

Catalytic Reforming of Heavy Naphtha- Modeling and Simulate

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Abstract:

Catalytic reforming is a chemical process used to convert low-octane naphtha's into high-octane gasoline blending components called reformates to be used either as a motor fuel blending stock or as a source for specific aromatics, such as benzene, toluene and xylene (BTX). Considering the importance of this process for the production of gasoline, the catalytic reforming process is simulated and important parameters such as octane number, reactor inlet and outlet temperatures, and PONA moles of the gas leaving the reactor are predicted. This paper uses the Smith model to simulate and estimate process parameters.

A computer program is used to simulate a model of the catalytic reforming process.

The accuracy of the model results was compared with data collected at the Zawia refinery. The results are validated with operating data from a catalytic reformer unit.

Keywords: catalytic naphtha reforming, heavy naphtha, kinetic model, catalyst.

التهديب بواسطة العامل المساعد للنافثا الثقيلة و النمذجة والمحاكاة

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الملخص

التهديب بواسطة العامل المساعد هو عملية كيميائية تستخدم لتحويل النفط المقطرة من النفط الخام إلى منتجات سائلة عالية الأوكتان تسمى التهديبات. وهي عبارة عن مخزونات مزج ممتازة للبنزين عالي الأوكتان والمواد العطرية القيمة مثل البنزين والتولين والزيلين (BTX) التي يتم انتاجها. بالنظر الى أهمية هذه العملية لإنتاج البنزين، تم محاكاة عملية التهديب بواسطة العامل المساعد والتنبؤ بالعوامل الحيوية مثل درجة حرارة مدخل ومخرج المفاعلات ذات رقم الأوكتان ومولات (PONA) من الغازات الخارجة من المفاعلات. في هذا البحث تم استخدام نموذج سميت لمحاكاة وتقدير معالم العملية. وتم مقارنة دقة نتائج النموذج مع البيانات المجمعة من مصفاة الزاوية للنفط. وقد تم التحقق من صحة النتائج من خلال بيانات التشغيل المأخوذة من وحدة التهديب بواسطة العامل المساعد. حيث تم استخدام برنامج الحاسوب لمحاكاة نموذج عملية التهديب بواسطة العامل المساعد.

الكلمات المفتاحية: اصلاح النافثا التحفيزي ، النافثا الثقيلة ، النموذج الحركي ، المحفز

1. Introduction

The catalytic reforming unit (CRU) is one of the major units for gasoline production in refineries. It can produce about 37% gasoline by weight [1]. This unit is developed for the production of automotive fuel components to meet the engine's requirements for high antiknock quality [2]. The process goal is to convert low-octane C₇-C₁₀ hydrocarbons into high-octane aromatics and isoparaffins, called reformates, which are components of high-

octane gasoline [3]. Catalytic reforming can be produce reformed feed with an octane number between 90 and 95 [4].

In addition, CR is suitable for the production of petrochemical products such as benzene, toluene, xylene (BTX) and other aromatics used in the petroleum industry. Hydrogen is an important by-product that is separated from reformed feed for recovery and used in hydrocracking, hydrotreating and other hydrogen-consuming processes. It can also be used as a clean combustible [5,6].

Catalytic reforming is carried out in the presence of a catalyst. Depending on the catalyst, a certain sequence of reactions occurs [7], including the reconstruction of the hydrocarbons in the feedstock without changing the boiling point range [8].Catalytic reforming processes are divided into (1) moving-bed process, which uses mixed non-precious metal oxide catalysts in devices equipped with independent regeneration facilities, (2) fluid-bed process, and (3) fixed-bed process, mainly using platinum-containing catalyst [7].The naphtha stream is obtained from the distillation column and is primarily liquid, with a mixture boiling in the range C5-140°C (called straight-run naphtha, SRN). Further separation in the column (splitter) into two fractions, the lighter one at the top, C5–90°C, and the bottom 90°C–140°C (heavy naphtha or heavy straight-run naphtha, HSR) [1,9]. The light naphtha from the naphtha cracker is essentially a low-octane fraction. If necessary, it can be hydro refined and sent directly to the gasoline pool for mixing, or to the isomerization process to improve Its octane rating[10]. In a hydrogen environment, the heavy naphtha fraction is converted into high-octane gasoline through the reaction of a platinum (or platinum-rhenium) catalyst in a reactor [1]. HSR requires hydro treatment prior to the catalytic reforming process to remove olefins and other contaminants that may poison the reforming catalyst, such as sulfur and nitrogen compounds [11].

