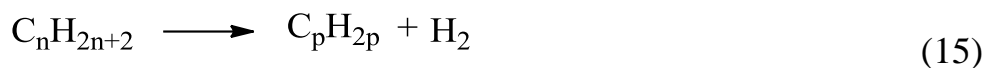
3. Hydrogen Transfer:



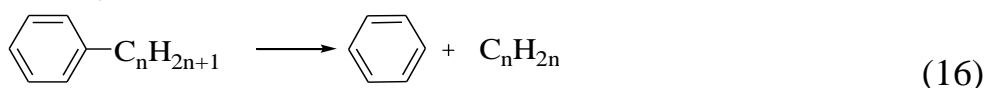
4. Trans-alkylation / Alkyl-group Transfer

5. Cyclization of Olefines to Naphthenes

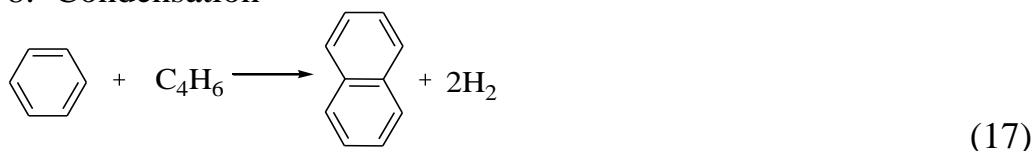
6. Dehydrogenation:



7. Dealkylation:



8. Condensation



The distribution of products depends on many factors, including the nature and strength of the catalyst acid sites. Although most cracking in the FCC is catalytic, thermal cracking reactions also occur.

A typical catalytic cracking unit is shown in Fig. 7. The unit comprises two large vessels – one to react feed with hot catalyst and the other to regenerate the catalyst by burning off the carbon deposits with air. The key feature of the catalytic cracking operation is the short contact time between the catalyst and feed to produce the desired products. Extended contact between the feed and catalyst promotes overcracking and the creation of gases. The activity of newer catalysts selectively promotes primary cracking reactions. New catalysts use a distributed matrix structure; zeolites are applied to the surface and pores of the catalyst, thus increasing the number of active sites. With more active sites, the activity of the catalysts increases and less contact time is necessary.

The short contact time is accomplished by using a transfer line between the regenerator and the reactor vessels. Most of the reaction occurs within the riser section. A termination device can be used to separate the catalyst from the products that are taken quickly as overhead. The main reactor vessels contain cyclone separators to remove the catalyst from the products and provide additional space for cracking the heavier fraction of the feed.

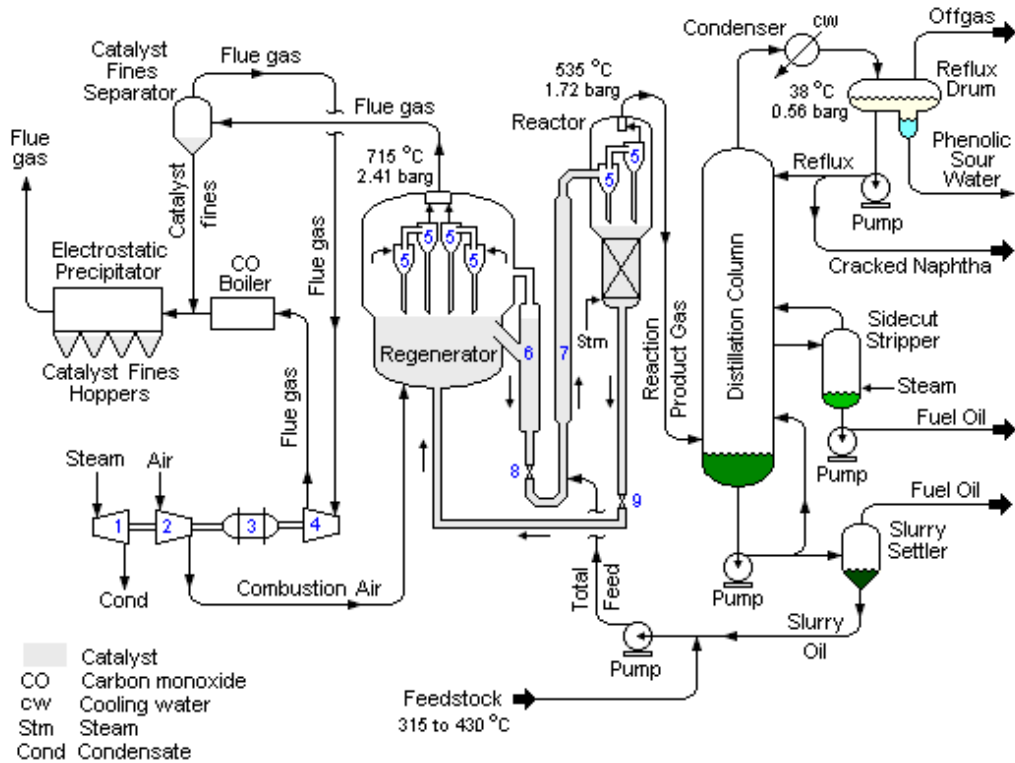


Fig. 7. A schematic flow diagram of a Fluid Catalytic Cracking unit as used in petroleum refineries [5]:

1 – Start-up steam turbine; 2 – Air compressor; 3 – Electric motor/generator; 4 – Turbo-expander; 5 – Cyclones; 6 – Catalyst withdrawal well; 7 – Catalyst riser; 8 – Re-generated catalyst slide valve; 9 – Spent catalyst slide valve

Fluid catalytic cracking (FCC) continues to play a key role in an integrated refinery as a primary conversion process. For many refiners, the cat cracker is the key to profitability in that the successful operation of the unit determines whether or not the refiner can remain competitive in today's market.

Approximately 350 cat crackers are operating worldwide, with a total processing capacity of over 12.7 million barrels per day [4]. Most of the existing FCC units have been designed or modified by six major technology licensors:

1. ABB Lummus Global
2. Exxon Research and Engineering (ER&E)
3. Kellogg Brown & Root – KBR (formerly The M.W.Kellogg Company)
4. Shell Oil Company
5. Stone & Webster Engineering Corporation (SWEC)/IFP
6. UOP (Universal Oil Products)

In the fluidized catalytic cracking (FCC) process, the feed is injected into the reactor (fig. 8) through a feed-nozzle system and mixed with the catalyst. The FCC unit uses a microspheroidal catalyst, which behaves like a liquid when properly aerated by gas. The atomized oil mixes with the catalyst and ascends the riser.

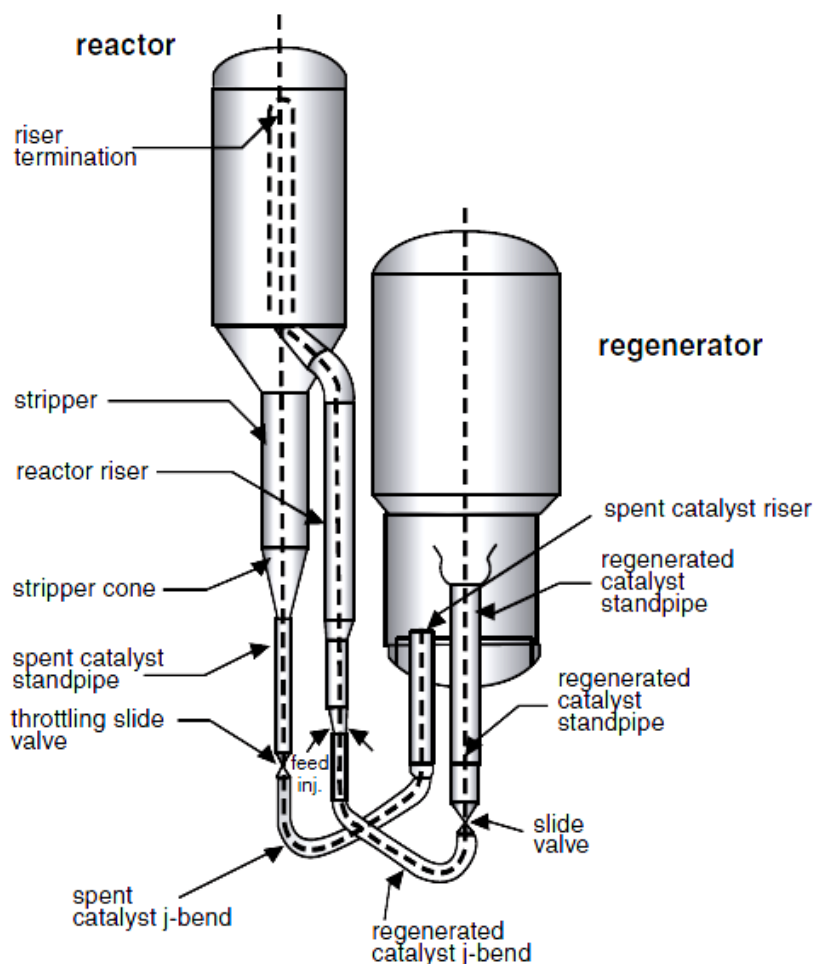


Fig. 8. Flexicracking Unit of Exxon Research and Engineering [4]

The cracking process – *riser cracking* or short-time contacting – has several advantages. This system can operate at high temperatures, thus promoting the conversion of feed into gasoline and olefins. It minimizes the destruction of any aromatics formed during cracking. The net effect is gasoline production with two to three higher octane.

The catalyst is regenerated at high temperatures (1300–1400 °F (705–760 °C)). Coke that is deposited on the catalyst is quickly burnt off with high-temperature air. Newer catalysts are rugged and can withstand the rigors of extreme heat and fluidizing.

The catalytic cracking unit is often referred to as the gasoline work-horse of a refining unit. As shown in Fig. 5, feeds to the catalytic cracking

unit are gas oils from the atmospheric and vacuum distillation columns and delayed coker. These heavier fractions also carry metals such as nickel, vanadium, and iron. More important, sulfur compounds concentrate in the heavier product fractions.

Table 4

Typical Gasoline Pool Composition of a Refinery

Gasoline Blendstocks	% of Pool Volume	% of Pool Sulfur
Alkylate	12	–
Coker naphtha	1	1
Hydrocracked naphtha	2	–
FCC naphtha	36	98
Isomerate	5	–
Light straight-run naphtha	3	1
Butanes	5	–
MTBE	2	–
Reformate	34	–
Total	100	100

Table 4 lists a typical mass balance for sulfur. FCC blendstocks comprise 36 percent of the volume of the gasoline pool. However, this stream also contributes 98 percent of the sulfur concentration to blended products. As specifications on sulfur concentrations in diesel and gasoline tighten, more efforts are focused on how feeds and product streams from the FCC are pre- and post-treated for sulfur concentrations.

3.4 Hydrocracking

Before the late 1960s, most hydrogen used in processing crude oil was for pretreating catalytic reformer feed naphtha and for desulfurizing middle-distillate products. Later, sulfur requirements for fuels were lowered and became an important consideration. The heavier fractions of crude oil are the fractions with the highest sulfur concentrations and are more difficult to treat. With a constant decline in demand for heavy fuel oils, refiners needed to convert heavier fractions into lighter products. Thus, hydrocracking became a possible solution to the problem.

Basically, catalytic hydrocracking involves three primary chemical processes [11]:

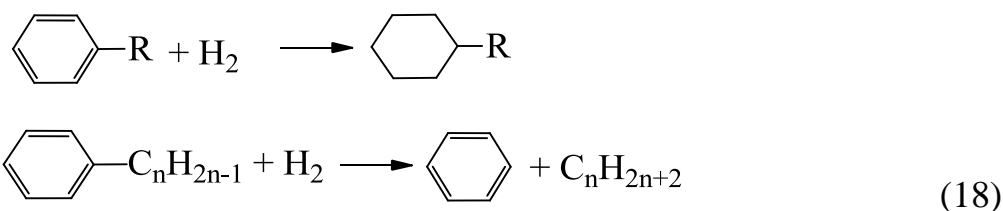
- ~ Cracking of high-boiling, high molecular weight hydrocarbons found in petroleum crude oil into lower-boiling, lower molecular weight hydrocarbons.

~ Hydrogenating unsaturated hydrocarbons (whether present in the original feedstock or formed during the cracking of the high-boiling, high molecular weight feedstock hydrocarbons) to obtain saturated hydrocarbons usually referred to as paraffins or alkanes.

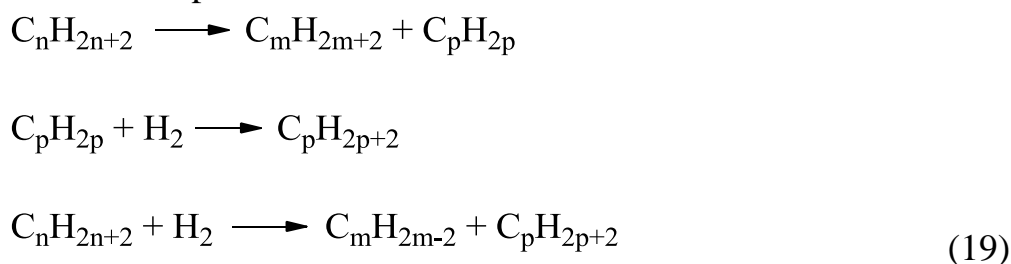
~ Hydrogenating any sulfur, nitrogen or oxygen compounds in the original feedstock into gaseous hydrogen sulfide, ammonia and water.

The above primary processes include too many complex reactions to describe each of them in detail. The following four reactions are provided as examples of those complex reactions:

1. Addition of hydrogen to aromatics converts them into hydrogenated rings. These are then readily cracked using acid catalysts.



2. Acid catalyst cracking opens paraffinic rings, breaks larger paraffins into smaller pieces and creates double bonds.



3. Addition of hydrogen to olefinic double bonds to obtain paraffins.



4. Isomerization of branched and straight-chain paraffins.



Hydrocracking catalysts consist of active metals on solid, acidic supports and have a dual function, specifically a cracking function and a hydrogenation function. The cracking function is provided by the acid catalyst support and the hydrogenation function is provided by the metals.

The solid acidic support consists of amorphous oxides such as silica-alumina, crystalline zeolite or a mixture of amorphous oxides and crystalline

zeolite. Cracking and isomerization reactions (reactions 2 and 4 above) take place on the acidic support. Metals provide the hydrogenation reactions (reactions 1 and 3 above).

The metals that provide the hydrogenation functions can be the noble metals palladium and platinum or the base metals (i.e., non-noble metals) molybdenum, tungsten, cobalt or nickel.

Catalyst cycle life has a major impact on the economics of hydrocracking. Cycles can be as short as 1 year or as long as 5 years. Two years are typical.

