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KINETIC MODELING OF A DEACTIVATION PROCESS IN A HYDROCRACKER

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

San Jose State University

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

by

Philip Caesar Alemania

May 2003

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ABSTRACT

KINETIC MODELING OF A DEACTIVATION PROCESS IN A HYDROCRACKER

By Philip C. Alemania

The hydrocracking catalyst system is known to deactivate during normal operations. The rate of deactivation depends on run conditions. As a result, the run temperature is gradually increased to compensate for the deactivation. The kinetic model developed by Ashok Krishna and a curve fitting program were used to treat the temperature-time data.

$$T = [\ln(1-t/z)/Q + 1/T_o]^{-1}$$

$$\text{where: } z = \exp([E_d/RT_o]/A_d\{(E_d/E_a) - n + 1\}), Q = (E_d - nE_a + E_a)/R$$

This equation was used at different hydrogen partial pressures to obtain n , the activation energy of deactivation (E_d) and the pre-exponential (A_d) for four catalyst systems. These parameters were in turn used to calculate catalyst life. The results showed that the governing equation did describe the pilot plant data. Three out of the four systems were 1st order kinetic mechanism and the other was 2nd order. A relationship between A_d , E_d , and hydrogen partial pressure was also observed.

Table of Contents

	List of Tables	vii
	List of Figures	viii
	<u>Topic</u>	<u>Pages</u>
I	Introduction	1
	Kinetic Model	4
II	Literature Search	8
	Model for the Time-Temperature Data Analytical Solution	9
	Formation of Polycyclic Nuclear Aromatics	17
III	Thesis Proposal	18
IV	Pilot Plant Systems	
	Description of Pilot Plant Setup	20
	Pilot Plant Runs	27
V	Data Preparation and The Curve Fitting Program	37
VI	Results	
	Data Obtained for System A	44
	Data from System B	51
	Data from System C	54
	Data Obtained for System D	60
VII	Discussion	
	Introduction	69
	Impact of E_A on the Design Equation	72
	Relating Pressure to A_d and E_d	76
	Determination of A_d and E_d Values at Other pressures	77
	Relating k_A , k_d , and Temperature	80
	Determination of Kinetic Order	82
	Catalyst Life Calculation	84
VIII	Conclusion	87
	References	88

	Bibliography	89
IX	Appendices	
	Appendix A: Definition of Variables	91
	Appendix B: List of Acronyms	94
	Appendix C: Raw Data for 4 Systems	95
	Appendix D: Predicted Values for A_d and E_d using an Excel Spreadsheet	106
	Appendix E: Statistics for A_d and E_d Values	107
	Appendix F: System A 585 psia at $(n) = 1.3$ and $(n) = 1.6$	109
	Appendix G: System C at 1150 psia for $(n) = 0.9$ and $(n) = 1.3$	111

<u>List of Tables:</u>	<u>Page</u>
Table 1. Desired Products from a Hydrocracker	1
Table 2. Deactivating parameters from Krishanswamy and Kittrell Paper	15
Table 3. Feed Properties of Catalyst Systems A, B, C, and D	25
Table 4. Summary of Pilot Plant Data	36
Table 5. Preparing Raw Data for the Software Curve-Fitting Program	39
Table 6. Data for System A at 3 Pressures	45
Table 7. Data of the Data for System B at 1000 and 800 psia	51
Table 8. Summary of Values for System C at 3 pressures	54
Table 9. Summary of values for System D at 3 Pressures from time 0 to 190 hours and 330 to 430 hours	61
Table 10. Summary of Calculated A_d and E_d using Pilot Plant Data	70
Table 11. Result from varying the E_a value on the quality of the fit to Equation 17	73
Table 12. Values for calculating k_a and k_d	80
Table 13. Calculation of $\log(k_A / k_d)$ from Equation 31 and Table 12	82
Table 14. Catalyst Life Values using Equation 28 for Systems A-D	84
Table 15. Combination of Table 12 and Table 13	86

<u>List of Figures:</u>	<u>Page</u>
Figure 1. Schematic for a Hydrocracker inside a refinery	2
Figure 2. Hydrocracking Reactor Reactions	5
Figure 3. Parallel Deactivation	8
Figure 4. Temperature-Time Trajectories for Deactivating Hydrocracking Catalyst	16
Figure 5. Initiation Step	17
Figure 6. Propagation Steps for PNA Formation	18
Figure 7. Flow Diagram of a Pilot Plant	20
Figure 8. A typical Total Boiling Point Curve	25
Figure 9. Structure of Coronene	26
Figure 10. The Pilot plant run of System A at 1000 psia	28
Figure 11. The Pilot plant run of System A at 800 psia	28
Figure 12. The Pilot plant run of System A at 650 psia	29
Figure 13. The Pilot plant run of System B at 1000 psia	29
Figure 14. The Pilot plant run of System B at 800 psia	30
Figure 15. The Pilot Plant run of System C at 2000 psia	31
Figure 16. The Pilot plant run of System C at 2000 psia from 50 to 210 hours	31
Figure 17. The Pilot plant run of System C at 1600 psia	32
Figure 18. The Pilot plant run of System C at 1150 psia	32
Figure 19. The Pilot plant run of System D at 1774 psia	33
Figure 20. The Pilot plant run for System D at 1576 psia	34

<u>List of Figures:</u>	<u>Page</u>
Figure 21. The Pilot plant run for System D at 1320 psia and run hours from 0 to 430 hours	34
Figure 22. The Pilot plant run for System D at 1320 psia and run hours 0 to 190 hours	35
Figure 23. The Pilot plant run for System D at 1320 psia and run hours 330 to 430	35
Figure 24. Example of the Raw data and line created for Equation 17 using Table 2D	43
Figure 25. The Plot of the temperature against time was obtained from the run at 1000 psia with System A. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$	46
Figure 26. The Plot of the temperature against time was obtained from the run at 800 psia with System A. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$	47
Figure 27. The Plot of the temperature against time was obtained from the run at 650 psia with System A. The solid line was calculated from Equation 17 using $n = 1$	48
Figure 28. The Plot of the temperature against time was obtained from the run at 650 psia with System A. The solid line was calculated from Equation 17 using $n = 2$	49
Figure 29. The Plot of the temperature against time was obtained from the run at 650 psia with System A. The solid line was calculated from Equation 17 using $n = 1.3$	50
Figure 30. The plot of the temperature against time obtained from the run at 1000 psia with System B. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$	52
Figure 31. The Plot of the temperature against time was obtained from the run at 800 psia with System B. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$	53

<u>List of Figures:</u>	<u>Page</u>
Figure 32. The Plot of the temperature against time was obtained from the run at 2000 psia with System C. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$	56
Figure 33. The Plot of the temperature against time was obtained from the run at 1600 psia with System C. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$	57
Figure 34. The Plot of the temperature against time was obtained from the run at 1150 psia with System C. The solid line was calculated from Equation 17 using $n = 1$	58
Figure 35. The Plot of the temperature against time was obtained from the run at 1150 psia with System C. The solid line was calculated from Equation 17 using $n = 1$	59
Figure 36. The Plot of temperature against time was obtained from the run at 1597 psia and the line from Equation 17 for $n=1$ and $n=2$	63
Figure 37. The Plot of temperature against time was obtained from the run at 1418 psia and the line from Equation 17 for $n=1$ and $n=2$	64
Figure 38. The Plot of temperature against time was obtained from the run hours 0 to 190 hours at 1188 psia and the line from Equation 17 for $n=1$ and $n=2$	65
Figure 39. The Plot of temperature against time was obtained from the run hours 330 to 430 hours at 1188 psia and the line from Equation 17 for $n=1$	66
Figure 40. The Plot of temperature against time was obtained from the run hours 330 to 430 hours at 1188 psia and the line from Equation 17 for $n=2$	67
Figure 41. Comparison of Line Fit Data at 2000 and 1150 psia for System C	71

<u>List of Figures:</u>	<u>Page</u>
Figure 42. Plot of A_d , E_d against pressure for 1 st order for System A	77
Figure 43. The Plot of A_d , E_d against Pressure for Order for System B	78
Figure 44. The Plot of A_d , E_d against Pressure for 1 st Order for System C. Note for 1150 psia value used was for $n= 1.0$	78
Figure 45. Plot of A_d , E_d against Pressure for from run hours 0 to 190 hours for System D. Note for 1188 psia value used was for $n= 1.0$	79
Figure 46. Plot of A_d , E_d against Pressure for from run hours 330 to 430 hours 1 st Order for System D. Note for 1188 psia value used was for $n= 1.0$	79

I) Introduction

Unrefined crude oil cannot be used as finished products because it contains a large fraction of big molecules. Thus, the hydrocracking reactor was developed specifically to convert large hydrocarbon molecules into smaller hydrocarbon molecules and hydrogenate the aromatic compounds. Aromatic compounds are unsaturated ringed hydrocarbons with low hydrogen content and must be hydrogenated before the hydrocracking reaction can occur. The hydrogenation process also adds hydrogen and upgrades the quality of the product. This improves the of cetane number of the diesel product. Table 1 lists products from a hydrocracker that are commercially important.

Table 1. Desired Products from a Hydrocracker

<u>Product</u>	<u>Boiling Range (°F)</u>
Naphtha (Gasoline)	100-250
Jet	250-550
Diesel	550-700
Lube Oil	700-1000

A hydrocracking unit is one of the most important units in an oil refinery and is a key for maximizing the production of valuable products. The hydrocracker further cracks the vacuum gas oil (large hydrocarbons) coming off the distillation columns producing the desired hydrocarbon products. This process is shown schematically in Figure 1. In the early crude oil process, the refining of oil consisted mostly of a distillation column and a couple of down stream units that simply cleaned up the distilled products coming from the distillation column. This type of refinery was called a topping refinery.

Topping refineries did not have the capacity to crack larger hydrocarbons into smaller hydrocarbons. As the demand for more transportation fuel increased and the demand for the other petroleum products decreased, oil companies had to find other new ways to produce the more valuable products.

Figure 1. Schematic for a Hydrocracker inside a refinery

Hydrocracking reactor dimensions range from 100 to 1000 feet tall and up to 20 feet in diameter. Reactors are made of stainless steel and can be split up into a series of beds, which are filled with a catalyst. Reactor temperatures are measured by thermocouples located inside the reactor and then covered by catalyst. The measured temperatures of the system are used to calculate the catalyst average temperature (CAT) in the reactor. Reactors are usually operated at 650-800 °F and 2000 psia with 1.0-hour retention time. Typically the end temperature of a reactor is set at 800-815 °F which is

the metallurgical limit of the reactor. Lower initial temperatures give the reactor a longer activation period (catalyst life). Most hydrocracking catalyst systems require a catalyst life of two years.

There are two types of hydrocracking reactors. The first type is called a hydrotreating reactor. The hydrotreating reactor was designed to reduce the amount of sulfur and nitrogen, hydrogenate the unsaturated feed molecules and produce some cracking.

The second type is called a hydrocracking reactor. The hydrocracking reactor was designed to make products by cracking the big feed molecules into smaller product molecules. In the hydrocracking systems where both types of reactors are used, the hydrocracking reactor follows the hydrotreating reactor. The catalyst for either reactor allows the reaction to initiate at a lower temperature and prevents the larger hydrocarbons from burning (thermal degradation). Catalyst deactivation was a major concern because it slows down the reaction of feed to products. Deactivation depends on the rate of catalyst deactivation and loss of available active sites.

There are three proposed descriptions of catalyst deactivation [1]. First there is poisoning, which occurs when sulfur, nitrogen and/or metals impurities contaminate the active site of the catalyst and prevent large hydrocarbons from adsorbing on to the catalyst surface. This deactivation mode is avoided by removing the sulfur, nitrogen and metals from the vacuum gas oil (VGO) feed. This is accomplished by passing the VGO feed over a demetalizing, sulfur removing (HDS) and nitrogen removing (HDN) catalyst.

The second type is sintering, which involves changes in the lattice structure of the catalyst. Sintering clogs catalyst pores and causes a large pressure gradient across the catalyst bed. The high pressure produces strain in the catalyst bed structure and crushes the catalyst.

The third type is called coking and fouling and is caused by the adsorption and retention of aromatic compounds on the active sites of the catalyst. Coking and fouling inhibits the adsorption of other feed components from adsorbing on the active sites and inhibits hydrogenation of the unsaturated compounds. This adsorption also produces polycyclic aromatic (PNA) compounds, which cause the catalyst to degrade further and slows down the hydrocracking reaction. The undesired PNA production is part of the coking and fouling path.

Development of the Deactivation Kinetics:

The governing equation for catalyst deactivation must be developed to understand how the deactivation process behaves. The deactivation of the catalyst can be expressed as the following equation:

$$- da/dt = k_d a^n \quad (1)$$

Where a is the activity, t is the time, k_d is the rate constant and n is the kinetic order.

