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A Thermodynamic Analysis of Naphtha Catalytic Reforming Reactions to Produce High-Octane Gasoline

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Abstract: The catalytic naphtha reforming process is key to producing high-octane gasoline. Dozens of components are involved in this process in hundreds of individual catalytic reactions. Calculations of concentrations at equilibrium, using equilibrium constants, are commonly performed for a small number of simultaneous reactions. However, the Gibbs free energy minimization method is recommended for the solution of complex reaction systems. This work aims to analyze, from the point of view of thermodynamic equilibrium, the effect of temperature, pressure, and the H_2/HC ratio on the reactions of the catalytic reformation process and evaluate their impact on the production of high-octane gasoline. Gibbs's free energy minimization method was used to evaluate the molar concentrations at equilibrium. The results were compared with those obtained in the simulation of a catalytic reforming process to evaluate the optimal conditions under which the process should operate.

Keywords: thermodynamic equilibrium; Gibbs free energy; catalytic reforming; Research Octane Number

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1. Introduction

The maximum amounts of products formed from a specific reaction are achieved at equilibrium under specific pressure and temperature [1]. Therefore, knowing equilibrium compositions can help design new catalysts and processes and improve existing plant operations by maximizing the production of desired products and eliminating or reducing the undesired side reactions [1].

There are two general approaches for calculating chemical equilibrium compositions for multi-reaction systems based on the minimum free energy: the constant equilibrium method and the free energy minimization method. In the first method, the overall reactions are written, and their equilibrium constants are calculated. The mathematical expressions for the equilibrium reaction equations are usually non-linear, and their number and complexity increase as the number of species in a reaction increases. Some of the disadvantages of this method are complications for the appropriate component selection; numerical troubles with compositions that become extremely small; inconvenience in testing for the presence of some condensed species; difficulties in extending the generalized method to non-ideal equations of state [1–3].

Free energy minimization is a more direct and general method for solving complex chemical systems [4,5]. Gibbs's free energy minimization method does not consider individual equilibrium constants nor the chemistry of reactions; it is based on the principle that the total Gibbs free energy of the system has its minimum value at chemical equilibrium [4]. Gibbs's free energy minimization problems are typically based on equation solving methods and direct optimization strategies and are widely discussed elsewhere [2,3,6,7]. Equation-solving methods solve the non-linear equations obtained from the stationary conditions subjected to mass balance and chemical equilibrium constraints [8]. However, this method

fails to converge to the correct solution when initial estimates are unsuitable, especially for non-ideal multicomponent and multi-reactive systems [6,8]. The use of Lagrange multipliers is usually the preferred approach for Gibbs minimization, but its performance is highly dependent on initial estimates of Lagrange multipliers [2,3,6,9]. Alternatively, stochastic optimization techniques have also been applied for minimizing the Gibbs free energy [3,6].

Gibbs's free energy minimization method has been used to study chemical systems of moderate complexity such as methanation reactions [4], steam reforming of methanol, ethanol, and glycerin for hydrogen production [10–12], reduction of silicon dioxide [13] and the esterification reaction [14]; and more complex systems such as the Claus process [1].

One of the objectives of this work is to apply Gibbs's free energy minimization method to the naphtha reforming process for calculating equilibrium compositions. Catalytic naphtha reforming is a key process to produce high-octane gasoline and aromatic feedstocks for petrochemical industries [15]. It is a multi-reactive system with more than 100 compounds participating in hundreds of individual catalytic reactions [16]. Since catalysts do not change the thermodynamics of a chemical reaction, we compared the equilibrium compositions with those obtained for a catalytic process.

The present work aims to thermodynamically analyze the effect of temperature, pressure, and H_2/HC ratio on catalytic naphtha reforming. We compared the thermodynamic calculations with the simulated results obtained for a catalytic naphtha reforming plant. We analyzed the impact of the operating conditions on the Research Octane Number, one of the main parameters used in the quality control of gasoline.

To our knowledge, no thermodynamic analysis has been made for the catalytic naphtha reforming process based on Gibbs's free energy minimization method.

2. Methodology

2.1. Problem Delimitation

The naphtha feed to the catalytic reformer is a fraction of crude oil that boils between approximately 70 and 200 °C. It is a very complex mixture consisting of about three hundred components with the carbon number range from 5 to 9+ [17,18], mainly alkanes and cycloalkanes, although there may also be a small fraction of aromatics [19].

The naphtha reforming process aims to increase the low Research Octane Number (RON). A Pt/Re bifunctional catalyst promotes the dehydrogenation and dehydroisomerization of naphthenes to aromatics, dehydrogenation of paraffins to olefins, dehydrocyclization of paraffins and olefins to aromatics, isomerization or hydroisomerization to iso-paraffins, isomerization of alkyl cyclopentanes and substituted aromatics and hydrocracking of paraffins and naphthenes to lower hydrocarbons [18,19].

Many studies related to new catalyst development, kinetic and deactivation models, reactor configuration, and operation modes have been accomplished for the catalytic naphtha reforming process and are widely discussed in [18,20].

A detailed reaction network, considering all components and reactions, is beyond the scope of this work. Subsequently, for the thermodynamics analysis, we grouped the components in gases, paraffins, naphthenes, and aromatics, and we assumed that they could be well represented for the model compounds given in Table 1.

Table 1. Model compounds for the thermodynamics analysis.

Symbol	Model Compound	Symbol	Model Compound
Gases		Isoparaffins	
H ₂	Hydrogen	ip ₆	2-Methylpentane
C ₁	Methane	ip ₇	2-Methylhexane
C ₂	Ethane	ip ₈₊	2-Methylheptane
C ₃	Propane	Naphthenes	
C ₄	Butane		Methylcyclopentane
C ₅	Pentane		Methylcyclohexane
Paraffins		N ₆	Ethylcyclohexane
		N ₇	
		N ₈₊	
		Aromatics	
np ₆	<i>n</i> -hexane	A ₆	Benzene
np ₇	<i>n</i> -heptane	A ₇	Toluene
np ₈₊	<i>n</i> -octane	A ₈₊	Ethylbenzene

2.2. Thermodynamic Analysis

According to Gibbs's free energy minimization method, the total Gibbs free energy of a reactive system reaches a minimum value at equilibrium [4,21]. Equilibrium calculations involve the global minimization of Gibbs free energy constrained by the material balances and chemical equilibrium restrictions.

