

Institut Français du Pétrole Publications

PETROLEUM REFINING

2

SEPARATION PROCESSES

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Institut Français du Pétrole

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Translation of

Le raffinage du pétrole.

Tome 2. Procédés de séparation.

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PETROLEUM REFINING

2 SEPARATION
PROCESSES

FROM THE SAME PUBLISHER

Petroleum Refining

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Jean-Claude COMPANY <i>Total Raffinage Distribution</i>	Foreword
André DESCHAMPS <i>Institut Français du Pétrole</i>	Chapters 10 and 11
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Thierry HOMBOURGER <i>Mobil Oil Française</i>	Chapters 7, 8 and 9
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Presentation of the Series

"PETROLEUM REFINING"

The series "**Petroleum Refining**" includes five volumes covering the following aspects of the technology involved in the oil refining industry:

- Crude oil. Petroleum products. Process flowsheets.
- Separation processes.
- Conversion processes.
- Materials and equipment.
- Refinery operation and management.

The series is designed for the engineers and technicians who will be operating the refineries of the twenty-first century. Two types of problems will have to be solved at the same time: increasingly severe product specifications and, even more importantly, protecting our air and water from pollution. It will provide operational people in the field with an understanding of the fundamentals of oil refining as well as an overview of the specific technology they will be using.

The collection was written by a group of eminent specialists whose names will be found at the beginning of each volume. We would like to thank them all for being so dynamic and enthusiastic in their work on this project.

Michel VERWAERDE
Institut Français du Pétrole

Foreword

*Jean-Claude
Company*

The eighties and nineties were a period of considerable change for the refining industry in the world and in Europe in particular.

It was during this period that the very basis of the industry, which was entering its mature phase, was critically re-examined. The tried-and-true expressions such as maximum flow, standard products, and "bigger is better" were gradually replaced by optimum choice of feed, added value, energy savings, products suited to the market, refinery hinterland, niche effect, etc. The consequences were considerable, since in France 23 refining sites dwindled to 11 in the space of a few years, with consumption going from a forecast 200 million tons a year to some 80 million tons. The same story could be told all over Europe in general or in the United States. The special case of the Far East with its double-digit development figures, or of the former Eastern bloc in the midst of social and economic upheaval, should not make us forget that our industry has today reached maturity and that it must be dealt with as such.

Finally, how can we fail to mention the recent phenomenon that refiners have been somewhat defenseless in dealing with: what is termed the "paper" market? It means that players with no connection to our industry (mainly large financial operators) involuntarily influence the refiner's margin, multiplying or dividing it by a factor of three or even seven in the space of a few months, sometimes a few days.

How can refiners respond to this three-pronged challenge?

- Technical: manufacture products that are more and more "suited" to the market and as disconnected as possible from the major international quotations.
- Economic: invest massively in strategic choices with a highly volatile future looming ahead.
- Financial: generate enough cash-flow over a ten-year period to finance the huge needs of this atypical industry that is both massive and specialized.

There will probably never be a definite solution to this equation and this is where the refiner must focus his thinking: how to make the transition from the certain or almost certain universe of the engineer and the economic forecaster to the moving fuzzy logic universe of the futurologist and the strategist? The change is already underway and the only ones who survive — probably very successfully — will be those who have identified the parameters they have to control soon enough.

Although there are no guarantees, in this connection responses or even habits exist that pave the way for just about any scenario:

- Avoid assumptions such as: processing heavy and high-sulfur crudes is the trend for the future.
- Prioritize a great degree of flexibility in industrial facilities, possibly at the expense of the sacred cow of economic optimums.
- Reduce costs intelligently while avoiding any adverse effect on flexibility, reliability or operational safety.

In the background fortunately — or unfortunately for some — is the refiner's technique and skill that can provide a lot of answers.

Does he want to consolidate his margins and manufacture high added-value products? He knows how to couple up the olefin-producing catalytic cracker and a high-quality distillate-producing hydrocracker.

Does he want to reduce costs? He knows how to install advanced control to run his refinery automatically, implement preventive maintenance methods to space out his maintenance operations or process less "noble" feed than crude oil.

Does he want to lessen his impact on the environment? He knows how to treat his effluents, manufacture increasingly purer products, optimize energy consumption and even make less noise.