The deactivation rate equation, the decrease of catalyst activity with time, can be developed using the overall reaction $A \rightarrow B$ shown in Figure 2. [2]

Adsorption Reaction Transformation Reaction Desorption Reaction Poison Reaction

Figure 2. Hydrocracking Reactor Reaction

The reaction of A to B occurs in several steps. The reaction begins with an adsorption reaction. The adsorption reaction occurs when a feed compound (A) combines with an active site (S) to produce an intermediate state (AS). The intermediate state reacts to form the product (BS) on the active site (transformation reaction). The transformation product is separated from the active site to produce product (B) and the active site (S). The overall reaction is $\text{A} \rightarrow \text{B}$. The competing reaction of A to B is the production of other compounds that are not B. These reactions produced poison compounds (P) and fouled (deactivated) the catalyst. The poisoning (fouling) reaction

can be a different kinetic order (n) than the product reaction. Equation 1 for the deactivation reaction can be derived in the following way:

The rate for the adsorption reaction (r_A) is given as:

$$r_A = k_A C_A C_v - k_d C_{As} \quad (2)$$

Transformation reaction (r_t) is given as:

$$r_t = k_r C_{As} \quad (3)$$

Poisoning reaction (r_p) is given as:

$$r_p = k_p (C_v)^n C_p \quad (4)$$

In the above rate expressions, C_v is the concentration of active sites and is equal to $C_m - [C_{ps} + C_{As} + C_{bs}]$, where C_m is the total number of active sites, C_{ps} is the number of poison sites, C_{As} is the number of feed sites, C_p is the concentration of poison, and C_{bs} is the number of product sites. The reaction rate constants are: $k_{\text{absorption}}$ (absorption of A), $k_{\text{desorption}}$ (desorption of A), k_r (transformation) and k_p (poison).

For rate of adsorption reaction, a quasi-steady state is assumed and $r_A = 0$.

Substituting Equation 4 into Equation 2 gives:

$$0 = k_A C_A * (C_m - [C_{ps} + C_{As} + C_{bs}]) - k_d * C_{As} \quad (5)$$

Which rearranged gives an equation for C_{As} :

$$C_{As} = (k_A C_A / k_d) (C_m - [C_{ps} + C_{bs}]) \quad (6)$$

Substituting Equation 6 into Equation 3 gives an expression for the reaction rate equation:

$$r_r = k_r \{ (k_A C_A / k_A C_A + k_d) (C_m - [C_{ps} + C_{bs}]) \} \quad (7)$$

Substituting C_v into Equation 4 gives an equation for the poisoning reaction rate:

$$r_p = k_p C_p * (C_m - [C_{ps} + C_{as} + C_{bs}])^n = dC_{ps} / dt \quad (8)$$

Conversion of Reaction Rate Expressions into Function of Activity

Since the rate of poisoning in fixed bed reactors was slow, C_p is equal to C_{pb} (the concentration of the poison) in the liquid phase.

$$C_p = C_{pb} = \text{Constant} \quad (9)$$

The catalyst activity (a) was defined as:

$$a = (C_m - C_{ps}) / C_m = 1 - C_{ps} / C_m \quad (10)$$

Taking the derivative of a with respect to time gives:

$$da/dt = \frac{dC_{ps}/dt}{C_m} \quad (11)$$

Rearrange Equation 11 to defines dC_{ps}/dt :

$$dC_{ps}/dt = da/dt * C_m \quad (12)$$

Substituting Equations 12 into 8, gives Equation 13:

$$- da/dt * C_m = k_p * C_p * (C_m - C_{ps} - C_{As} - C_{bs})^n \quad (13)$$

For C_{As} and $C_{bs} \ll 1$, Equation 13 becomes

$$-da/dt * C_m = k_p * C_p (C_m - C_{ps})^n \quad (13b)$$

Dividing by C_m gives an expression for $-da/dt$:

$$-da/dt = \frac{k_p * C_p * (C_m - C_{ps})^n}{C_m} \quad (13c)$$

Which can be rewritten as:

$$-da/dt = k_p C_p C_m^{n-1} a^n \quad (14)$$

$$\text{Where: } a^n = \left[\frac{C_m - C_{ps}}{C_m} \right]^n$$

$$\text{Defining } k_d = k_p * C_p * C_m^{n-1} \quad (15)$$

Substitute Equation 15 into Equation 14 gives Equation 16:

$$-da/dt = k_d * a^n \quad (16)$$

Equation 16 was the same as Equation 1 as seen above.

II) Literature Search

Of the three types of processes which can contribute to the deactivation of the catalyst, only coking and fouling will be addressed in this thesis. In the report titled *Analysis of Temperature-Time Data for Deactivating Catalyst*, by S. Krishnaswamy and J.R. Kittrell, the coking and fouling deactivation reaction was described as occurring parallel to the desired reactions [3]. This is shown schematically in Figure 3, where the r_b is the rate for the production of the desired products and r_{pa} for the undesired products.

The k_1 is the reaction rate constant for the desired products and k_2 is the reaction rate constant for the undesired reactions. The C_A is the concentration of A in the feed.

Where: r_n - reaction rate, k_n - reaction rate constant, C_A - concentration of reactant (A)

Figure 3. Parallel Deactivation

In the Krishanaswamy report, the temperature and pressure were monitored and controlled in the hydrocracking reactor. As the deactivation of the catalyst proceeded, the temperature of the reactor was increased to maintain a constant conversion of the feed to desired products. A rise in temperature was the indicator of the catalyst deactivation. Pressure was used to regulate the amount of hydrogen available to the catalyst system. Hydrogen saturates the aromatics and other large unsaturated compounds in the feed so that they can be subsequently cracked into smaller compounds. The pressure was held constant throughout each run. In these runs, the feed was continuously fed into a hydrocracking reactor. During the run, temperature was adjusted to maintain a constant 60% conversion of compounds boiling below 700 °F from feed to products. As the run proceeded, deactivation occurred and the temperature of the reactor was elevated to maintain conversion.

Model for the Time-Temperature Data Analytical Solution

An analytical solution was developed by Krishnaswamy and Kittrell to relate deactivation reaction of the catalyst, hydrocracking reaction and temperature to fit the data [4]. Equation 17 was a way of presenting deactivation in terms of temperature as a function of time.

$$T = [\ln (1-t /z)/ Q + 1 / T_0]^{-1} \quad (17)$$

The derivation of Equation 17 is based on the deactivation rate equation defined as in Equation 1 where (a) is the fractional catalyst activity, k_d is the deactivation rate constant and (n) is the order of reaction. The derivation of this equation was shown above.

$$-da/ dt = k_d a^n \quad (1)$$

An Arrhenius Equation for Equation 1 was shown in Equation 18 where A_d was the preexponential factor for deactivation, 1/hr, E_d was the activation energy for deactivation, calories/mole, R is the gas constant, and T was the temperature in degrees Kelvin.

$$k_d = A_d \exp (-E_d/ RT) \quad (18)$$

The cracking reaction in the Krishnaswamy paper was assumed to be an irreversible reaction. There was constant conversion of A to B so Equation 19 proves

true, where k_0 was the initial reaction rate constant at the start of the run temperature (SOR) and $k(T)$ was the observed reaction rate constant, at Temperature T , and $T < T_0$.

$$k(T) = a(T) k_0 \quad (19)$$

Inserting $k(T)$ and k_0 into Equation 17 gives the Arrhenius Equation for the two reaction rate constants. Where A_A , was the preexponential factor for the primary reaction and was set equal to 0.52×10^{12} , hr^{-1} and E_A was the activation energy for the reaction and was set equal to 30000 cal/g-mol [5]. T_0 , was the initial set temperature (SOR) in degrees Kelvin.

$$k_0 = A_A \exp(-E_A / RT_0) \quad (\text{at } T=T_0) \quad (20a)$$

$$k = A_A \exp(-E_A / RT) \quad (20b)$$

Combining Equations 20a and 20b with Equation 19, provides the expression for $1/T$ (Equation 21) and a (Equation 22):

$$1/T = (R/E_A * \ln a) + 1/T_0 \quad (21)$$

$$a = \exp\{E_A/R * (1/T - 1/T_0)\} \quad (22)$$

From Equation 21 and Equation 18, k_d was related to a as:

$$k_d = A_d \exp [((-E_d/E_A) \ln a) - E_d/RT_0] \quad (23)$$

Substituting k_d into Equation 1 provides:

$$-da/dt = A_d \exp [((-E_d/E_A) \ln a) - E_d/RT_0] a^n \quad (24)$$

Integration of Equation 24 provided:

$$t = \frac{\exp(E_d/RT_o)}{A_d((E_d/E_A) - n + 1)} [1 - a^{((E_d/E_A) - n + 1)}] \quad (25)$$

The limits for Equation 24 are t ranges from, 0 to t ; T ranges from, T_o to T ; a ranges from, 1 to a .

Herein the initial catalyst activity was assumed to be unity.

Substituting Equation 20 into Equation 24 provides the relationship between t and T :

$$t = \frac{\exp(E_d/R * T_o)}{A_d ((E_d/E_A) - n + 1)} \{ [1 - \exp[\{ (E_d - n * E_A + E_A) / R \} (1/T - 1/T_o)]] \} \quad (26)$$

Rearranging Equation 26 provides, where z is equal:

$\exp ([E_d / R T_o] / A_d \{ (E_d / E_A) - n + 1 \})$, and Q is equal to $(E_d - n * E_A + E_A) / R$.

$$T = [\ln (1 - t / z) / Q + 1 / T_o]^{-1} \quad (17)$$

Inspection of Equation 17 will determine its application. In industry, the hydrocracking reaction was assumed to be first order ($n = 1$) and z and Q are simplified:

$$z = \exp[E_A / (A_d * R * T_o)]$$

$$Q = E_d / R$$

In Equation 17, T , T_o and (t) are experimentally provided to the catalyst system, but feed properties, and pressure are not specified. Equation 17 was used with (n) equal

to 1 to model the data. In determining the limits of Equation 17, certain special cases were explored:

- 1) When n is equal to 2.
- 2) When E_A is much larger than E_d .

For the case where n is equal to 2, the z and Q are changed to:

$$z = \exp[E_A/(R \cdot T_o)] / ((A_d \cdot (E_d/E_A)) - 1)$$

$$Q = (E_d - E_A) / R$$

Equation 17 will increase at a faster pace because of the subtraction of E_d from E_A .

If E_A is much greater than E_d , then z and Q are changed to:

$$z = \exp[E_d/(RT_o)]$$

$$Q = (E_A (1 - n)) / R$$

When (n) is equal to 1, then Q is equal to 0 that makes Equation 17 invalid.

When (n) is equal to 2, the T_o term is subtracted from the constant that makes the temperature decrease as the reaction proceeds. The reactor should be increasing temperature as the run progresses.

When E_d is much larger than E_A or equivalent to E_A , the calculated z and Q is larger than the $1/T$ and the temperature decreases as the run progresses.

Equation 17 will not work under the following conditions:

- 1) When E_d is much larger than E_A and n is equal to 2.
- 2) When E_d is much larger than E_A .
- 3) When E_d is equivalent to E_A .

Determination of Preexponential Factor(C) and Deactivation Activation Energy

In the Krishnaswamy paper, pilot plant data was used to calculate E_d , the activation energy of the deactivation reaction and A_d , the reaction rate constant, as provided by Equation 10. Equation 25 was written in the following form:

$$t = C (1 - e^{A \cdot Y}) \text{ or } \ln(1 - t / C) = A \cdot Y \quad (27)$$

where C is equal to $\frac{\exp(E_d/R T_0)}{A_d ((E_d / E_a))}$, A is equal to E_d / R , and Y is equal to $(1 / T - 1 / T_0)$.

The constant C was calculated using the following formula:

$$C = (t_1 \cdot t_4 - t_2 \cdot t_3) / [(t_1 + t_4) - (t_2 + t_3)] \quad (28)$$

Where t_1, t_2, t_3, t_4 are corresponding times for the reciprocal temperatures $1/T_1, 1/T_2, 1/T_3, 1/T_4$. The values reported in the paper are listed Krishnaswamy and Kittrell in Table 2. Equation 17 was used with the constant and calculated factors to produce curves that fit the pilot plant data. These plots are shown in Figure 4. The activation energy value is 30,000cal/mole.

Table 2. Deactivating parameters from Krishnaswamy and Kittrell paper. [6]
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Run Number	$T_o, ^\circ R$	$E_d, \text{ cal/g.mol}$	$A_d, \text{ h}^{-1}$
1	1049.0	40592.3	2.4E12
2	1045.0	6715.4	0.43E00
3	1200.0	42145.1	1.54E11
4	1053.0	37581.1	2.08E11
5	1211.0	49833.3	9.00E12
6	1192.0	64988.3	1.35E18
7	1225.0	60015.1	5.84E15
8	1109.0	9681.0	1.36E00
9	1054.0	12948.6	2.63E02
10	1052.0	17187.6	5.07E02

Figure 1. Temperature-time trajectories for deactivating hydrocracking catalyst, runs 1 and 2.

Figure 2. Temperature-time trajectories for deactivating hydrocracking catalyst, runs 3 and 4.

Figure 3. Temperature-time trajectories for deactivating hydrocracking catalyst, runs 5 and 6.

