

CATALYSIS AND REFINERY

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Contents

1. Brief presentation of the refinery and its products
 - 1.1. Introduction
 - 1.2. Simplified Refinery Process Scheme
 - 1.3. Refinery Products
 - 1.4. Production of Environmental Fuels in the Refinery
 - 1.5. Future Trends –Biofuels
2. Catalytic reforming
 - 2.1. Introduction
 - 2.2. Simplified Process Flow Diagram
 - 2.3. Chemistry and Reaction Pathways of Catalytic Reforming
 - 2.4. Factors affecting yields and quality of the process products
 - 2.5. Future Trends in Catalytic Reforming Process
3. Isomerization
 - 3.1. Introduction
 - 3.2. Process Diagram
 - 3.3. Isomerization Chemistry and Reaction Pathways
 - 3.5. Isomerization of Light Products-Future Trends
4. Fuel production from fluid catalytic cracking of heavy petroleum fractions
 - 4.1. Introduction
 - 4.2. Flow Diagram Description
 - 4.3. Chemistry of Catalytic Cracking
 - 4.4. FCC Feed and its Effect on Yield and Quality of Products Formed
 - 4.5. Catalytic Cracking Catalysts
5. Alkylation
 - 5.1. Introduction
 - 5.2. Process Flow Diagram
 - 5.3. Chemistry of Alkylation
 - 5.4. Factors Affecting the Yield and Quality of the Alkylate
 - 5.5. Future Trends in Alkylation
6. Hydroprocessing of petroleum products
 - 6.1. Introduction
 - 6.2. Flow Diagram Description
 - 6.3. Hydrotreating

Acknowledgments

Glossary

Bibliography

Biographical Sketches

Summary

Catalysis plays a key role in petroleum refining as most of the processes are catalytic. Petroleum fractions produced via fractional distillation of crude oil do not fulfill the quality standards to be used as fuels and the increasing market demands. The present topic describes the key conversion processes, which operate in modern refineries producing high quality fuels, mostly gasoline and diesel. The high demand in gasoline with anti-knocking characteristics is fulfilled with catalytic cracking of heavy petroleum fractions at high temperature in the presence of highly active and selective catalysts, zeolites. Improvements in octane number of light and heavy naphtha are accomplished in isomerization and reforming processes respectively in the presence of hydrogen and metallic noble catalysts. High quality gasoline without aromatics is also formed via alkylation reactions of light olefins with isobutane in the presence of strong acid catalysts. Catalytic addition of hydrogen to various refinery streams results to the removal of heteroatoms mainly of S and N, which have a negative environmental impact, the reduction in olefins and to a lesser extent to aromatics. Hydroprocessing of final product and intermediate hydrocarbon streams and hydrocracking units for upgrading heavy intermediate products operating under various conditions consist an important part of a modern refinery.

The text is organized in six sections. The first one is related with a brief introduction to the modern refinery and the main fuels produced. It continues with the other five sections dealing with isomerization, reforming, catalytic cracking, alkylation and hydroprocessing of petroleum fractions. The quality of products formed, the characteristics of catalysts used, the chemistry and kinetics of the reactions, the operating variables, the process schemes applied and the future trends are discussed.

1. Brief Presentation of the Refinery and its Products

1.1. Introduction

Crude oil is today the major energy source for transportation fuels worldwide and also a source for the production of a wide variety of chemical products. More than 85 millions barrels of crude oil are processed daily in petroleum refineries. Crude oil is a complex mixture of hydrocarbons, with main components carbon (C) and hydrogen (H). The C and H composition varies between 83-87 w.t.% in C and 10-14 w.t.% in H, respectively. Hundreds of hydrocarbon compounds are present in crude oil ranging from the simplest, methane, to heavy compounds containing 300 and more carbon atoms. The major types of hydrocarbons in the crude oil are paraffinic, naphthenic and aromatic. Besides carbon and hydrogen, crude oil also contains low concentrations in sulfur (0-5 wt%), nitrogen (0-1 wt%), oxygen (0-2wt%) and metals (0-0.1wt%), mainly iron, nickel, chromium and vanadium. The composition and properties strongly depend on the origin of the crude oil.