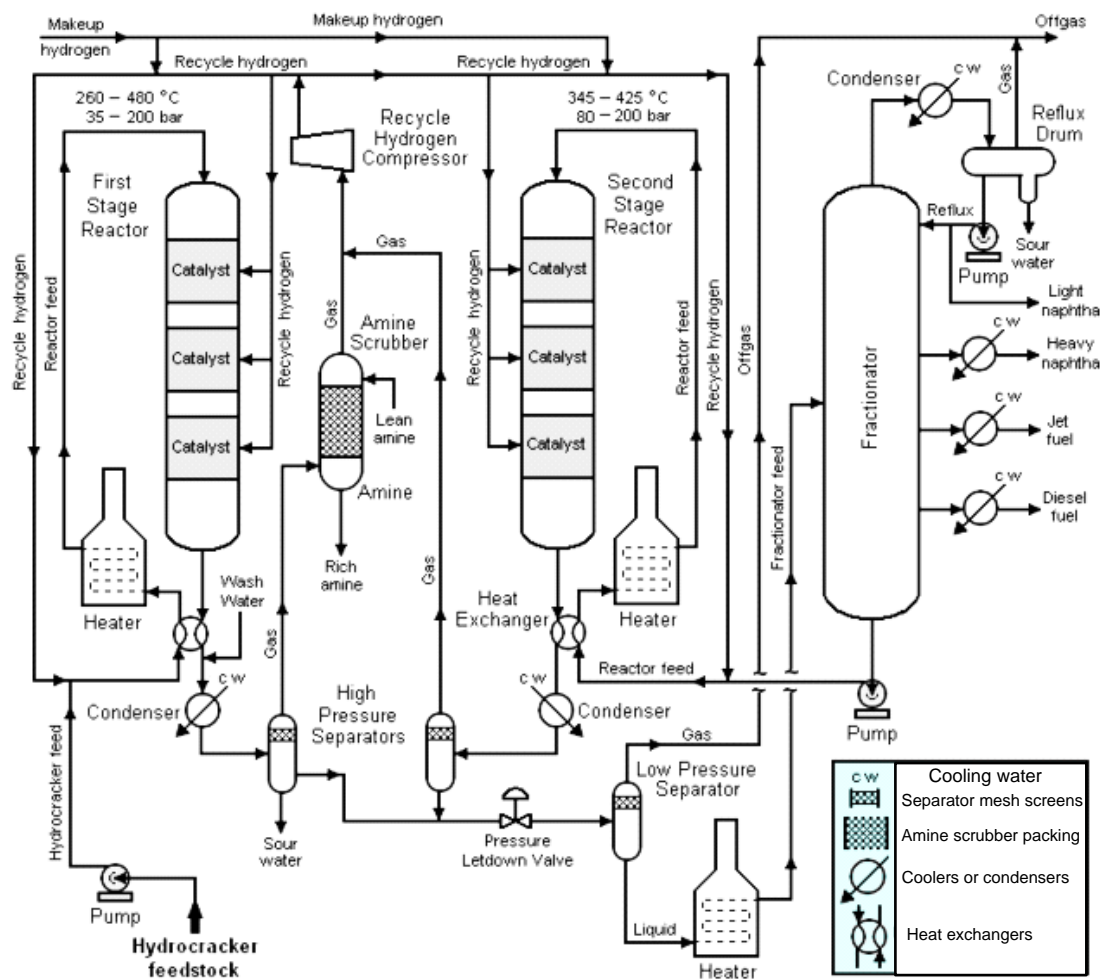


Fig. 9. Schematic flow diagram of a typical hydrocracker

Figure 9 is a typical flow diagram of a hydrocracking process. The process is similar to hydrotreating. The feed is pumped to operating pressure, mixed with hydrogen-rich gas, heated, passed through a catalytic reactor, and distributed among various fractions. Yet this process does significantly differ from hydrotreating. In the hydrocracking process, operating pressures

are very high – 1500–3500 psia (10.34–24.13 MPa). Hydrogen consumption is also greater – 1200–1600 scf (34–45.3 m³) of hydrogen per barrel of feed, depending on the extent of cracking. If the refinery has a high hydrogen demand due to hydrocracking needs, construction of an onsite hydrogen plant may be necessary.

Hydrocracking catalysts perform a dual function. They provide both hydrogenation and dehydrogenation reactions and have a highly acidic support to foster cracking reactions. The hydrogenation–dehydrogenation components of the catalyst are metals such as cobalt, nickel, tungsten, vanadium, molybdenum, platinum, palladium, or a combination of these metals. The acidic support can be silica–alumina, silica–zirconia, silica–magnesia, alumina–boria, silica–titania, acid-treated clays, acidic-metals phosphates, or alumina, to name a few.

Greater flexibility is attributed to most hydrocracking processes. Under mild conditions, the process can function as a hydrotreater. Under severe conditions – high pressure and temperatures – this process can produce a variety of motor fuels and middle distillates, depending on the feedstock and operating variables. Even greater flexibility is possible if the process is tailored to convert naphthas into liquefied petroleum gases or convert heavy residues into lighter products.

Hydrocracking is a swing process; it is a treater and a cracker. Thus, this process function can be incorporated into a number of different places within a refining scheme. As a cracker, it can convert feeds that are too heavy or too contaminant-laden to go to catalytic cracking. As a treater, it can handle high boiling point fractions such as heating oil and saturate this fraction to provide good burning quality.

With pending low-sulfur fuels specifications, hydrocracking efforts will be increased to break complex hydrocarbon compounds and expose embedded sulfur molecules. Hydrocracking significantly upgrades feeds to downstream processes and fuel products, especially diesel products.

3.5 Catalytic Reforming

This process upgrades naphtha (light distillates) into aromatic-rich streams that can be used for octane enhancers for gasoline blending or as a petrochemical feedstock. Originally the process was developed in the 1950s to upgrade low-octane, straight-run gasoline to high-octane liquid. This process converts naphthenes into corresponding aromatics and isomerizes paraffinic structures to isomeric forms. The naphtha charge is a varying mixture of C₆–C₁₁ paraffins, naphthenes, and aromatics. In a catalytic reformer, aro-

matic compounds pass through the system unchanged, while naphthalenes react selectively to form aromatics.

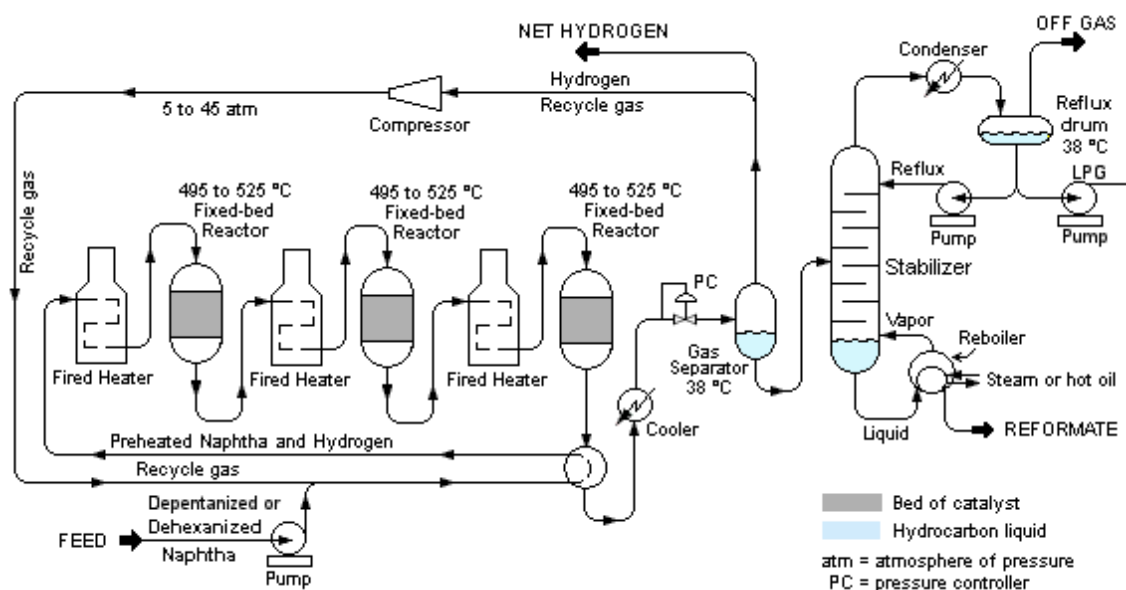
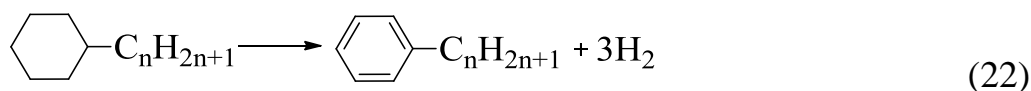


Fig. 10. Schematic diagram of a typical semi-regenerative catalytic reformer unit in a petroleum refinery [12]

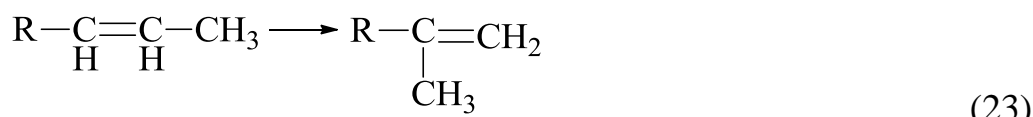
In the reformer, multiple reactions occur simultaneously. This process is endothermic and is subject to carbon laydown; thus, refiners must regenerate reforming catalysts. Several catalyst-regenerating approaches are possible. Semi-regenerative processes use moving-bed catalyst reactors. The catalyst bed reactors are placed side-by-side, and hydrogen is used to lift and convey the catalyst to the next bed, except for the last bed where it is regenerated, as shown in Fig. 10. Other reforming designs use a continuous moving bed to continuously regenerate a portion of the catalyst. The reactors are stacked on top of each other, and gravity moves the catalyst through the bed. From the last reactor, the catalyst is lifted by nitrogen or hydrogen to a catalyst collection vessel. The catalyst is regenerated in a regeneration tower and returned to process.

In the catalytic reforming process, the feed is pumped to operating pressure and mixed with a hydrogen-rich gas before heating to reaction temperatures. The net hydrogen produced is a by-product of the dehydrogenation and cyclization reactions. Several reactions occur:

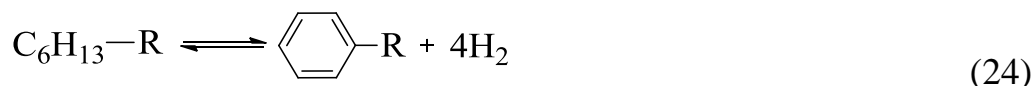
~ dehydrogenation of naphthene:



~ isomerization of paraffins and naphthenes:



~ dehydrocyclization of paraffins:



~ hydrocracking and dealkylation of paraffins:



Reforming catalysts promote these reforming reactions. Isomerization is a desired reaction, especially to raise the octane value of the products. However, hydrocracking is an undesired side-reaction that produces light gases. Higher operating pressures are used to suppress hydrocracking. Unfortunately, higher operating pressures suppress reforming reactions also. Generally, a compromise is made between the desired reforming and undesired hydrocracking.

In the late 1960s, it was discovered that adding certain promoters such as rhenium, germanium, or tin to the platinum-containing catalyst would reduce cracking and coke formation. The resulting bi-metallic and tri-metallic catalysts facilitate a lower operating pressure without fostering hydrocracking conditions. Earlier reforming pressures ranged around 500 psig (3.45 MPa); with improved catalyst systems, such operations now use operating pressures of 170–370 psig (1.2–2.6 MPa). Advances in continuous catalyst design permit using operating pressures as low as 50 psig (0.345 MPa).

Operating temperatures are also critical. The listed reactions are endothermic. The best yields occur along isothermal reaction zones, but are difficult to achieve. Instead, the reaction beds are separated into a number of adiabatic zones operating at 500–1000 °F (260–540 °C) with heaters between stages to supply the necessary energy to promote heat of reaction and hold the overall train near or at a constant temperature. Three or four zones are commonly used to achieve high-octane products.

3.6 Alkylation

Another method to convert light olefins into gasoline blending stocks is alkylation. In this process, light olefins – propylene, butylenes, and amylenes with isobutene – are reacted in the presence of strong acids to form branched chain hydrocarbons. These branched hydrocarbons, often referred

to as alkylate, have a high-octane value; thus, it is an excellent contributor to the octane pool.

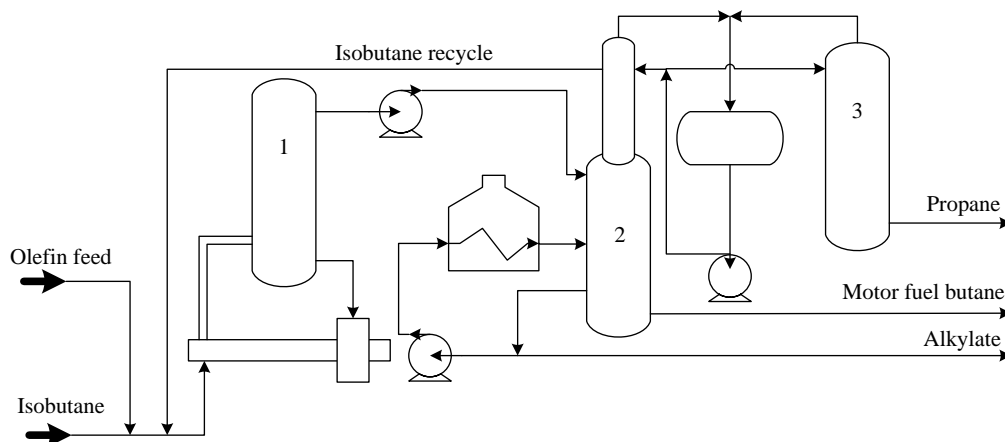


Fig. 11. Alkylation – Fuels Technology Division of Phillips Petroleum Co [3]:
 1 – combination reactor/settler; 2 – main fractionator; 3 – small propane stripper

A flow diagram of an alkylation unit using sulfuric acid is shown in Fig. 11. Alkylation traditionally combines isobutane with propylene and butylene using an acid catalyst, either hydrofluoric (HF) acid or sulfuric acid. The reaction is favored by high temperatures, but competing reactions among the olefins to give polymers prevent high-quality yields. Thus, alkylation is usually done at low temperatures to deter polymerization reactions. Temperatures for HF acid-catalyzed reactions are approximately 100 °F (40 °C), and for sulfuric acid they are approximately 50 °F (10 °C). Notably, some acid loss occurs with this process. Approximately 1–1.2 lb of HF acid/bbl of alkylate is consumed, while 25–30 lb of sulfuric acid/bbl of alkylate is consumed. The alkylation feed should be dried and desulfurized to minimize acid loss. Since the sulfuric-acid-catalyzed reactions are carried out below normal atmospheric temperatures, refrigeration facilities are included.

As shown in Fig. 11, dry liquid feed containing olefins and isobutane is charged to a combined reactor–settler. In this example, the reactor uses the principle of a differential gravity head to circulate through a cooler before contacting a highly dispersed hydrocarbon feed in the reactor pipe. The hydrocarbon phase, generated in the settler, is sent to a fractionator, which separates LPG-quality propane, isobutane recycle, *n*-butane, and alkylate products. A small amount of dissolved catalyst is also removed from the propane product by a small stripper tower.

Environmental and safety concerns on acid-based processes are promoting research and development efforts on solid-acid alkylation processes. Liquid catalysts pose possible risks to the environment, employees, and the

general public from accidental atmospheric releases. Also, these acid catalysts must be regenerated—another reliability and safety issue. Thus, research efforts are directed at investigating other methodologies to produce high-octane alkylation gasoline component streams.



Glossary

Alkylation [ˌælkɪˈleɪʃ(ə)n] (n) – in petroleum refining, it is a chemical process in which light, gaseous hydrocarbons are combined to produce high-octane components of gasoline. The liquid fraction of this mixture, known as alkylate, consists mainly of isooctane, a compound that lends excellent antiknock characteristics to unleaded gasolines.