Figure 4. Temperature-time trajectories for deactivating hydrocracking catalyst, runs 7 and 8.

Figure 5. Temperature-time trajectories for deactivating hydrocracking catalyst, runs 9, 10, and 11.

Figure 6. Temperature-time trajectories for deactivating reforming catalyst.

Figure 4. Temperature-Time Trajectories for Deactivating Hydrocracking Catalyst.
Copied from Time-Temperature paper by Ashok Krishna. [7] Permission
Granted

As shown, Equation 17 fits the data. There was a large variance in deactivation energy (E_d) and deactivating pre-exponential factor (A_d), which can be seen in Table 2. This may have resulted in variances between the different runs, but the operating conditions and feed properties were not provided when the calculation was made.

Formation of Polycyclic Nuclear Aromatics (PNA's)

Many mechanisms for coke formation in a hydrocracker are described in literature [8]. Julius Scherizer and A.J. Garia suggested that coking is a complicated process and produces the Polycyclic Aromatics (PNA). A 3-step process for the formation of PNA's produced from benzene through a series of addition reactions via a carbenium intermediate was suggested by Gates et al. [9], and is shown in Figures 5 and 6. The process initiates in a step that involves formation of a carbenium ion seen in Figure 5.

Figure 5. Initiation Step

The carbenium ion was the transition intermediate. If there is a large excess of hydrogen, then the carbenium intermediate becomes saturated and produces cyclohexane, as shown in Figure 6a. The hydrocracker will further process the cyclohexane and crack

into smaller molecules. If there is insufficient hydrogen, then the carbenium ion reacts with the benzene ring adding on to the carbenium ion, as shown in Figure 6b. The propagation continues with the addition of another benzene ring, shown in Figure 6c. The process keeps adding a benzene ring until the molecule reacts with hydrogen to form the PNA compound. The PNA production increases in the hydrocracker because the amount of hydrogen was not enough to saturate the benzene. Higher pressure provides a greater amount of hydrogen, which is available to saturate the aromatics. Saturation of the aromatics is faster at higher temperature. Hydrogen demand in the hydrocracker increases because of the formation of the types of molecules in Figure 6, all of which consume hydrogen.

Figure 6. Propagation Steps for PNA Formation.

III) Thesis Proposal

In this thesis, a curve fitting program was used to apply Equation 17 as an alternative to the analytical solution used in the time-temperature paper. The use of the program makes the following assumptions:

1. The model simplifies the feed, products, and deactivating molecules by lumping them into one type of compound. In the hydrocracking refinery unit, the feed and products consists of many different kinds of compounds.
2. While some of the deactivating compounds are present in the feed, this treatment assumes that there were no deactivating compounds in the feed.
3. The activity (a) in Equation 17 was caused by the overall catalyst deactivation not just the coking and fouling reactions.

The deactivation parameters obtained from the initial data fit will be reinserted into Equation 17 to optimize the fit to the pilot plant data. The data obtained at different temperatures on the same catalyst system will also be treated in this way. The resulting deactivation parameters and the line created by Equation 17 will be analyzed to determine the following:

1. The quality of the fit of Equation 17 to the pilot plant data.
2. The impact of E_A on Equation 17.
3. Compare the reaction rate constant k_A to the deactivation rate constant k_d .
4. The variation in A_d and E_d resulting from the change in pressure.
5. The appropriate kinetics order for each deactivation system.
6. The catalyst life for each system.

Chevron pilot plants will provide the data used in this thesis to test the deactivation model. The pilot plant runs chosen for the thesis had hydrocracking fouling and catalyst deactivation. The pressure simulated accelerated fouling.

IV) Pilot Plant System

Description of Pilot Plant Setup

The Chevron pilot plant system consists of the pilot plant, the catalyst and the feed. The pilot plants all have similar setups, but different catalysts and feeds. Since the catalysts and feeds are proprietary to Chevron, alphanumeric letters will be used to designate each system. The pilot plants are set up to simulate the refineries hydrocracking units. Figure 7 shows the flow diagram for the pilot plant.

The process starts by adding the feed and hydrogen gas simultaneously to the top of the hydrocracking reactor. In the reactor, the combined feed is then stripped of nitrogen and sulfur and the unsaturated molecules are hydrogenated and cracked into products. The product stream is sent to the fractionator and separated into separate product effluents. In the recycle model, part of the product effluent is recycled back to the reactor. Recycled mode, shown in Figure 7, is used when complete conversion of the feed was required.

Figure 7. Flow Diagram of a Pilot Plant.

Types of Hydrocracking Reactor Configurations

There are three types of hydrocracking reactor schemes that are used for the hydrocracking processes shown in Figure 7. The Single Stage Once Through (SSOT) reactor scheme, recycle first stage reactor scheme and second stage reactor scheme.

These types of hydrocracking reactors are described in the introduction section.

In the SSOT scheme the feed is passed over the catalyst bed in the reactor only once. The advantage of a SSOT reactor scheme is that the polycyclic aromatics (PNA's) do not have a chance to build up. The disadvantage was that there is an incomplete cracking of the feed compounds. This reactor scheme can be used for hydrotreating, and/or hydrocracking depending on the nature of the feed and the catalyst in the reactor.

In recycle first stage reactor scheme, some of the bottom product coming off the fractionator was recycled back to the reaction section. This is shown in Figure 7. The advantage of the recycling scheme is that all the feed is cracked to product. The disadvantage of the recycling reactor is that the PNA's build up quickly and deactivate the catalyst.

In the second stage reactor scheme, a first stage once-through reactor treats the feed before it goes to the second stage recycle reactor. The advantage of the second stage reactor is the extension of catalyst life. The disadvantage is the capital investment and added complexity. Each type of scheme is used for this thesis.

Catalyst

The catalyst used in the reactor is the platform for the reactions. Catalysts are designed to promote reactions at a lower temperature. The lattice structure of the catalyst consists of interconnecting Al/Si units. Reactions occur on active sites that are located both inside and outside of the lattice structure. Hydrocracking catalysts are bi-functional, and reactions occur at two types of active sites. One type is the metal site, which hydrogenates the aromatic and other unsaturated hydrocarbon compounds in the feed. The other is the acid site, which cracks the large hydrocarbon compounds into smaller ones. There two types of acid sites are the Lewis acid sites, such as the cavities in the matrix of the Al_2O_3 and the Bronsted acid sites, or zeolite catalyst. Both types of catalyst functions were selected to increase the amount of middle distillate (b.p. 350-550 °F). Middle distillates are the kerosene and whole diesel products.

Feeds

The feeds used in this study come from two sources. One source is from an upstream processing unit, which is the first unit in the processing of crude oil. This unit was called a residue unit and serves to remove water, metals, and large particulate in the crude oil, as well as to reduce the amount of nitrogen and sulfur. The product from this residue unit is called de-sulfurized vacuum gas oil and is used in hydrocracking reactors. The second type of feed is called a clean service feed and is used in the second stage.

Both the resid unit and the first stage unit have processed this clean service feed. Feeds are categorized by the following properties:

1. Total Boiling Point Curve (TBP)
2. API (function of Specific Gravity)
3. Nitrogen and Sulfur Content
4. Saturates (Paraffin's), Naphthalenes, and Aromatics content.
5. Polycyclic Aromatics (PNA) Content.

The TBP curve is an indication of the amount of higher boiling compounds in the feed. Figure 8 shows an example of a TBP curve. The portion of the feed that is easier to process was the liquid boiling below 700 °F. The portion of the feed boiling above 700 °F will require higher temperature and more hydrogen to process.

Removal of nitrogen containing compounds in the feed is important because these compounds deactivate the catalyst and render them inactive and consume hydrogen. Nitrogen is removed from the feed by reacting with hydrogen to produce ammonia gas.

Removal of free sulfur and sulfur containing compounds in the feed is important because it deactivates the catalyst acid sites and also consumes hydrogen. The sulfur consumes hydrogen to produce H_2S gas, which is removed from the system by diffusing out of the catalyst matrix.

A low API number indicates a high content of large compounds that need to be cracked. The API number was used to screen potential catalysts since some catalysts can't withstand the heat required to crack the bigger compounds. Aromatics in the feed

have to be saturated with hydrogen before they can be cracked into products. The aromatic molecules are categorized by size; aromatics with one or two rings, those with three to five rings, and those with five or more rings (PNA). The PNA with a greater number of rings require more hydrogen to saturate the compound. PNA compound called coronene was especially monitored because it was very effective in deactivating the catalyst. In refinery terms, the production of Coronene is called “Red Death”. The structure of the Coronene molecule is shown in Figure 9. The feed properties and operating conditions of each catalyst system used in this thesis are summarized in Table 3. The values of nitrogen, API gravity, sulfur, LHSV, and H_2 pressure are explained in the previous section. According to a Chevron expert, the hydrogen partial pressure was calculated by multiplying the total pressure by 0.90 [10]. The pilot plant run pressures were unclear on whether the pressure was hydrogen partial pressure or absolute pressure. The thesis viewed the pressures in the pilot plant runs as absolute pressure. The PCI value indicates the amount of aromatic compounds with five rings or more present in the feed. The EP value is the end point of the feed distillation curve. The Per Pass Conversion (PPC) values are the conversion of the feed that occurs below a designated boiling point per pass through the catalyst bed in a recycle scheme.

Table 3. Feed Properties for Catalyst Systems A,B,C,D.

Catalyst System	Nitrogen, ppm	Gravity API	EP	PCI, ppm	LHSV	PPC	Pressure, H ₂
A							
	1.2	NA	810	40	1.5	60% <500 °F	900
							720
							585
B							
	1.2	NA	910	40	1.4	75% <380 °F	1000
							800
C							
	NA	33.6	987	NA	NA	NA	2000
							1600
							1150
D							
	NA	33.6	987	NA	NA	NA	1597
							1418
							1188

Figure 8. A typical Total Boiling Point Curve.

Figure 9. Structure of Coronene

Time vs Temperature Data

From the Chevron pilot plants showed the temperature during a run was a measure of the deactivation of the catalyst system, since the system temperature was raised to maintain the required conversion of feed to products. The required conversion for the reactor employed in this study was 60% conversion at temperatures < 700°F. This means that 60 % of the compounds that boil below 700°F must be converted to product. The rise in temperature was different at each different pressure because the amount of hydrogen available to the system varies. The Catalyst Average Temperature (CAT) used in this thesis was calculated for one type of catalyst per system. The CAT temperature was the average temperature of the catalyst bed.

LHSV and Pressure

The objective of the catalyst system was to optimize the conversion of feed to products and to saturate the aromatic and unsaturated compounds. This was accomplished by varying operating conditions of the reactor. The important operating

conditions were liquid hourly space velocity (LHSV) and pressure. LHSV has units of time^{-1} and is the inverse of the time the feed stays in contact with the catalyst. A lower LHSV produced longer contact times and produced more reaction. The LHSV was the same for all cases to maintain a constant contact time. The pressure of the system was a measure of the amount of hydrogen in the system. The hydrogen moves the fluid through the pilot plant reactor, which affects the LHSV and reacts with the aromatic and unsaturated compounds. At the higher pressures, the contact time with the catalyst was shorter, but more hydrogen saturation occurs.

Pilot Plant Runs

For each pilot plant run, provided by Chevron, the data from the rolling chart paper was transcribed into an excel spreadsheet. In general, the pilot plant runs at higher pressures were longer than runs at lower pressures. The data for each system are shown as excel spreadsheets in the Appendix A. The summaries for the runs are found in Table 4. The delta temperature at the higher pressures was lower than the lower pressures except for system D and the temperature- time ratio at higher pressures was about 1000 times less than lower pressures.

System A: Runs for the system A pilot plants were made using pressures of 1000, 800 and 650 psia. The temperature changes during runs are shown in Figures 10, 11, and 12, respectively.

Figure 10. Pilot plant run of System A at 1000 psia

Figure 11. Pilot plant run of System A at 800 psia

Figure 12. Pilot plant run of System A at 650 psia

System B: Runs for the system B pilot plant plots were made using pressures of 1000 and 800 psia. The temperature change during the runs is shown in Figures 13 and 14.

Figure 13. Pilot plant run of System B at 1000 psia

Figure 14. Pilot Plant Run of System B at 800 psia

System C: Runs for the system C pilot plant plots were made using hydrogen partial pressures of 2000, 1600 and 1150 psia. Temperature change during the runs is shown in Figures 15, 16, 17, and 18. Figure 15 shows the whole run at 2000 psia. From 0 to 40 hours, the pilot plant was adjusting to new conditions. Figure 16 shows the pilot plant temperature increase, from 50 to 120 hours, due to the deactivation of the pilot plant. Figure 16 was used as the data for 2000 psia. The plots at 2000 and 1600 psia were similar to systems A and B. The plot for 1150 started out with the same trend as 2000 and 1600 psia, but the temperature rate increased as the run proceeded. The accelerated catalyst fouling at the end of run caused the increased temperature rate.