The main objective of this study is the production of fuel with a high octane number using catalytic reforming and uses the smith model to simulate and estimate process parameters.

2. Catalyst

Many types of reforming catalysts used contain platinum or rhenium as active catalyst [12], which can be supported on alumina or silica-alumina [7]. In most cases, platinum is combined with rhenium (bimetallic, Pt-Re/Al₂O₃) to form a more stable catalyst that permits operation at lower pressures [9]. Pt-Re bimetallic catalysts are favored due to their lower coking rate and higher resistance to deactivation [13]. As the platinum catalyst is easily poisoned by the presence of the sulfur, oxygen, nitrogen, and metallic components, it is essential to pretreat naphtha before reforming. This fact is carried out simultaneously in the catalytic hydrogen pretreatment reactor [1].

There are three basic types of catalytic reforming catalyst regeneration operations: continuous, cyclic and semi-regenerative. The catalyst regenerator of the continuous catalytic reforming unit operates continuously, and a small amount of catalyst slipstream is circulated between the catalytic reforming unit and the regenerator. In a circulating CRU, there are basically additional CRU reactors. When regeneration is required, one reactor is cycled offline and regenerated. Regeneration of offline reactors is an intermittent process. Upon completion, the reactor is resumed and the next reactor is cycled offline and regenerated. This process continues until all reactors are regenerated. In a cycling CRU, 1000 to 4000 hours of regeneration may occur per year. Semi-regenerative CRUs operate without regeneration for 8 to 18 months before the entire unit is taken offline and relocated. The entire regeneration cycle usually takes 1 to 2 weeks [11].

3. Feedstock:

The feed to the CRU is the heavy naphtha (or HSR) stream from the naphtha redistillation column, which is typically desulfurized in a catalytic hydrogenation unit [1]. It consists of four main hydrocarbon groups; paraffin's, alkenes, cycloalkanes, and aromatic hydrocarbons (PONA) [9]. HSR is easy to produce aromatic gasoline, is the easiest to reform, and has the highest gasoline yield [1]. The composition of a given HSR depends on the crude oil type, the boiling range of the heavy naphtha, and whether it is obtained

directly from crude oil distillation. HSR accounts for 15-30% of crude oil [14,15]. A typical HSR has the following PONA analysis; 40–70 wt% paraffins, 20–50 wt% naphthenes, 5–20 wt% aromatics, and only 0–2 wt% olefins [8] Figure 1 illustrates the catalytic reforming process in a refinery.

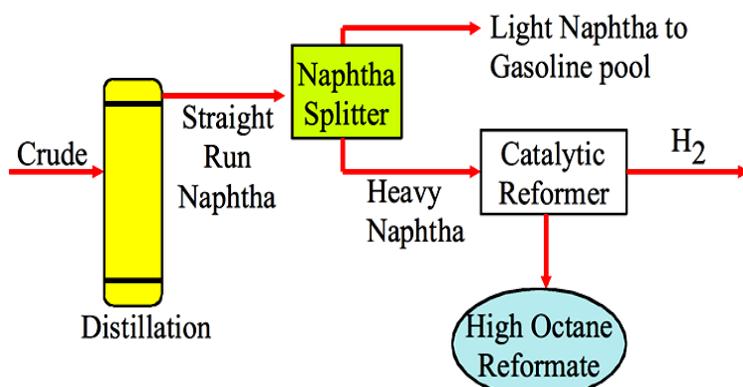


Figure 1: Placement of catalytic reforming process in a refinery.

Table(1) shows the hydrocarbon composition of three different naphtha streams.

Table 1: Composition and characteristics of three different types of Libyan naphtha feed.