Burton process [ˈbɜːtn ˈprəʊsɪs] – a thermal cracking process invented by William M. Burton; the oil industry first used it to produce gasoline in 1913. It is still in use today to produce Diesel.

Cracking [ˈkrækiŋ] (n) – the process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules (e.g. light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors.

Catalysis [kəˈtæləsis] (n) – the process in which the rate of a chemical reaction is increased by means of a chemical substance known as a catalyst. Unlike other reagents that participate in a chemical reaction, a catalyst is not consumed. Thus the catalyst may participate in multiple chemical transformations, although in practice catalysts are secondary processes.

Catalytic cracking [ˌkætəˈlɪtɪk ˈkrækiŋ] – the process of thermal catalytic processing of oil with the purpose of gasoline obtaining. It is carried out at 450–550 °C and 50–400 kPa at the fine-dispersed catalyst presence (rare-earth metals, vanadium).

Dehydrogenation [dɪˌhaɪdrədʒ(ə) ˈneɪʃ(ə)] (n) – **1.** Removal of water from a substance. **2.** A chemical reaction in which a compound loses hydrogen and oxygen in the ratio 2:1. For instance, ethanol passed over hot pumice undergoes dehydration to ethene:



Substances such as concentrated sulphuric acid, which can remove H₂O in this way, are known as *dehydrating agents*.

Fluid catalytic cracking [ˈfluːɪd ˌkætəˈlɪtɪk ˈkrækiŋ] – a commonly used process and a modern oil refinery which typically includes *a cat cracker*,

particularly at refineries in the USA due to the high demand for gasoline.

Gasification [ˌgæsɪfɪˈkeɪʃ(ə)n] (n) – a process that converts carbonaceous materials, such as coal, petroleum or biomass into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam.

Hydrocracking [ˌhaɪdrə(u)'krækɪŋ] (n) – a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. It is carried out at the catalyst presence by hydrogen action on highly boiling oil fractions (namely vacuum distillate with boil-off limits 300–540 °C), on easily boiling and medium distillate straight-run fractions and secondary products of their thermo catalytic processing.

Isomerisation [ˌaɪsəməraɪˈzeɪʃ(ə)n] (n) – the chemical process by which a compound is transformed into any of its isomeric forms, *i.e.*, forms with the same chemical composition but with different structure or configuration and, hence, generally with different physical and chemical properties.

Oil refinery [oɪl rɪˈfaɪn(ə)rɪ] (n) – an industrial process plant where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene and liquefied petroleum gas.

Polymerization [pəˈlɪməraɪˈzeɪʃ(ə)n] (n) – in petroleum refining is the process of converting light olefin gases including ethylene, propylene, and butylene into hydrocarbons of higher molecular weight and higher octane number that can be used as gasoline blending stocks.

Pyrolysis [ˌpaɪˈrəʊl(ə)sɪz] (n) – is a form of incineration that chemically decomposes organic materials by heat in the absence of oxygen.

Reforming [rɪˈfoːmɪŋ] (n) – secondary process of processing of petrochemicals conducted for obtaining of individual aromatic hydrocarbons, hydrogen or petrol/gasoline with excessive content of aromatic hydrocarbons.

Residue refining [ˈrezɪdjuː rɪˈfaɪnɪŋ] – the term is used to describe the number of processes to upgrade fuel oil to catalytic cracker feed, for example by using pressurized hydrogen gas and a catalyst.

Secondary oil refining [ˈsekənd(ə)rɪ oɪl rɪˈfaɪnɪŋ] (secondary processes) – are different processes of petrochemicals processing obtained by the straight-run method. These processes are considered to be chemical,

because they result in nature change of and destructive conversions of hydrocarbons contained in petrochemicals.

Steam cracking [sti:m 'krækiŋ] – a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethylene and propylene.

Review Questions and Exercises



Answer the questions

1. Describe the similarities and the differences between straight thermal cracking and catalytic cracking as oil modification procedures. How do the details of the process parameters affect the types and proportions of the observed products from the two processes?
2. Explain the chemical basis for the inevitable formation of olefins and/or coke (as well as saturated paraffins) from cracking reactions.
3. Explain and give equations to illustrate your explanation of the mode of formation of a high proportion of branched, rather than straight chain products formed during the formation of polymer alkylate for use in gasoline. What property is contributed by this component of gasoline that is valued by refiners?
4. What is the major acid gas component, and what are the more minor acid gases present in “flue gas” that provide a low cost way to acidify aqueous alkaline waste water streams to assist recovery of pollutants, such as phenols and hydrogen sulfide?



Exercise 3.1

In table 2 find out statistical data on oil production, consumption, export and import in different countries and at different times. Summarize the information and report it in English describing:

- main idea of the table,
- comparison where possible,
- trend where possible,
- inference.

Use appendix B to help you.



Exercise 3.2.

For question 1-9 choose the fragment (A, B, or C) that best completes the gap.

1..... is a petroleum-derived liquid mixture consisting primarily of hydrocarbons, used as fuel in internal combustion engines.

A gasoline B crude oil C kerosene

2..... is an industrial process plant where crude oil is processed and refined into useful petroleum products.

A oil pipeline B surface equipment C oil refinery

3..... is the process whereby complex organic molecules are converted to simpler molecules by the breaking of carbon-carbon bonds in the precursors.

A reforming B cracking C oil stabilization

4..... is a solid carbonaceous residue derived from low-ash, low-sulfur bituminous coal from which the volatile constituents (including water, coal-gas and coal-tar) are driven off by baking.

A coke B asphalt C petroleum coke

5..... uses a catalyst to help the process of breaking down petroleum vapor to fractions. Typical catalysts are Al_2O_3 , SiO_2 , and various types of clay.

A hydrocracking B catalytic cracking C steam cracking

6. involves the cracking of heavier hydrocarbons in the presence of hydrogen.

A steam cracking B thermal cracking C hydrocracking

7. It is a that easily converts to aromatics.

A coke B naphtha C diesel oil

8..... is a complex, high molecular weight (>3000), three-dimensional polymeric solid precursor to petroleum which is intimately distributed through the rock.

A bitumen B oil shale C kerogen

9. Commercial production of began in 1979, shortly after the discovery of its octane-improving capability for motor fuels. Although a higher proportion of this additive was required for equivalent octane enhancement, it was less costly and eliminated the lead particles.

A methyl tertiary-butyl ether B LRP C organonitrogen compounds



Exercise 3.3.

For questions 1-4, 5-8, 9-12 find one of the words on the right (a-d) that best completes the gap in the text. You can use each word only once.

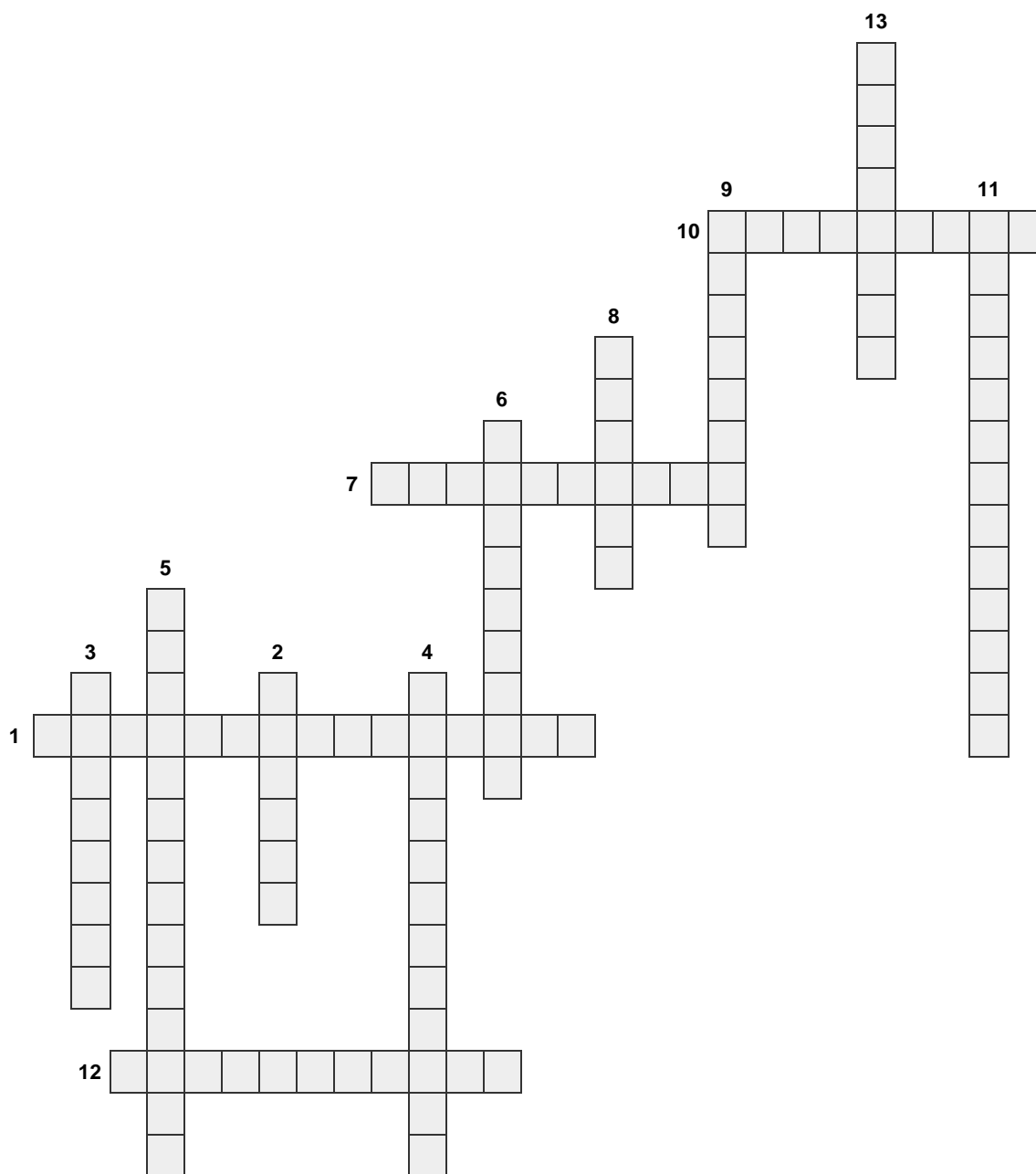
How to Refine Oil

<p>The naphtha fraction is useful for making many (1). Heating (2) in the absence of air makes the molecules split into shorter ones. This is called (3), because heat is used. Some of the hydrocarbons made by cracking larger molecules contain double bonds. Hydrocarbons with double bonds are called (4).</p>	<ul style="list-style-type: none">a. alkenesb. naphthac. thermal crackingd. petrochemicals
<p>Larger hydrocarbons split into shorter ones at low temperatures if a catalyst is used - a process called (5). The products include useful short chain hydrocarbons. The main use of catalytic cracking used in (6) is to convert surplus (7) into (8) and diesel fuels, which would otherwise be in shortage.</p>	<ul style="list-style-type: none">a. gasolineb. fuel oilc. oil refineryd. catalytic cracking
<p>Naphtha molecules can be altered by heating them to 500°C in the presence of hydrogen and a platinum catalyst. The resulting molecules are blended with other (9) to make petrol. The reformed naphtha molecules improve the (10) which means that the fuel burns better in a car engine. (11) contains (12). If these are present in fuels they will produce polluting emissions when burned. This is because the sulphur combines with oxygen, forming sulphur dioxide. This gas is soluble in water and makes it acidic. It is the main cause of acid rain, which damages wildlife by making lakes and soil more acid. To clean the emissions and remove sulphur, the hydrocarbon fractions are heated, mixed with hydrogen under pressure and fed into a reactor vessel. There is a metallic salt catalyst in the vessel which enables the sulphur compounds to change to hydrogen sulphide. Pure sulphur is recovered from this and sold.</p>	<ul style="list-style-type: none">a. hydrocarbonsb. crude oilc. organosulfurcompoundsd. octane number



Exercise 3.4.

Crossword



1. A chemical reaction that involves the elimination of hydrogen (H_2).
2. A process for thermally converting the heavy residual bottoms of crude oil entirely to lower-boiling petroleum products.
3. A combustible hydrocarbon liquid.

4. A process that converts carbonaceous materials, such as coal, petroleum or biomass into carbon monoxide and hydrogen by reacting the raw material at high temperatures with a controlled amount of oxygen and/or steam.
5. A process of reacting monomer molecules together to form long chains or three-dimensional networks.
6. A form of incineration that chemically decomposes organic materials by heat in the absence of oxygen.
7. In petroleum refining, it is a chemical process in which light, gaseous hydrocarbons are combined to produce high-octane components of gasoline.
8. A thermal cracking process invented by him. William M. ...
9. The process whereby complex organic molecules such as kerogens or heavy hydrocarbons are broken down into simpler molecules (e.g. light hydrocarbons) by the breaking of carbon-carbon bonds in the precursors.
10. The process in which the rate of a chemical reaction is increased by means of a chemical substance known as a catalyst.
11. The chemical process by which a compound is transformed into any of its isomeric forms, *i.e.*, forms with the same chemical composition but with different structure or configuration and, hence, generally with different physical and chemical properties.
12. Thermally cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons.
13. A transparent, petroleum-derived liquid that is used primarily as a fuel in internal combustion. The second name is petrol.

UNIT 4

Refining crude oil involves breaking carbon-to-carbon (C–C) bonds of the complex hydrocarbon compounds and adding hydrogen. Such efforts are done thermally and catalytically. The distinction between *refined products* and *petrochemicals* often is subtle. In general, when the product fraction is from crude oil that includes a fairly large group of hydrocarbons, the fraction is classified as a refined product. Examples of refined products are: gasoline, diesel fuel, heating oil, lubricants, waxes, asphalts, and petroleum coke.

By contrast, when the product from crude oil is limited to only one or two specific hydrocarbons of fairly high purity, the fraction is called a petrochemical. Examples of petrochemicals are: ethylene, propylene, benzene, toluene, and styrene. Refined products are defined by the fraction's boiling point and may be composed of various hydrocarbons. Many compounds compose refined-product fractions. In contrast, petrochemicals are single-compound fractions, which are required for feedstocks for other petrochemicals and polymers. More processing and separation (distillation, extraction, etc.) operations are used to extract petrochemical products from processing streams. Thus, more identifiable petrochemical products are processed as compared to the categories of refined products. Many specific hydrocarbon compounds can be derived from crude oil. However, these hydrocarbons lose their individual identity when they are grouped together as a refined product.

4.1 Refined Products

Most refined products at the consumer level are blends of several refinery streams. Product specifications determine which streams are suitable for a specific blend. Part of the difficulty in learning about refining lies in the industry's use of stream names that are different from the names of consumer products.

Refining is considered a “dirty” processing effort. Product separation of refined product streams is not as clean as efforts to process petrochemicals. Refiners have the flexibility to blend final fuel products. Thus, there is no exact recipe used by all refiners to produce consumer products. Multiple crude oils are processed and then blended to meet consumer fuel product specifications. Table 5 lists the refining streams that are blended to produce consumer products. The consumer products are familiar. However, within a refinery these products are blended from portions of crude oil fractions from the listed reforming process units. To complicate the situation further, not all

refineries are configured identically. Many different processing operations can be used to refine and separate product streams to blend the products listed in Table 5.