Last but not least, does he want to improve safety? Although the refining industry is considered hazardous — and rightly so — it is one of the most well structured in its approach to safety problems. The latest developments in management methods, which no longer consider safety as a separate subject but integrate it into a concept of loss control, have made considerable progress in the approach to operating problems that is in complete harmony with safety concerns.

What shortfalls still need to be overcome and what developments can be expected?

- In the area of economics, we will have to cut ourselves free from the "paper" market, which has now come to the point where it is based on only a few percent of real operations.
- In the field of finance, investments will probably continue to be relocated to efficient refineries. Benchmarking studies¹ are there to guide us.

1. Benchmarking is the procedure that consists in improving by comparing with the best ("competitive sampling" method), according to IBC, International Benchmarking Council.

- In the area of technology — and this is probably where the refiner's skill will find its greatest expression — enormous challenges are waiting to be taken up, whether in the field of conversion or separation, where the same scientific concepts have been in use ever since the industry was born.

Without reviewing the history of the last hundred years, it is still useful to look back on our predecessors' thinking when they were facing their own challenges.

With crude oil, nature has given us an almost infinite variety of mainly organic molecules which exist in mixtures in the natural state. They are hydrocarbons, but also compounds containing heteroatoms (S, N, O, etc.) and even metallic elements, which we would be better off without.

The refiner's job is to separate this mixture of uncommon complexity out into categories, which have long been identified according to a physical characteristic called distillation range. Roughly speaking, distillation range is the boiling point of the most and the least volatile component of a specified mixture at atmospheric pressure.

It soon became apparent with the uses that could be imagined for these categories called "petroleum cuts" that identification by boiling point alone was insufficient. It was necessary to complete the characterization by other parameters involving the prevailing chemical structure of the components in the cut and also to be able to modify them. However, almost every time the refiner was confronted with separation problems, and that was when he realized that the potential uses of the cuts required more and more sophisticated processes to sort the molecules. In addition, since certain categories were more appreciated than others, conversion processes created new cuts (see Vol. 3).

This is where the refiner's skill came into play, by creating the gigantic entropic system that is the separation processes found in refineries and petrochemical plants today, whether the products to be separated come from crude oil or from chemical conversion units.

The principle of the processes is always the same: matter usually exists in three states, solid, liquid and vapor. When two phases of a mixture coexist in equilibrium in given temperature and pressure conditions, the concentration of each chemical substance in each phase is generally different. So the equilibrium of the phases needs only to be established recurrently in other pressure and temperature conditions for any given phase to contain a greater concentration of the target chemical substance until the required quality has been achieved.

This is of course generally true, but there are many special cases:

- The phase equilibrium may not be reached in feasible industrial conditions.
- There is a particular point which is such that the phase concentrations at equilibrium are identical for a given mixture.

Other conditions, or even other phases, will then be needed, in order to apply these principles. It is often helpful to use additional recyclable compounds (furfural, NMP, MEK, DEA, etc.). This has given rise to a number of ingenious processes that are often low on energy consumption and material investments.

The scientific disciplines that describe these phenomena and remain the basis for the engineer's understanding are:

- Thermodynamics, in particular as applied to phase equilibria, which determines what can be achieved.
- Mass transfer, which explores what is reasonable to achieve, ie. introducing the time factor into sizing units.

In addition to scientific disciplines, the control of separation processes also involves the choice of technique (distillation, extractive distillation, extraction, absorption, percolation, adsorption, crystallization, etc.) and the choice of technology (mixer-settlers, different types of columns, centrifuges, membranes, etc.)

These few words of introduction provide an overview of the field of investigation that the refiner has at his disposal. Separation processes would therefore seem to play a leading role in the future of the refining industry, since they fit in with several general objectives:

- They separate molecules and yield specific high added-value products.
- The relevant investments are usually lower than for conversion processes.
- The operating costs involved, although sometimes high, are open to considerable progress.
- Their impact on the environment and safety can be controlled, since they seldom use extreme operating conditions.

Separation processes will therefore often be preferred to other more chemical approaches, synthesis for example.

Nomenclature

As for Volume 1, the nomenclature used in Volume 2 is based on the recommendations of the IUPAC (International Union of Pure and Applied Chemistry) for the system of units utilized (SI) as well as for their symbols. The reference is entitled,

"Quantities, Units and Symbols in Physical Chemistry"

prepared by I. Mills, T. Cvitaš et al., edited by Blackwell Scientific Publications, Oxford, UK, 1993.