Figure 15. Pilot plant run of System C at 2000 psia

Figure 16. Pilot plant run of System C at 2000 psia from 50 to 210 hours

Figure 17. Pilot plant run of System C at 1600 psia

Figure 18. Pilot plant run of System C at 1150 psia

System D: Runs for the system D pilot plant plots were made using pressures at 1774, 1576 and 1320 psia. The temperature change during the run is seen in Figures 19 thru 23. The plots at 1774 (Figure 19) and 1576 psia (Figure 20) were similar to system C. The plot for 1320 (Figure 21) started with the same trend as 1774 and 1576 psia, but

the temperature rate increased as the run proceeded. The plot for 1320 psia was split into two different plots. The first plot, run hours 0 to 190, had temperature increase similar to 1774 and 1576 psia. This is seen in Figure 22. The middle part of the plot, hours 200 to 320, shows the system in transition from a lower to a higher deactivation rate. The second plot, run hours 330 to 430, shows the temperature rate increasing to the end of run. This is seen in Figure 23. The accelerated catalyst fouling caused the increase in temperature rate.

Figure 19. Pilot plant run of System D at 1774 psia

Figure 20. Pilot plant run for System D at 1576 psia

Figure 21. Pilot plant run for System D at 1320 psia and run hours from 0 to 430 hours.

Figure 22. Pilot plant run for System D at 1320 psia and run hours 0 to 190 hours.

Figure 23. Pilot plant run for System D at 1320 psia and run hours 330 to 430.

Table 4. Summary of Pilot Plant Data.

System	Pressure, PSIA	T _i , °F	T _f , °F	Delta Temperature	Time, Hrs.	Delta T/Time
A	1000	570	575	5	1650	0.003
A	850	610	613	3	350	0.009
A	650	638	687	49	170	0.290
B	1000	572	574	2	1200	0.002
B	800	586	595	9	700	0.013
C	2000	689	695	6	160	0.038
C	1600	697	702	5	340	0.015
C	1150	730	820	90	270	0.334
D	1774	660	688	28	2800	0.010
D	1576	688	692	4	660	0.006
D	1320	708	760	52	430	0.121

V) Data Preparation and The Curve Fitting Program

This chapter describes how the data was prepared for analysis using the hydrocracking model. Data obtained from the pilot plant studies are; feed properties, operating conditions, and the time against temperature data. The monitoring system for the pilot plants is computer-based, which records temperatures, pressures, and calculates Catalyst Average Temperature (CAT) as well as other parameters at constant time intervals. The monitoring system plots the data in intervals of minutes to hours. The pilot plant engineer continuously checks the performance of the pilot plant. The engineer monitors the temperature in the reactor to maintain the right conversion and instructs the pilot plant operator of any changes required in the pilot plant. Pilot plants are manned on a 24 hour basis and cost about \$1000 a day to operate.

Data Treatment

A curve fitting program was used to solve Equation 17. Table Curve 2D is a software program developed by Jandel Scientific. This program is a 32-bit Windows application curve fitting program. It requires that the data be entered in a certain format that is then used by the Table Curve 2D. The Chevron pilot plant data was prepared in the following manner:

- 1) The following literature values were entered: E_A (30,000 cal/mole), LHSV (1.0), Pressure (From Chart), and Reaction Order (n).
- 2) The time-temperature data from the chart paper was entered into an Excel spreadsheet.

- 3) The SOR temperature was entered as T_o .
- 4) The initial time was recorded with the change of pressure in the run.
- 5) The temperatures were converted from $^{\circ}\text{F}$ to $^{\circ}\text{K}$.

$$T = [\ln(1-t/z)/Q + 1/T_o]^{-1} \quad (17)$$

where: $z = \exp([E_d/RT_o]/(A_d\{(E_d/E_A) - n + 1\}))$, $Q = (E_d - nE_A + E_A)/R$

The pilot plant data, Equation 17, R , T_o , n , and E_A is inserted into Table 2D Curve using the programs format. Estimates are entered for A_d and E_d and the program creates a line using Equation 17. The program plots the newly created line against the pilot plant data. If the line is not a good fit, then adjust A_d and E_d until the best fit is found. An example of the spreadsheet is seen in Table 4. Values of the predicted parameters are found in Appendix B. The procedure to use Table Curve 2D software is as follows:

Table 5. Preparing raw data for the software curve-fitting program

	n	1.00					
	Ea	30000.00			5106.21	41558.92	4884.19
	To	572.04					
	Ad	0.38					
	Ed	9700.00					
	R	1.99					
Hydrogen Partial Pressure		900					
Raw Data				Calculated Using Equation 17			
	X	Y		X	1/T	T	Delta
Time, Hours	Time, Normalized	Temperature, °K	Temperature, °F				
200	0	572.04	570.00	0	0.00	572.04	0.00
210	10	572.06	570.03	10	0.00	572.06	0.00
220	20	572.07	570.06	20	0.00	572.07	0.00
230	30	572.09	570.09	30	0.00	572.09	0.00
240	40	572.11	570.12	40	0.00	572.10	0.00
250	50	572.12	570.15	50	0.00	572.12	0.00
260	60	572.14	570.18	60	0.00	572.14	0.00
270	70	572.16	570.21	70	0.00	572.15	0.00
280	80	572.17	570.24	80	0.00	572.17	0.00
290	90	572.19	570.27	90	0.00	572.18	0.00
300	100	572.21	570.30	100	0.00	572.20	0.01
310	110	572.22	570.33	110	0.00	572.22	0.01
320	120	572.24	570.36	120	0.00	572.23	0.01
330	130	572.26	570.39	130	0.00	572.25	0.01
340	140	572.27	570.42	140	0.00	572.27	0.01
350	150	572.29	570.45	150	0.00	572.28	0.01
360	160	572.31	570.48	160	0.00	572.30	0.01
370	170	572.32	570.51	170	0.00	572.31	0.01
380	180	572.34	570.54	180	0.00	572.33	0.01
390	190	572.36	570.57	190	0.00	572.35	0.01
400	200	572.37	570.60	200	0.00	572.36	0.01
410	210	572.39	570.63	210	0.00	572.38	0.01
420	220	572.41	570.66	220	0.00	572.39	0.01
430	230	572.42	570.69	230	0.00	572.41	0.01
440	240	572.44	570.72	240	0.00	572.43	0.01
450	250	572.46	570.75	250	0.00	572.44	0.01
460	260	572.47	570.78	260	0.00	572.46	0.01
470	270	572.49	570.81	270	0.00	572.48	0.01
480	280	572.51	570.84	280	0.00	572.49	0.01
490	290	572.52	570.87	290	0.00	572.51	0.01
500	300	572.54	570.90	300	0.00	572.52	0.01
510	310	572.56	570.93	310	0.00	572.54	0.01
520	320	572.57	570.96	320	0.00	572.56	0.01
530	330	572.59	570.99	330	0.00	572.57	0.02
540	340	572.61	571.02	340	0.00	572.59	0.02
550	350	572.62	571.05	350	0.00	572.61	0.02
560	360	572.64	571.08	360	0.00	572.62	0.02
570	370	572.66	571.11	370	0.00	572.64	0.02
580	380	572.67	571.14	380	0.00	572.65	0.02
590	390	572.69	571.17	390	0.00	572.67	0.02
600	400	572.71	571.20	400	0.00	572.69	0.02
610	410	572.72	571.23	410	0.00	572.70	0.02
620	420	572.74	571.26	420	0.00	572.72	0.02
630	430	572.76	571.29	430	0.00	572.74	0.02
640	440	572.77	571.32	440	0.00	572.75	0.02
650	450	572.79	571.35	450	0.00	572.77	0.02
660	460	572.81	571.38	460	0.00	572.79	0.02
670	470	572.82	571.41	470	0.00	572.80	0.02
680	480	572.84	571.44	480	0.00	572.82	0.02
690	490	572.86	571.47	490	0.00	572.83	0.02
700	500	572.87	571.50	500	0.00	572.85	0.02
710	510	572.89	571.53	510	0.00	572.87	0.02
720	520	572.91	571.56	520	0.00	572.88	0.02
730	530	572.92	571.59	530	0.00	572.90	0.02
740	540	572.94	571.62	540	0.00	572.92	0.02
750	550	572.96	571.65	550	0.00	572.93	0.02
760	560	572.97	571.68	560	0.00	572.95	0.02
770	570	572.99	571.71	570	0.00	572.97	0.02
780	580	573.01	571.74	580	0.00	572.98	0.02
790	590	573.02	571.77	590	0.00	573.00	0.02
800	600	573.04	571.80	600	0.00	573.01	0.02
810	610	573.06	571.83	610	0.00	573.03	0.02
820	620	573.07	571.86	620	0.00	573.05	0.02

Inputting Pilot Plant Data

- 1) Copy the Raw Data X (Time, Normalized) and Y (Temperature, °K).
- 2) Go into the Curve Fitting program and access the **Import Clipboard**.
- 3) Choose the X and Y columns from the **X-Y Data Table**.
- 4) In the **Variable Names and Description** table input the following:
 - a) MainTitle: **Name.wk1**
 - b) X Title: **Time, Hours.**
 - c) Y Title: **Temperature, K.**
 - d) Press OK.
 - e) Save Data.

Inputting Equation 17:

- 1) Access the Enter or Edit User Defined Function (UDF) equation button. ( )
- 2) Enter Equation 17 in the **function box** using the following:
 - i) First Order Treatment
$$EA=30000$$

$$R=1.986$$

$$T0=573.15$$

$$B=EXP(A1/(R*T0))/(A0*(A1/EA))$$

$$Q=A1/R$$

$$Y=1/(LN(1-(X/B))/Q+1/T0)$$

Let $B = z$, $A0 = A_d$ and $A1 = E_d$

ii) Second Order Treatment was the same as first order with B and z having different equations.

$$EA=30000$$

$$R=1.986$$

$$T_0=573.15$$

$$B=\text{EXP}(A_1/(R \cdot T_0))/(A_0 \cdot ((A_1/EA)-1))$$

$$Q=(A_1-EA)/R$$

$$Y=1/(\text{LN}(1-(X/B)))/Q+1/T_0$$

Let $B = z$, $A_0 = A_d$ and $A_1 = E_d$

Running the Program:

- 1) Access the **Import** pull down menu.
- 2) Pick the file from the box.
- 3) The file will show up as a graph of points.
- 4) Access the User Defined Function (UDF) equation button. ( )
- 5) Click the **Read** button.
- 6) Click on the **Firstorder** file.
- 7) Enter the estimate values for A_d and E_d from Table 4 into A_0 (A_d) and A_1 (E_d) of the adjustable parameters.
- 8) Enter the starting temperature (T_0) for each case at different pressure.
- 9) Click on the **Adjust** button. The program will use the adjustable parameters to fit Equation 17 to the inputted data. The graph should look like Figure 26.

- 10) If the equation line does not fit the data, then adjust A_d (AO) and E_d (A1) until the line fits the data.
- 11) To save the final fit, click on the **Fit UDF** button.
- 12) Save the Graph as an **Excel** file.
- 13) Repeat Steps 5 through 12 for the **Secondorder** file in the read button.
- 14) Repeat steps 5 through 13 for each pressure and system.

This data treatment was performed on all the pilot plant data.

The inset in Figure 24 of statistical values shows an example of the statistics calculated by the curve-fitting program for the example in Figure 24 where: r^2 is The Coefficient of Determination, DF Adj r^2 is Degree of Freedom Adjusted r^2 , Fit Std Err is Fit Standard Error (Root Mean Square Regression), and F-statis = F-Statistic. Completed equations for statistical values are given in Appendix C.

Figure 24. Example of the Raw data and line created for Equation 17 using Table 2D

VI) Results

Temperature-Time data were treated for systems A, B, C, and D from the Chevron pilot plants and show the temperature adjustments made during a run to maintain constant conversion. The data is presented in Figures 25 to 40 of temperature against time plots for the various pressures. The data was fit to Equation 17 using the Table Curve 2D curve-fitting program using different reaction orders (n). The fits were used to determine the deactivation parameters, A_d and E_d , and are listed in Tables 6, 7, 8, and 9.

$$T = [\ln(1 - t/z) / Q + 1 / T_o]^{-1} \quad (17)$$

$$\text{where: } z = \exp([E_d / (R * T_o)] / (A_d * \{(E_d / E_a) - n + 1\})),$$

$$Q = (E_d - n * E_a + E_a) / R$$

Data obtained for System A: The process temperature for the runs in System A are plotted against time in Figures 25 through 29. Data was fit using reaction order (n) values of 1 and 2. The calculated line is also included in the figures. As shown Figure 25, the data for the run at 1000 psia is equally well fit by Equation 17. Both for (n) equal 1 and 2, where r^2 was 0.999. This result points to a limitation in the use of Equation 17 that does not permit the discrimination between first and second order behavior. The A_d and E_d values obtained from this fit are effectively equal and have a 95% confidence level. These values are listed in Table 6. The A_d values are near equal, for (n) equal 1 and 2. Thus, the system deactivates at the same rate regardless of the kinetic order.