Table 5

Several Names for the Same Material

Crude Oil Cuts	Refinery Blends	Consumer Products
Gases	Still gases	Fuel gas
	Propane/Butane	Liquefied petroleum gas (LPG)
Light/heavy naphtha	Motor Fuel	Gasoline
	Aviation turbine, Jet-B	Jet fuel (naphtha type)
Kerosine	Aviation turbine, Jet-A	Jet fuel (kerosine type)
	No. 1 Fuel oil	Kerosine (range oil)
Light gas oil	Diesel	Auto and tractor diesel
	No. 2 fuel oil	Home heating oil
Heavy gas oil	No. 4 fuel oil	Commercial heating oil
	No. 5 fuel oil	Industrial heating oil
	Bright stock	Lubricants
Residuals	No. 6 fuel oil	Bunker C oil
	Heavy residual	Asphalt
	Coke	Coke

For example, gasoline at the consumer level may be called benzol or petrol, depending upon the country where it is sold. In the early stages of crude oil processing, most gasoline components are called naphthas. Kerosine is another example. It may be called coal oil to denote that it replaces stove oil (or range oil) once derived from coal. Historically, kerosine gained significant importance as a replacement for whale oil for lamps. In the early 1900s, refining efforts were directed to supplying kerosine–lamp oil. However, in the 1920s, a new energy form – electricity – began to displace kerosine usage. Thus, early refiners sought other products to compensate for this market loss. Today, kerosine fractions are directed to jet fuel and high-quality No. 1 heating oil.

4.2 Crude Oil Fractions

Product applications and customer acceptance set detailed specifications for various products properties. In the United States, the American Society for Testing Materials (ASTM) and the American Petroleum Institute

(API) are recognized for establishing specifications on both products and methods for testing. Other countries have similar referee organizations. For example, in the United Kingdom it is the Institute of Petroleum (IP). In Germany, it is the Deutsches Institut fuer Normung (DIN). In Japan, it is the Ministry of International Trade and Industry (MITI).

As regards to Russia, any type of activity is regulated by the system of government standards (GOST) in the development of which different core organizations take part. Besides, the government standard is validated by the administration or appropriate ministry. Oil and as complex in Russia on the whole (from oil extraction to oil refining) is a part of Ministry of Energy of Russian Federation which, in its turn, regulates the quality of products from oil [13].

Boiling range is the major distinction among refined products, and many other product properties are related to the products in these boiling ranges. The simplest form of refining would isolate crude oil into fractions having boiling ranges that would coincide with the temperature ranges for consumer products. Some treatment steps might be added to remove or alter undesirable compounds, and a very small quantity of various chemical additives would be included to enhance final properties.

Crude oil distillation separates the desalted crude oil into fractions of different boiling ranges. Instead of trying to match final product boiling ranges, the fractions are defined by the number and type of downstream processes.

The desalting and distillation units are shown in Figs 5, 12, 13 along with the crude fractions from the crude distillation column. The relationships between some finished products and downstream processing steps will be expanded upon later in this unit.

Gasoline

Gasoline is blended from several refining processes, as shown in Fig. 11. Depending on the individual refinery configuration, gasoline blending streams are separated and refined. Figure 5 depicts a light-fraction processing scheme. A straight-run gasoline stream is separated from the top portion of the atmospheric crude distillation column, which has a boiling range of 90–200 °F (32–93 °C) and is very paraffinic.

The next cut gasoline stream from the crude distillation column is the naphtha cut. This stream has a boiling range of 200–365 °F (93–185 °C) and contains a significant portion of naphthenes, aromatics, and paraffins. Thus, the naphtha cut is hydrotreated and reformed to upgrade this stream into a gasoline blending stock.

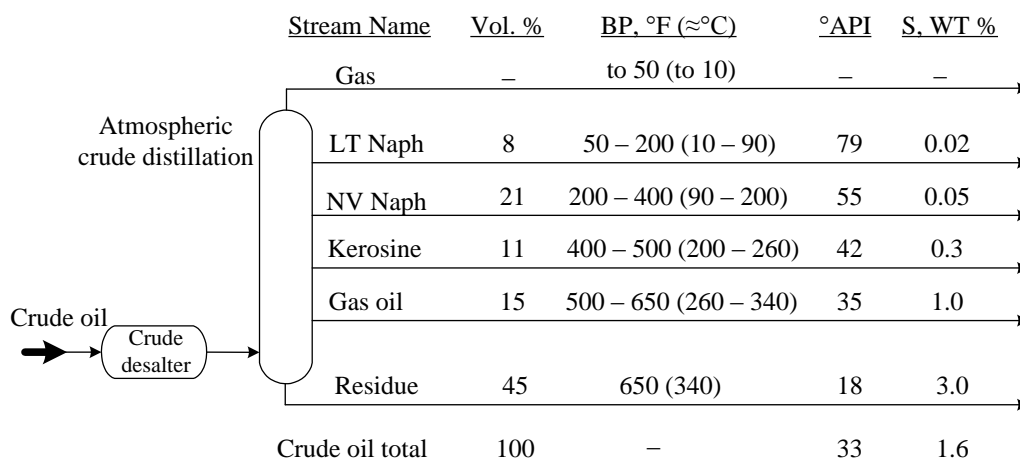


Fig. 12. Separating desalted crude oil into fractions.

In present-day refineries, the fluid catalytic cracking (FCC) unit has become the major gasoline producing unit. The FCC's major purpose is to upgrade heavy fractions, that is, gas oil from the atmospheric and vacuum distillation columns and delayed coker, into light products. Atmospheric gas oil has a boiling range of between 650 and 725 °F (343–385 °C).

Table 6
Anticipated Fuel Specifications under Auto Oil Program, U.S. [3] and Russian Requirements [14]

Period	2000	2005	2008	2000 (U.S. only)	2006	GOST R51866-2002
Gasoline						
Sulfur content	<150 ppm	<50 ppm ^b		<170 ppm	30 ppm	500 ppm
Benzene content	<1% v/v	<1% v/v ^a		<1 % v/v	–	1 %
Aromatics content	<42% v/v	<35% v/v		<25 v/v	–	–
Diesel fuel						
Sulfur content, ppm	<350	<50	<30	<500	<10	–
Cetane number, min	51	53 ^a	54–58	40	–	50
Polynuclear aromatics	<11% w/w	<6% w/w ^a	<4–1% w/w	–	–	–
Density, kg/l max	<0.845	<0.845 ^a	<0.830–0.825	–	–	
Distillation T95, °C	<360	<360 ^a	<350–340	–	–	

% v/v: percent by volume; % w/w: percent by weight; ^aExpected values; ^bGermany is promoting 10 ppm sulfur for gasoline by 2003.

The crude oil feedstock heavily influences the product slate for the refinery and the downstream processing required to meet the refinery's product goals. Fuels are blended to meet product specifications – of volatility, sulfur content, and octane number. Most important, refiners constantly seek to optimize their blending programs to meet product goals without giving up product.

The automobile's engine-drive train sets the specifications for gasoline. Notably, as automobile manufacturers design more sophisticated engines, in response refiners must adjust their operation to refine and blend fuels that are compatible with newer engines. Worldwide, new environment legislation has set product specifications for fuels. Table 6 lists the quality standards for automotive gasoline and diesel. These mandates are geared to lower tail-pipe emission from vehicles. Sulfur content and volatility will be strictly limited in future fuel requirements.

4.3 Sulfur Content

Sulfur compounds are corrosive and foul-smelling. When burned in an engine these compounds form sulfur dioxide and other oxides referred to as SO_x in engine exhaust. These compounds recombine and form sulfur trioxide and sulfuric acid mist, which is released as engine exhaust. Efforts to improve air quality are targeted at reducing vehicle engine exhaust of toxins and SO_x compounds. Thus, many new environmental regulations (Table 6) are focused on reducing the sulfur content of fuels. All crude oils contain some sulfur concentration. How much desulfurization that is needed is dependent on the feedstock and product slate.

Caustic wash or other enhanced solvent-washing methods are a sufficient pretreatment to remove sulfur compounds from light naphtha. The sulfur compounds in light naphtha are mercaptans and organic sulfides that are readily removed by these washing processes. Heavy naphtha is harder to desulfurize. This stream has a higher sulfur content, and, equally important, the sulfur is embedded in complex hydrocarbon compounds and rings. Washing efforts are more effective on mercaptans, which are not usually present in heavy naphtha. More aggressive methods are needed to break the compound structures and release the sulfur. Hydrotreating is one effective method to reduce sulfur content in hydrocarbon streams.

Hydrotreating is a catalytic process that converts sulfur-containing hydrocarbons, that is, sulfides, disulfides, and ring compounds such as thiopenes, into low-sulfur liquids and hydrogen sulfide. This technology is widely used throughout the refinery, as shown in Figs 5 and 13. This process is operated under a hydrogen-rich blanket at elevated temperatures and pres-

sure. The process is a hydrogen-consuming step, since the hydrogen replaces the sulfur bond on the hydrocarbon molecule.

Nitrogen and oxygen compounds are also dissociated by hydrotreating. Consequently, hydrotreating provides additional benefits of hydrodenitrification, which improves downstream operations. For nitrogen and oxygen compounds, the products from hydrotreating are ammonia and water, respectively. Thus, these contaminants will be separated in the off-gas and are easily removed by conventional gas-treating processes.

4.4 Octane Number

Another condition to keep gasoline engines running smoothly is that the fuel–air mixture starts burning at a precise time in the combustion cycle. An electrical spark starts the ignition. The remainder of the fuel–air mix should be consumed by a flame front moving out from the initial spark.

Under some conditions, a portion of the fuel–air mix will ignite spontaneously instead of waiting for the flame front from the spark. The extra pressure pulses that occur from spontaneous combustion are usually audible above the background sounds of the engine running and give rise to a condition known as “engine knock”. The engine pings and rumbles when under “knock conditions”. This condition is undesirable; it is a waste of available power.

The *octane number* is a measure of a fuel's ability to avoid knocking. The octane number of gasoline is determined in a special single-cylinder engine where various combustion conditions can be controlled. The test engine is adjusted to trace the knock from the fuel being rated. Various mixtures of *iso*-octane and normal heptane (*n*-heptane) are used to find the ratio of the two reference fuels that will give the same intensity of knock as that from an unknown fuel. Defining *iso*-octane as 100 octane number and *n*-heptane as 0 octane number, the volumetric percentage of *iso*-octane in heptane that matches knock from the unknown fuel is reported as the octane number of the fuel. For example, 90 volume percent (vol. %) of *iso*-octane and 10 vol. percent *n*-heptane establishes a 90 octane number reference fuel.

Two types of octane number ratings are specified, although other methods are often used for engine and fuel development. Both methods use the same reference fuels for essentially the same test engine. Engine operating conditions are the difference. In the *research method*, the spark advance is fixed, the air inlet temperature is 125 °F (52 °C), and the engine speed is 600 rpm. The other method is called the *motor method*; it uses variable spark

timing, a higher mixture temperature (300°F (150 °C)), and a faster engine speed (900 rpm).

The more severe conditions of the motor method have a greater influence on commercial blends than they do on the reference fuels. Thus, a motor octane number (MON) of a commercial blend often has a lower research octane number (RON). Consequently, blended fuels use an arithmetic average of both ratings – MON and RON – and can be abbreviated as (R + M)/2.

Catalytic reforming is a principal process used to upgrade low-octane, straight-run gasoline to high-octane liquid, as shown in Table 7.

Table 7

Aromatics have Higher Octane Numbers

Hydrocarbon	Homologs	Octane Number, Clear	
		Motor	Research
C ₇ hydrocarbons			
<i>n</i> -paraffin	C ₇ H ₁₆ (<i>n</i> -heptane)	0.0	0.0
naphthene	C ₇ H ₁₄ (cycloheptane)	40.2	38.8
	C ₇ H ₁₄ (methylcyclohexane)	71.1	74.8
aromatic	C ₇ H ₈ (toluene)	103.5	120.1
C ₈ hydrocarbons			
<i>n</i> -paraffin	C ₈ H ₁₈ (<i>n</i> -octane)	-15 ^a	-19 ^a
naphthene	C ₈ H ₁₆ (cyclooctane)	58.2	71.0
	C ₈ H ₁₆ (ethylcyclohexane)	40.8	45.6
aromatic	C ₈ H ₁₀ (ethylbenzene)	97.9	10.4
	C ₈ H ₁₀ (<i>o</i> -xylene)	100.0	120 ^a
	C ₈ H ₁₀ (<i>m</i> -xylene)	115.0	117.5
	C ₈ H ₁₀ (<i>p</i> -xylene)	109.6	116.4

^aBlending value at 20 vol.% in 60 octane number reference fuel.

Reforming uses catalysts to reshape the molecular structure of hydrocarbons to raise the octane number of the process stream. Naphthenes are converted to aromatics; paraffins are isomerized to isomeric forms. Reforming efforts are most effective when used on heavier molecules; a greater increase in octane number can be attained by reforming heavy naphtha cuts.

Reforming catalysts typically contain platinum or a mixture of platinum and other metal promoters on a silica–alumina support. Only a concentration of platinum is used, averaging about 0.4 wt. percent. The reforming process is a highly endothermic process. Desulfurized feeds are preheated to 900°F, and the reactions are done at various pressures (50–300 psig (0.345–2.068 MPa)), which are dependent on the licensed process used. At

elevated temperatures and pressures, the catalyst is susceptible to coking, which decreases catalyst efficiency. Thus, refiners must regenerate the catalyst to maintain process efficiency. Reforming catalyst can be regenerated in situ by burning off the coke from the catalyst. Newer developments now use continuous regeneration of the reforming catalyst in which three reforming reactors are stacked one on top of the other. Gravity flow moves the catalyst from the top to the bottom and sends it to a regeneration step in which a dry burn removes the coke. The regenerated catalyst is then returned to process. Also, reforming feeds are pretreated to remove poisons that can kill precious-metal catalysts.

Hydrotreating is an effective method to pretreat reforming feedstocks (Fig. 13). Combining hydrotreating with reforming is most effective. Due to cyclization and dehydrogenation of hydrocarbon molecules in the reformer, hydrogen is a by-product from this operation. Notably, by-product hydrogen from the reform can be directed to the hydrotreating operations. Thus, the reformer can provide the refinery with the hydrogen supply for hydrotreating. A rule of thumb is that the catalytic reformer produces 800–1,200 scf/bbl for naphtha. The excess hydrogen is available for hydrotreating other fractions in separate hydrotreaters.