The total Gibbs free energy of the system is given as follows [5]:

$$nG(n_i, T, P) = \sum_{i=1}^N n_i \Delta G_{fi}^0 + \sum_{i=1}^N n_i RT \ln P + \sum_{i=1}^N n_i RT \ln y_i + \sum_{i=1}^N n_i RT \ln \hat{\phi}_i \quad (1)$$

The global optimization problem can be solved by finding the set of n_i that minimizes nG (Equation (1)) for specified T and P . In a reactive system, molecular species are not conserved; nevertheless, the total number of atoms of each element remains constant [21]. Subsequently, the material balance constraints are formulated as follow:

$$\sum_i n_i a_{ij} = b_j, \quad j = 1, \dots, K \quad (2)$$

The subscript j identifies a particular atom, and K is the total number of the different elements present in the system. The b_j parameter is the total number of atomic masses of the k th element in the system, while the a_{ij} parameter is the number of atoms of the k th element present in each molecule of chemical species i .

When liquid and gas phases are both present in an equilibrium mixture of reacting species, a vapor/liquid equilibrium criterion must be satisfied along with Equations (1) and (2). In our particular case, it is assumed that reforming reactions occur only in the gas phase, since they are carried out at high temperatures (>600 K).

2.3. Standard Gibbs-Energy Change of Reaction

The Standard Gibbs-energy change for the reactions at equilibrium is calculated as follows [21]:

$$\frac{\Delta G^0}{RT} = \frac{\Delta G_0^0 - \Delta H_0^0}{RT_0} + \frac{\Delta H_0^0}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^0}{R} dT - \int_{T_0}^T \frac{\Delta C_P^0}{R} dT \quad (3)$$

Calculation of the Fugacity Coefficients

The fugacity coefficients were calculated according to the Soave–Redlich–Kwong equation of state [22]:

$$\ln \hat{\phi}_i = \frac{B_i}{B} (z - 1) - \ln(z - B) + \frac{A}{B} \left[\frac{B_i}{B} - \frac{2}{a\alpha} \sum_j y_j (a\alpha)_{ij} \right] \ln \left(1 + \frac{B}{z} \right) \quad (4)$$

Binary interaction parameters k_{ij} were taken as 0 for hydrocarbon pairs and hydrogen as given in [22].

The SRK equation of state gives the compressibility factor z :

$$f(z) = z^3 - z^2 + (A - B - B^2)z - AB = 0 \quad (5)$$

The critical properties and ideal gas standard Gibbs free energy at standard conditions and constants for C_p calculations are shown in Tables 2 and 3, respectively.

Table 2. Critical properties and ideal gas standard Gibbs free energy [21].

Compound	w	T _c , K	P _c , bar	ΔH ⁰ ₂₉₈ , J/mol	G ⁰ ₂₉₈ , J/mol
H ₂	−0.2160	33.19	13.13	0	0
C ₁	0.0120	190.60	45.99	−74,520	−50,460
C ₂	0.1000	305.30	48.72	−83,820	−31,855
C ₃	0.1520	369.80	42.48	−104,680	−24,290
C ₄	0.2000	425.10	37.96	−125,790	−16,570
C ₅	0.2520	469.70	33.70	−146,760	−8650
ip ₆	0.3010	507.60	30.25	−174,300 *	−2800 *
ip ₇	0.3500	540.20	27.40	−196,200 *	5620 *
ip ₈ +	0.4000	568.70	24.90	−215,500 *	14,040 *
np ₆	0.2774	497.50	30.05	−166,920	150
np ₇	0.3277	530.37	27.34	−187,780	8260
np ₈ +	0.3772	559.64	24.84	−208,750	16,260
N ₆	0.2300	532.80	37.85	−108,100 *	36,190 *
N ₇	0.2350	572.2	34.71	−154,770	27,480
N ₈ +	0.2455	609.15	30.40	−172,600 *	40,930 *
A ₆	0.2100	562.20	48.98	82,930	129,665
A ₇	0.2620	591.80	41.06	50,170	122,050
A ₈ +	0.3030	617.20	36.06	29,920	130,890

* Taken from Chemical and Physical Properties by Cheméo [23].

Table 3. Constants for ideal gas heat capacity [24].

Compound	A	$\frac{\Delta C_p^0}{R} = \Delta A + \Delta BT + \Delta CT^2 + \Delta DT^3 + \Delta ET^4$			
		B × 10 ³	C × 10 ⁶	D × 10 ¹⁰	E × 10 ¹⁴
C	−0.50686	6.45776	−4.70494	15.59118	−19.04428
H ₂	3.24631	1.43467	−2.89398	25.8003	−73.9095
C ₁	4.34610	−6.14488	26.62607	−219.29980	588.89965
C ₂	4.00447	−1.33847	42.86416	−452.24460	1440.48530
C ₃	3.55751	10.07312	39.13602	−475.72200	1578.16560
C ₄	2.91601	28.06907	15.37435	−292.92550	1028.04620
C ₅	4.06063	29.87141	30.46993	−461.35230	1559.89710
ip ₆	0.44073	60.77573	−10.93570	−180.70573	833.40865
ip ₇	0.57808	70.71556	−15.00679	−187.48705	899.92106
ip ₈ +	0.92650	78.42561	−11.24742	−281.97592	1265.61161
np ₆	3.89054	41.42970	24.35860	−457.52220	1599.41000
np ₇	4.52739	47.36877	31.09932	−570.22085	1999.68224
np ₈ +	4.47277	57.81747	29.07465	−621.09106	2265.33690
N ₆	−6.81073	80.58175	−50.42977	141.93915	−107.77270
N ₇	−8.75751	100.20540	−62.47659	169.33320	−123.27361
N ₈ +	−5.50074	91.59292	−26.04906	−192.84542	1021.80248
A ₆	−7.29786	75.33056	−69.66390	336.46848	−660.39655
A ₇	−2.46286	57.69575	−19.66557	−106.61110	−654.52596
A ₈ +	4.72510	9.02760	141.18870	−1989.23470	8167.18050

The fmincon Matlab function was used to find the n_i set that minimizes the total Gibbs free energy (Equation (1)), constrained to the elemental balances (of Equation (2)), and the

z function (Equation (5)). To evaluate the equilibrium, we use the molar flow composition at the inlet of the catalytic naphtha reforming process given in Table 4.