Feed (HSR)	Paraffin (Wt. %)	Olefin (Wt. %)	Naphthene (Wt. %)	Aromatic (Wt. %)	IBP-FBP (°C)	Sulfur content (Wt. %)	M.W
Brega crude oil	56.078	0.275	30.573	10.787	88 – 162	0.031	113.2
Hamada crude oil	68.888	0.500	19.686	6.8670	81 – 180	0.026	113.9
Sedra crude oil	50.484	0.573	35.807	10.348	66 – 178	0.020	111.6

4. Feed Preparation:

Platinum is the active material in most catalytic reforming catalysts. Certain metals, hydrogen sulfide, ammonia, and organic nitrogen

and sulfur compounds can deactivate catalysts. Feed pretreatment in the form of hydrotreating is often used to remove these species. Hydrotreaters use cobalt-molybdenum catalysts to convert organic sulfur and nitrogen compounds into hydrogen sulfide and ammonia, which are then removed from the system along with unreacted hydrogen. The hydrotreater catalyst retains metals in the feed. The hydrogen required for the hydrotreating unit is obtained from the catalytic reforming unit. If the boiling range of the feed must be changed, the feed must be re-distilled before being added to the catalytic reformer. When the feed enters the first reactor, the feed should meet the requirements of Table 2 [9]

Table 2: Feed specifications for CRU.

S	< 1.0 ppm
N	< 1.0 ppm
H ₂ O	< 4.0 ppm
Pb, As, Cu	< 20.0 ppb

5. Process Description:

The catalytic reforming unit consists of a reactor part, a circulating gas compression part and a fractionation part, as shown in Figure 2. The reactor part consists of a feeding system, three heaters or furnaces and three reactors in series [2]. Typically a mixture of heavy naphtha and hydrogen is fed into a furnace, the mixture is heated to the desired temperature of 450°C–520°C, and then reacted through a semi-regenerative fixed-bed catalytic reaction at a hydrogen pressure of 20–500°C. 25 kg/cm² Catalysts are used mainly to accelerate the reaction [7]. The product stream from the preheated first reactor enters the second reactor and, after preheating, enters the third reactor. Since the reaction is endothermic, the reactor feed is raised to the appropriate temperature by a heater located in front of the reactor. The temperature distribution of the reactor is shown in Figure 3. The product from the last reactor is cooled to 50°C and sent to the separator where the hydrogen-rich gas stream is separated from the product and then recycled back to the gas compression section and

mixed with the first reactor fresh feed [12]. The liquid product from the bottom of the separator is sent to the fractionator section, which includes a distillation column that serves as a product stabilizer (for the butanizer). The distillate stream extracts light gases from the flashed liquid, producing liquefied petroleum gas (LPG) and waste gas as fuel. The main product is a bottoms stream called reformat, which is the raw material for gasoline blending. [12, 7]. Reformer operating pressure and hydrogen/feed ratio are a compromise between obtaining maximum yield, long operating time between regenerations, and stable operation. Typically operation at pressures of 50 to 350 psig and hydrogenation ratios of 3-8 mol H₂/mol feed (2800-7600 scf/bbl) is required. The liquid space-time velocity is commonly used in the range of 1 to 3 [9].

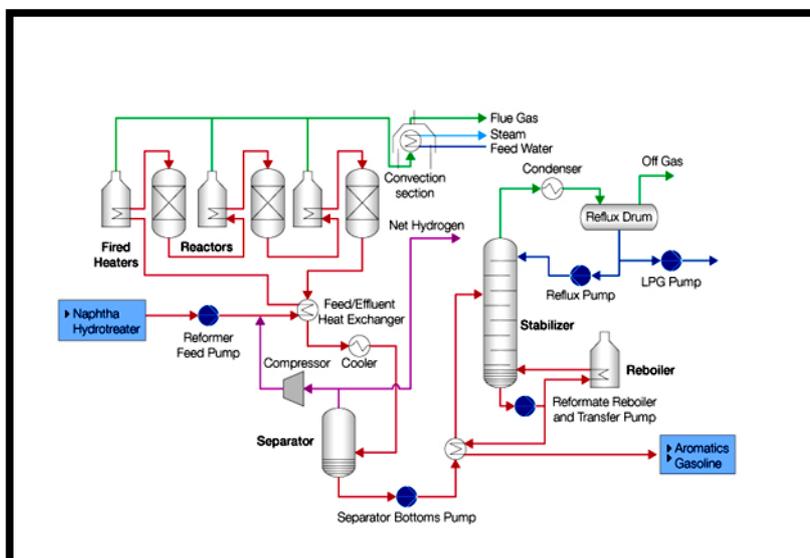


Figure 2: Catalytic reforming flowchart (semi-regenerative).