Any deviations result from a deliberate choice, either to conform to current usage in the profession, or to avoid ambiguity in the interpretation of symbols.

In addition to fundamental units from the SI system, i.e. m, kg, s, mol, K, A and cd, multiples and sub-multiples of these units as well as derived or combined units are also used and are indicated in the list below by parentheses.

Symbols

γ	activity	-
κ	equation of state parameter	$\text{m}^6 \cdot (\text{bar}) / \text{mol}^2$
σ	interfacial area per unit of volume	m^2 / m^3
A	interfacial area	m^2
Q	flow rate of solute A (liquid-liquid extraction)	$\text{kg/s}, \text{mol/s}$
k	pre-exponential factor	$\text{s}^{-1} / \text{m}^3$

$a_{i,j}$	binary parameter of interaction between components (UNIQUAC model)	K
$a_{k,l}$	binary parameter of interaction between groups (UNIFAC model)	K
B	flow rate of diluent B (liquid-liquid extraction)	kg/s, mol/s
B	adsorption coefficient	(variable)
b	equation of state parameter (covolume)	m ³ /mol
B	residual amount in the drum (batch distillation)	mol
c	translation parameter	m ³ /mol
C_p	molar heat capacity at constant pressure	J/(mol·K)
C	concentration	kg/m ³ , mol/m ³
c	reduced concentration (Chapter 3)	—
C	flow rate of feed C (liquid-liquid extraction)	kg/s, mol/s
$C_{i,j}$	binary parameter (NRTL model)	J/mol
D	diffusion coefficient	m ² /s
D	distillate flow rate	mol/s
d	thickness, diameter, diagonal length, characteristic dimension, etc.	m
D	amount distilled (batch distillation)	mol
e	extract flow rate, excluding solvent (liquid-liquid extraction)	kg/s, mol/s
E	extract flow rate (liquid-liquid extraction)	kg/s, mol/s
E	efficiency in number of stages	—
E	tension gradient (Chapter 5)	V/m
E_{og}	local efficiency	—
E_M	Murphree efficiency	—
E	activation energy	J/mol
f	fugacity	(bar)
F	feed flow rate	mol/s
F	Helmholtz free energy (Chapter 10)	J
F	filterability (Chapter 8)	m ² /s
F	driving force (Chapter 12)	(variable)
g	acceleration of gravity	9.81 m/s ²
g	Gibbs molar free energy	J/mol
G	Gibbs free energy	J
G	gas flow rate	mol/s
$G_{i,j}$	binary parameter (NRTL model)	—
h	molar enthalpy	J/mol

\mathcal{H}	heat film transfer coefficient	W/(m ² ·K)
H	enthalpy	J
h	height	m
H , HTU	height of transfer unit	m
J	diffusion flow	mol/(m ² ·s)
\mathcal{H}_{ij}	Henry's constant of solute i in solvent j	(bar)
k	rate constant	(variable)
k, k'	mass film transfer constant	m/s, mol/(m ² ·s)
$k_{i,j}$	binary interaction parameter (in equations of state)	—
K	K value (equilibrium)	—
\mathcal{H}, K	overall transfer coefficient	m/s, mol/(m ² ·s)
L	liquid flow rate	mol/s
L	length	m
l_i	combined parameter (UNIQUAC and UNIFAC models)	—
m	equation of state parameter (Soave law)	—
m	partition coefficient (liquid-liquid extraction)	—
m, M	mass	kg
M	molar mass	kg/mol
M_0, M_1, M_2	equation of state parameters (Soave law)	—
N	amount of matter	mol
N	matter flow	mol/(m ² ·s), mol/(m ³ ·s)
N	mass flow	mol/s
\mathcal{N}	Avogadro number	$6.023 \times 10^{23} \text{ mol}^{-1}$
n, N	number of stages, number of components	—
ng	number of groups (ASOG and UNIFAC models)	—
Nu	Nusselt number	—
N , NTU	number of transfer units	—
p, m	slope	—
P	pressure	(bar)
P^σ	vapor pressure	(bar)
\mathcal{P}	Poynting correction	—
P	permeability (of a membrane)	mol/(m ² ·s·Pa)
Pe	Peclet number	—
q, q'	amount adsorbed	kg/kg, mol/kg, mol/m ³
Q, F	volume flow rate	m ³ /s
Q, Φ	heat flow rate	W

