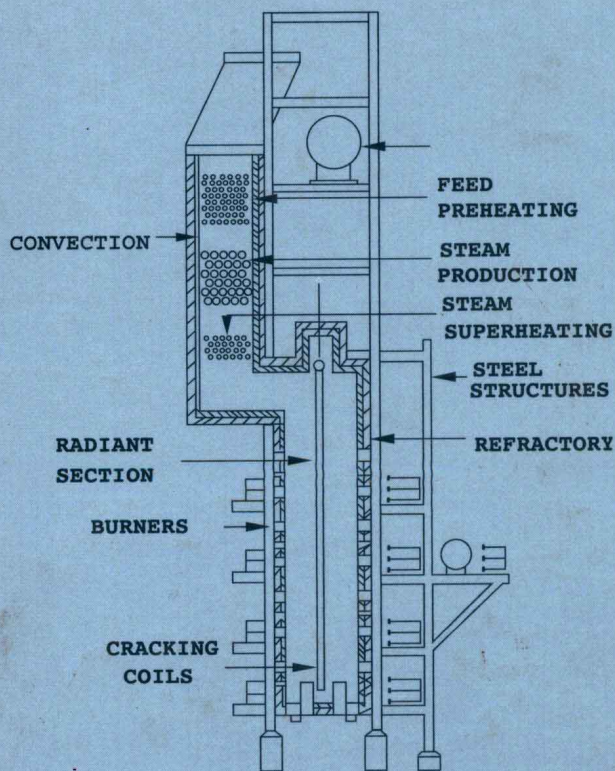


Thermal and Catalytic Processes in Petroleum Refining



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Thermal and Catalytic Processes in Petroleum Refining

To my dear wife Irena

Preface

This book is considered to be a completely new version of the original book published in 3 volumes in Romania, in 1996–1997 under the title *Conversia Hidrocarburilor* (“the conversion of hydrocarbons”).

Recent developments in petroleum processing required the complete revision of some of the chapters, the elimination of outdated material and bringing up to date the processes in which the technology was significantly improved. Furthermore, the presentation of theoretical aspects has been somewhat expanded and deepened.

The processes discussed in this book involve the conversion of hydrocarbons by methods that do not introduce other elements (heteroatoms) into hydrocarbon molecules. The first part is devoted to thermal conversion processes (pyrolysis, vis-breaking, coking). The second part studies catalytic processes on acidic catalysts (catalytic cracking, alkylation of isoalkanes, oligomerization). The third and fourth parts analyze catalytic processes on metal oxides (hydrofining, hydrotreating) and on bifunctional catalysts (hydroisomerization, hydrocracking, catalytic reforming), respectively.

The importance of all these processes resides in the fact that, when required, they allow large variations in the proportion of the finished products as well as improvement of their quality, as required by increasingly stringent market demands. The products of primary distillation are further processed by means of secondary operations, some fractions being subjected to several processing steps in series. Consequently, the total capacity of the conversion processes is larger than that of the primary distillation.

The development of petroleum refining processes has made it possible to produce products, especially gasoline, of improved quality and also to produce synthetic chemical feedstocks for the industry. The petrochemical branch of the refining industry generates products of much higher value than does the original refining industry from which the feedstocks were derived.

One should not overlook the fact that the two branches are of quite different volume. A few percentage points of the crude oil processed in the refineries are sufficient to cover the needs for feeds of the whole petrochemical and synthetic organic industry and of a large portion of the needs of the inorganic chemicals industry. The continuous development of new products will result in a larger fraction of the crude oil than the approximately 10% used presently being consumed as feedstocks for the chemical industry.

Hydrocarbons conversion processes supply hydrocarbons to the petrochemical industry, but mainly they produce fuels, especially motor fuels and quality lubricating oils. The same basic processes are used in all these different applications. The specific properties of the feedstocks and the operating parameters are controlled in order to regulate the properties of the product for each application. In this book, the processes are grouped by these properties, in order to simplify the presentation and to avoid repetitions.

The presentation of each group of processes begins with the fundamentals common to all the processes: thermodynamics, reaction mechanisms (including catalysis when applicable), and, finally, process kinetics. In this manner, operating parameters practiced in commercial units result as a logical consequence of earlier theoretical discussion. This gives the reader a well-founded understanding of each type of process and supplies the basis on which improvements of the process may be achieved.