Table 4. Molar composition of the feed flow rate [25].

Model Compound	Molar Flow kmol/h	mol%	Model Compound	Molar Flow kmol/h	mol%
H ₂	4173.8	69.69	ip ₆	4.53	0.08
C ₁	579.25	9.67	ip ₇	52.80	0.88
C ₂	292.33	4.88	ip ₈₊	143.11	2.39
C ₃	232.78	3.89	N ₆	1.16	0.02
C ₄	113.68	1.90	N ₇	7.94	0.13
C ₅	21.66	0.36	N ₈₊	18.35	0.31
np ₆	15.83	0.26	A ₆	88.50	1.48
np ₇	65.95	1.10	A ₇	81.02	1.35
np ₈₊	91.93	1.53	A ₈₊	4.60	0.08

2.4. Composition of the Catalytic Reforming Products

Experimental results and ample plant experience have shown that catalytic naphtha reforming reactions are quite sensitive to operating temperature and pressure and on the hydrogen to hydrocarbon ratio (H₂/HC). However, their effect on the various reforming reactions can differ. A simplified classification of the main reactions that take place during naphtha reforming is exemplified in Figure 1 and consist of: (a) Naphtenes dehydrogenation to aromatics, (b) alkyl cyclopentanes dehydroisomerization to aromatics, (c) alkanes dehydrocyclization to aromatics, (d) n-alkanes isomerization to branched alkanes, and (e) cracking reactions leading to lower carbon products with regard to the reactants [26]. These reactions are not affected in the same way by the operating conditions, while reactions that form aromatics (Figure 1a–c) are highly endothermic and thermodynamically benefit from higher temperatures and lower hydrogen partial pressures, operating under such conditions will clearly have negative effects on catalyst deactivation by coke deposition. Furthermore, exothermic reactions such as paraffin isomerization to alkenes and hydrocracking and hydrogenolysis (Figure 1e,d) will be facilitated by lower temperatures and the latter higher hydrogen partial pressure. Therefore, it is evident that the mutual interference of the operating factors on the main reactions makes naphtha reforming a complicated process.

For the simulation of catalytic naphtha reforming, we used the kinetic model reported by Arani et al., 2009, and the naphtha composition given in Table 4. In the kinetic model, C₁–C₅ hydrocarbons are considered light paraffins. The C₆ to C₈₊ naphtha cuts are labeled as iso-paraffins, normal paraffins, and naphthenes aromatics. In reaction network, the reversible reactions of iso-paraffins produce normal paraffins, normal paraffins react to form naphthenes, and naphthenes form aromatics. Light paraffins are formed from the irreversible hydrocracking reactions of the iso-paraffins and aromatic fractions. The main difference between Arani et al. and this work is that in the first, the mole fractions of naphtha cuts with more than eight carbon numbers are lumped together, while we assume that a model compound can effectively represent eight carbon cuts.

The reaction section is split into three catalytic reactors. A furnace heats the feedstock back to the desired temperature to maintain an appropriate temperature between each reactor. Reactors are of different sizes, with the smallest one located in the first position and the largest one in the last. The typical reactor inlet temperature is around 774 K, and the typical pressure is around 2.8 MPa.

A typical Pt/Al₂O₃ catalyst promotes the reforming reactions. Both Pt and Alumina provide a different role in the reforming reactions. The metal sites catalyze hydrocarbons' hydrogenation and dehydrogenation reactions, while the alumina's acid sites are known to catalyze hydrocarbon rearrangements reactions [26].

Figure 1. Catalytic reforming reactions. (a) Naphtenes dehydrogenation to aromatics, (b) alkyl cyclopentanes dehydroisomerization to aromatics, (c) alkanes dehydrocyclization to aromatics, (d) n-alkanes isomerization to branched alkanes, and (e) cracking reactions to lower carbon products.

Tables 5–8 summarize the expected reforming reactions according to the model compounds given in Table 1.

Table 5. Isomerization of paraffins.

Chemical Reaction	Reaction Rate
$i\text{-C}_6\text{H}_{14} \rightleftharpoons n\text{-C}_6\text{H}_{14}$ <i>iso-hexane</i> <i>2-Methylpentane</i>	$r_{Iso \ i P_6} = \phi k_{I \ i P_6} e^{(-E_a/RT)} \frac{\left(\frac{P_{i P_6}}{P_{H_2}} - \frac{P_{n P_6}}{K_{i P_6 \leftrightarrow n P_6}} \right)}{P_{H_2} \Gamma}$
$i\text{-C}_7\text{H}_{16} \rightleftharpoons n\text{-C}_7\text{H}_{16}$ <i>iso-heptane</i> <i>2-Methylhexane</i>	$r_{Iso \ i P_7} = \phi k_{I \ i P_7} e^{(-E_a/RT)} \frac{\left(\frac{P_{i P_7}}{P_{H_2}} - \frac{P_{n P_7}}{K_{i P_7 \leftrightarrow n P_7}} \right)}{P_{H_2} \Gamma}$
$i\text{-C}_8\text{H}_{18} \rightleftharpoons n\text{-C}_8\text{H}_{18}$ <i>iso-octane</i> <i>2-Methylheptane</i>	$r_{Iso \ i P_8} = \phi k_{I \ i P_8} e^{(-E_a/RT)} \frac{\left(\frac{P_{i P_8}}{P_{H_2}} - \frac{P_{n P_8}}{K_{i P_8 \leftrightarrow n P_8}} \right)}{P_{H_2} \Gamma}$

Table 6. Dehydrocyclization of paraffins.