q	ordinate at the origin	(variable)
q_i	surface parameter of component i (UNIQUAC and UNIFAC models)	—
Q_k	surface parameter of group k (UNIQUAC and UNIFAC models)	—
R	reflux flow rate (Chapter 5)	(m ³ /h)
r	reflux ratio	—
r	reaction rate	mol/s
r_i	volume parameter of component i (UNIQUAC and UNIFAC models)	—
r_1, r_2	equation of state parameters	—
r	raffinate flow rate, excluding solvent (liquid-liquid extraction)	kg/s, mol/s
R, r	radius	m
R	residue flow rate	mol/s
R	retention	mol
R	raffinate flow rate (liquid-liquid extraction)	kg/s, mol/s
R	ideal gas constant = $83 \cdot 10^{-6} \text{ m}^3 \cdot \text{bar}/(\text{mol} \cdot \text{K})$	= 8.31 J/(mol·K)
R_k	volume parameter of group k (UNIQUAC and UNIFAC models)	—
Re	Reynolds number	—
s	reboil ratio	—
S	entropy	J/K
S	area	m ²
S	draw off flow rate	mol/s, (m ³ /h)
S	stripping coefficient	—
S	solubility coefficient (Chapter 12)	mol/(m ³ ·Pa)
Sc	Schmidt number	—
Sh	Sherwood number	—
Sh_0	infinite dilution Sherwood number	—
T	second solvent flow rate (liquid-liquid extraction)	kg/s, mol/s
T	absolute temperature	K
t	step	—
t_D	response delay	s
t	time	s

u	equation of state parameter	—
u	coordinate	m
u	internal molar energy	J/mol
u, v, V	velocity, superficial velocity	m/s
U	internal energy (Chapter 10)	J
U	equation of state characteristic function	—
U	control variable	—
v, V_m	molar volume	m ³ /mol
v	coordinate	m
v, V	volume	m ³
V	vapor flow rate	mol/s
V_d	settling velocity	m/s
\bar{v}, \bar{V}	partial molar volume	m ³ /mol
(Σv)	diffusion volume	(cm ³ /gram atom)
V	variance	—
w	equation of state parameter	—
w, W	mass, volume fraction	—
W	energy flow rate (power)	W
W	adsorbed volume (Chapter 10)	m ³ /kg
W_0	adsorbent micropore volume	m ³ /kg
x	mole (or mass) fraction, usually liquid	—
X	reduced mass fraction (liquid-liquid extraction)	—
X_k	mole fraction of group k (ASOG and UNIFAC models)	—
y	mole (or mass) fraction, usually vapor	—
Y	reduced mass fraction (liquid-liquid extraction)	—
z	height	m
z	mole (or mass) fraction, mixture, feed, etc.	—
z	coordination degree (UNIQUAC and UNIFAC models)	—
Z	compressibility factor	—

Greek letters

α	equation of state parameter	—
α	separation factor, selectivity	—
α	relative volatility	—
α	macroporosity	—
$\alpha_{j,i}$	binary parameter (NRTL model)	—
β	affinity coefficient (Chapter 10)	—
γ	activity coefficient	—
Γ_k	activity coefficient of group k (ASOG and UNIFAC models)	—
δ	solubility parameter	$(\text{J}/\text{m}^3)^{1/2}$
δ	film thickness	m
Δh_i°	enthalpy of vaporization of component i	J/mol
ϵ	bed void fraction	—
ϵ	adsorption potential	J/mol
η	yield	—
θ	temperature (Celsius)	(°C)
θ	contact time	s
θ	contact angle	(degree)
θ	porosity, void fraction	—
θ	convergence parameter (Holland method, Chapter 4)	—
θ_i	surface fraction of component i (UNIQUAC and UNIFAC models)	—
Θ	coverage ratio (Chapter 10)	—
Θ_k	surface fraction of group k (UNIFAC model)	—
κ	Boltzman constant	1.380×10^{-23} J/K
λ	thermal conductivity	W/(m·K)
Λ	equation of state parameter	—
Λ	extraction factor, absorption factor	—
μ	chemical potential	J/mol
μ	dynamic (or absolute) viscosity	Pa·s
ν	kinematic viscosity	m ² /s
$\nu_{k,i}$	number of k groups in the molecule of component i (ASOG and UNIFAC models)	—
π	spreading pressure	N/m
ρ	density	kg/m ³
ρ	recovery ratio (liquid-liquid extraction)	—