The presentation of commercial implementation is followed by a discussion of specific issues pertaining to the design of the reaction equipment, which results in the unity of the theoretical bases with the design solutions adopted for commercial equipment and the quantitative aspects of implementation.

My warmest thanks to Prof. Sarina Feyer-Ionescu, to my son Prof. George Raseev, and especially to my technical editor Dr. G. Dan Suci, for their support in preparing the English-language version of this book.

Serge Raseev

Preface to the Romanian Edition

This book is the fruit of many years of work in the petrochemical industry, and in research, and of university teaching. It sums up my technical and scientific background and reflects the concepts that I developed over the years, of the manner in which the existing knowledge on chemical process technology—and especially on the processing of hydrocarbons and petroleum fractions—should be treated and conveyed to others.

While initially the discipline of process technology was taught mainly by describing the empirical information, it soon changed to a quantitative discipline that considers the totality of phenomena that occur in the processes of chemical conversion of industrial interest.

The objective of process technology as a discipline is to find methods for the continual improvement of commercial processes. To this purpose it uses the latest advances in chemistry, including catalysis, and applies the tools of thermodynamics and kinetics toward the quantitative description of the processes. In this manner it became possible to progress from the quantitative description provided by the reaction mechanisms to the mathematic formulation for the evolution in time of the processes.

In order to implement the chemical process on a commercial scale, a series of additional issues need to be addressed: the effect of the operating parameters and the selection of the optimal operating conditions, selection of the reactor type, the design of the reaction equipment and of the other processing steps, the limitations due to the heat and mass transfer, and the limitations imposed by the materials of construction.

Process technology thus becomes the convergence point of several theoretical and applicative disciplines called upon to solve in an optimal manner the complex interrelations among quite different sciences and phenomena (chemistry, hydraulics, heat transfer, etc.). This situation requires a multifaceted competence and the full understanding and control of the entire complex phenomenon that is the implemen-

tation of chemical conversions in the conditions of the commercial units. Without it, one cannot address the two basic questions about process technology: first, why the commercial processes have been developed in the manner they are presently implemented and second, how they can be continually improved.

In this manner, by mastering the complex phenomena involved, the process engineer is fully equipped to answer the “why” and “how” questions, and will be able to become one of the important driving forces of technical progress. This is the concept that has guided me during my entire professional activity.

This book treats the conversion of hydrocarbons and petroleum fractions by thermal and catalytic methods, while attempting to answer the “why” and “how” questions at the level of the current technical knowledge. In this manner, I hope to contribute to the education of specialists who will advance continuing developments in processing methods.

I am thankful to Mr. Gavril Musca and Dr. Grigore Pop for their help in creating this book. My special gratitude goes to Prof. Sarina Feyer-Ionescu, for her special contributions.

Serge Raseev

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Thermodynamic Analysis of Technological Processes

The thermodynamic study of technological processes has two objectives:

- Determination of the overall thermal effect of chemical transformations that take place in the industrial process
- Determination of the equilibrium composition for a broad range of temperatures and pressures in order to deduce optimum working conditions and performances

The manner in which the two objectives are approached within the conditions of chemical technology is different from the classical approach and requires the use of the specific methodology outlined in this chapter.

1.1 CALCULATION OF THE OVERALL THERMAL EFFECT

In practical conditions under which technological processes operate, the main reaction may be accompanied by secondary reactions. In many cases the transformation is of such complexity that it cannot be expressed by a reasonable number of chemical reactions.

When calculating the heat of reaction in such situations, in order to avoid the difficulties resulting from taking into account all reactions many times in the calculation, simplified approaches are taken. Thus, one may resort to the approximation of limiting the number of the reactions taken into consideration, or to take account only the main reaction. Such approximations may lead to significant errors.

Actually, the exact value of the thermal effect can be calculated without having to resort to such approximations. Since the thermal effect depends only on the initial and the final state of the system (the independence of path, as stipulated by the second principle of thermodynamics), it may be calculated based on the initial and final compositions of the system, without having to take in account the reactions that take place.