Crude oil after pumping it is transported to a refinery, a process plant for producing fuels such as gasoline and diesel and chemical intermediates such as propylene. The crude oil is first submitted to distillation under atmospheric or reduced pressure, in order to separate it in streams and produce petroleum fractions used in downstream refining processes. The refinery besides the distillation columns includes a variety of catalytic processes aiming at improving product yields and properties. These include: reforming, isomerization, hydroprocessing, alkylation and catalytic cracking.

The main refinery products are gasoline and diesel. Gasoline, which is a blend of many refinery streams, is a light fuel with high octane number, appropriate volatility and distillation range that facilitates its combustion in an internal combustion engine. Diesel is a middle distillate fuel with the appropriate properties (such as high cetane number) in order to be used in internal combustion engines. Besides automobiles fuels, other fuels are also produced in the refinery, such as domestic fuels and industrial fuels with standard specifications.

Catalysis plays a crucial role in several stages of fuel production. Many catalytic processes are necessary to convert crude oil to final commercial products, with strictly defined specifications. Approximately 30% of the total amount of catalysts produced by the industry is consumed in refinery processes.

1.2. Simplified Refinery Process Scheme

Crude oil, is first treated for the removal of dissolved salts (mainly sodium chloride), and then is preheated in a furnace at predetermined temperature around 370 to 400°C. The hot and partially vaporized crude is “flashed” in a trayed distillation tower, where it is separated to lighter fractions and a residue. The physical separation of the petroleum-distillation- is carried out at atmospheric pressure or more precisely in a little higher pressure than atmospheric (1.3 bar).

The atmospheric tower bottom is further processed in a vacuum distillation column, which operates at reduced pressure (5-10 mmHg) in order to facilitate separation of heavier compounds without heating at high temperatures which would cause thermal decomposition of hydrocarbons. Usually one additional side fraction and the residuum of the vacuum column are obtained. For an Arabian Light type crude oil the distillation ranges of the major products and the yields obtained from the fractional distillation are given in Table 1.1.

Distillation range, °C	Product	% vol. of the crude
Start – 50	Light products (butanes and lighter)	1.7
45 – 105	Light naphtha*, (light straight run, LSR naphtha)	5.18
90 – 200	Heavy naphtha* (HSR naphtha)	16.33
180 – 250	Kerosene	7.44
235 – 335	Light Gas Oil or diesel (light gas oil – LGO)	14.06
300 – 440	Atmospheric or Heavy Gas Oil (HGO)	12.99
400 – 565	Vacuum Gas Oil (VGO)	20.00
565+	Residue (VRC)	22.3

*The term naphtha is used to describe petroleum fractions directly derived from the column with distillation components similar to those of gasoline.

Table 1.1. Distillation ranges and fraction yields obtained from the fractional distillation of an Arabian Light type of crude oil

Products obtained from the atmospheric and vacuum towers do not have the appropriate properties and characteristics as engine fuels or heating fuels. Distillation products are submitted to a series of successive processes aiming to improve fuel properties, and increase yields of high market demand products.

The main conversion processes and the fractions used as feedstocks are:

- Light naphtha, the lightest liquid fraction of the atmospheric column, is subjected to a treatment to increase the octane number via isomerization. The isomerization process is the subject of Section 3.
- Heavy naphtha, the second side stream of the atmospheric column, is fed to the unit of catalytic reforming, where it is submitted to treatment to improve its engine burning properties. This process is described in detail in Section 2.
- Atmospheric heavy gas oil and vacuum gas oil comprise the main feed of the Fluid Catalytic Cracking Unit. This process is particularly important for a refinery and is extensively described in Section 4.
- Another important unit in the refinery is the alkylation unit, described in Section 5, which produces gasoline using isobutene and a mixture of olefins with 3 to 4 carbon atoms as feed.
- Almost all fractions either before their final disposal or before they are fed to other conversion units, are subjected to hydroprocessing for the removal of environmentally harmful heteroatoms and for improving their properties. The importance of hydroprocessing for improving fuel properties is significant and therefore it is described in detail in Section 6.