The data for the run at 800 psia also fit equally well with Equation 17 for both (n) equal 1 or 2 where r^2 was 0.992. This plot is shown in Figure 26. The A_d and E_d values

were again effectively equal and had a 95% confidence level. The E_d values are equal within experimental error for both 800 psia and 1000 psia. The A_d values were again near equal and 100 times bigger than the values for the 1000 psia run. These are listed in Table 6.

Table 6. Summary of the Data for System A at 3 Pressures.

Pressure,psia	SOR Temp., °K	n	Ad, 1/h**	Ed , cal./mole**	r ²
900	572	1	0.3800	9700	0.9992
900	572	2	0.5300	10000	0.9995
720	594	1	0.7800	9700	0.9998
720	594	2	0.8100	9700	0.9999

*SOR = Start of Run, ** = Values have 95% Confidence Level

Data for the run at 650 psia are plotted in Figures 27 through 29 with the corresponding line fits for (n) equal 1 or 2. As can be seen, the fit is good with (n) equal to 1, but not as good with (n) equal 2. Several other values of (n) between 1 and 2 were tested, and it was found that the data fit best using 1.3 where r^2 was 0.9998. The A_d values were 4 times greater at (n) equal 1 and 2 as compared to 1.3. This result is plotted in Figure 28. Plot of the fit generated for (n) equal to 1.6 is shown in the Appendix D.

Figure 25. Plot of the temperature against time obtained from the run at 1000 psia with System A. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

Figure 26. Plot of the temperature against time obtained from the run at 800 psia with System A. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

Figure 27. Plot of the temperature against time obtained from the run at 650 psia with System A. The solid line was calculated from Equation 17 using $n = 1$.

Figure 28. Plot of the temperature against time obtained from the run at 650 psia with System A. The solid line was calculated from Equation 17 using $n = 2$.

Figure 29. Plot of the temperature against time obtained from the run at 650 psia with System A. The solid line was calculated from Equation 17 using $n = 1.3$.

Data from System B: The process temperatures for runs in System B are plotted against time in Figures 30 and 31. The data taken at 1000 and 800 psia, were fit equally well by Equation 17, for both the first and second orders forms. A_d increases and E_A appears to stay unchanged as the pressure decreases. The statistics show that all r^2 are effectively 0.999. This can be seen in Figure 30. The fit values of A_d and E_d are listed in Table 7. Each line fit has a 95% confidence level. The A_d value was lower for the first order reaction than for the second order reaction at 1000 psia, and equal at 800 psia.

Table 7. Summary of the Data for System B at 1000 psia and 800 psia.

Pressure,psia	SOR Temp, °K*	n	A_d , 1/h**	E_d , cal/mole**	r^2
1000	573	1	0.135	9000	0.9986
1000	573	2	3.000	12,5000	0.9993
800	581	1	4.255	11000	0.9991
800	581	2	4.666	11000	0.9991

* SOR = Start of Run, ** = Values have 95% Confidence Level

Figure 30. Plot of the temperature against time obtained from the run at 1000 psia with System B. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

Figure 31. Plot of the temperature against time obtained from the run at 800 psia with System B. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

System B. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

Data from System C: The process temperature for runs in System C are plotted against time in Figures 32 through 35, along with the fitted line calculated from Equation 17. Figure 32 shows that at 2000 psia, the A_d value and E_d value fit equally with both the first and second order treatments, where r^2 is 0.9911-0.9917 for both. The A_d and E_d values obtained from this fit had a 95% confidence for both first and second order treatments and are listed in Table 8. The E_d for the second order reaction model was 300 calories/mole and was higher for the first order reaction model. Again, indicating that more activation energy was required to initiate the deactivation reaction.

At 1600 psia, again the data fit for the first and second order treatment was very good and had r^2 of 0.9998. This is seen in Figure 33. The A_d and E_d values had a 95% confidence level and were experimentally equal for both reaction order models.

Table 8. Summary of Values for System C at 3 Pressures.

Pressure	SOR Temp., °K*	n	A_d , 1/h**	E_d , cal./mole**	r^2
2000	638	1	2.10	10000	0.9911
2000	638	2	2.20	10000	0.9917
1600	643	1	7.80	13000	0.9998
1600	643	2	8.20	13000	0.9994
1150	661	1	8.70	10000	0.9611
1150	661	2	13.80	10000	0.8423

* SOR = Start of Run, ** = Values have 95% Confidence Level

Data taken at 1150 psia is plotted in Figures 34 and 35, along with corresponding line fits, for (n) equal to 1 and 2. The fit was not good with either treatment and additional values of (n) were tested. Plots generated for (n) values of 0.9 and 1.3 did not show any improvement. These plots are found in Appendix E. It appears that the data fit best using (n) equal to 1. The statistics show that the order had a fit of r^2 of 0.9611. The A_d and E_d values are listed in Table 8 and have a 95% confidence level as was found with the data of 2000 psia.

In conclusion, the A_d rate is higher at lower pressure but decreases as the run progresses. The E_d values for first and second order models have a bell shaped curve as the pressure increases with the maximum value on 1600 psia. The start of run temperature for both models is lowered when the pressure is higher.

Figure 32. Plot of the temperature against time obtained from the run at 2000 psia with System C. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

Figure 33. Plot of the temperature against time obtained from the run at 1600 psia with System C. The solid line was calculated from Equation 17 using $n = 1$ and $n = 2$.

Figure 34. Plot of the temperature against time obtained from the run at 1150 psia with System C. The solid line was calculated from Equation 17 using $n = 1$.

Figure 35. Plot of the temperature against time obtained from the run at 1150 psia with System C. The solid line was calculated from Equation 17 using $n = 2$.

Data Obtained for System D: The process temperature for runs in System D are plotted against time in figures 38 through 42, along with the resulting line fit. As shown in Figure 38, the data for the run at 1597 psia, was fit equally well by Equation 17, for both the first and second order reaction models. The statistics for the fit was r^2 of 0.9964 for both. The A_d and E_d values have a 95% confidence level and are the same for both reaction order models. These are listed in Table 9. The data suggests that deactivation proceeds at the same rate for both the first order and second order. Thus, the line produced by Equation 17 was in good agreement with the pilot plant data.

Data for the run at 1418 psia fit well with Equation 17 for both the first and second order reaction models. This is shown in Figure 39. The statistics for the fit was r^2 of 0.9988 for both. The A_d and E_d values have a 95% confidence level, as was the case for the run at 1597 psia. The A_d and E_d values are listed in Table 9. The A_d values and the E_d values were the same for both reaction models.

Data taken at 1188 psia was treated in two parts. The first part of the reaction, 0 to 190 run hours, is shown in Figure 40. In this case, the deactivation rates were smaller than the rates found with 1597 and 1418 psia. The time interval between 190 hours and 330 hours was not treated. The portion from 330 to 430 run hours was treated and is shown in Figure 41. This deactivation rate was larger than the plot for 0 to 190 hours.

Table 9. Summary of values for System D at 3 Pressures from time 0 to 190 hours and 330 to 430 hours

Pressure, psia	SOR Temp., °K*	n	Ad, 1/h**	Ed, cal./mole**	r ²
1597	622	1	4.80	12500	0.9964
1597	622	2	6.10	12500	0.9963
1418	638	1	5.30	13500	0.9988
1418	638	2	5.40	13500	0.9999
1188	660				
(0-190) hrs.	660	1	1.00	10000	0.9992
(0-190) hrs.	660	2	1.00	10000	0.9927
(330-430) hrs.	660	1	9.50	10000	0.9272
(330-430) hrs.	660	2	11.50	10000	0.8831

* SOR = Start of Run, ** = All values have a 95% Confidence Level

The data taken at 1188 psia, from run time 0 to 190 were well fit with Equation 17, although the second order reaction model fit better than the first order. This is seen in Figure 40. The statistics show that both orders had a fit with r^2 of 0.999. The A_d and E_d values had a 95% confidence level, as was the case with 1597 psia. The A_d and E_d values are listed in Table 9. The A_d and E_d values were the same for both models. Figure 43 shows plots for (n) equal to 1 and Figure 44 shows the plot for (n) equal to 2.

Data from run time 330 to 430 hours is plotted in Figure 41 and Figure 42, with corresponding line fits for (n) equal to 1 and 2. As shown, the fit was not good for either reaction, thus additional fits were tried. The plots for (n) equal to 0.9 and 1.3 are shown in the Appendix E. It appears that the data was best fit when using (n) equal to 1. The A_d and E_d values from (n) equal 1 are listed in Table 9. The statistics show that the

fit had r^2 of 0.9272, and there was a 95% confidence level for these values. Figure 45 shows plots for (n) equal to 1 from Table 9.

Figure 36. Plot of temperature against time from the run at 1597 psia and the line from Equation 17 for $n = 1$ and $n = 2$.

Figure 37. Plot of temperature against time from the run at 1576 psia and the line from Equation 17 for $n = 1$ and $n = 2$.

Figure 38. Plot of temperature against time from run hours 0 to 190 hours at 1320 psia and the line from Equation 17 for $n = 1$ and $n = 2$.

Figure 39. Plot of temperature against time from the run hours 330 to 430 hours at 1320 psia and the line from Equation 17 for $n = 1$.

Figure 40. Plot of temperature against time from run hours 330 to 430 hours at 1320 psia and the line from Equation 17 for $n = 2$.

In summary, the A_d rates for the reactions at all pressures tested are slow. A_d rates were faster at lower pressure. A higher start of run temperature was needed when the pressure was lower. The E_d increases to a maximum then decreases as the pressure continues to increase. The highest E_d value was found at ~1418 psia for both orders. For run time 0 to 190 hours, the fit was the same at (n) equal 1 or n equal to 2. For the run time of 330 to 430 hours, the best fit was found with (n) equal to 1. An increase in the rate of temperature change was seen in the 330 to 430 hour interval. This would indicate that the catalyst was deactivating faster during the latter part of the run.

VII) Discussion

Introduction

This discussion addresses seven points; the appropriateness of Equation 17 for treating the raw data, the impact of E_A value on A_d and E_d values, the selection of (n) either 1 or 2, comparison of k_d , k_A and k_A/k_d , and the relationship of A_d , E_d , and pressure, the relationship of k_A/k_d to temperature, and to calculation of catalyst life for each system.

The appropriateness of Equation 17 as a model for the raw data was evaluated by the fitness parameter r^2 . Complete listings of r^2 values are found in Appendix B and are also listed in the last column of Table 11. The closer the r^2 value is to unity, the better the fit of the pilot plant data to the model. The r^2 values for the four systems ranged between 0.999-0.8831.

In general, the fits were good at higher hydrogen pressures for each system. An example of this fit is shown in Figure 46, which is System C at 2000 psia hydrogen pressure. As seen in this plot, there was a constant slow rise in reactor temperature indicating a steady slow deactivation of the catalyst. Bad fits were found for systems C and D at lower pressures of 1188 and 1150 psia. The plot in Figure 46, for System C at 1150 psia, is an example of a bad fit. As shown, the temperature rise is faster than at 2000 psia. In this run, the temperature rise was linear from 0 to 90 hours of the run, but then the rise accelerates beyond linearity from 100 hours to the end of the run. Two different linear lines were fit for two different periods of time. At the lower pressures, the lower amount of hydrogen available to the feed, as well as the formation of PNAs,

can cause an accelerated rise in the rate of the reaction temperature. Equation 17 accounts for the increase in temperature required to maintain a constant conversion of feed, but not for a system where the temperature rise is not constant.

Table 10. The Summary Calculated of A_d and E_d using Pilot Plant Data.

Pressure, psia	SOR** Temp., °K	n	** A_d , 1/h	** E_d , cal/mole	r^2
System A					
1000	572.0	1	0.38	9700	0.9992
850	594.3	1	0.78	9700	0.9998
650	609.8	1	21.10	10000	0.9919
1000	572.0	2	0.53	10000	0.9995
850	594.3	2	0.81	9700	0.9999
650	609.8	2	27.50	9800	0.9877
System B					
1000	573.2	1	0.14	9000	0.9986
800	580.9	1	4.26	11000	0.9992
800	580.9	2	3.00	11000	0.9994
1000	573.2	2	4.67	9000	0.9993
System C					
2000	689	1	2.10	10000	0.9911
1600	730	1	7.80	10000	0.9611
1150	697	1	12.00	13000	0.9998
2000	730	2	5.80	10000	0.9917
1600	697	2	8.20	13000	0.9994
1150	689	2	13.80	13000	0.8423
System D					
1774	622	1	4.80	12500	0.9964
1576	638	1	5.30	13500	0.9988
1320***	660	1	5.00	9940	0.9272
1774	622	2	6.10	12500	0.9963
1576	638	2	5.40	13500	0.9999
1320	660	2	11.50	9000	0.8831

** = Equation 17 and $E_a = 30,000$ Cal/Mole, *** = Run Hours 330 to 430

Figure 41. Comparison of Line fit of Data at 2000 psia to Data at 1150 psia for System C.