Accordingly, the classic equations, which give the thermal effect of a chemical reaction:

$$\Delta H_{rT}^0 = \sum v_p \Delta H_{fT}^0 - \sum v_r \Delta H_{fT}^0 \quad (1.1)$$

$$\Delta H_{rT}^0 = \sum v_r \Delta H_{cT}^0 - \sum v_p \Delta H_{cT}^0 \quad (1.2)$$

may be written under the form:

$$\Delta H_{rT} = \sum n_e \Delta H_{fT} - \sum n_i \Delta H_{fT} \quad (1.3)$$

$$\Delta H_{rT} = \sum n_i \Delta H_{cT} - \sum n_e \Delta H_{cT} \quad (1.4)$$

The heats of formation ΔH_f and of combustion ΔH_c for hydrocarbons and organic compounds, which are of interest in studying petrochemical processes, are given in thermodynamic data books [1,2]. The values are usually given for temperature intervals of 100 K, within which linear interpolation is accurate. Thus, the calculations that use the heat capacities may be avoided.

Example 1.1 shows how to perform the calculations by means of relations (1.3) and (1.4).

Example 1.1. Compute the overall thermal effect of an industrial dehydrogenation process of isopentane to isoprene at 600°C.

The composition of the streams at the inlet and outlet of the reactor is given in Table 1.1. The coke composition by weight, is 95% carbon and 5% hydrogen.

The calculations of the heat of formation at the inlet and the outlet of the reactor at 600°C are collected in Table 1.2.

Table 1.1

Component	Reactor inlet feed + recycle (wt %)	Reactor Outlet (wt %)
H ₂	-	1.0
CH ₄	-	0.6
C ₂ H ₆	-	0.7
C ₂ H ₄	-	0.7
C ₃ H ₈	-	0.7
C ₃ H ₆	-	1.4
C ₄ H ₁₀	0.3	1.2
C ₄ H ₈	-	2.2
C ₄ H ₆	-	0.2
<i>i</i> -C ₅ H ₁₂	79.3	55.8
<i>i</i> -C ₅ H ₁₀	16.6	17.1
C ₅ H ₈	0.8	12.1
<i>n</i> -C ₅ H ₁₂	1.8	0.8
<i>n</i> -C ₅ H ₁₀	1.7	1.7
1,3-C ₅ H ₈	-	2.0
coke	-	1.8

Table 1.2

Component	Heat of formation ΔH_f^0 (kcal/mol) [2]			Inlet		Outlet	
	800 (K)	900 (K)	873 = 600 (K) (°C)	n_i (mol/kg)	$n_i \Delta H_{f873}^0$ (kcal/kg)	n_e (mol/kg)	$n_e \Delta H_{f873}^0$ (kcal/kg)
H ₂	0	0	0	-	-	9.92	0
CH ₄	-20.82	-21.15	-21.05	-	-	0.37	-7.79
C ₂ H ₆	-24.54	-24.97	-24.85	-	-	0.23	-5.72
C ₂ H ₄	9.77	9.45	9.54	-	-	0.25	2.39
C ₃ H ₈	-30.11	-30.58	-30.45	-	-	0.16	-4.87
C ₃ H ₆	0.77	0.35	0.46	-	-	0.33	0.15
C ₄ H ₁₀	-36.41	-36.93	-36.79	0.05	-1.84	0.21	-7.73
C ₄ H ₈	-6.32	-6.84	-6.70	-	-	0.39	-2.61
C ₄ H ₆	23.25	22.95	23.03	-	-	0.04	0.92
<i>i</i> -C ₅ H ₁₂	-44.13	-44.65	-44.61	10.99	-489.16	7.73	-344.06
<i>i</i> -C ₅ H ₁₀	-13.45	-13.93	-13.80	2.37	-32.71	2.44	-33.67
C ₅ H ₈	14.16	13.82	13.91	0.12	1.67	1.78	24.76
<i>n</i> -C ₅ H ₁₂	-42.28	-42.85	-42.70	0.25	-10.68	0.11	-4.70
<i>n</i> -C ₅ H ₁₀	-12.23	-12.78	-12.63	0.24	-3.03	0.24	-3.03
1,3-C ₅ H ₈	14.17	13.73	13.85	-	-	0.29	4.02
C	0	0	0	-	-	-	-
Total {				-	-535.75	-	-381.94
kcal/kg				-	-2243.1	-	-1599.1
kJ/kg				-	-2243.1	-	-1599.1

According to Eq. (1.3), the overall thermal effect per unit mass (kg) of feed will be:

$$\Delta H_{r,873} = \sum n_e \Delta H_{f873} - \sum n_i \Delta H_{f873} = -1599 - (-2243.1) = 644 \text{ kJ/kg}$$

Since the process is performed at a temperature much above the critical point and at low pressure, no deviations from the ideal state have to be considered.