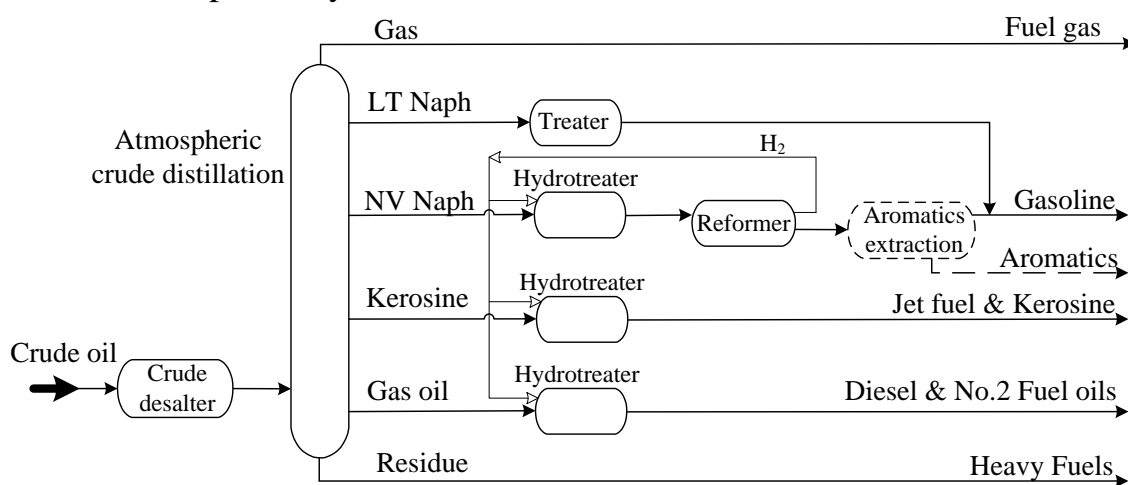


Fig. 13. Low-investment route to modern products

4.5 Distillates

Jet fuel, kerosine (range oil), No. 1 fuel oil, No. 2 fuel oil, and diesel fuel are all popular distillate products from the 365–650 °F (185–343 °C) fractions of crude oil. Distillates are further classified as light distillates with a true boiling point range of 365–525 °F (185–275 °C), and heavy distillate cuts have a true boiling point range from 525 to 650 °F (from 275 to

343 °C). Light distillates are blended into kerosine and jet fuels. Heavy distillate cuts are used to blend diesel fuels and home heating oils.

Some heating oil (generally No. 2 heating oil) and diesel fuel are very similar and are sometimes substitutes for each other. Home heating oil is intended to be burned in a furnace for space heating. Diesel fuel is intended for compression – ignition engines.

Distillates are lower cuts from the atmospheric crude distillation column (Fig. 13); thus, these refinery streams may have high sulfur concentrations due to the feedstock that is processed. Newer product specifications limit sulfur concentrations in consumer products, especially diesel. Consequently, distillate streams must be upgraded. Hydrotreating improves the product properties of distillate products; notably it reduces sulfur content. More important, hydrotreating hydrogenates unsaturated hydrocarbons so that they will not contribute to smoke and particulate emissions – whether the fuel is burned in a furnace or used in an engine.

4.6 Residuals

Crude oil is seldom distilled at temperatures above 650 °F (343 °C). At higher temperatures, coke will form and plug the lower section of the crude oil distillation tower. This bottom fraction from the atmospheric crude column has a true boiling point range of 650–725 °F (343–385 °C) and is often referred to as *atmospheric gas oil* or *residuals*. This fraction is traditionally not vaporized. Atmospheric gas oil must be upgraded extensively; it can be severely hydrotreated to break apart the complex ring compounds and saturate them into lighter products. This stream can be sent to a catalytic cracker to further upgrade this heavy fraction into gasoline, diesel, and home heating fuel. The heaviest cut of the atmospheric crude distillation is often referred to as the *long residuum*. This fraction is further processed via a vacuum distillation column.

The residue from crude distillation is usually processed to an asphalt product as much as possible, since as a component of residual fuel oils it generally fetches a lower price than as asphalt itself. The residual fuel oil market is quite competitive since ships and tankers can choose to load at centers, which offer the lowest cost fuels. Also the price of the heavier grades of bunker fuel used to supply power stations has to be comparable to coal to be competitive.

Asphalts made from different crudes are not always mutually soluble and may require instrumental work before mixing to determine compatibility. Asphalts are marketed in liquid and low-, medium-, and high-melting

point solid grades, depending on the intended end use. The melting point and degree of hardness of an asphalt is affected by the completeness of removal of volatile fractions [2]. If the melting point or hardness of a crude separated asphalt product is too low, it is oxidized by blowing air through the heated asphalt until the melting point is raised to the extent desired.

Lower melting point asphalts are used for the waterproofing of flat, built-up roofs and the like, where the self-sealing qualities are an attraction. For sloping built-up roofs, higher melting asphalts are required. For asphalt shingles, roll roofing, and similar sheet roofing products, the melting point has to be high enough to give an essentially nonsticky surface after fabrication, under ordinary ambient conditions. Road asphalts normally have to pass a melting point specification, a penetration test (“pen test”), and other requirements. The pen test is the extent to which an asphalt sample at 25 °C is penetrated by a steel ball or pin of standard dimensions, while a force of 100 g is applied for 5 seconds. It is an important measure of the suitability of the asphalt for various paving applications. For application as road surfacing small crushed gravel aggregate is blended into hot asphalt, which serves as the binder.

By the variety of processing procedures outlined very little of the crude oil processed is wasted. From the high volatility dissolved gases present, all the way to the nearly involatile asphaltenes, and suspended carbon, etc. present in the original oil are converted to a host of useful products. Any combustible components that are not directly used toward the formulation of a product are used to generate energy for the refinery itself.

4.7 Petrochemicals

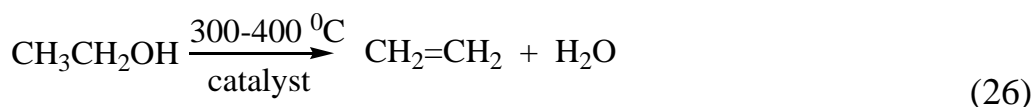
Organic chemicals, such as dyestuffs and derivatives of benzene and heterocyclic compounds, were first produced from coal-based raw materials. Since the mid-nineteenth century these products were obtained by the further processing of discrete volatile fractions recovered during the coking of coal. A large fraction of the coke product was destined for the reduction of iron ore to produce pig iron. Although volatile fractions from the coking of coal, such as benzene, toluene, and the xylenes are still items of commerce, petroleum-based sources for these materials have now become much more important [2]. The attractiveness of petroleum-based feedstocks grew as both the reliability and scale of petroleum production increased. These aspects, plus the gradually increased sophistication of refining methods of the oil industry of the early twentieth century contributed to the increased appeal of petroleum as a resource for chemicals production.

As a consequence of its recent development the petrochemical industry is relatively much younger than the major inorganic chemicals industry. However, one can easily be misled by the classification of products that are termed “petrochemical”. Basically a petrochemical is derived directly or indirectly from a petroleum or natural gas fraction. It may be organic, such as ethylene, benzene, or formaldehyde, or it may be inorganic, such as ammonia, nitric acid, and ammonium nitrate. So a “petrochemical” is not synonymous with an organic chemical, although most petrochemicals are also organic chemicals.

What is the incentive to produce petrochemicals? It is producer accessibility to profit from the additional value-added stages that are obtained from conversion of a refined petroleum or gas fraction into a petrochemical, compared to the value of crude petroleum. Depending on the complexity and number of stages involved, a petrochemical product may command a price that is five or six times the price of the oil or gas used to produce it. If more value-added stages are used to convert a petrochemical commodity into a consumer product, this may fetch a price as high as 20 times that of the oil from which it is derived. In short, oil (or natural gas) is worth far more when converted to chemicals than as fuel.

The majority of the chemical processes of the modern petrochemical industry rely on just three refinery streams, methane (or natural gas), olefins, and aromatics comprising just seven hydrocarbons – methane, ethylene, propylene, the butylenes, benzene, toluene, and the xylenes (dimethyl benzenes). A few of the other hydrocarbons listed also occur to a varying extent in crude oil streams but in concentrations that are inadequate to meet the demand. Thus molecular changes are necessary to convert these hydrocarbon streams. Some of the procedures used to do this, such as polymerization, cyclo-alkylation, and aromatization, produce components of gasoline as has already been described. Others differ in important respects but still employ similar principles to obtain the desired product, namely sufficiently high temperatures to cause carbon–carbon and/or carbon–hydrogen bond homolytic cleavage, plus suitable conditions (contact time, catalyst, concentration, etc.) to achieve the optimum product yield. Since many refinery operations lead to several of these products simultaneously, computer programs are used to aid in process optimization to produce the currently required ratio of products. The tendency to get several simultaneous products from a single process will be evident from the following discussion of related product groups.

Ethylene, the largest scale petrochemical, is probably also the oldest to have had confirmed preparation in the laboratory. The initial method used, catalytic dehydration of ethanol, was reported as early as 1797 (Eq. 26).



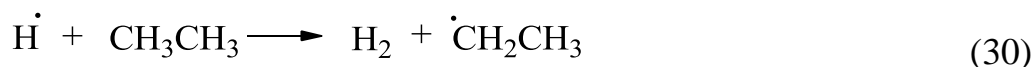
Although this method is capable of well over 90% yields of ethylene, and may be used when the local availability and price of ethanol (e.g., occasionally fermentation sources, Brazil) are attractive, other methods are usually more important.

Refinery ethylene is usually made by the catalytic cracking of ethane, propane, or a mixed hydrocarbon stream, such as recovered natural gas liquids, naphthas, or gas oil [2]. Cracking conditions are quite severe: 750–900 °C and 0.1–0.6 second residence time for a low partial pressure hydrocarbon stream. A number of metal oxide catalysts have recently been evaluated for this purpose [6]. The usual diluent is steam, used at a weight ratio of steam to hydrocarbon of 0.2:1 for ethane feed, to progressively higher ratios with the higher molecular weight hydrocarbons of up to 2.0:1 for gas oil.

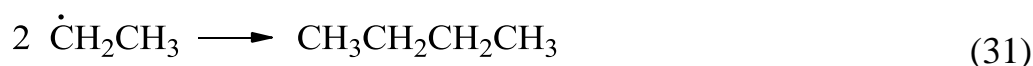
With an ethane feed the dominant cracking reaction is to ethylene and hydrogen, together with traces of methane and higher hydrocarbons. The initiation step involves the homolysis of the carbon–carbon bond (Eq. 27).



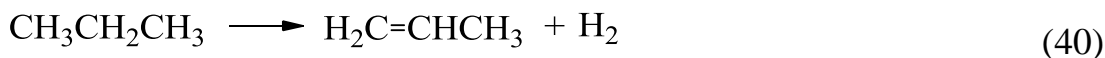
Carbon hydrogen bonds, which are stronger, are much less affected. The methyl radicals formed can then abstract hydrogen atoms from ethane in the first of a series of rapid propagation reactions (Eqs. 28–30).



Termination reactions are one of the ways in which the higher hydrocarbons are formed in the cracking of ethane (Eqs. 31 and 32).



Propane cracks to both ethylene and methane, and to propylene and hydrogen (Eqs. 39 and 40) with product proportions, which change with the cracking temperature (Fig. 14).



The initial step in the process with propane is still predominantly carbon-carbon bond cleavage, with methyl and ethyl radicals and to lesser extent hydrogen atoms serving in the propagation steps, which lead to the products.

Naphtha, or gas oil, may also be efficiently cracked to ethylene and propylene, although the proportion of ethylene in the product stream is generally lower for these feedstocks than from ethane or propane. However, this flexibility of possible feedstocks to ethylene enables a refinery to process those streams in current excess in order to produce the olefins that it may currently need.

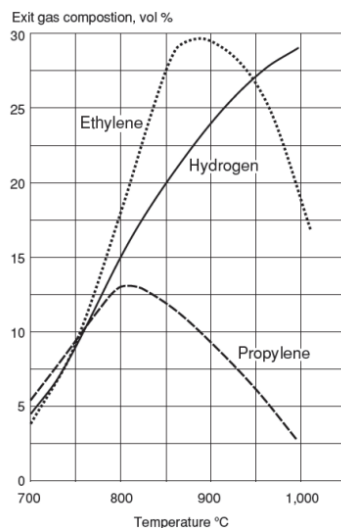


Fig. 14. Changes in the product distribution with temperature on the thermal cracking of propane [2]

Recovery of ethylene (b.p. $-103.7\text{ }^{\circ}\text{C}$) from the mixed hydrocarbon product vapors is accomplished by compression, condensation, and then fractionation at progressively lower temperatures. Ethane (b.p. $-88.6\text{ }^{\circ}\text{C}$) is the most difficult constituent to separate from ethylene, but even this is technically feasible.

The bulk of the worldwide annual commercial production of ethylene is based on thermal cracking of petroleum hydrocarbons with steam; the process is commonly called pyrolysis or steam cracking. The principal arrangement of such a cracking reactor is shown in Figure 15. A hydrocarbon stream is heated by heat exchange against flue gas in the convection section, mixed with steam, and further heated to incipient cracking temperature ($500\text{--}680\text{ }^{\circ}\text{C}$, depending on the feedstock). The stream then enters a fired

tubular reactor (radiant tube or radiant coil) where, under controlled residence time, temperature profile, and partial pressure, it is heated from 500–650 to 750–875 °C for 0,1–0,5 s. During this short reaction time hydrocarbons in the feedstock are cracked into smaller molecules; ethylene, other olefins, and diolefins are the major products. Since the conversion of saturated hydrocarbons to olefins in the radiant tube is highly endothermic, high energy input rates are needed. The reaction products leaving the radiant tube at 800–850 °C are cooled to 550–650 °C within 0.02–0.1 s to prevent degradation of the highly reactive products by secondary reactions. The resulting product mixtures, which can vary widely, depending on feedstock and severity of the cracking operation, are then separated into the desired products by using a complex sequence of separation and chemical-treatment steps. The cooling of the cracked gas in the transfer line exchanger is carried out by vaporization of high-pressure boiler feed water (BFW, $p = 6\text{--}12\text{ MPa}$), which is separated in the steam drum and subsequently superheated in the convection section to high-pressure superheated steam (HPSS, 6–12 MPa).

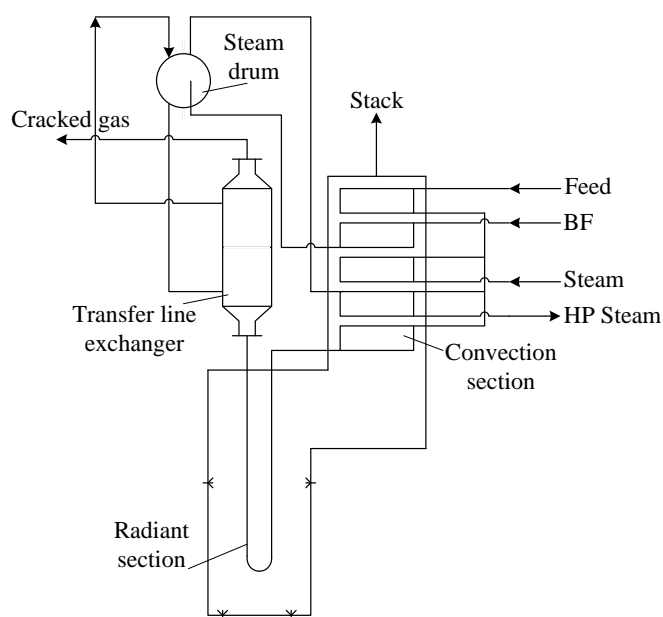


Fig. 15. Principal arrangement of a cracking furnace

Ethylene (ethene), the first member of the alkenes, is a colorless gas with a sweet odor. It is slightly soluble in water and alcohol.