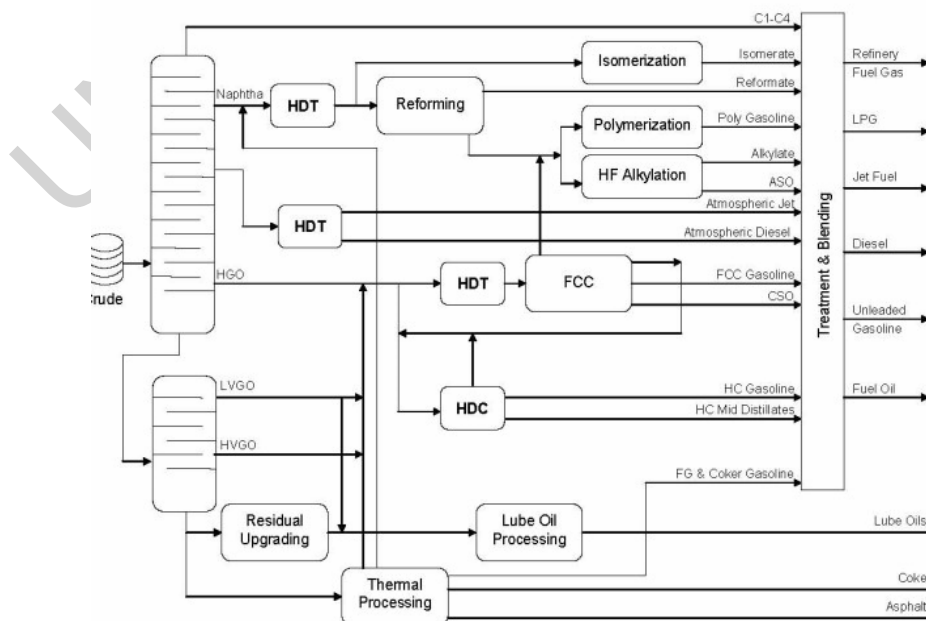


Figure 1.1. Simplified schematic diagram of a refinery

A simplified schematic diagram of a refinery is given in Figure 1.1.

1.3. Refinery Products

The main categories of products obtained from crude oil are:

- Engine fuels (gasoline, diesel, aviation fuels)
- Heating fuels (liquid gases, heating diesel, residual fuel oils, petrocoker)
- Several non-combustible products (asphalt, lubricants, illuminant petroleum, solvents, waxes, etc.)
- Feedstock for the production of petrochemicals (naphtha, C₃-C₄, gas oil)

Gasoline: Gasoline is a complex mixture of hydrocarbons having typical boiling ranges from 38 to 221°C. Today, gasoline production represents the 45% of the total production in a refinery. The main streams used in blending gasoline are:

- Isomerization gasoline (isomerate)
- Catalytic cracking gasoline
- Catalytic reforming gasoline (reformate)
- Alkylation gasoline and (alkylate)
- Oxygenated additives that increase octane number and small amounts of n-butane to control the vapor pressure.

Diesel: Diesel is a middle distillate product used in internal combustion engines with a continuously increasing market demand. This product is obtained by blending fractions of direct distillation (light gas oil) and other intermediate fractions produced from refinery processes with distillation limits 230- 370°C and cetane number higher than 45. It should be underlined that the most crucial property of this fuel, also characterizing its smooth ignition in the engine is the cetane number, which should be higher than 51.

Kerosene: Kerosene is the main component of aviation fuels for the aircrafts of civil and military aviation. The aviation fuels (jet fuels) are mainly blends of kerosene and a fraction of similar boiling range from the hydrocracking unit. The major characteristics of these fuels are the narrow distillation ranges (180-250°C), the upper limit in aromatics content 20%-22% and the low pour point (-40 to -50°C) necessary for the safe operation of the aviation engines.

The general term **fuels** refers also to fuels used domestically (heating diesel) and heavy fuels like bunker oils, used only in specific industrial applications. Liquefied petroleum gases, LPG, are of significant importance both for domestic use and for automobiles.