Impact of E_A on the Design Equation

The design equation (Equation 17) has only three variables. The activation energy of hydrocracking (E_A), pre-exponential (A_d) and the activation energy of deactivation (E_d). In this equation (z) equals $\exp [E_d / R * T_o] / (A_d \{ (E_d / E_A) - n + 1 \})$ and Q equals $(E_d - n * E_A + E_A) / R$:

$$T = [\ln(1 - t / z) / Q + 1 / T_o]^{-1} \quad (17)$$

In a given run, the hydrocracking activation energy (E_A) establishes the pre-exponential (A_d) and relates to how fast the system reaches the final deactivation temperature. The temperature values from Equation 17 start with the initial time and temperature (SOR) and end with final time and temperature (800°F)[8]. As shown in Table 12 each system deactivated more quickly in an environment where the hydrocracking activation energy (E_A) was high.

In Equation 17, the values for rate constant and the activation energy of deactivation were selected to fit the pilot plant data. The 30,000 cal/mole is used for E_A and value was chosen because most hydrocracking reactions activate at 30,000 cal/mole [11]. To determine the effect of a higher E_A on E_d , A_d , and the quality of the fit, the data was again fit by Equation 17 using the following E_A values; 20,000 cal/mole, 40,000 cal/mole, 50,000 cal/mole, and 60,000 cal/mole. Equation 17 adequately provided the deactivation parameters and the results are shown in Table 11. At the high pressure conditions, r^2 did not significantly change. As shown in Table 11 the activation energy of deactivation (E_d) was not affected in any of the cases when E_A was varied. However, the

pre-exponential (A_d) increased in every case when the E_A was increased. The A_d values were higher when the run pressure was lower.

Appropriateness of the E_A values was based on A_d since the r^2 values were generally quite high. A lower A_d value means a longer catalyst life, and lower A_d values were generally found when E_A was 20,000 cal/mole. The A_d values increased faster for second order than first order fits. In System C at the 1150 psia and (n) equal 2, the catalyst deactivated faster and significantly reduced catalyst life.

Table 11. Results from varying the E_A value on the quality of the fit to Equation 17.

System A					
Pressure	Order	E_A	r^2	A_d	E_d
1000	1	20000	0.9985	0.26	9700
	1	30000	0.9992	0.38	9700
	1	40000	0.9997	0.51	9700
	1	50000	0.9999	0.64	9700
	1	60000	0.9999	0.77	9700
	2	20000	0.9993	0.35	10000
	2	30000	0.9995	0.53	10000
	2	40000	0.9983	0.73	10000
	2	50000	0.9989	0.91	10000
	2	60000	0.9985	1.10	10000
850	1	20000	0.9988	0.28	9000
	1	30000	0.9998	0.78	9700
	1	40000	0.9999	1.05	9700
	1	50000	0.9998	1.30	9700
	1	60000	0.9986	1.60	9700
	2	20000	0.9985	0.51	9700
	2	30000	0.9999	0.81	9700
	2	40000	0.9994	1.10	9700
	2	50000	0.9982	1.40	9700
	2	60000	0.9977	1.70	9700
650	1	20000	0.9916	14.20	10000
	1	30000	0.9919	21.10	10000

	1	40000	0.9916	28.00	10000
	1	50000	0.9916	35.00	10000
	1	60000	0.9762	40.00	10000
	2	20000	0.9956	16.30	9800
	2	30000	0.9877	27.50	9800
	2	40000	0.9729	42.00	9800
System B					
Pressure	Order	E_A	r^2	A_d	E_d
1000	1	20000	0.9951	0.09	9000
	1	30000	0.9986	0.14	9000
	1	40000	0.9997	0.19	9000
	1	50000	0.9999	0.23	9000
	1	60000	1.0000	0.28	9000
	2	20000	0.9954	1.88	12500
	2	30000	0.9993	3.00	12500
	2	40000	0.9983	4.00	12500
	2	50000	0.9969	5.00	12500
	2	60000	0.9951	6.00	12500
800	1	20000	0.9999	3.05	11000
	1	30000	0.9992	4.26	11000
	1	40000	0.9995	5.70	11000
	1	50000	0.9993	7.10	11000
	1	60000	0.9996	8.60	11000
	2	20000	0.9994	3.10	11000
	2	30000	0.9994	4.67	11000
	2	40000	0.9980	6.50	11000
	2	50000	0.9973	8.30	11000
	2	60000	0.9958	10.20	11000
System C					
Pressure	Order	E_A	r^2	A_d	E_d
2000	1	20000	0.9923	1.40	10000
	1	30000	0.9911	2.10	10000
	1	40000	0.9923	2.80	10000
	1	50000	0.9923	3.50	10000
	1	60000	0.9923	4.20	10000
	2	20000	0.9932	1.45	1000
	2	30000	0.9917	2.20	10000
	2	40000	0.9935	3.00	10000
	2	50000	0.9934	3.80	10000
	2	60000	0.9930	4.60	10000

1600	1	20000	0.9994	5.20	13000
	1	30000	0.9998	7.80	13000
	1	40000	0.9986	9.90	13000
	1	50000	0.9989	12.50	13000
	1	60000	0.9986	15.10	13000
	2	20000	0.9999	5.35	13000
	2	30000	0.9994	8.20	13000
	2	40000	0.9955	12.00	13000
	2	50000	0.9944	15.50	13000
	2	60000	0.9929	19.00	13000
1150	1	20000	0.9611	5.80	10000
	1	30000	0.9611	8.70	10000
	1	40000	0.9611	11.60	10000
	1	50000	0.9611	14.50	10000
	1	60000	0.9604	17.60	10000
	2	20000	0.8839	8.00	10000
	2	30000	0.8423	13.80	10000
	2	40000	0.7755	25.10	10000
	2	50000	0.7629	31.40	10000
	2	60000	0.7261	43.70	10000

System D					
Pressure	Order	E_A	r²	A_d	E_d
1774	1	20000	0.9964	3.70	12500
	1	30000	0.9964	4.80	12500
	1	40000	0.9964	6.40	12500
	1	50000	0.9964	8.00	12500
	1	60000	0.9964	9.60	12500
	2	20000	0.9995	3.70	12500
	2	30000	0.9963	6.10	12500
	2	40000	0.9919	8.60	12500
	2	50000	0.9851	11.60	12500
	2	60000	0.9767	15.00	12500
1576	1	20000	0.9997	3.50	13500
	1	30000	0.9988	5.30	13500
	1	40000	0.9997	7.00	13500
	1	50000	0.9999	8.70	13500
	1	60000	0.9998	10.40	13500
	2	20000	0.9999	3.57	13500
	2	30000	0.9999	5.40	13500
	2	40000	0.9997	7.30	13500
	2	50000	0.9997	9.20	13500

	2	60000	0.9993	11.20	13500
1320	1	20000	NA	NA	NA
	1	30000	0.9272	9.50	10000
	1	40000	0.9257	13.00	10000
	1	50000	0.9267	16.00	10000
	1	60000	0.9267	19.00	10000
	2	20000	NA	NA	NA
	2	30000	0.8831	11.50	10000
	2	40000	0.8675	16.00	10000
	2	50000	0.8523	21.00	10000
	2	60000	0.8376	27.00	10000

Relating Pressure to A_d and E_d

While Equation 17 relates A_d and E_d with time and temperature, it does not address the pressure. Figures 42 thru 46 show the relationship between the A_d and E_d values and pressure. Figure 42 shows that above 850 psia, the A_d and E_d values are constant, while below 850 psia the values are higher. E_d slightly increases as the pressure increases. In system B (Figure 43), both A_d and E_d are lower at the higher pressure. In System C (Figure 44), A_d remains fairly constant until 1600 psia but is lower at 2000 psia. The E_d was higher at 1600 psia than at 1100 or 2000 psia. In system D (Figure 45), at 1320 psia from 0 to 190 hours, the A_d and E_d was higher at 1450 psia than at 1200 and 1600 psia. Figure 46 is the run plot for 1188 psia from hours 330 to 430 and showed that A_d was higher at 1450 psia and 1600 psia. There was no more deactivation affect after 1450 psia. The E_d had the same response as Figure 46.

Determination of A_d and E_d Values at Other Pressures

The plots in Figures 42 to 46 can be used to determine A_d and E_d values at other pressures for use in Equation 17. This would apply to systems similar to those described in this thesis. The values could be used in Equation 17 to create time versus temperature data. This procedure would provide the run data and deactivation temperature without requiring pilot plant data.

Figure 42. Plot of A_d , E_d against Pressure for 1st order for System A. Note that 650 psia value used was for $n = 1.3$.

Figure 43. Plot of A_d , E_d against Pressure for 2nd order for System B.

Figure 44. Plot of A_d , E_d against Pressure for 1st order for System C. Note that 1150 psia value used was for $n = 1.0$.

Figure 45. Plot of A_d , E_d against Pressure for run hours 0 to 190 hours System D. Note that 1320 psia value used was for $n = 1.0$.

Figure 46. Plot of A_d , E_d against Pressure for run hours 330 to 430 hours 1st order for System D. Note that 1320 psia value used was for $n = 1.0$.

Relating k_A , k_d , and Temperature

Another measure of deactivation of the catalyst system is comparing the reaction rate constant (k_A) and the deactivation rate constant (k_d). The corresponding Arrhenius Equations for the product reaction (Equation 20a) and deactivation reactions (Equation 18) are shown in Equation 20a and Equation 18, respectively. For this comparison, k_A and k_d were calculated using A_A equal to 0.52×10^{12} 1/hr, E_A equal to 30,000 cal/mole [12], and the n , A_d and E_d from the fits. The A_A value was not the pre-exponential for reaction of any of the four systems, but was used to measure the reaction rate to deactivation rate. These values are listed in Table 12. From these values, k_A , k_d and k_A/k_d were calculated using SOR temperatures for T in Equations 18 and 20a. These values are listed in Table 12. In systems A and B, the log of k_A / k_d became smaller as the SOR temperature became bigger. In systems C and D, the log of k_A / k_d is not linear with temperature. System D had its biggest value at the middle SOR temperature.

$$k_A = A_A \exp (-E_A / RT) \quad (20a)$$

$$k_d = A_d \exp (-E_d / RT) \quad (18)$$

Table 12. Values for calculating k_A and k_d

Pressure,psia	SOR Temp., °K	n	A_d , 1/h	E_d , cal/mole	k_d	k_A	k_A/k_d
System A							
1000	572	1	0.38	9700	0.0001	2	24,636
800	594	1	0.78	9700	0.0002	5	23,381
650	610	1	21.10	10000	0.0056	10	1,715
System B							
1000	573	2	4.67	9000	0.0002	3	12,621
800	581	2	3.00	11000	0.0017	2	1,124
System C							
2000	689	1	2.10	10000	0.0014	164	114,512
1600	730	1	7.80	10000	0.0080	559	69,948
1150	697	1	12.00	13000	0.0010	210	206,031
System D							
1774	622	1	4.80	12500	0.0002	16	78,523

The parameters used in Equation 20a and Equation 18, had a wide range of values. The SOR temperatures ranged between 572 °K to 730 °K. The A_d values ranged from 0.38 to 21.1, hour^{-1} . The E_d values ranged from 9400 to 13,500 calories/mole. The (n) values was 1 for systems A, B, and C and 2 for system B.

In systems A and B, the k_d values were higher and the ratio of k_A/k_d was lower when the pressure was lower. In systems C and D, the intermediate pressure had the highest k_d and k_A/k_d values.

Another measure of catalyst deactivation is comparing the ratio of k_A / k_d and the SOR temperature. Beginning with the Arrhenius Equations (20a and 18) and the ratio of k_A / k_d , the relationship can be written as:

$$k_A / k_d = A_A / A_d \exp (-E_A / R * T) / (-E_d / R * T) \quad (29)$$

or as:

$$2.303 * \log (k_A / k_d) = 1 / T * ((E_A - E_d) / R) + 2.303 * \log (A_A / A_d) \quad (31)$$

Equation 31 is used to calculate the $\log (k_A / k_d)$ and k_A / k_d . These k_A / k_d values can be compared with those in Table 12. These values are listed in Table 13.

Table 13. Calculation of $\log (k_A / k_d)$ from Equation 31 and Table 12.

Pressure, psia	SOR Temp., °K	1/T, °K	n	A_d	E_d	Log k_A/k_d
System A						
1000	572	0.0017	1	0.38	9700	4.21
850	594	0.0017	1	0.78	9700	4.19
650	610	0.0016	1	21.10	10000	3.10
System B						
800	581	0.0017	2	3.00	11000	3.93
1000	573	0.0017	2	4.67	9000	2.93
System C						
2000	689	0.0015	1	2.10	10000	4.85
1600	730	0.0014	1	7.80	10000	4.65
1150	697	0.0014	1	12.00	13000	5.10
System D						
1774	622	0.0016	1	4.80	12500	4.70
1576	638	0.0016	1	5.30	13500	5.13
1320	660	0.0015	1	5.00	9940	4.20

Determination of Kinetic Order

In industry, deactivation reactions are assumed to follow first order kinetics with (n) equal to 1 [13]. To test this assumption, the kinetic order (n) for the deactivation reaction from the best fit (r^2), was further analyzed for compliance with the following characteristics of the A_d and E_d parameters:

- 1) A_d was smaller when the pressure was higher.
- 2) E_d was smaller when the start of run (SOR) temperature was lower.