The chemical properties of ethylene result from the carbon – carbon double bond, with a bond length of 0.134 nm and a planar structure. Ethylene is a very reactive intermediate, which can undergo all typical reactions of a short-chain olefin. Due to its reactivity ethylene gained importance as a chemical building block. The complex product mixtures that have to be separated during the production of ethylene are also due to the reactivity of eth-

ylene. Ethylene can be converted to saturated hydrocarbons, oligomers, polymers, and derivatives thereof. Chemical reactions of ethylene with commercial importance are: addition, alkylation, halogenation, hydroformylation, hydration, oligomerization, oxidation, and polymerization.

The following industrial processes are listed in order of their 1993 worldwide ethylene consumption:

- 1) Polymerization to low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE)
- 2) Polymerization to high-density polyethylene (HDPE)
- 3) Addition of chlorine to form 1,2-dichloroethane
- 4) Oxidation to oxirane (ethylene oxide) over a silver catalyst
- 5) Reaction with benzene to form ethylbenzene, which is dehydrogenated to styrene
- 6) Oxidation to acetaldehyde
- 7) Hydration to ethanol
- 8) Reaction with acetic acid and oxygen to form vinyl acetate
- 9) Other uses, including production of linear alcohols, linear olefins, and ethylchloride, and copolymerization with propene to make ethylene – propylene (EP) and ethylene – propylene – diene (EPDM) rubber

Chemicals Derived from Ethylene

Ethylene surpasses all other organic petrochemicals in production and in the amount sold. It is used as raw material for a greater number of commercial synthetic organic chemical products than is any other single chemical. Figure 16 shows the more important derivatives of ethylene.

Ethylene consumption has grown explosively since 1940 when 300 million lb were used, mostly for making ethanol and ethylene oxide. During World War II, styrene use grew markedly, and polyethylene was developed as insulation for the then – new radar electronics. These materials later found a multitude of applications, which were responsible in large part for ethylene consumption reaching nearly 5 billion lb in 1960. Strong growth in ethylene dichloride and ethylene oxide contributed to over 18 billion lb of ethylene consumption in 1970. Continued growth raised this figure to 27 billion lb in 1978 and over 58 billion lb in 2000, which is almost two hundred times the 1940 volume. The overall growth for 48 years averaged a remarkable 10 percent/year.

Nowadays Global ethylene production was 107 million tons in 2005 [18], 109 million tonnes in 2006. NNFCC Renewable Chemicals Factsheet: Ethanol, 138 million tonnes in 2010 and 141 million tonnes in 2011 [19] By 2010 ethylene was produced by at least 117 companies in 55 countries. [20]

To meet the ever increasing demand for ethylene, sharp increases in production facilities are added globally, particularly in the Mideast and in China.

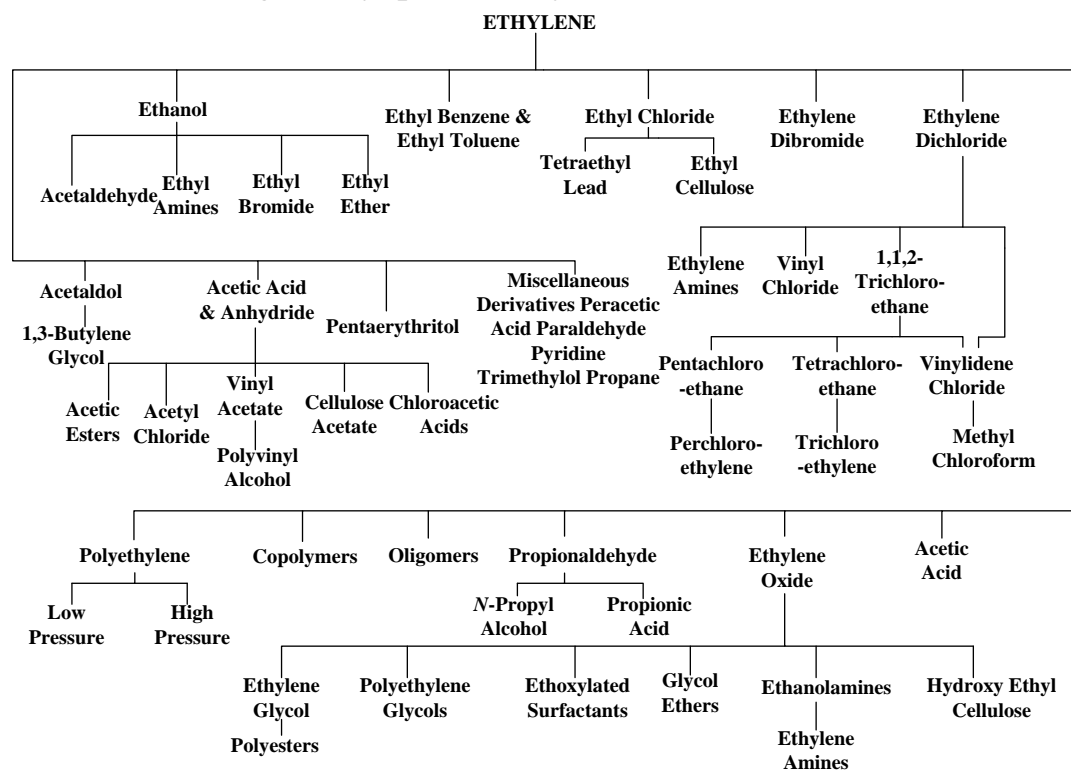


Fig. 16. Important derivatives of ethylene [3]

Propylene (Propene)

Propylene, or propene by IUPAC (International Union of Pure and Applied Chemistry) nomenclature, is probably the oldest petrochemical feedstock, employed as it was in the early processes to isopropanol. It is produced by the cracking of propane or higher hydrocarbons in the presence of steam under conditions very like those outlined for ethylene. Propane is the feedstock of choice for a product stream to contain the maximum concentration of propylene. The yield of propylene rises as the cracking severity of the propane is increased, but reaches a maximum before the maximum conversion of ethylene is achieved. Thus, even with use of propane as the feedstock for propylene production, it is common to have more moles of ethylene than propylene product in the exit stream for optimum cracking economics.

Propylene is also recovered as a by-product of other refinery operations, principally from the fluid catalytic cracking (FCC) of gas oils and to a lesser extent from the volatile products of coking, when coking is used. All refinery streams containing recoverable fractions of propylene will be combined into a mixed C₃ stream for propylene separation. Distillation of this

combined stream then gives propylene (b.p. $-47.7\text{ }^{\circ}\text{C}$) as the overhead product and propane (b.p. $-42.1\text{ }^{\circ}\text{C}$) plus traces of other higher boiling point products as the bottom fraction.

Chemicals Derived from Propylene

Propylene consumption for chemical synthesis in 1998 in the United States was 30 billion lb. This demand was exceeded by that of only one other synthetic organic chemical, ethylene. The demand was projected to grow at about 4.7 percent/year through 2003. Major uses of propylene are in polypropylene, acrylonitrile, propylene oxide, and cumene. A breakdown of propylene consumption by product is:

~ Polypropylene	45 %
~ Acrylonitrile	12 %
~ Propylene oxide	11 %
~ Cumene	8 %
~ Oxo alcohols	8 %
~ Isopropyl alcohol	4 %
~ Oligomers	4 %
~ Acrylic acid	5 %
~ Export, other	3 %

Benzene, Toluene, and the Xylenes (BTX)

Aromatics are typically concentrated in product streams from the catalytic reformer. When aromatics are sought for petrochemical applications, they typically are extracted from the reformer product stream by solvent extraction or distillation extraction. A common solvent used is sulfolane; new processes now use *n*-formylmorpholin as the extractive solvent.

The mixture of aromatics is typically referred to as BTX and is an abbreviation for benzene, toluene, and xylene. The first two components – benzene and toluene – usually are separated by distillation, and the isomers of the third component – xylene – are separated by partial crystallization. Benzene is the starting chemical for materials such as styrene, phenol, and many fibers and plastics. Toluene is used to make a number of chemicals, but most is blended into gasoline. Xylene usage is dependent on its isomer. *Para-xylene* (*p*-xylene) is a precursor compound for polyester. *Ortho-xylene* (*o*-xylene) is the building block for phthalic anhydride. Both compounds are widely used to manufacture consumer products.

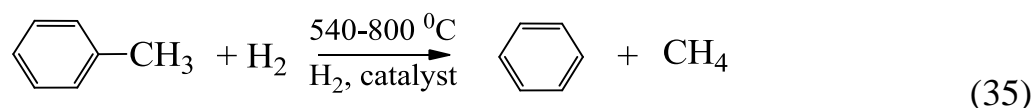
This BTX monoaromatic product stream is usually produced in several different refinery operations. Each of these rank in the top 30 chemicals produced in the United States by volume. They have reached this signifi-

cance because of their large demand as feedstocks for many of the important plastics. Preparation of these materials is discussed together because several are produced at the same time from many of the processes from which they arise. The chief sources of these aromatics may be conveniently divided into three groups.

In *the first group*, the production of aromatics is a complementary objective to the refinery processing of gasoline fractions to raise the aromatic content, which evidently links these refining functions. Catalytic reforming processes are used to convert paraffins to naphthenes (cycloparaffins) to be followed by dehydrogenation of naphthenes to aromatics. Since aromatization of naphthenes is an easier process to accomplish than cycloalkylation, the emphasis in refinery operations is on maximization of the second step in this sequence, when there is an adequate supply of naphthenes. The demand for the aromatics component of gasoline will compete with the feedstock aromatic need from this source.

The second group includes some of the processes used for ethylene production, particularly those using naphtha or gas oil as feedstocks, which may also produce large amounts of BTX. The conditions used (temperature, pressure, feedstock ratios, etc.) to operate these processes provide some flexibility to alter the product distribution slightly in response to the distribution of the demand.

The third group of processes to benzene, toluene, and xylenes, or p-xylene is discretionary and depends on the proportion of these products that are available from the first two classes of processes in comparison to the current demand. Benzene consumption is more than twice that of toluene. It may be conveniently produced in almost 90% yields by the catalytic hydrodealkylation of toluene (Eq. 35) [7]. Or if both benzene and xylenes are in short supply, toluene may be catalytically transalkylated to mainly benzene and xylenes [8].



Ethylbenzene, too, may be isomerized to xylenes. Xylenes are normally recovered from a mixed aromatics stream by extraction with sulfolane or a glycol. If the market for one xylene isomer is greater than that available by separation of the mixture, the low demand isomers may be isomerized to raise the proportion of the desired isomer(s).

About half of the benzene produced as a chemical feedstock is for styrene production, followed by large fractions for phenol and cyclohexane-

based products. As much as half of the toluene produced is converted to benzene, depending on the price and demand differential. The largest use of toluene itself is as a component of gasoline. Much smaller amounts are used as a solvent, or in the manufacture of dinitrotoluene and trinitrotoluene for military applications. Xylenes are also used in gasoline formulations and function as octane improvers like toluene. *para*-Xylene and *o*-xylene are the dominant isomers of value as chemical feedstocks, for the production of terephthalic acid (and dimethyl terephthalate) and phthalic anhydride, respectively. Polyester and the synthetic resin markets, in turn, are major consumers of these products. *meta*-Xylene is oxidized on a much smaller scale to produce isophthalic acid, of value in the polyurethane and Nomex aramid (poly(*m*-phenylene isophthalamide)) technologies.



Glossary

Asphalt ['æsfəlt] (n) – a sticky, black and highly viscous liquid or semi-solid that is present in most crude oils and in some natural deposits sometimes termed asphaltum. It is most commonly modeled as a colloid.

Bitumen ['bɪtjʊmɪn] (n) – a mixture of organic liquids that are highly viscous, black, sticky, entirely soluble in carbon disulfide and composed primarily of highly condensed polycyclic aromatic hydrocarbons.

Burner ['bɜ:nə] is a device which produces heat or a flame, especially as part of a cooker, stove, or heater.

Catalyst ['kæt(ə)lɪst] a substance that increases the rate of a chemical reaction without itself undergoing any permanent chemical change.

Coil [kɔɪl] (n) a length of something wound or arranged in a spiral or sequence of rings.

Coke [kəuk] (n) – a solid-fuel product containing about 80 percent of carbon produced by distillation of coal to drive off its volatile constituents: used as a fuel and in metallurgy as a reducing agent for converting metal oxides into metals.

Conversion [kən'veɜ:ʃ(ə)n] – the process of changing or causing something to change from one form to another

Convection section [kən'vekʃ(ə)n 'sekʃ(ə)n] – the part of the furnace in which tubes receive heat from the flue gases by convection.

- Diesel oil ['di:z(ə)l oɪl] – a fuel obtained from petroleum distillation that is used in diesel engines. It has a relatively low ignition temperature (540 °C) and is ignited by the heat of compression, also called (Britain): derv.
- Endothermic [ˌendə(u)'θɜ:mɪk] (adj) – accompanied by or requiring the absorption of heat.
- Exothermic [eksə(u)'θɜ:mɪk] (adj) – requiring a net input of heat for its formation from its constituent elements.
- Explosive [ɪk'spləʊsɪv] is a substance or device that can cause an explosion.
- Feedstock ['fri:dstɒk] (n) – raw material to supply or fuel a machine or industrial process.
- Fermentation [ˌfɜ:men'teɪʃ(ə)n] (n) – the chemical breakdown of a substance by bacteria, yeasts, or other micro-organisms, typically involving effervescence and the giving off of heat.
- Fuel oil [fjuəl oɪl] – fraction obtained from petroleum distillation, either as a distillate or a residue. Generally, fuel oil is any liquid petroleum product that is burned in a furnace or boiler for heat generation or power generation in an engine, except oils having a flashpoint of approximately 40 °C (104 °F) and oils burned in cotton or wool-wick burners. Fuel oil is made of long hydrocarbon chains, particularly alkanes, cycloalkanes and aromatics. The term fuel oil is used in a stricter sense to refer only to the heaviest commercial fuel that can be obtained from crude oil, heavier than gasoline and naphtha.
- Gasoline ['gæs(ə)lɪ:n] (n) – US and Canadian, any one of various volatile flammable liquid mixtures of hydrocarbons, mainly hexane, heptane, and octane, obtained from petroleum and used as a solvent and a fuel for internal-combustion engines. Usually petrol also contains additives such as antiknock compounds and corrosion inhibitors, also called (especially in Britain): petrol.
- Halogenation [ˌheɪləʊədʒɪ'neɪʃ(ə)n] (n) – is a chemical reaction that incorporates a halogen atom into a molecule. More specific descriptions exist that specify the type of halogen: fluorination, chlorination, bromination, and iodination.
- Heavy crude oils or Extra heavy crude oil – any type of crude oil which doesn't flow easily. It is referred to as “heavy” because its density or specific gravity is higher than of light crude oil.
- Hydration [haɪ'dreɪʃ(ə)n] (n) – a chemical addition reaction where a hydroxyl group and proton are added to a compound.

Hydroformylation [ˌhaɪdrəʊfɔːmjʊˈleɪʃ(ə)n] (n) - also known as *oxosynthesis*, is an important industrial process for the production of aldehydes from alkenes. This chemical reaction entails the addition of a formyl group (CHO) and a hydrogen atom to a carbon-carbon double bond.

Kerogen [ˈkærədʒən] (n) – the solid organic material found in some rocks, such as oil shales that produce hydrocarbons similar to petroleum when heated.

Kerosene [ˈkerəsiːn] (n) – a combustible hydrocarbon liquid, sometimes spelled kerosine in scientific and industrial usage. The name is derived from Greek *keros* meaning wax.