1.4. Production of Environmental Fuels in the Refinery

For the identification and determination of improved fuels specifications for lower exhaust emissions, large projects were realized in USA (CAAA Phase I και II) and EU (AUTO-OIL I and II) by collaboration between car industries and refineries. The main outcome of these projects was the development of mathematical models for the prediction of emitted pollutants as a function of fuel characteristics (e.g. aromatic and sulfur content, T90, vapor pressure etc). Among others, the US projects showed that benzene emissions are related with total aromatics and the initial benzene content while

the two EU AUTO-OIL projects demonstrated the linear correlation of HC and NO_x emissions with the sulfur content in the fuels (Figure 1.2).

Based on all previous remarks, new, stringent specifications were set the last years in automotive fuels. Changes started with the reduction of sulfur and aromatics. Undoubtedly fuel specification levels are chronically determined from the available technology in the refineries that could accomplish these specifications. In Table 1.2 current and future fuel specifications are presented. After 2010 in EU, fuels (gasoline and diesel) of zero S (zero S fuels) are required meaning S levels <10 ppmw. Besides transport fuels, properties of all other fuels are also improved especially concerning sulfur. For example S concentration of heating diesel for domestic use is 2000 ppm, while this value was 10000 ppm a few years ago.

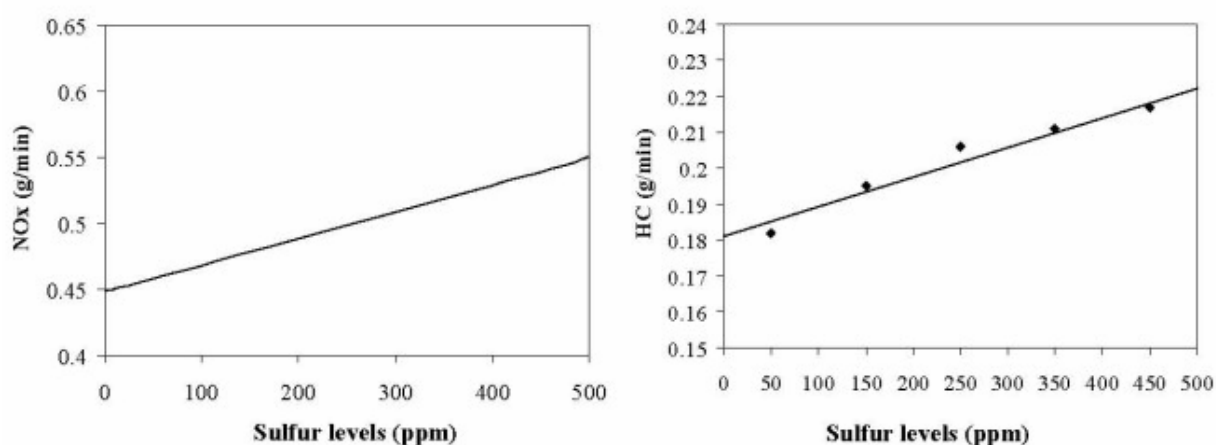


Figure 1.2. Correlation between S concentration in the fuel and NO_x and hydrocarbon (HC) emissions from the car exhaust

Gasoline	2005	2010	2020*
RON/MON, minimum	95/85		95
Sulfur (ppm), maximum	50	10	10
Aromatics (% v.v.), maximum	35	35	30
Olefins (% v.v.), maximum	18	12	10
Benzene (% v.v.), maximum	1	0.5	0.5
Vapor pressure at 38°C (kPa) maximum, summer period	60	60	60
Final boiling point (°C), maximum	210	210	200
Distillate at 100°C (% v.v.), minimum	46		
Distillate at 150°C (% v.v.), minimum	75		
Oxygen (% wt.), maximum	2.7		
Diesel	2005	2010	2020*
Density at 15°C (kg/lit), maximum	845	845	840
Sulfur (ppm maximum)	50	10	10
Cetane number (minimum)	51	54	54
T95 (°C), maximum	360		340
Aromatics (% v.v.)	-		10
Polyaromatics (PNA) (% wt.)	11		1

*Suggested specifications

Table 1.2. Fuel specifications in EU

The final commercial fuels derive from blending streams of various refinery processes described previously in this chapter. In Table 1.3 characteristic properties of gasoline streams (concerning pollutants-related components) from a typical refinery are presented. This specific refinery uses MTBE as oxygenated additive and butane to control vapor pressure of gasoline.