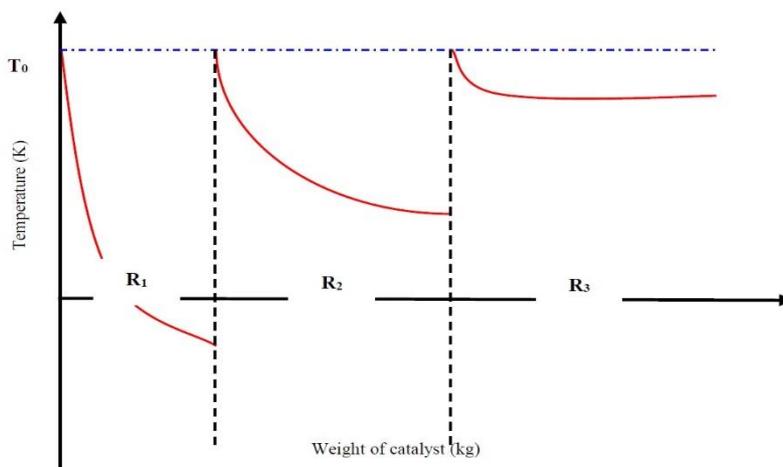


Figure 3: Temperature distribution in reactors length.

5. Kinetics Model:

Naphtha is a very complex mixture of hydrocarbons with more than 300 components present in the mixture [16]. Different reactions such as dehydrogenation, hydrocracking, isomerization and dehydrocyclization occur during this process [1]. Smith's model feeds will be divided into three categories as seen in figure 4; paraffinic, naphthenic and aromatic hydrocarbons. Additionally, hydrogen and light gases are considered. The Smith model involves five pseudo-components; four reactions of alkanes, cycloalkanes, aromatics and hydrogen [18].

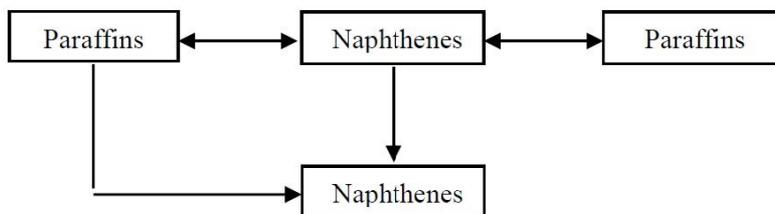


Figure 4: Reaction schemes of the Smith model.

The reaction rate is usually expressed in terms of simple first order with respect to the hydrocarbon partial pressure, and the pressure drop across the reactor is neglected [19].

$$a A + b B \leftrightarrow c C + d D$$
$$-\left(\frac{dN_R}{dV_R}\right) = k_f P_A^a P_B^b \dots - k_r P_C^c P_D^d$$

The reaction rates components are expressed in the form of a modified Arrhenius law as follows;

$$k_f = k_{of} \exp\left(\frac{-E}{RT}\right) A_c$$

Reaction 1:

Naphthenes \leftrightarrow Aromatics + Hydrogen

The rate of disappearance of naphthenes is given by;

$$-\left(\frac{dN_N}{dV_R}\right)_1 = \frac{k_{f1}}{K_{eq1}} (K_{eq1} P_N - P_A P_{H_2}^3) \rightarrow (1)$$

The contribution of this reaction to the total rate of change of temperature is given by;

$$\left(\frac{dT}{dN_R}\right)_1 = \left(\frac{dN_N}{dV_R}\right)_1 \left[\frac{\Delta H_1}{N_T C_p (MW)_R} \right] \rightarrow (2)$$

Reaction 2:

Naphthenes + Hydrogen \leftrightarrow Paraffins

The rate of disappearance of naphthenes is given by;

$$-\left(\frac{dN_N}{dV_R}\right)_2 = \frac{k_{f2}}{K_{eq2}} (K_{eq2} P_N P_{H_2} - P_P) \rightarrow (3)$$

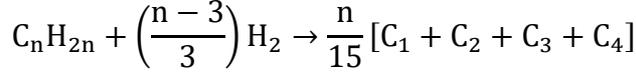
And the corresponding change in temperature is;

$$\left(\frac{dT}{dN_R}\right)_2 = \left(\frac{dN_N}{dV_R}\right)_2 \left[\frac{\Delta H_2}{N_T C_p (MW)_R} \right] \rightarrow (4)$$