LRP – Lead (Pb) Replacement Petrol [led rɪˈpleɪsmənt ˈpetr(ə)l] (also called LPG, GPL, LP Gas, or autogas) – is a mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles, and increasingly replacing chlorofluorocarbons as an aerosol propellant and a refrigerant to reduce damage to the ozone layer.

Lubricating oilstream [ˈluːbrɪkətɪŋ oɪl ˈstriːm] – the highest boiling distillate (i.e., volatile) fraction from the crude, b.p. 400–520 °C, which also contains much of the grease and wax yield of the crude oil.

Mineral oil [ˈmɪn(ə)r(ə)l oɪl] (n) – 1) Britain: any oil of mineral origin, especially petroleum; 2) US and Canadian: a colorless almost tasteless oily liquid obtained by petroleum distillation and used as a laxative, also called (in Britain and certain other countries): liquid paraffin.

MTBE methyl tertiary-butyl ether [ˈmeθ(ə)l ˈteɪʃ(ə)rɪ-ˈbjuːtɪl ˈɪːθə] – a lead-free antiknock petrol additive. It is highly refined and high octane light distillate used in the blending of petrol.

Naphtha [ˈnæfθə] (n) – 1) a distillation product from coal tar boiling in the approximate range 80–170 °C and containing aromatic hydrocarbons; 2) a distillation product from petroleum boiling in the approximate range 100–200 °C and containing aliphatic hydrocarbons: used as a solvent and in petrol.

Octane number [ˈɒkteɪn ˈnʌmbə] – a measure of petrol’s resistance to pre-ignition which is the sound made by an engine when pre-ignition occurs, particularly at low revs and high speed.

Oligomerization [ˌɒlɪg(ə)məraɪˈzeɪʃ(ə)n] – a chemical process only converts monomers to a finite degree of polymerization.

Oxidation [ˌɒksɪˈdeɪʃ(ə)n] – is a process in which a chemical substance changes because of the addition of oxygen.

- Paraffin wax [ˈpærəfɪn wæks] (or simply "paraffin", but see alternative name for *kerosene*, above) – is mostly found as a white, odorless, tasteless, waxy solid, with a typical melting point between about 47 °C to 64 °C (116.6 °F to 147.2 °F), and having a density of around 0.9 g/cm³.
- Petrochemical [ˌpetrəˈkemɪk(ə)l] (n) – any chemical derived from fossil fuel. These include purified fossil fuels such as methane, propane, butane, gasoline, kerosene, diesel fuel, aviation fuel, or fuel oil, and also include many agricultural chemicals such as pesticides, herbicides and fertilizers, and other items such as plastics, asphalt and synthetic fibers. Also a wide variety of industrial chemicals are petrochemicals.
- Petroleum coke [pəˈtrɔɪləm kəʊk] (n) – often abbreviated petcoke, is a carbonaceous solid derived from oil refinery coker units or other cracking processes. Other coke has traditionally been derived from coal.
- Petroleum products [pəˈtrɔɪləm ˈprɒdʌkts] – useful materials derived from crude oil (petroleum) as it is processed in oil refineries.
- Purge [ˈpɜːdʒ] to remove (impurities and other elements) by or as if by cleansing.
- Radiant section [ˈreɪdɪənt ˈseɪʃ(ə)n] – is where the tubes receive almost all their heat by radiation from the flame.
- Reactor [rɪˈæktə] – a device for containing and controlling a chemical reaction.
- Refinery gas [rɪˈfaɪn(ə)rɪ ɡæs] – is produced in petroleum refineries by cracking, reforming, and other processes; principally methane, ethane, ethylene, butanes, and butylenes.
- Stack [stæk] – the industrial terminology for an industrial plant chimney.
- Steam drum [ˈstiːm drʌm] – is a standard feature of a water-tube boiler. It is a reservoir of water/steam at the top end of the water tubes. The drum stores the steam generated in the water tubes and acts as a phase-separator for the steam/water mixture.
- Stripper [ˈstri:pə] – a device used for stripping/cleaning/removing something.
- Transfer line exchanger – after the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger.
- Vent [vent] – an opening that allows air, gas, or liquid to pass out of or into a confined space.



Review Questions and Exercises

1. Enumerate the areas of final products application obtained from ethylene and propylene.
2. Can we obtain the same final products from another feedstock without olefin synthesis? And why?
3. Give “for” and “against” arguments of oil employment for olefin synthesis.
4. Using data from Fig. 16 write down a flowsheet of polyvinyl alcohol synthesis and give real life examples of its application. Explain, is it possible to get polyvinyl from another raw material?



Exercise 4.1.

Match the terms with their definitions:

1. Petrochemical
 2. Petrol (gasoline in the United States and Canada)
 3. Oil refinery
 4. Cracking
 5. Coke
 6. Steam cracking
 7. Hydrocracking
-
- A. a solid carbonaceous residue derived from low-ash, low-sulfur bituminous coal
 - B. a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons.
 - C. the process whereby complex organic molecules are converted to simpler molecules by the breaking of carbon -carbon bonds in the precursors.
 - D. any chemical derived from fossil fuel.
 - E. a petroleum-derived liquid mixture consisting primarily of hydrocarbons, used as fuel in internal combustion engines.
 - F. an industrial process plant where crude oil is processed and refined into useful petroleum products.
 - G. the cracking of heavier hydrocarbons in the presence of hydrogen.



Exercise 4.2.

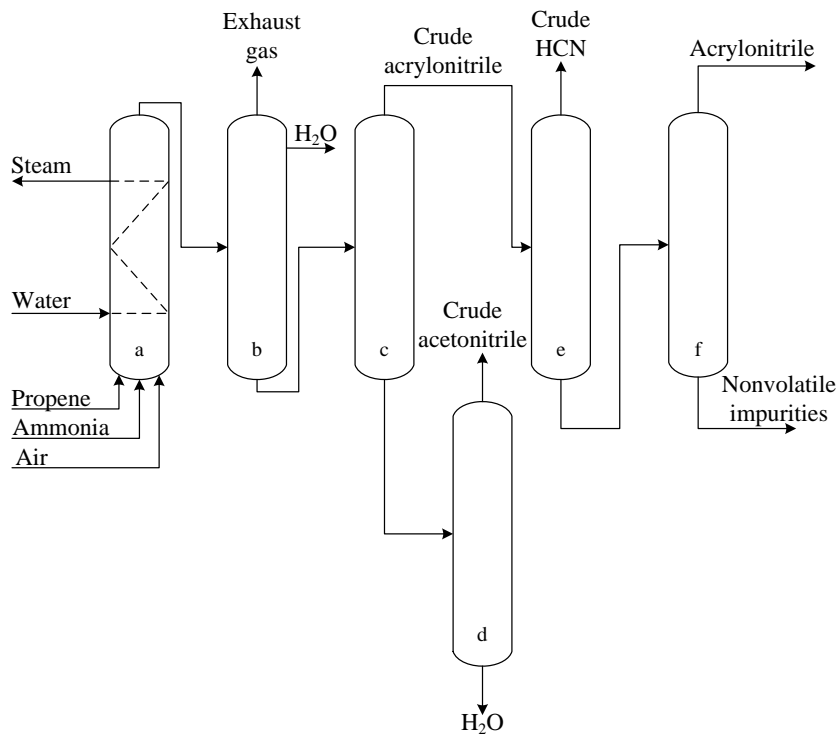
Find Russian equivalents 1-10 to English ones 1-10:

- | | |
|--------------------------|--------------------------------|
| 1. Cut | 1. Обессеривание нефти |
| 2. Straight run gasoline | 2. Гидроочистка |
| 3. Virgin naphtha | 3. Алкилирование |
| 4. Naphtha | 4. Изомеризация |
| 5. Fuel oil | 5. Сырая нефть |
| 6. Asphalt | 6. Дезактивация |
| 7. Alumina | 7. Битуминозный |
| 8. Silica | 8. Углистый |
| 9. Gas oil | 9. Аморфный, некристаллический |
| 10. Coal-tar | 10. Малозольный |



Exercise 4.3.

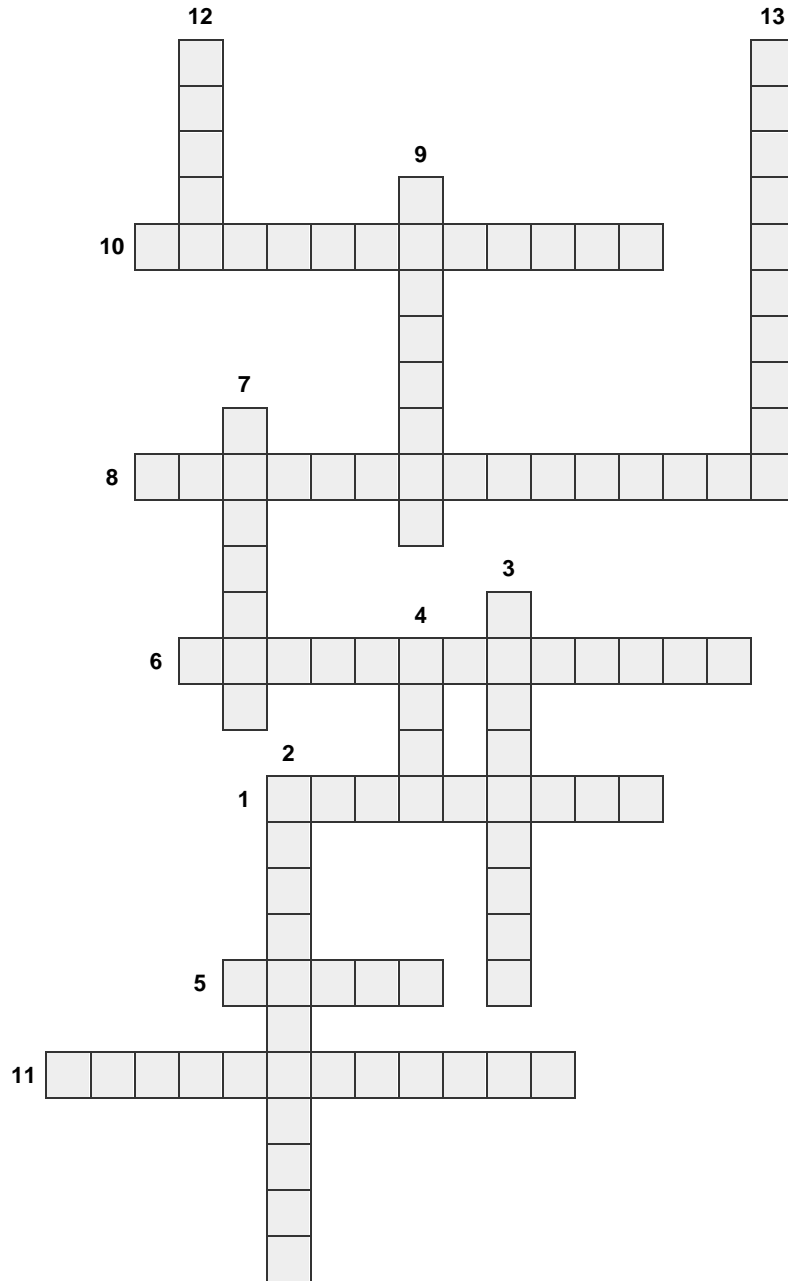
Describe the technological process of acrylonitrile synthesis via propylene oxidation in terms of its chemical reaction and technological parameters. Could you please describe the situation/sphere where is it applied?





Exercise 4.4.

Crossword



1. A substance or device that can cause an explosion.
2. Accompanied by or requiring the absorption of heat.
3. Raw material to supply or fuel a machine or industrial process.
4. A length of something wound or arranged in a spiral or sequence of rings.
5. The industrial terminology for an industrial plant chimney.
6. Any chemical derived from fossil fuel.
7. A mixture of organic liquids that are highly viscous, black, sticky, entirely soluble in carbon disulfide and composed primarily of highly condensed polycyclic aromatic hydrocarbons.
8. A chemical process only converts monomers to a finite degree of polymerization.
9. A device used for stripping/cleaning/removing something.
10. The chemical breakdown of a substance by bacteria, yeasts, or other microorganisms, typically involving effervescence and the giving off of heat.
11. A chemical reaction that incorporates a halogen atom into a molecule.
12. To remove (impurities and other elements) by or as if by cleansing.
13. The process of changing or causing something to change from one form to another.

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Appendix A



Exercise A.1.

Mind the meaning of the following phrasal verbs.

Phrasal verbs

- 1) To bring about – осуществлять
- 2) To build up – образовывать
- 3) To consist in – заключаться в
- 4) To consist of – состоять из
- 5) To carry out – осуществлять
- 6) To draw up – составлять документ
- 7) To end up – закруглять, заканчивать что-либо
- 8) To give off – выделять, испускать
- 9) To give up – выполнять
- 10) To leave over – откладывать (вопрос, решение)
- 11) To leave up – оставлять
- 12) To make up – составлять (план, перечень и т.д.), состоять из
- 13) To result from – быть результатом чего-либо
- 14) To result in/ to lead to – приводить к чему-либо
- 15) To put down/to cut down – урезать расходы
- 16) To put forward – выдвигать/предлагать идею
- 17) To set up – устанавливать, учреждать
- 18) To take up – браться за что-либо, приниматься за что-либо
- 19) To use up – расходовать
- 20) To take-off (casing-head gas) – отбирать нефтяной газ на устье скважины



Exercise A.2.

Translate the following sentences into Russian.

- 1) Iron **makes up** about 4 percent of solid rocks of the earth crust.
- 2) Higher temperatures **bring about** more frequent collisions between molecules.
- 3) If we pass an electric current through water using platinum or gold electrodes we found two gases **to be given off** at the electrodes and the water **to be used up**.

- 4) Supersaturated solutions are unstable; they readily **give up** their excess solute if shaken.
- 5) Each of the sodium atoms **gives off** an electron and forms an ion which goes into solution.
- 6) The flow of electrons in one direction **results in** an electric current.
- 7) Convection **is resulted from** the change in density that takes place when the substance is heated.
- 8) The transmission of heat energy by conduction **consists in** the transmission of kinetic energy from particle to particle within the substance.
- 9) We know steam **to consist of** minute drops of water.
- 10) The technological scheme of the process **must be drawn up**.
- 11) We need **to leave over** the issue about the additional instrumentation use.
- 12) To make the enterprise economically profitable we need **to cut down** the expenses.
- 13) A new installation **has been set up**.
- 14) Separation method of stabilization **leaves up** to 2 % of hydrocarbons C₁-C₄ in oil.
- 15) The casing-head gas **is taken off** at the top of the well or at the separator.

Exercise A.3.


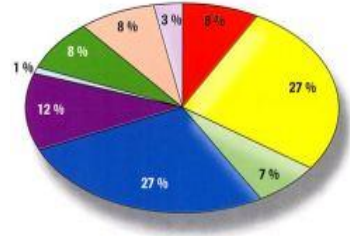
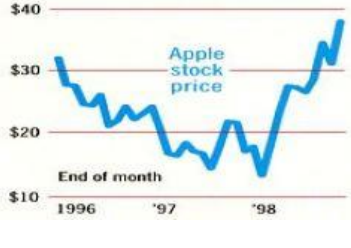

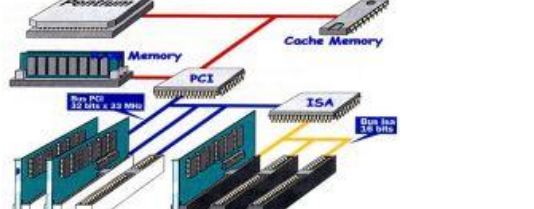


Make up your own examples on oil refining using the phrasal verbs above.