A_d values that did not change with pressure and E_d values that did not change with SOR temperature were suspect even if the r^2 value was close to 1. The A_d and E_d values are listed in Table 11. The r^2 values are in the last column and the A_d and E_d values are in columns 4 and 5.

Since each system met compliance 1, the order was selected based on r^2 value and compliance 2. For system A, C, and D, (n) equal 1 provided a better fit of the data than (n) equal 2. For system A, the E_d values at (n) equal 1 were consistent with criteria 2, while those with (n) equal 2 were not. For system C, the r^2 value was closer to (n) equal 1 as compared to (n) equal 2 at 1150 psia. For system D, the r^2 value was closer for (n) equal 1 as compared to (n) equal 2 at 1188 psia. The results for system B were different from the others. In this system, the E_d values with (n) equal 2 were consistent with criteria 2, but not with (n) equal 1.

Inconsistencies with criteria 2 each system was caused by the variability in the operation of the pilot plants and not the selection of the A_d and E_d parameters. Since a different run was performed at each pressure the operating conditions could have been different for each run. Any of number of parameters could have caused a change in pilot plant temperature rate.

In contrast with these results, Ashok's paper was able to model both linear and exponential type data using Equation 17 [14]. Ashok's paper split the each run into different regime and calculated a different pre-exponential factor depending on the regime of the graph [17]. The average run times from Ashok's paper ranged from 200 to 3500 hours [15]. The temperature ranged from 590 to 1000 °F [16]. Ashok's paper did not mention the pressures for any of the runs. The feed, catalyst, and operating conditions used in the paper are different than in this thesis. Since the operating conditions were not provided for Ashok's runs, the systems in the paper and the thesis cannot be compared.

Catalyst Life Calculation

Catalyst life is affected by two competing reactions, the production of desired product and the production of deactivation product (PNA's). When hydrogen is plentiful, the feed is converted into desired product, but as the hydrogen depletes, A_d and PNA production increases. Since more energy is required to convert PNA to desired product, the temperature of the system will increase more rapidly. The catalyst life for each system was calculated using Equation 26, and using the SOR temperature for T_o , T equal to 800 °F, E_A was 30,000 cal. / mole, and (n) , A_d and E_d values were determined from data fits. The results are shown in Table 14. The final temperature (700 °K) was based on the integrity limit of the metal used in the reactor [18]. The time to reach the final temperature was considered to be the catalyst life.

$$t = \frac{\exp(E_d / R * T_o)}{A_d ((E_d / E_A) - n + 1)} * \{ [1 - \exp\{ ((E_d - n * E_A + E_A) / R) (1 / T - 1 / T_o) \}] \} \quad (26)$$

Table 14. Catalyst Life values using Equation 28 for Systems A-D. *

Pressure, psia	SOR Temp., °K	n	A _d , 1/h	E _d , cal/mole	Catalyst Life		r ²
					Days	Years	
System A							
1000	572.0	1	0.38	9700	1368	3.75	0.9992
850	594.3	1	0.78	9700	436	1.19	0.9998
650	609.8	1	21.10	10000	15	0.04	0.9919
System B							
1000	573.2	2	3.0	12500	21333	58.45	0.9993
800	580.9	2	4.7	11000	3042	8.33	0.9994

Pressure, psia	SOR Temp., °K	n	A _d , 1/h	E _d , cal/mole	Catalyst Life		r ²
					Days	Years	
System C							
2000	689	1	2.1	10000	127	0.35	0.9911
1600	697	1	7.8	13000	299	0.82	0.9998
1150	730	1	12.0	10000	22	0.06	0.9611
System D							
1774	622	1	4.8	12500	349	0.96	0.9964
1576	638	1	5.3	13500	485	1.33	0.9988
1320	660	1	5.0	9940	21	0.06	0.9231

* The EOR temperature was 700 °K in every case

Catalyst behavior and life was unique for each system. However, the catalyst life was longer in every case when the pressure was higher and the SOR temperatures were lower. System B was the only system where the second order fit was better and the catalyst life had the greatest difference between high and low pressures. Catalyst in Systems C and D had a shorter life and did not follow the trend in the pressure. In system C, the A_d and SOR was higher when the pressure was lower, and E_d was higher at the intermediate pressure. In system D, the SOR was lower at the higher pressure and A_d and E_d had the highest value at the intermediate pressure.

The rate constants (k_A , k_d , k_A/k_d) and catalyst lives are shown in Table 15. When k_A / k_d were higher, the catalyst life was higher. The (A_d) values give an indication of the catalyst life, when A_A was a constant.

Table 15. Combination of Table 12 and Table 13.

Pressure, psia	SOR Temp., °F	n	A_d , $^1/h$	E_d , cal/mole	r^2	k_d	k_A	k_A/k_d	Catalyst Life, Days
System A									
900	572	1	0.38	9700	0.9992	0.0001	1.87	24,636	1368
720	594	1	0.78	9700	1.0000	0.0002	5.00	23,381	436
585	610	1	21.10	10000	0.9999	0.0056	9.54	1,715	15
System B									
1000	573	2	3.00	9000	0.9993	0.0002	2.79	12,621	21333
800	581	2	4.67	11000	0.9994	0.0017	1.96	1,124	3042
System C									
2000	689	1	2.1	10000	0.9911	0.0014	163.53	114,512	127
1600	697	1	7.8	13000	0.9998	0.0080	558.86	69,948	299
1150	730	1	12.0	10000	0.9611	0.0010	210.22	206,031	22
System D									
1597	622	1	4.80	12500	0.9964	0.0002	15.51	78,523	349
1418	638	1	5.30	13500	0.9988	0.0001	28.02	220,821	485
1188	660	1	0.10	9940	0.9231	0.0026	62.13	24,103	21

VIII) Conclusion

Catalyst deactivation is difficult to model because of the complexity of the systems. Feed type, catalyst types, and conditions are all variables in the conversion reactions. The data from four systems were fit to Equation 17 in an attempt to describe them. To fit the data, E_A was set equal to 30,000 calorie/mole and A_A value was set equal to 0.52×10^{12} 1/hr for the product reaction. The system pressures for the runs were between 585 psia and 2000 psia and the SOR temperature ranged between 570 °F and 660 °F. The fit to Equation 17 was made using a curve-fitting program called Tablecurve 2D. The deactivation parameters (n), A_d , and E_d were adjusted in each run until the best fit was obtained as judged by the r^2 value. The A_d values obtained were in the range of 0.38 to 21.1 1/hr. The E_d values obtained ranged from 940 to 13000 calorie/mole. The r^2 value ranged from 0.8831 to 0.9999. There was a set of compliances to test the reality of the results. In most cases, compliance 1 and 2 were satisfied. The E_d values did not satisfy compliance 2, but this did not affect the quality of the fit.

In general, Equation 17 accommodated the pilot plant data and worked well for E_A values between 20,000 to 60,000 cal/mole. The life of the catalyst was calculated using Equation 17 and the experimentally determined values of (n), A_d , E_d , SOR and pressure. With systems A and B, the catalyst life increased with the increase in pressure. There were not enough data points to obtain an equation to describe catalyst life as a function of pressure.

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Appendix A: Definition of Variables

$-da/dt$ = Rate of Activity, activity/hr.

k_d = Rate Constant, production/hr.

n = Order of Kinetics

a^n = Activity of Catalyst

A = Feed molecule A

S = active Site On Substrate

$A-S$ = Molecule of A on S

$B-S$ = Product B on S

B = Product

P = Poison

$P-S^n$ = Poison on S

r_A = Reaction Rate of A, Production of A/time

k_A = Rate Constant of A, 1/hr.

C_A = Concentration of A, grams of a/ ml of Feed

C_v = Concentration of vacant sites, Number of Vacant sites/ area^2 of Catalyst

k_d = Rate of Deactivation, 1/hr.

C_{As} = Concentration of Feed on Active site, # of site/ area^2 of catalyst

r_r = Transformation Reaction, # of sites/ area^2 of catalyst x hr

k_r = Rate of Reaction, 1/hr

r_p = Poisoning Reaction, grams/ml hr.

k_p = Rate of poisoning, 1/hr.

C_p = Concentration of Poison in the bulk Phase, grams/ml of feed

C_m = Concentration of total number of active sites, # of sites/area² of catalyst

C_{ps} = Concentration of poison attached to active sites, # of sites/area² of catalyst

C_{bs} = Concentration of product attached to active sites, # of sites/area² of catalyst

C_{pb} = Concentration of poison in the bulk phase to active sites, grams/ml of feed

r_b = Reaction rate of products, grams B/ ml x hr.

k_1 = Rate constant of hydrocracking reaction, 1/hr.

r_{pa} = Reaction rate of poisoning reaction, grams P/ ml x hr.

k_2 = Rate constant of Poison reaction, 1/hr.

k_d = Rate of Deactivation, 1/hr.

A_d = Pre-exponential of Deactivation, 1/h

E_d = Activation energy of Deactivation, calories/mole

R = Gas Constant, 1.99

T = Temperature, °F or °K

k_A = Rate Constant of A, 1/h

A_A = Exponential of Reaction, 1/hr.

E_A = Activation Energy of Reaction, calories/mole

t_1 = Time of First Point, time

t_2 = Time of Second Point, time

t_3 = Time of Third Point, time

t_4 = Time of Fourth Point, time

T_1 = Temperature of First Point, °F

T_2 = Temperature of Second Point, °F

T_3 = Temperature of Third Point, °F

T_4 = Temperature of Fourth Point, °F

Appendix B: List of Acronyms

API = Function of Specific Gravity

CAT = Catalyst Average Temperature

EP = End Point

HDN = Hydrocracking De-Nitrification Unit

HDS = Hydrocracking Desulfurization Unit

LHSV = Liquid Head Space Velocity

PCI = Polycyclic Index

PNA = Polycyclic Nuclear Aromatics

PPC = Per Pass Conversion

SOR = Start of Run Temperature

SSOT = Single Stage Once Through

TBP = Total Boiling Curve

UDF = User Defined Function

VGO = Vacuum Gas Oil

Appendix C: Raw Data for 4 Systems

System A:

Hydrogen Partial Pressure 900 psia

Time, Normalized	Temperature, °F	Time, Normalized	Temperature, °F
0	570.00	480	571.44
10	570.03	490	571.47
20	570.06	500	571.50
30	570.09	510	571.53
40	570.12	520	571.56
50	570.15	530	571.59
60	570.18	540	571.62
70	570.21	550	571.65
80	570.24	560	571.68
90	570.27	570	571.71
100	570.30	580	571.74
110	570.33	590	571.77
120	570.36	600	571.80
130	570.39	610	571.83
140	570.42	620	571.86
150	570.45	630	571.89
160	570.48	640	571.92
170	570.51	650	571.95
180	570.54	660	571.98
190	570.57	670	572.01
200	570.60	680	572.04
210	570.63	690	572.07
220	570.66	700	572.10
230	570.69	710	572.13
240	570.72	720	572.16
250	570.75	730	572.19
260	570.78	740	572.22
270	570.81	750	572.25
280	570.84	760	572.28
290	570.87	770	572.31
300	570.90	780	572.34
310	570.93	790	572.37
320	570.96	800	572.40
330	570.99	810	572.43
340	571.02	820	572.46
350	571.05	830	572.49
360	571.08	840	572.52
370	571.11	850	572.55
380	571.14	860	572.58
390	571.17	870	572.61
400	571.20	880	572.64
410	571.23	890	572.67
420	571.26	900	572.70
430	571.29	910	572.73
440	571.32	920	572.76
450	571.35	930	572.79
460	571.38	940	572.82
470	571.41	950	572.85

Hydrogen Partial Pressure 900 psia (cont.)