Reaction 3:

Naphthenes \rightarrow Lighter ends

Assuming that in the different partitions of the hydrocracking products, i.e. methane, ethane, propane, butane and pentane are all produced in approximately equal molar proportions, the chemical reaction can be written as:



Taking the hydrocracking reaction to be first order regarding the precursor, the rate of change of concentration and temperature can be represented by equations (5) and (6) respectively as;

$$-\left(\frac{dN_N}{dV_R}\right)_3 = \left(\frac{k_{f_3}}{P_T}\right) P_N \rightarrow (5)$$

$$\left(\frac{dT}{dN_R}\right)_3 = \left(\frac{dN_N}{dV_R}\right)_3 \left(\frac{n_c}{3}\right) \left[\frac{\Delta H_3}{N_T C_p (MW)_R}\right] \rightarrow (6)$$

Reaction 4:

Paraffins \rightarrow Lighter ends

Assuming paraffins hydrocracking to be similar to naphthene hydrocracking with reaction rate constant to be the same;

$$-\left(\frac{dN_N}{dV_R}\right)_4 = \left(\frac{k_{f_4}}{P_T}\right) P_P \rightarrow (7)$$

$$\left(\frac{dT}{dN_R}\right)_4 = \left(\frac{dN_N}{dV_R}\right)_4 \left(\frac{n_c-3}{3}\right) \left[\frac{\Delta H_4}{N_T C_p (MW)_R}\right] \rightarrow (8)$$

In the first reactions, the forward rate constants k_{fi} ($i = 1,2$) can be expressed as;

$$k_{fi} = 9.869 \times 10^{-3} \exp\left(C_i - \frac{X_i}{RT}\right) A_c \rightarrow (9)$$

For reactions (3) and (4), the rate constant k_{fi} ($i = 3,4$) is given by;

$$k_{fi} = \exp\left(C_i - \frac{X_i}{RT}\right) A_c \rightarrow (10)$$

Parameters C_i and ΔH_i are given in table 3. Also in this table are the equilibrium constants for the first two reactions, which are reversible.

Table 3: Kinetics and thermodynamic parameters.

i	C _i (kmol/m ³)	X _i (kJ/kmol)	ΔH _i × 10 ⁵ (kJ/kmol)	Keq
1	23.21	1.37672×10 ⁵	- 2.12783	5.441×10 ⁹ kPa ³
2	35.98	2.66348×10 ⁵	- 0.44185	5.474×10 ⁻³ kPa ⁻¹
3	42.94	2.79484×10 ⁵	- 0.51860	-
4	-	-	- 0.56508	-

Adding the contribution of all the four reactions, we finally have;

$$\frac{dN_P}{dV_R} = - \left(\frac{dN_N}{dV_R} \right)_2 + \left(\frac{dN_P}{dV_R} \right)_4 \rightarrow (11)$$

$$\frac{dN_N}{dV_R} = \left(\frac{dN_N}{dV_R} \right)_1 + \left(\frac{dN_N}{dV_R} \right)_2 + \left(\frac{dN_N}{dV_R} \right)_3 \rightarrow (12)$$

$$\frac{dN_A}{dV_R} = - \left(\frac{dN_N}{dV_R} \right)_1 \rightarrow (13)$$

$$\frac{dN_{H_2}}{dV_R} = -3 \left(\frac{dN_N}{dV_R} \right)_1 + \left(\frac{dN_N}{dV_R} \right)_2 + \frac{n_c}{3} \left(\frac{dN_N}{dV_R} \right)_3 + \left(\frac{n_c - 3}{3} \right) \left(\frac{dN_P}{dV_R} \right)_4 \rightarrow (14)$$

$$\left(\frac{dT}{dV_R} \right) = \left(\frac{dT}{dV_R} \right)_1 + \left(\frac{dT}{dV_R} \right)_2 + \left(\frac{dT}{dV_R} \right)_3 + \left(\frac{dT}{dV_R} \right)_4 \rightarrow (15)$$

Equations (11) through (15) were integrated using a fourth order Rung–Kutta method to obtain calculated values of aromatics yield and temperature at the exit for each set of plant data.