	FCC gasoline	Reforming gasoline	Isomerization gasoline	MTBE	n-butane
S content, ppmw	700	0	0	0	0
Olefins, %v.v	37	0	0	0	0
Benzene, % v.v.	0.9	3.5	0	0	0
Aromatics, %v.v	25	65	0	0	0
Octane number RON	92.5	99.5	77.5	117.5	100.5
Octane number MON	80	88	75	99	88.5
Vapor pressure RVP, psi	7.5	7	13	8	75
Specific gravity at 15°C	0.75	0.8	0.66	0.75	0.57

Table 1.3. Properties of gasoline from various processes

It is obvious that for a reduction in S and olefins of the final gasoline product one should improve FCC gasoline. To reduce aromatics (and benzene) reforming gasoline is the crucial parameter. To control octane numbers contribution of MTBE and reforming gasoline is of significant importance, while for any control of vapor pressure the added n-butane and isomerization gasoline are specifically important.

The major changes (and investments) realized in refineries the last decades to accomplish fuel specifications concern:

New units for diesel hydrotreating. Hydrotreatment can reduce S and aromatics from diesel.

New units for FCC-gasoline hydrotreating. These units can remove S, olefins and aromatics from FCC gasoline. Since hydrotreatment significantly lowers gasoline octane number specific gasoline fractions should be submitted to hydrogenation.

Benzene hydrotreating unit. This unit premises separation of the light reforming gasoline fraction and then hydrotreatment of this fraction.

Units for hydrocracking of catalytic pyrolysis feed. The FCC feed hydrocracking units help to remove sulfur and aromatics from the FCC feed. In addition, this unit contributes to increased diesel production in the refinery.

Isomerization and alkylation units. Both units significantly contribute to the production of high quality gasoline

Units for separation of olefins in FCC. Iso-olefins are separated to be used for the production of oxygenates (gasoline additives)

Oxygenates production unit. Depending on the olefins available, most refineries invest in a MTBE or/and a TAME unit. We should underline here that MTBE is not further used in California due to its high solubility in water and its low biodegradability.

1.5. Future Trends –Biofuels

The need to decreased CO₂ emissions in the atmosphere is becoming more urgent. Biomass (lignocellulosic raw materials, e.g. wood) is considered as an alternative raw material for energy production, as it is renewable and CO₂ neutral. Biomass derived fuels (Biofuels) are alternative fuels for the transportation sector. EU directives suggest introducing up to 5.75% of biofuels in the fuel market until 2010. It must be noted that the use of biodiesel is considered to contribute in the reduction of greenhouse gases at least 3.2 kg equivalent of CO₂ for each kg of biodiesel. Other advantages of biofuels (besides that they do not contribute to CO₂ and not contain sulfur) are that they limit energy dependence from fossil fuels, while simultaneously help rural economy. New cultivations are currently promoted aiming exclusively to the production of biofuels.

The first generation of biofuels (biodiesel, biethanol) is already in the fuel market. However, their major drawback is the high production cost compared with conventional fuels and the concern about use of edible feedstocks (edible oils, corn etc). For this reason second generation biofuels are now under development. It is important to mention the technologies almost ready for commercialization for diesel production from hydrogenation of triglycerides: “Green diesel” technology of UOP, Non-Ester Biomass to Liquid “NexBTL” technology of Neste Oil, H-BIO technology of Petrobras and “Super Cetane” technology of CANMET Energy Technology Center in Canada.

Petrobras is additionally planning to apply H-BIO technology in at least three refineries in Brazil to produce diesel from soybean oil. Applying similar technology, BP in the Bulwer refinery in Australia, is expected to produce biodiesel from tallow oil in a unit of 1900 bpd capacity by the end of 2007. Finally, Neste Oil is about to install a new unit of 3500 bpd capacity in a refinery in Finland and producing biodiesel from hydrotreating vegetable oils. Second generation bioethanol for enzymatic conversion of lignocellulosic materials are also under development. Finally synthetic diesel and synthetic DME production are under demonstration stage in Germany and Sweden respectively. These biofuels are produced through a biomass gasification step following by Fischer-Tropsch synthesis of the produced synthesis gas.