Appendix B

How to talk about a visual aid

Choosing the right visual aid

<p>A flow chart is a diagram showing the progress of material through the <i>steps</i> (étapes) of a manufacturing <i>process</i> (processus) or the succession of operations in a complex activity</p>	<p>A pie chart displays the <i>size</i> (taille) of each part as a percentage of a <i>whole</i> (tout).</p>																																																																																										
 <pre> graph TD DF[Digital Flowers plc] --> BD[Board of Directors] BD --> MD[Managing Director] MD --> RDM[R&D Manager] MD --> PM[Personnel Manager] MD --> PROD[Production Manager] MD --> FM[Finance Manager] MD --> MM[Marketing Manager] RDM --> TM[Training Manager] PM --> WM[Works Manager] PROD --> AM[Accounts Manager] FM --> SM[Sales Manager] </pre>																																																																																											
<p>A line chart depicts changes over a period of time, showing data and trends</p>	<p>A table is a convenient way to show large amount of <i>data</i> (données, informations) in a small space</p>																																																																																										
	<table border="1" data-bbox="837 1052 1372 1299"> <thead> <tr> <th></th> <th>AUST Sch</th> <th>BELG Fr</th> <th>DAN Kr</th> <th>GER Dm</th> <th>NETH Fl</th> <th>FIN Markka</th> <th>FR Fr</th> <th>GREEC Drach</th> </tr> </thead> <tbody> <tr> <td>30 Jan 2003</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> </tr> <tr> <td>AUSTRIA Schilling</td> <td>-</td> <td>0.341</td> <td>1.839</td> <td>7.036</td> <td>6.270</td> <td>2.355</td> <td>2.085</td> <td>0.044</td> </tr> <tr> <td>BELGIUM Franc</td> <td>2.929</td> <td>-</td> <td>5.387</td> <td>20.61</td> <td>18.36</td> <td>6.897</td> <td>6.107</td> <td>0.130</td> </tr> <tr> <td>DENMARK Krone</td> <td>0.544</td> <td>0.186</td> <td>-</td> <td>3.825</td> <td>3.409</td> <td>1.280</td> <td>1.134</td> <td>0.024</td> </tr> <tr> <td>GERMANY Deutschmark</td> <td>0.142</td> <td>0.049</td> <td>0.261</td> <td>-</td> <td>0.891</td> <td>0.335</td> <td>0.296</td> <td>0.006</td> </tr> <tr> <td>NETHERLANDS Guilder</td> <td>0.159</td> <td>0.054</td> <td>0.293</td> <td>1.122</td> <td>-</td> <td>0.376</td> <td>0.333</td> <td>0.007</td> </tr> <tr> <td>FINLAND Markka</td> <td>0.425</td> <td>0.145</td> <td>0.781</td> <td>2.988</td> <td>2.663</td> <td>-</td> <td>0.885</td> <td>0.019</td> </tr> <tr> <td>FRANCE Franc</td> <td>0.480</td> <td>0.164</td> <td>0.882</td> <td>3.374</td> <td>3.007</td> <td>1.129</td> <td>-</td> <td>0.021</td> </tr> <tr> <td>GREECE Drachma</td> <td>22.49</td> <td>7.679</td> <td>41.37</td> <td>158.2</td> <td>141.0</td> <td>52.96</td> <td>46.90</td> <td>-</td> </tr> </tbody> </table>		AUST Sch	BELG Fr	DAN Kr	GER Dm	NETH Fl	FIN Markka	FR Fr	GREEC Drach	30 Jan 2003									AUSTRIA Schilling	-	0.341	1.839	7.036	6.270	2.355	2.085	0.044	BELGIUM Franc	2.929	-	5.387	20.61	18.36	6.897	6.107	0.130	DENMARK Krone	0.544	0.186	-	3.825	3.409	1.280	1.134	0.024	GERMANY Deutschmark	0.142	0.049	0.261	-	0.891	0.335	0.296	0.006	NETHERLANDS Guilder	0.159	0.054	0.293	1.122	-	0.376	0.333	0.007	FINLAND Markka	0.425	0.145	0.781	2.988	2.663	-	0.885	0.019	FRANCE Franc	0.480	0.164	0.882	3.374	3.007	1.129	-	0.021	GREECE Drachma	22.49	7.679	41.37	158.2	141.0	52.96	46.90	-
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<p>A (vertical or horizontal) bar chart is used to compare <i>unlike</i> (different) items</p>	<p>A diagram is a drawing showing arrangements and situations, such as <i>networks</i> (réseaux), distribution, fluctuation ...</p>																																																																																										
																																																																																											

Presenting a visual

Introduction	Topic	Circumstances
This graph shows ...	the results of our products ...	over 10 years.
The diagram outlines ...	rates of economic growth ...	between 1990 and 1996.
This table lists ...	the top ten agencies ...	in the industrial world.
This pie chart represents	the company's turnover ...	for this year in our sector.
This line chart depicts ...	the changes in sales ...	over the past year.
This chart breaks down (<i>ventile</i>) ...	the sales of each salesman ...	during the past ten weeks.

Indicating upward movement

Verbs	Nouns
(to) go/be up	(an) increase
(to) grow	(a) raise (US), a rise (UK)
(to) increase	(an) upswing
(to) rise (rose, risen)	(a) growth
(to) push/put/step up	(an) extension, expansion
(to) extend, (to) expand	(a) progression
(to) progress	(a) boom
(to) boom/soar/climb	(a) jump
(to) jump, (to) skyrocket	(a) peak
(to) reach a peak, (to) peak	
(to) reach an all-time high	

Indicating no movement

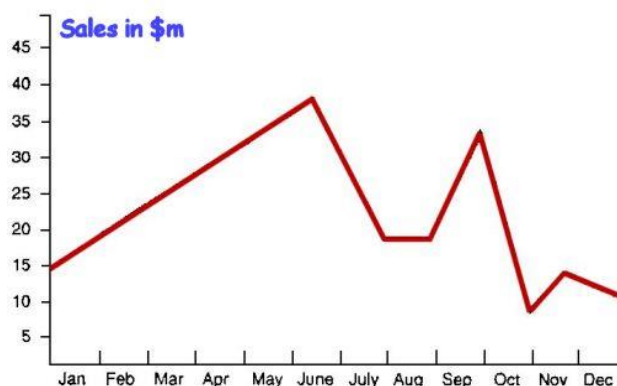
Verbs	Nouns
(to) keep ... stable	stability
(to) hold ... constant	constancy
(to) stabilize	permanency
(to) remain stable	
(to) stay constant	

Indicating downward movement

Verbs	Nouns
(to) decrease	(a) decrease
(to) cut, (to) reduce	(a) cut, (a) reduction
(to) fall (off) (fall, fell, fallen)	(a) fall
(to) plunge, to plummet	(a) plunge
(to) drop (off)	(a) drop
(to) go down	(a) downswing
(to) decline	(a) decline
(to) collapse	(a) collapse (dramatic fall)
(to) slump, (to) go bust	(a) slump
(to) bottom out	

Example of answer

The x axis of this graph shows the twelve months of the past year while our sales in millions of dollars appear on the y axis. It may be seen clearly that sales rose steadily in the first half of the year (from January to May) and reached their peak in June. Then they dropped off in July and levelled out in August. After rising sharply during September, they suffered a **dramatic** (*spectaculaire*) fall in October but then made a **significant** (*sensible*) **recovery** (*redressement*) in November. However, the year ended with a slight downturn.



Appendix C

Useful expressions for writing and speaking in English

<i>Addition to what has been previously indicated: above all indeed</i>	
first furthermorefinally	particularly
one a second a third	especially
actually	furthermore
in addition	too
additionally	what is more
moreover	also
again	notably
not only	as well (as)
besides	obviously
to begin/start with	but also
in the second place	specifically
further	then
to conclude	
<i>Comparison</i>	
also	in the same way
too	likewise
similarly	both and
correspondingly	equally
<i>Example</i>	
for example	to illustrate
for instance	as an illustration
such as	to demonstrate
<i>Result</i>	
accordingly	as a result
now	so that
as a consequence	in order that
because of	therefore
thus	consequently
so	hence
then	for this/that reason
the result is	the consequence is
<i>Summary</i>	
in conclusion	to conclude
in short	to summarise

hence	overall
therefore	to sum up
in brief	altogether
<i>Speaking expressions</i>	
<i>Agreement</i>	<i>Disagreement</i>
I agree	I'm afraid I disagree
I completely / entirely / totally/agree	I wouldn't say so
Yes, definitely	I can't agree
Yes, that's right	I disagree with that completely
Sure	It is a disputable question
That is out of the question	I guess you are wrong

<i>LINKING DEVICES:</i>	
To make contrasting points	however, nevertheless, in spite of, but, while, despite, even if, even though, at the same time, although, yet,
To list points	firstly, in the first place, first of all, to start with, secondly, thirdly, finally
To add more points to a topic	what is more, furthermore, also, apart from this/that, in addition to, moreover, besides, too, not to mention the fact that
To list advantages/disadvantages	one/another/one other /the first/the greatest advantage/disadvantage of...
To express personal opinion	in my opinion/view, to my mind/way of thinking, personally I believe, it strikes me that, I feel very strongly that, I am inclined to, believe that, it seems to me that, as far as I am concerned
To refer to other Sources	according to, with reference to
To conclude	finally, lastly, above all, taking everything into account, on the whole, all things considered, in conclusion, as I have said, as was previously stated, to sum up
To express cause	because of, owing to, due to, for this reason
To express effect	therefore, thus, as a result, consequently, so, as a consequence
To emphasise what you say	clearly, obviously, of course, needless to say, in particular

To express reality	in fact, actually, as a matter of fact, in practice, the fact of the matter is that
To express difference between appearance and reality	on the face of it, at first sight, apparently
To state an argument against your opinion	it is popularly believed that, people often claim that, contrary to popular belief, it is a fact that, it is often alleged that, people argue that
To state other people's opinions	many people are in favour of/against, some people argue that, a lot of people think/believe
To express balance	while, on the one hand, on the other hand, whereas
To introduce the other side of the argument	opponents of this view say, however there are people/those who oppose... claim that
To refer to what actually happens	for example, for instance
To make general statements	as a rule, generally, in general, as a general rule, on the whole
To make partly correct statements	up to a point, to a certain extent, to some extent, in a way, in a sense
To express limit of knowledge	to the best of my knowledge, for all I know, as far as I know
To rephrase	that is to say, in other words
To bring up other points or aspects	as far as ... is concerned, regarding, with regard to, as for
To imply that nothing else needs to be said	anyway, at any rate, in any case
Accepting the situation	as it is, under the circumstances, things being as they are

Appendix D

List of acronyms in oil and gas exploration and product

AADE – American Association of Drilling Engineers
AAPG – American Association of Petroleum Geologists
AAODC – American Association of Oil well Drilling Contractors
AGRU – acid gas removal unit
API – American Petroleum Institute
APS – active pipe support
ASME – American Society of Mechanical Engineers
B or b – prefix denoting a number in billions
bbl – barrel
BBSM – behavior-based safety management
BCPD - barrels condensate per day
boe – barrel(s) of oil equivalent
BOP – bottom of pipe
bopd – barrel(s) of oil per day
BPH – barrels per hour
BPV – back pressure valve (goes on the end of coiled tubing a drill pipe tool strings to prevent fluid flow in the wrong direction)
BSML – below sea mean level
BS&W – basic sediments and water
BTEX – benzene, toluene, ethyl-benzene and xylene
BTHL – bottom hole log
BTO/C – break to open/close (valve torque)
BTU – British thermal units
BU – bottom up
BUL – bottom up lag
BUR – build-up rate
BVO – ball valve operator
bwd – barrels of water per day (often used in reference to oil production)
bwpd – barrels of water per day
C&E – well completion and equipment cost
C&S – cased and suspended
C1 – methane
C2 – ethane
C3 – propane
C4 – butane
C6 – hexanes
C7+ – heavy hydrocarbon

CDU – control distribution unit
CDP – common depth point (geophysics)
CDP – comprehensive drilling plan
CDRCL – compensated dual resistivity
CHESM – contractor, health, environment and safety management
CHKSR – checkshot survey report
CCR Cyclic catalytic reforming
DECC – Department for Energy and Climate Change (UK)
DOE – Department of Energy, United States
DTI – Department of Trade and Industry (UK)
E&P – Exploration and Production
EAGE – European Association of Geoscientists & Engineers
ECD – Equivalent Circulating Density
ECP – External Casing Packer
ECRD – Electrically Controlled Release Tool
EDP – Exploration Drilling Program Report
EDP – Emergency Disconnect Package
EDR – Exploration Drilling Report
EDR - Electronic Drilling Recorder
EDS – Emergency Disconnection Sequence
EFL – Electrical Flying Lead
EFR – Engineering Factual Report
EHT – Electric Heat Trace
ESP – Electric Submersible Pump
FCC Fluid catalytic cracking or cracker
G/C – Gas Condensate
GAS – Gas Log
GASAN – Gas Analysis Report
GDE - Gross Depositional Environment
GIS – Geographic Information System
GTL – Gas to Liquid
GTW – Gas to Wire
GUN – Gun Set Log
GWC – Gas-Water Contact
GWREP – Geo Well Report
HDC Hydrocracking or hydrocracker
HDS Hydrodesulfurization
HDT Hydrotreating or hydrotreater
HAZ – Heat Affected Zone
HSE – Health, Safety and Environment or Health & Safety Executive (UK)
HPU – Hydraulic Power Unit

HVDC – High Voltage Direct Current
IADC – International Association of Drilling Contractors
IPAA – Independent Petroleum Association of America
IWCF – International Well Control Federation
LNG – Liquefied Natural Gas
MEG – Mono-Ethylene Glycol
MMS – Minerals Management Service, (United States)
MPQT – Manufacturing Procedure Qualification Test
MWD – Measurement While Drilling
NACE – National Association of Corrosion Engineers
NOC – National Oil Company
NPD – Norwegian Petroleum Directorate
O&G – Oil and Gas
ONAN – Oil Natural Air Natural cooled transformer
OWC – Oil Water Contact
PCDM – Power and Control Distribution Module
PEDL – Petroleum Exploration and Development License
PESBG – Petroleum Exploration Society of Great Britain
QC – Quality control
ROCT – Rotary Coring Tool
SCHLL – Schlumberger
SCO – Synthetic crude oil
SPE – Society of Petroleum Engineers
TCF – Temporary Construction Facilities
TD – Total Depth
TOFD – Time of first data sample
USGS – United States Geological Survey
VISME – Viscosity Measurement
XC – Cross-connection
YP – Yield Point

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КУКУРИНА Ольга Сергеевна
РОЗАНОВА Яна Викторовна

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Научный редактор *доктор хим. наук,*
профессор А.Н. Пестряков
Редактор
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Дизайн обложки А. И. Сидоренко


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ИЗДАТЕЛЬСТВО  **ТПУ**. 634050, г. Томск, пр. Ленина, 30
Тел./факс: 8(3822)56-35-35, www.tpu.ru

O.S. Kukurina, Ya.V. Rozanova

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