Chemical Reaction	Reaction Rate
$\text{C}_6\text{H}_{14} \rightleftharpoons \text{C}_6\text{H}_{12} + \text{H}_2$ <i>n-hexane</i> <i>Methylcyclopentane</i>	$r_{DHC \ n P_6} = \phi k_{DHC \ n P_6} e^{(-E_a/RT)} \frac{\left(\frac{P_{n P_6}}{P_{H_2}} - \frac{P_{N_6} P_{H_2}}{K_{n P_6 \leftrightarrow N_6}} \right)}{P_{H_2} \Gamma}$
$\text{C}_7\text{H}_{16} \rightleftharpoons \text{C}_7\text{H}_{14} + \text{H}_2$ <i>n-heptane</i> <i>Methylcyclohexane</i>	$r_{DHC \ n P_7} = \phi k_{DHC \ n P_7} e^{(-E_a/RT)} \frac{\left(\frac{P_{n P_7}}{P_{H_2}} - \frac{P_{N_7} P_{H_2}}{K_{n P_7 \leftrightarrow N_7}} \right)}{P_{H_2} \Gamma}$
$\text{C}_8\text{H}_{18} \rightleftharpoons \text{C}_8\text{H}_{16} + \text{H}_2$ <i>n-octane</i> <i>Ethylcyclohexane</i>	$r_{DHC \ n P_8} = \phi k_{DHC \ n P_8} e^{(-E_a/RT)} \frac{\left(\frac{P_{n P_8}}{P_{H_2}} - \frac{P_{N_8} P_{H_2}}{K_{n P_8 \leftrightarrow N_8}} \right)}{P_{H_2} \Gamma}$

Table 7. Dehydrogenation of naphthenes.

Chemical Reaction				Reaction Rate
C_6H_{12} Methylcyclopentane	$\rightleftharpoons$	C_6H_6 Benzene	$+ 3H_2$	$r_{DH\ N_6} = \phi k_{DH\ N_6} e^{(-E_a/RT)} \frac{(P_{N_6} - \frac{P_{A_6} P_{H_2}}{K_{N_6} P_6 \leftrightarrow N_6})}{P_{H_2} \Gamma}$
C_7H_{14} Methylcyclohexane	$\rightleftharpoons$	C_7H_8 Toluene	$+ 3H_2$	$r_{DH\ N_7} = \phi k_{DH\ N_7} e^{(-E_a/RT)} \frac{(P_{N_7} - \frac{P_{A_8} P_{H_2}}{K_{N_7} P_7 \leftrightarrow A_7})}{P_{H_2} \Gamma}$
C_8H_{16} Ethylcyclohexane	$\rightleftharpoons$	C_8H_{10} Ethylbenzene	$+ 3H_2$	$r_{DH\ N_8} = \phi k_{DH\ N_8} e^{(-E_a/RT)} \frac{(P_{N_8} - \frac{P_{A_8} P_{H_2}}{K_{N_8} P_8 \leftrightarrow A_8})}{P_{H_2} \Gamma}$

Table 8. Hydrocracking reactions.

Chemical Reaction				Reaction Rate
$n-C_5H_{12} + H_2 \rightarrow$	$1/2 CH_4 + 1/2 C_2H_6 + 1/2 C_3H_8 + 1/2 C_4H_{10}$			$r_{HDCrack\ iP_5} = \phi k_{HDCrack\ iP_5} e^{(-E_a/RT)} \frac{P_{iP_5}}{\Gamma}$
$i-C_6H_{14} + H_2 \rightarrow$	$1/3 CH_4 + 1/3 C_2H_6 + 2/3 C_3H_8 + 1/3 C_4H_{10} + 1/3 C_5H_{12}$			$r_{HDCrack\ iP_6} = \phi k_{HDCrack\ iP_6} e^{(-E_a/RT)} \frac{P_{iP_6}}{\Gamma}$
$i-C_7H_{16} + H_2 \rightarrow$	$1/3 CH_4 + 1/3 C_2H_6 + 1/3 C_3H_8 + 1/3 C_4H_{10} + 1/3 C_5H_{12} + 1/3 i-C_6H_{14}$			$r_{HDCrack\ iP_7} = \phi k_{HDCrack\ iP_7} e^{(-E_a/RT)} \frac{P_{iP_7}}{\Gamma}$
$i-C_8H_{18} + H_2 \rightarrow$	$1/4 CH_4 + 1/4 C_2H_6 + 1/4 C_3H_8 + 1/2 C_4H_{10} + 1/4 C_5H_{12} + 1/4 i-C_6H_{14} + 1/4 i-C_7H_{16}$			$r_{HDCrack\ iP_8} = \phi k_{HDCrack\ iP_8} e^{(-E_a/RT)} \frac{P_{iP_8}}{\Gamma}$
C_7H_8 Toluene	$+ H_2 \rightarrow$	C_6H_6 Benzene	$+ CH_4$	$r_{HDCrack\ A_7} = \phi k_{HDCrack\ A_7} e^{(-E_a/RT)} \frac{P_{A_7}}{\Gamma}$
C_8H_{10} Ethylbenzene	$+ H_2 \rightarrow$	$1/2 C_7H_8$ Toluene + $1/2 C_6H_6$ Benzene	$+ 1/2 CH_4$ $+ 1/2 C_2H_6$	$r_{HDCrack\ A_8} = \phi k_{HDCrack\ A_8} e^{(-E_a/RT)} \frac{P_{A_8}}{\Gamma}$

The catalyst deactivation function is as follow:

$$\phi = \left[-k_d e^{(-\frac{E_d}{R} [\frac{1}{T} - \frac{1}{T_R}])} (-m+1)(t) + 1 \right]^{\frac{1}{(-m+1)}} \quad (6)$$

The kinetic parameters for the reaction rate expressions given in Tables 5–8 and the deactivation parameters for Equation (15) were taken from Arani et al., 2009.