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Biographical Sketches

Angeliki A. Lemonidou was born in Tichero Evrou Greece in 1957. Angeliki Lemonidou received her Diploma in Chemistry from Aristotle University of Thessaloniki, Greece in 1979 and her PhD in Chemical Engineering from the same University in 1990.

She joined Aristotle University as research associate and she served the Department of Chemical Engineering as Lecturer (1992-1998) and Assistant Professor (1999-2004). From 2005 she is Associate Professor and Head of the Lab of Petrochemical Technology in the same Department. She is author and co-author of 50 publications in refereed journals and numerous publications in conferences. She has over 15 years of teaching experience in Chemical Engineering. She served as a member in the Editorial Board of *Applied Catalysis: A Journal* (2004-2007) and Guest Editor in a special issue of *Catalysis Today*. She is co-author of a textbook for graduate studies in Environmental Catalysis “Environmental fuels production via catalytic processes (in Greek), Greek Open University, Athens (2006) and of a chapter of a book “Carbon Dioxide Recovery and Utilisation”, Ed. M. Aresta, Kluwer Academic Publishers, Dordrecht (2003). The main areas of interest include applied catalysis in refining and petrochemical processes and alternative fuels production.

Prof. Lemonidou is a member of American Chemical Society and member of the Council of Greek Catalysis Society.

Angelos A. Lappas was born in Karditsa Greece in 1962. Angelos A. Lappas received his diploma in Chemical Engineering from Aristotle University of Thessaloniki, Greece in 1986 and holds a PhD degree in Chemical Engineering from the same university working in the area of Lignite Pyrolysis for fuel production.

He joined the Chemical Process Engineering Research Institute (CPERI) as Post Doctoral student from 1993 till 1994. Then he continued in the same institute as Assistant Researcher (1995-1999), Associate Researcher (2000-2003) and he is now a Principal Researcher in the laboratory of Environmental Fuels and Hydrocarbons of CPERI and a deputy director of CPERI. CPERI is one of the research institutes of Center of Research and Technology Hellas (CERTH). CERTH is a research organization located in Thessaloniki Greece.

He has 45 publications in ISI scientific journals and more than 100 papers in various symposia and conferences. He is a Guest Editor in a special issue of *Catalysis Today* and co-author of a textbook for graduate studies in Environmental Catalysis “Environmental fuels production via catalytic processes” (in Greek), Greek Open University, Athens (2006). He participates, as main researcher, in more than 35 EU and National sponsored research projects and in many industrial contracts. His research fields are: catalytic reaction engineering, refining processing, production of reformulated fuels, biomass thermochemical conversion processes, production of new fuels and biofuels, fuel quality and characterization.

Dr. Lappas is a member of the Council of Greek Catalysis Society and a member of the chamber of Greek Engineers.

Iacovos A. Vasalos was born in the island of Sifnos, Greece in 1938. He received his Diploma in Chemical Engineering, Technical University of Athens, in 1963. He served in the Greek Army till October 1965 and he received from M.I.T. a M.Sc. degree in 1967 and a Ph.D. degree in 1969. He holds an M.B.A. from Northwestern University, USA

His Research/professional activities include industrial employment in Amoco Research Center for 10 years and consulting services with Amoco Oil for 20 years. He has served as Professor in the Department of Chemical Engineering in University of Thessaloniki from 1979 till 2005. He was one of the founders and Director of Chemical Process Engineering Research Institute, the Center for Research and Technology Hellas, the Thessaloniki Technology Park, and the Center for Research and Technology Thessaly. He is currently Chairman in the Alexander Innovation Zone in Thessaloniki.

He has served in many national and European Commission Committees shaping both research policy and implementation. He is currently a Member in National Advisory Research Council and a member in the Advisory Group Energy EU DG Research. He has co authored more than 110 refereed publications and 43 international patents. His scientific interests mainly are in Chemical Reactors Engineering and Catalytic Technologies with emphasis in Petroleum Refining, Natural Gas Conversion, Biofuels, and Environmental Technologies of Gaseous Pollutants.