6. Results:

After performing the simulation process using computer program in c++ the results for each feed stream was tabulated as follows:

Table 4-a: Brega crude oil.

Reactor Number	1	2	3
Catalyst Distribution	1	1	2.75
Inlet Temperature, °C	514	512	510
Outlet Temperature, °C	416	497	508
Temperature Drop, °C	98	15	2
Octane Number (RON)	58.52	69.65	86.13
Moles;			
Moles N, Leaving Reactor	13.920	5.124	2.102
Moles P, Leaving Reactor	157.02	98.55	38.12
Moles A, Leaving Reactor	44.321	71.04	93.02

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Moles Gases Leaving Reactor	88.000	196.3	312.2
Moles Hydrogen Leaving Reactor	286.24	314.3	334.3
Total Moles	589.501	685.314	779.742

Table 4-b: Hamada crude oil.

Reactor Number	1	2	3
Catalyst Distribution	1	1	2.75
Inlet Temperature, °C	514	512	510
Outlet Temperature, °C	402	490	506
Temperature Drop, °C	112	22	4
Octane Number (RON)	51.40	68.75	86.34
Moles;			
Moles N, Leaving Reactor	15.821	6.254	3.001
Moles P, Leaving Reactor	143.22	84.22	31.20
Moles A, Leaving Reactor	38.937	65.28	88.70
Moles Gases Leaving Reactor	82.084	191.0	307.2
Moles Hydrogen Leaving Reactor	274.35	301.2	319.9
Total Moles	554.412	647.954	750..001

Table 4-c: Sedra crude oil.

Reactor Number	1	2	3
Catalyst Distribution	1	1	2.75
Inlet Temperature, °C	514	512	510
Outlet Temperature, °C	424	499	510
c	90	13	0
Octane Number (RON)	61.77	72.10	87.60
Moles;			
Moles N, Leaving Reactor	12.854	4.562	1.889
Moles P, Leaving Reactor	159.22	99.21	39.90
Moles A, Leaving Reactor	47.801	73.22	98.40
Moles Gases Leaving Reactor	90.221	201.2	323.0
Moles Hydrogen Leaving Reactor	297.02	328.8	345.2
Total Moles	607.116	706.992	808.389

7. Conclusion

The Smith model, although old and simple, can provide acceptable estimates of operating conditions such as reactor outlet temperature, octane number, yield, and PONA. In this study, the Smith model is

used to simulate the catalytic reforming unit. The Smith model is based on solving the mass and energy equations for all species in the reactor. Three reactors were simulated in series. The simulation results show that the highest conversion occurs in the first reactor and most species react in this reactor. Most reactions are exothermic and result in an increase in temperature. Furthermore, the model predictions were compared with the resulting data obtained from the catalytic reforming unit of the Zawia refinery and the results were in good agreement.

Nomenclature:

A	Aromatics
A_c	Catalyst activity
C_p	Specific heat, $\text{kJ} \cdot \text{kmol}^{-1}$
E	Activation energy, $\text{kJ} \cdot \text{kmol}^{-1}$
ΔH	Heat of reaction, $\text{kJ} \cdot \text{kmol}^{-1}$
K_p	Equilibrium constant
K_c	Hydrocracking reaction constant
k_f	Forward reaction rate constant, $\text{kmol} \cdot \text{hr}^{-1} \cdot \text{kg cat}^{-1} \cdot \text{kPa}^{-1}$ for reaction 1 and 2, $\text{kmol} \cdot \text{hr}^{-1} \cdot \text{kg cat}^{-1}$ for reaction 1 and 4
k_o	Backward reaction rate constant, $\text{kmol} \cdot \text{hr}^{-1} \cdot \text{kg cat}^{-1} \cdot \text{kPa}^{-1}$
k	Preexponential factor
MW	Molecular weight
N	Naphthenes
N_i	Molar flow rate, $\text{kmol} \cdot \text{s}^{-1}$
n_c	Average carbon number for naphtha
P	paraffins
ppm	Part per million
ppb	Part per billion
P_i	Partial pressure of component i, kPa
T	Temperature, K
P_T	Total pressure, kPa
X	Activation energy, $\text{kJ} \cdot \text{mol}^{-1}$

Subscript

A	Aromatics
F	Feed
N	Naphthenes

P Paraffins
R Reaction mixture
T Total

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