Pressure drops were calculated according to Ergun's Equation.

$$\frac{dP}{dw} = -\frac{G}{\rho d_p \varphi^3} \left[\frac{150(1-\varphi)\mu}{d_p} + \frac{1}{A_c \rho_c} \right] \quad (7)$$

Temperature variations in the catalytic bed were attained by the following differential equation:

$$\frac{dT}{dw} = \sum_{j=1}^{n_r} r_j \Delta H_{R_j} / \sum_{i=1}^{n_c} F_i C_{p_i} \quad (8)$$

Since radial and axial dispersion effects are minimal under usual reactor operating conditions [27], the material balances were defined in terms of molar flow by assuming a perfect plug flow reactor.

$$\frac{dF_{H_2}}{dw} = [r_{DHC\ nP_6}] + [r_{DHC\ nP_7}] + [r_{DHC\ nP_8}] + (3)[r_{DH\ N_6}] + (3)[r_{DH\ N_7}] + (3)[r_{DH\ N_8}] - [r_{HDCrack\ iP_5}] - [r_{HDCrack\ iP_6}] - [r_{HDCrack\ iP_7}] - [r_{HDCrack\ iP_8}] - [r_{HDCrack\ A_7}] - [r_{HDCrack\ A_8}] \quad (9)$$

$$\frac{dF_{C_1}}{dw} = (1/2)[r_{HDCrack\ iP_5}] + (1/3)[r_{HDCrack\ iP_6}] + (1/3)[r_{HDCrack\ iP_7}] + (1/4)[r_{HDCrack\ iP_8}] + [r_{HDCrack\ A_7}] + (1/2)[r_{HDCrack\ A_8}] \quad (10)$$

$$\frac{dF_{C_2}}{dw} = (1/2)[r_{HDCrack\ iP_5}] + (1/3)[r_{HDCrack\ iP_6}] + (1/3)[r_{HDCrack\ iP_7}] + (1/4)[r_{HDCrack\ iP_8}] + (1/2)[r_{HDCrack\ A_8}] \quad (11)$$

$$\frac{dF_{C_3}}{dw} = (1/2)[r_{HDCrack\ iP_5}] + (2/3)[r_{HDCrack\ iP_6}] + (1/3)[r_{HDCrack\ iP_7}] + (1/4)[r_{HDCrack\ iP_8}] \quad (12)$$

$$\frac{dF_{C_4}}{dw} = (1/2)[r_{HDCrack\ iP_5}] + (1/3)[r_{HDCrack\ iP_6}] + (1/3)[r_{HDCrack\ iP_7}] + (2/4)[r_{HDCrack\ iP_8}] \quad (13)$$

$$\frac{dF_{C_5}}{dw} = -[r_{HDCrack\ nP_5}] + (1/3)[r_{HDCrack\ iP_6}] + (1/3)[r_{HDCrack\ iP_7}] + (1/4)[r_{HDCrack\ iP_8}] \quad (14)$$

$$\frac{dF_{nP_6}}{dw} = [r_{Iso\ iP_6}] - [r_{DHC\ nP_6}] \quad (15)$$

$$\frac{dF_{nP_7}}{dw} = (1)[r_{Iso\ iP_7}] - (1)[r_{DHC\ nP_7}] \quad (16)$$

$$\frac{dF_{nP_8}}{dw} = [r_{Iso\ iP_8}] - [r_{DHC\ nP_8}] \quad (17)$$

$$\frac{dF_{iP_6}}{dw} = -[r_{Iso\ iP_6}] - [r_{HDCrack\ iP_6}] + (1/3)[r_{HDCrack\ iP_7}] + (1/4)[r_{HDCrack\ iP_8}] \quad (18)$$

$$\frac{dF_{iP_7}}{dw} = -[r_{Iso\ iP_7}] - [r_{HDCrack\ iP_7}] + (1/4)[r_{HDCrack\ iP_8}] \quad (19)$$

$$\frac{dF_{iP_8}}{dw} = -[r_{Iso\ iP_8}] - [r_{HDCrack\ iP_8}] \quad (20)$$

$$\frac{dF_{N_6}}{dw} = [r_{DHC\ nP_6}] - [r_{DH\ N_6}] \quad (21)$$

$$\frac{dF_{N_7}}{dw} = [r_{DHC\ nP_7}] - [r_{DH\ N_7}] \quad (22)$$

$$\frac{dF_{N_8}}{dw} = [r_{DHC\ nP_8}] - [r_{DH\ N_8}] \quad (23)$$

$$\frac{dF_{A_6}}{dw} = [r_{DH\ N_6}] + [r_{HDCrack\ A_7}] + (1/2)[r_{HDCrack\ A_8}] \quad (24)$$

$$\frac{dF_{A_7}}{dw} = [r_{DH\ N_7}] - [r_{HDCrack\ A_7}] + (1/2)[r_{HDCrack\ A_8}] \quad (25)$$

$$\frac{dF_{A_{8+}}}{dw} = [r_{DH\ N_8}] - [r_{HDCrack\ A_8}] \quad (26)$$

To validate the assumption of the model compounds given in Table 1, Equations (6)–(26) were solved simultaneously by using the Runge-Kutta fourth order method to simulate the industrial data reported for a catalytic naphtha reforming process given in [25].

The results are given in Table 9. We satisfactorily predict the aromatic fractions and for most cases, the absolute error is below 5% when compared with the plant data. For the cases where the error is higher than 5%, we can observe that it is close to the error reported by Arani et al., 2009.

Table 9. Model prediction of the industrial plant data.

	Molar Composition			% Abs Error	
	Plant Data	Arani et al.	This Work	Arani et al.	This Work
H ₂	68.89	69.02	68.30	0.19	0.85
C ₁	9.62	9.56	9.87	0.62	2.64
C ₂	5.05	5.29	5.12	4.75	1.40
C ₃	4.53	4.36	4.71	3.75	4.04
C ₄	2.89	2.87	2.95	0.69	2.12
C ₅	1.3	1.16	1.19	10.77	8.81
np ₆	0.27	0.23	0.24	14.81	10.27
np ₇	0.26	0.26	0.27	0.0	4.52
np ₈₊	0.08	0.07	0.07	12.5	9.47
ip ₆	0.63	0.67	0.65	6.35	3.83

Table 9. Cont.