In many cases it is convenient to express the thermal effect on the basis of the reacted isopentane or of the formed isoprene.

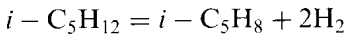
For this example, according to Table 1.1, 793 - 558 = 235g, isopentane reacts and 121 - 8 = 113g, isoprene is formed. In these conditions, the thermal effect expressed per mole of reacted isopentane is:

$$\Delta H_r = \frac{644}{235} \times 72.15 = 197.7 \text{ kJ/mole}$$

and per mole of produced isoprene:

$$H_r = \frac{644}{113} \times 68.11 = 388.2 \text{ kJ/mole}$$

If only the main reaction:



is taken into account, then according to the Eq. (1.1) one obtains:

$$\begin{aligned}\Delta H_r &= (\Delta H_f)_{C_5H_8} - \Delta H_f)_{C_5H_{12}} = 13.91 - (-44.51) = 58.42 \text{ kcal/mol} \\ &= 244.59 \text{ kJ/mol}\end{aligned}$$

the value being the same whether expressed per mole of isopentane or of isoprene.

This example shows that large errors may result if the computation of the overall thermal effect is not based on the real compositions of the inlet and outlet streams of the reactor.

Eq. (1.4) makes it possible to compute the thermal effects by using the heats of combustion. This is useful for the conversion of petroleum fractions of other feedstocks consisting of unknown components. In such cases it is usually more convenient to perform the calculation in weight units, by modifying the terms n and ΔH accordingly.

For liquid petroleum fractions, the heats of combustion may be determined by using the graph of Figure 1.1 [3], from the known values of the specific gravity and the characterization factor.

The characterization factor of residues may be determined graphically from the viscosity, by means of Figure 1.2 [3].

The heat of combustion of coke is determined experimentally or less precisely on the basis of the elementary composition.

The heats of combustion of gaseous components may be found in data books [1,2], or may be calculated from the heats of formation [2], by applying Eq. (1.1). For hydrocarbons, this equation takes the form:

$$(\Delta H_a)_{C_nH_m} = n(\Delta H_f)_{CO_2} + \frac{m}{2}(\Delta H_f)_{H_2O} - (\Delta H_f)_{C_nH_m} \quad (1.5)$$

This heat of combustion of gases must be brought to the same reference state as that of liquid fractions, i.e. 15°C and liquid water. For these conditions, Eq. (1.5) becomes:

$$(\Delta H_a)_{C_nH_m} = -393.77n - 143.02m - (\Delta H_f)_{C_nH_m} \quad (1.6)$$

It must be noted that Eq. (1.6) gives the heat of combustion in thermodynamic notation, expressed in kJ/mole. Figure 1.1 gives the heat of combustion in technical notation, expressed in kJ/kg.

An illustration of these calculations is given in Example 1.2.

Example 1.2. Calculate the thermal effect of the processing of a vacuum residue by visbreaking. The composition of the produced gases is given in Table 1.3. The yields and the characterization factors, K_{UOP} for the feed and the fuel oil were obtained from Table 1.4.

The characterization factor and the specific gravities were used to determine the heats of combustion for all the liquid fraction from Figure 1.1.

SOLUTION. By introducing the values of the heats of combustion from Tables 1.3 and 1.4 into Eq. (1.4), one obtains:

$$\begin{aligned}Q_r &= 43,645 - (0.0244 \times 51,319 + 0.1166 \times 46,827 + 0.859 \times 43,233) \\ &= -204 \text{ kJ/kg}\end{aligned}$$

Calculation of the thermal effects for a specific reaction, usually a small number obtained as the difference of heats of combustion, usually larger numbers, is