	Molar Composition			% Abs Error	
	Plant Data	Arani et al.	This Work	Arani et al.	This Work
ip7	0.9	0.82	0.99	8.89	10.42
ip8+	0.32	0.36	0.35	12.5	10.64
N _{6–10}	0.1	0.09	0.11	10.0	7.64
A ₆	0.38	0.44	0.40	15.79	4.35
A ₇	1.81	1.86	1.8	2.76	0.6
A ₈₊	2.97	2.94	2.89	1.01	2.58

3. Results and Discussion

Catalytic reformers are designed for flexibility in operation, and changes in operating parameters, such as temperature, pressure, and H₂/HC ratio, which affect reformate quality and yield. Reformers generally consist of a series of reactors that operate at a different temperature. The weight average bed temperature (WAIT) is a parameter of everyday practice that refers to the sum of the inlet temperature to each reactor multiplied by the weight percent of the total catalyst in each reactor. Reaction temperatures are chosen to promote a catalyst activity that could counterbalance the catalyst deactivation rate. In this regard, maximum reaction temperatures are reported in the range 733–798 K. However, in order to optimize high octane products, some low-pressure processes operate at slightly higher temperatures. As reformate RON increases with reactor temperature, for instance, a RON range of 90–95, WAIT should increase approximately by a 2–3 K/RON increase, depending on feedstock [25].

Operating pressure is an important parameter that influences product quality and yield. Reformer reactors operate in the 0.5 to 1.1 MPa pressure range, and it is common practice that each of the reactors in series operates at different pressures. For instance, operation under a decreasing pressure scheme on one side increases aromatics and hydrogen yield, but on the other increases coke formation and hence, catalyst deactivation. It has been demonstrated that a decrease in pressure increases product yield. At a 100 RON level, liquid yield increases or decreases by about 2 volume percent of charge per each 0.8 MPa change in pressure [26].

Finally, the presence of hydrogen is essential to avoid catalyst deactivation and undesirable side reactions. However, operating at high hydrogen-to-hydrocarbon ratios implies increased energy costs from more significant hydrogen recycling rates. Therefore, the lower boundary is often dictated by the desired amount of hydrocracking and maximum acceptable catalyst deactivation to save energy. Former designs used H₂/HC ratios in the range 8–10 while modern reformers, that benefit from highly active catalysts, operate in the 2–5 range and 0.5–1.1 H₂ partial pressure range.

3.1. Temperature Effect

According to the equilibrium calculations, it can be seen in Figure 2c that aromatics and hydrogen formation are favored at temperatures higher than 800 K. Moreover, paraffins, naphthenes, and C₂–C₅ are entirely consumed in the range of 600–1300 K. At temperatures lower than 800 K, there is an important methane production (Figure 2a), while the hydrogen production is less than 1% (Figure 2c). Methane production is associated with the hydrocracking reactions, since they typically occur at temperatures in the range of 573–723 K [28–30]. Additionally, they demand a large amount of hydrogen, about 0.5–0.8 wt% relative to the feed, for saturating the cracking fractions [31]. At temperatures higher than 800 K, the isomerization reaction of iso-paraffins to paraffins, the hydroacylation reactions of paraffins to naphthene, and the dehydrogenation of naphthenes are highly favored to increase aromatic production.

Figure 2. Effect of temperature on molar composition at 2.86 MPa and 9.4 H₂/HC molar ratio: (a,c,e) Equilibrium. (b,d,f) Catalytic. (●) CH₄, (■) H₂, (◀) C₂–C₅, (◆) Paraffins, (◆) Naphthenes, (●) Aromatics.

The hydrogen production increase correlates to the dehydrogenation of naphthenes to aromatics, which boosts hydrogen production at temperatures higher than 900 K (Figure 2e). In Figure 2a, it can also be observed that methane production decreases as reaction temperature increases, indicating that reforming reactions become more favored than hydrocracking reactions at such conditions.

On the other hand, we observed in Figure 2d that for the catalytic reforming, there is a maximum in the production of the aromatics at 800 K, which matches with the maximum observed in the hydrogen production (Figure 2b) and the minimum observed in the paraffins and naphthenes composition (Figure 2f). The molar composition of methane remains almost constant in the temperature range of 600 to 1300 K. The C₂–C₅ production shows a maximum that agrees with the production of the aromatic. This confirmed that the dehydrogenation of naphthenes is favored by high reaction temperatures since they were almost wholly converted [32].

Whether or not a catalyst is present, thermodynamics determines the equilibrium composition of reactants and products. Nonetheless, the presence of a catalyst allows the system to reach equilibrium faster. Based on this, it can be said that the catalyst used in catalytic naphtha reforming can still be improved to increase aromatics production. At 800 K, molar composition for this fraction is only 1.5% for the catalytic process (Figure 2d), while at equilibrium it is about 2.5% (Figure 2c). Additionally, an increase in aromatics production will also result in an increase in hydrogen production.

3.2. Pressure Effect

It is shown in Figures 3 and 4 that high pressures at both thermodynamics and catalytic conditions are not favorable for the naphtha reforming process, which agrees with previous studies reported in the literature [20]. Higher pressures promote the formation of light hydrocarbons (Figure 3a,b), and the formation of C₁–C₅ gases (Figure 3e,f), which is mainly attributed to the hydrocracking reactions. This is confirmed by the increase in the hydrogen consumption observed in Figure 3c,d since such reactions consume high amounts of hydrogen [33].

It can be seen in Figure 4a,c that at the equilibrium paraffins and naphthenes are wholly converted to their corresponding intermediate compound to finally produce aromatics. Conversely, in the catalytic process, we observed that paraffins and naphthenes reach a minimum at 800 K (Figure 4b,d), which agrees with the maximum production of aromatic observed in Figure 4f.

Dehydrocyclization and dehydrogenation are desired reactions, since they produce hydrogen, and both are favored by low pressure and high temperature [34]. We observe in Figure 4b that the concentration of paraffin components increases as the pressure increases. This is probably because the dehydrocyclization reactions are favored at a higher reaction pressure and higher molecular weight of carbon number [32].

Figure 4e,f shows that low pressures favor aromatics production. The increase in pressure results in a lower rate of catalytic aromatization reactions [35], increasing naphthenes (Figure 4d) and decreasing aromatics (Figure 4f) composition.

Figure 3. Effect of pressure on gas products: (a,c,e) Equilibrium. (b,d,f) Catalytic. (●/○) CH_4 , (■/□) H_2 , (◀/◁) $\text{C}_2\text{-C}_5$.

Figure 4. Effect of pressure on liquid products: (a,c,e) Equilibrium. (b,d,f) Catalytic. (◆/◇) Paraffins, (●/○) Naphthenes, and (●/○) Aromatics.

3.3. Effect of the H_2/HC Ratio

The molar H_2/HC ratio (R) effect is depicted in Figures 5 and 6. We noted an increase in CH_4 (Figure 5a,b) and C_2-C_5 gas production (Figure 5e,f) when the molar H_2/HC ratio increased.

These indicate that a higher R-value reduces aromatization and increases hydrocracking [25]. Nonetheless, the C_2-C_5 contribution is less than 1% at both 10 MPa and 0.1 MPa in the catalytic process (Figure 5f).

An increase in the H_2/HC promotes the hydrocracking of paraffins, which decreases paraffins composition when the R-value is increased (Figure 6b). This is confirmed in Figure 6d since naphthenes's composition remains constant for all the R values at 800 K,

the temperature at which the production of the maximum aromatic was observed for the catalytic process (Figure 4f).

Figure 6e,f depict that an increase in the R-value significantly decreases aromatic production at low and high pressures. At 800 K, the production of the aromatic decreases about ten percentage points when the H_2/HC ratio increases from 2 to 12, at both 0.1 and 10 MPa.

Figure 5. Effect of H_2/HC molar ratio on gas products: (a,c,e) Equilibrium. (b,d,f) Catalytic. (●/○) CH_4 , (■/□) H_2 , (◀/▶) C_2-C_5 .

Figure 6. Effect of H₂/HC molar ratio on liquid products: (a,c,e) Equilibrium. (b,d,f) Catalytic. (◆/◇) Paraffins, (●/○) Naphthenes, and (●/○) Aromatics.

3.4. Aromatics Distribution

In Figure 7, we present the effect of pressure and temperature on the aromatic distribution. We observed that, at the equilibrium, high temperatures favor the A₆ aromatic production (Figure 7a), while low temperatures favor the production of A₇ and A₈₊ aromatics (Figure 7c,e). Regarding the pressure, we found that low pressure favors the A₆ aromatic production (Figure 7a), while high pressures favor the production of A₇ and A₈₊ aromatics (Figure 7c,e).

Figure 7. Effect of pressure on aromatics molar composition ($R = 9.4 \text{ H}_2/\text{HC}$): (a,c,e) Equilibrium. (b,d,f) Catalytic. ($\blacktriangle/\triangle$) C₆ Aromatics, ($\blacktriangleright/\triangleright$) C₇ Aromatics, ($\blacktriangledown/\triangledown$) C₈ Aromatics.

We analyzed the aromatic distribution at 800 K for the catalytic process, the temperature at which the maximum aromatic production was achieved. We observed in Figure 7b that the A₆ aromatic production increases, while A₇ and A₈₊ aromatic production decrease when pressure is increased (Figure 7d,f). It has been reported that C₇ and C₈₊ aromatics formation increases when pressure is increased [32], which is the opposite of the behavior observed in Figure 7d,f, respectively. However, it is important to highlight that the reactivity of dehydrogenation reactions increases with an increase in the carbon number of naphthenes [36]. The larger the hydrocarbon chain of the non-aromatic compounds of the naphtha feedstock, the larger the carbon number of the naphthene produced, so that the higher reactivity towards C₇ and C₈₊ aromatics.

Additionally, we also analyzed the effect of the H_2/HC ratio on the distribution of aromatics (Figure 8). We found that the low R-value favors the production of the A_6 , A_7 , and A_{8+} aromatics at the equilibrium conditions as shown in Figure 8a,c,e, respectively.

Figure 8. Effect of H_2/HC ratio on aromatics distribution: (a,c,e) Equilibrium. (b,d,f) Catalytic. ($\blacktriangle/\triangle$) C_6 Aromatics, ($\blacktriangleright/\triangleright$) C_7 Aromatics, ($\blacktriangledown/\triangledown$) C_{8+} Aromatics.

Otherwise, we noticed in Figure 8b,d,f that the H_2/HC ratio does not significantly impact the C_6 – C_{8+} aromatic production in the catalytic process, neither at high nor at low pressure.

3.5. Research Octane Number

If the composition of fuel is known, the Research Octane Number (RON) may be estimated in the following form [24]:

$$RON = \sum v_{NP_i}(RON)_{NP_i} + \sum v_{IP_i}(RON)_{IP_i} + \sum v_{OI_i}(RON)_{OI_i} + \sum v_{N_i}(RON)_{N_i} + \sum v_{A_i}(RON)_{A_i} \quad (27)$$

The Research Octane Number for individual hydrocarbons was calculated as follow:

$$RON = a + bT + cT^2 + dT^3 + eT^4 \quad (28)$$

$$T = \frac{T_b - 273.15}{100} \quad (29)$$

The coefficients a – e are given in Table 10.

Table 10. Coefficients for RON estimation [24].

Hydrocarbons	a	b	c	d	e
n-Paraffins	92.809	−70.97	−53	20	10
Isoparaffins					
2-Methyl-pentanes	95.927	−157.53	561	−600	200
3-Methyl-pentanes	92.069	57.63	−65	0	0
2,2 Dimethyl-pentanes	109.38	−38.83	−26	0	0
2,2 Dimethyl-pentanes	97.652	−20.8	58	−200	100
Naphthenes	−77.536	471.59	−418	100	0
Aromatics	145.668	−54.336	16.276	0	0

Figure 9 shows the value of the octane number obtained with molar composition obtained at both equilibrium and catalytic conditions. It is observed that an increase in temperature induces an increase in the octane number; however, an increase in pressure results in a decrease in this property (Figure 9a,b). The impact of the H_2/HC ratio on the RON at equilibrium is minimal. Increasing the R-value from 1 to 12 only increases the octane number by approximately 0.5 units (Figure 9c).

We can see in Figure 9c,d that there is a maximum increase in the octane number at temperatures close to 800 K for the different pressures and H_2/HC ratios that were analyzed. This behavior is linked to the hydrocracking reactions inasmuch as they are favored at temperatures higher than 800 K. Consequently, the fraction of aromatic compounds is diminished, and so is that of the RON value.

According to Figure 9, it is convenient to operate at low pressure. Nevertheless, it has been reported that decreasing the total pressure increases the coke formation over Pt/Al_2O_3 catalysts. The increase in operating pressure contributes to less coke deposition on the metal function and higher stability, which is similar to adding Re or Ir to Pt to the catalyst [20]. When analyzing the effect of the H_2/HC ratio on the RON value, we observed that it has no significant impact, but it has been found in previous literature reports that H_2/HC ratios lower than 3.6 decreases aromatic production and increase carbon deposition [37].

It is essential to highlight that the catalytic naphtha reforming process is accompanied by side reactions that lead to carbonaceous deposits on both catalyst support and metallic sites, causing catalyst deactivation. Coke significantly alters the catalyst activity, selectivity, and lifetime [38].

Decreasing the H_2/HC ratio at constant pressure produces more coke deposition on the support [20]. Carbon deposition decreased with increasing pressure [20]; nevertheless, it has been reported that coke deposits predominantly on the support at high pressures and can only be burned off at high temperatures, while the coke deposited under low pressure is more easily removed by regeneration [38]. Increasing the reaction temperature usually causes an increase in aromatics and reformat yields but also an increase in coke amount [20].

Figure 9. Effect of operating conditions on the Research Octane Number. Effect of pressure: (a) Equilibrium, (b) Catalytic. Effect of H₂/H ratio (10 MPa): (c) Equilibrium, (d) Catalytic.

High severity accelerates coke formation and produces a decrease in aromatics and reformat yields [28], resulting in a decrease in the research octane. The decrease in the research octane number observed in Figure 9b,d at temperatures higher than 800 K agrees with the catalyst deactivation, which is incorporated in the reaction rate expressions for the catalytic reforming process (Tables 5–8) through the catalyst deactivation function given in Equation (15). It is recommended to operate below 823 K, since an irreversible deactivation of the catalyst occurs beyond this temperature due to sintering and loss of surface area and mechanical resistance [37].

4. Conclusions

The effect of temperature, pressure, and H₂/HC ratio on the products obtained from the naphtha reforming process was studied at equilibrium conditions and in the presence of Pt/Al₂O₃ catalyst. In both cases, it is observed that an increase in temperature increases the production of aromatics. In contrast, an increase in pressure and H₂/HC ratio decreases aromatics production. This is directly related to the Research Octane Number since this parameter highly depends on the aromatic content in the reformat.

It is important to highlight that the dehydrogenation of naphthenes towards aromatics production is completely favored under equilibrium conditions. However, during catalytic reforming, the aromatization reaction competes with the hydrocracking of paraffins and aromatics, significantly reducing the production of high-octane number compounds.

According to equilibrium calculations, the highest value of the RON expected was 108. From the results of the simulation of the catalytic reforming, the highest RON value was 98, at 800 K. This gap in the RON value justifies the effort for the research for new catalysts

and to evaluate alternative process configurations to reduce the severity of the process to obtain reformed gasoline with RON values greater than 98.

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Nomenclature

a_{ij}	Number of gram atoms of element j in a mole of species i
A_c	Cross section of flow in reactor
ΔA	Sum of A coefficients in Table 3, according to reaction stoichiometry
A_{ij}	Matrix of a_{ji} 's
ΔB	Sum of B coefficients in Table 3, according to reaction stoichiometry
B_i	B value of the i -th component of the mixture
ΔC	Sum of C coefficients in Table 3, according to reaction stoichiometry
ΔC_p	Standard heat-capacity change of reaction
DH	Dehydrogenation of naphthenes
DHC	Dehydrocyclization of paraffins
d_p	Diameter of catalyst particle
ΔD	Sum of D coefficients in Table 3, according to reaction stoichiometry
E_a	Activation energy
E_d	Deactivation energy
ΔE	Sum of E coefficients in Table 3, according to reaction stoichiometry
F_i	Molar flow
G	Light gases in Figure 1
	Superficial mass flux, $\text{kg}/\text{s}\cdot\text{m}^2$ in Equation (7)
ΔG	Standard Gibbs-energy change of reaction at temperature T
ΔG_0	Standard Gibbs-energy change of reaction at reference temperature T_0 (298 K)
ΔG_{fi}^0	Standard Gibbs-energy change of formation of species i
ΔH_0	Standard heat of reaction at reference temperature T_0 (298 K)
$HDCrack$	Hydrocracking
i	Carbon number: 6, 7, and 8+
ip	Iso-paraffins
ISO	Isomerization of paraffins
K	Total number of atomic elements
K_i	Equilibrium constant
k_d	Deactivation constant
k_{DH}	Preexponential factor for the dehydrogenation reactions
k_{DHC}	Preexponential factor for the dehydrocyclization reactions
$k_{DHCrack}$	Preexponential factor for the hydrocracking reactions
k_I	Preexponential factor for the isomerization reactions
m	Deactivation order
np	Normal paraffins
N	Total number of species in the reaction mixture.
	Naphthenes in Figure 1

nG	Total Gibbs free energy of the system
n_i	Number of moles of specie i
P	Total pressure of the system
P_i	Partial pressure
P_c	Critical pressure
P_r	Reduced pressure
R	Gas constant
r	Reaction rate
RON	Research Octane Number
t	Time-on-stream
T	Temperature of the system
	Temperature for RON calculations defined in Equation (28)
T_b	Boiling point, K
T_c	Critical temperature
T_r	Reduced temperature
v_{A_i}	Volumetric fraction of aromatic i
v_{IP_i}	Volumetric fraction of iso-paraffin i
v_{N_i}	Volumetric fraction of naphthene i
v_{NP_i}	Volumetric fraction of normal paraffin i
v_{O_i}	Volumetric fraction of olefin i
y_i, y_j	Mol fraction of species i
w	Weight of catalyst
z	Compressibility factor
Greek letters	
Γ	Adsorption term for the acid function
θ	Adsorption term for the metal function
μ	Viscosity of the mixture
ρ	Density of the mixture
ρ_c	Density of solid catalyst
φ	Bed void fraction
ϕ	Catalyst activity
$\hat{\phi}_i$	Fugacity coefficient of species i in the gas mixture

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