Time, Normalized	Temperature, °F	Time, Normalized	Temperature, °F
960	572.88	1460	574.38
970	572.91	1470	574.41
980	572.94	1480	574.44
990	572.97	1490	574.47
1000	573.00	1500	574.50
1010	573.03	1510	574.53
1020	573.06	1520	574.56
1030	573.09	1530	574.59
1040	573.12	1540	574.62
1050	573.15	1550	574.65
1060	573.18	1560	574.68
1070	573.21	1570	574.71
1080	573.24	1580	574.74
1090	573.27	1590	574.77
1100	573.30	1600	574.80
1110	573.33	1610	574.83
1120	573.36	1620	574.86
1130	573.39	1630	574.89
1140	573.42	1640	574.92
1150	573.45	1650	574.95
1160	573.48		
1170	573.51		
1180	573.54		
1190	573.57		
1200	573.60		
1210	573.63		
1220	573.66		
1230	573.69		
1240	573.72		
1250	573.75		
1260	573.78		
1270	573.81		
1280	573.84		
1290	573.87		
1300	573.90		
1310	573.93		
1320	573.96		
1330	573.99		
1340	574.02		
1350	574.05		
1360	574.08		
1370	574.11		
1380	574.14		
1390	574.17		
1400	574.20		
1410	574.23		
1420	574.26		
1430	574.29		
1440	574.32		
1450	574.35		

Hydrogen Partial Pressure 725 psia

Hydrogen Partial Pressure 585 psia

Time,Hours	Temperature,°F	Time,Hours	Temperature,°F
0	610.00	0	638.00
10	610.09	10	640.90
20	610.18	20	643.80
30	610.27	30	646.70
40	610.36	40	649.60
50	610.45	50	652.50
60	610.54	60	655.40
70	610.63	70	658.30
80	610.72	80	661.20
90	610.81	90	664.10
100	610.90	100	667.00
110	610.99	110	669.90
120	611.08	120	672.80
130	611.17	130	675.70
140	611.26	140	678.60
150	611.35	150	681.50
160	611.44	160	684.40
170	611.53	170	687.30
180	611.62		
190	611.71		
200	611.80		
210	611.89		
220	611.98		
230	612.07		
240	612.16		
250	612.25		
260	612.34		
270	612.43		
280	612.52		
290	612.61		
300	612.70		
310	612.79		
320	612.88		
330	612.97		
340	613.06		
350	613.15		

System B:

Hydrogen Partial Pressure 1000 psia

Time, Normalized	Temperature, °F	Time, Normalized	Temperature, °F
0	572.00	480	572.96
10	572.02	490	572.98
20	572.04	500	573.00
30	572.06	510	573.02
40	572.08	520	573.04
50	572.10	530	573.06
60	572.12	540	573.08
70	572.14	550	573.10
80	572.16	560	573.12
90	572.18	570	573.14
100	572.20	580	573.16
110	572.22	590	573.18
120	572.24	600	573.20
130	572.26	610	573.22
140	572.28	620	573.24
150	572.30	630	573.26
160	572.32	640	573.28
170	572.34	650	573.30
180	572.36	660	573.32
190	572.38	670	573.34
200	572.40	680	573.36
210	572.42	690	573.38
220	572.44	700	573.40
230	572.46	710	573.42
240	572.48	720	573.44
250	572.50	730	573.46
260	572.52	740	573.48
270	572.54	750	573.50
280	572.56	760	573.52
290	572.58	770	573.54
300	572.60	780	573.56
310	572.62	790	573.58
320	572.64	800	573.60
330	572.66	810	573.62
340	572.68	820	573.64
350	572.70	830	573.66
360	572.72	840	573.68
370	572.74	850	573.70
380	572.76	860	573.72
390	572.78	870	573.74
400	572.80	880	573.76
410	572.82	890	573.78
420	572.84	900	573.80
430	572.86	910	573.82
440	572.88	920	573.84
450	572.90	930	573.86
460	572.92	940	573.88
470	572.94	950	573.90

Hydrogen Partial Pressure 1000 psia (cont.)

Time, Normalized	Temperature, °F
960	573.92
970	573.94
980	573.96
990	573.98
1000	574.00
1010	574.02
1020	574.04
1030	574.06
1040	574.08
1050	574.10
1060	574.12
1070	574.14
1080	574.16
1090	574.18
1100	574.20
1110	574.22
1120	574.24
1130	574.26
1140	574.28
1150	574.30
1160	574.32
1170	574.34
1180	574.36
1190	574.38
1200	574.40

Hydrogen Partial Pressure 800 psia

Time, Normalized	Temperature, °F	Time, Normalized	Temperature, °F
0	586.00	480	592.24
10	586.13	490	592.37
20	586.26	500	592.50
30	586.39	510	592.63
40	586.52	520	592.76
50	586.65	530	592.89
60	586.78	540	593.02
70	586.91	550	593.15
80	587.04	560	593.28
90	587.17	570	593.41
100	587.30	580	593.54
110	587.43	590	593.67
120	587.56	600	593.80
130	587.69	610	593.93
140	587.82	620	594.06
150	587.95	630	594.19
160	588.08	640	594.32
170	588.21	650	594.45
180	588.34	660	594.58
190	588.47	670	594.71
200	588.60	680	594.84
210	588.73	690	594.97
220	588.86	700	595.10
230	588.99		
240	589.12		
250	589.25		
260	589.38		
270	589.51		
280	589.64		
290	589.77		
300	589.90		
310	590.03		
320	590.16		
330	590.29		
340	590.42		
350	590.55		
360	590.68		
370	590.81		
380	590.94		
390	591.07		
400	591.20		
410	591.33		
420	591.46		
430	591.59		
440	591.72		
450	591.85		
460	591.98		
470	592.11		

System C:

Hydrogen Partial Pressure 2000 psia

Hydrogen Partial Pressure 1600 psia

Time,Hours	Temperature,°F	Time,Hours	Temperature,°F
0	689.0	0	697.0
10	689.5	20	697.3
20	690.0	40	697.6
30	690.4	60	697.9
40	690.5	80	698.2
50	690.9	100	698.5
60	691.3	120	698.8
70	691.6	140	699.1
80	692.0	160	699.4
90	692.5	180	699.6
100	693.0	200	699.9
110	693.6	220	700.2
120	694.0	240	700.5
130	694.1	260	700.8
140	694.5	280	701.1
150	694.7	300	701.4
160	695.0	320	701.7
		340	702.0

Hydrogen Partial Pressure 1150 psia

Time,Hours	Temperature,°F
0	730.0
10	731.0
20	731.9
30	733.7
40	735.5
50	737.3
60	739.1
70	741.1
80	742.7
90	745.4
100	748.1
110	749.9
120	753.0
130	755.3
140	758.9
150	761.6
160	766.1
170	769
180	773.3
190	776.9
200	782.3
210	787.7
220	793.1
230	798.5
240	803.9
250	809.3
260	814.7
270	820

System D:

Hydrogen Partial Pressure 1774 psia

Time, Hours	Temperature, °F	Time, Hours	Temperature, °F	Time, Hours	Temperature, °F
0	660.0	490	664.9	980	669.8
10	660.1	500	665.0	990	669.9
20	660.2	510	665.1	1000	670.0
30	660.3	520	665.2	1010	670.1
40	660.4	530	665.3	1020	670.2
50	660.5	540	665.4	1030	670.3
60	660.6	550	665.5	1040	670.4
70	660.7	560	665.6	1050	670.5
80	660.8	570	665.7	1060	670.6
90	660.9	580	665.8	1070	670.7
100	661.0	590	665.9	1080	670.8
110	661.1	600	666.0	1090	670.9
120	661.2	610	666.1	1100	671.0
130	661.3	620	666.2	1110	671.1
140	661.4	630	666.3	1120	671.2
150	661.5	640	666.4	1130	671.3
160	661.6	650	666.5	1140	671.4
170	661.7	660	666.6	1150	671.5
180	661.8	670	666.7	1160	671.6
190	661.9	680	666.8	1170	671.7
200	662.0	690	666.9	1180	671.8
210	662.1	700	667.0	1190	671.9
220	662.2	710	667.1	1200	672.0
230	662.3	720	667.2	1210	672.1
240	662.4	730	667.3	1220	672.2
250	662.5	740	667.4	1230	672.3
260	662.6	750	667.5	1240	672.4
270	662.7	760	667.6	1250	672.5
280	662.8	770	667.7	1260	672.6
290	662.9	780	667.8	1270	672.7
300	663.0	790	667.9	1280	672.8
310	663.1	800	668.0	1290	672.9
320	663.2	810	668.1	1300	673.0
330	663.3	820	668.2	1310	673.1
340	663.4	830	668.3	1320	673.2
350	663.5	840	668.4	1330	673.3
360	663.6	850	668.5	1340	673.4
370	663.7	860	668.6	1350	673.5
380	663.8	870	668.7	1360	673.6
390	663.9	880	668.8	1370	673.7
400	664.0	890	668.9	1380	673.8
410	664.1	900	669.0	1390	673.9
420	664.2	910	669.1	1400	674.0
430	664.3	920	669.2	1410	674.1
440	664.4	930	669.3	1420	674.2
450	664.5	940	669.4	1430	674.3
460	664.6	950	669.5	1440	674.4
470	664.7	960	669.6	1450	674.5
480	664.8	970	669.7	1460	674.6

Hydrogen Partial Pressure 1774 psia (cont.)

Time, Hours	Temperature, °F	Time, Hours	Temperature, °F	Time, Hours	Temperature, °F
1470	674.7	1970	679.7	2470	684.7
1480	674.8	1980	679.8	2480	684.8
1490	674.9	1990	679.9	2490	684.9
1500	675.0	2000	680.0	2500	685.0
1510	675.1	2010	680.1	2510	685.1
1520	675.2	2020	680.2	2520	685.2
1530	675.3	2030	680.3	2530	685.3
1540	675.4	2040	680.4	2540	685.4
1550	675.5	2050	680.5	2550	685.5
1560	675.6	2060	680.6	2560	685.6
1570	675.7	2070	680.7	2570	685.7
1580	675.8	2080	680.8	2580	685.8
1590	675.9	2090	680.9	2590	685.9
1600	676.0	2100	681.0	2600	686.0
1610	676.1	2110	681.1	2610	686.1
1620	676.2	2120	681.2	2620	686.2
1630	676.3	2130	681.3	2630	686.3
1640	676.4	2140	681.4	2640	686.4
1650	676.5	2150	681.5	2650	686.5
1660	676.6	2160	681.6	2660	686.6
1670	676.7	2170	681.7	2670	686.7
1680	676.8	2180	681.8	2680	686.8
1690	676.9	2190	681.9	2690	686.9
1700	677.0	2200	682.0	2700	687.0
1710	677.1	2210	682.1	2710	687.1
1720	677.2	2220	682.2	2720	687.2
1730	677.3	2230	682.3	2730	687.3
1740	677.4	2240	682.4	2740	687.4
1750	677.5	2250	682.5	2750	687.5
1760	677.6	2260	682.6	2760	687.6
1770	677.7	2270	682.7	2770	687.7
1780	677.8	2280	682.8	2780	687.8
1790	677.9	2290	682.9	2790	687.9
1800	678.0	2300	683.0	2800	688.0
1810	678.1	2310	683.1		
1820	678.2	2320	683.2		
1830	678.3	2330	683.3		
1840	678.4	2340	683.4		
1850	678.5	2350	683.5		
1860	678.6	2360	683.6		
1870	678.7	2370	683.7		
1880	678.8	2380	683.8		
1890	678.9	2390	683.9		
1900	679.0	2400	684.0		
1910	679.1	2410	684.1		
1920	679.2	2420	684.2		
1930	679.3	2430	684.3		
1940	679.4	2440	684.4		
1950	679.5	2450	684.5		
1960	679.6	2460	684.6		

Hydrogen Partial Pressure 1576 psia

Time, Hours	Temperature, °F	Time, Hours	Temperature, °F
0	688.0	490	690.9
10	688.1	500	691.0
20	688.1	510	691.1
30	688.2	520	691.1
40	688.2	530	691.2
50	688.3	540	691.2
60	688.4	550	691.3
70	688.4	560	691.4
80	688.5	570	691.4
90	688.5	580	691.5
100	688.6	590	691.5
110	688.7	600	691.6
120	688.7	610	691.7
130	688.8	620	691.7
140	688.8	630	691.8
150	688.9	640	691.8
160	689.0	650	691.9
170	689.0	660	692.0
180	689.1		
190	689.1		
200	689.2		
210	689.3		
220	689.3		
230	689.4		
240	689.4		
250	689.5		
260	689.6		
270	689.6		
280	689.7		
290	689.7		
300	689.8		
310	689.9		
320	689.9		
330	690.0		
340	690.0		
350	690.1		
360	690.2		
370	690.2		
380	690.3		
390	690.3		
400	690.4		
410	690.5		
420	690.5		
430	690.6		
440	690.6		
450	690.7		
460	690.8		
470	690.8		
480	690.9		

Hydrogen Partial Pressure 1320 psia

Time, Hours	Temperature, °F
0	708.0
10	708.2
20	708.4
30	708.7
40	708.9
50	709.1
60	709.3
70	709.5
80	709.8
90	710.0
100	710.2
110	710.4
120	710.6
130	710.9
140	711.1
150	711.3
160	711.5
170	711.7
180	712.0
190	712.2
200	726.0
210	730.0
220	728.0
230	728.0
240	728.0
250	730.0
260	722.0
270	724.0
280	724.0
290	726.0
300	729.0
310	730.0
320	732.0
330	728.0
340	730.0
350	730.0
360	732.0
370	736.0
380	738.0
390	740.0
400	744.0
410	748.0
420	754.0
430	760.0

Appendix D: Predicted Values for A_d and E_d using an Excel Spreadsheet.

Pressure,psia	n	A _d , 1/hr	E _d , cal./mole	A _d , 1/hr	E _d , cal./mole
		Spreadsheet		Equation 17	
System A					
900	1	0.38	9700	0.38	9700
720	1	0.78	9700	0.78	9700
585	1	21.10	10000	21.10	10000
900	2	0.53	10000	0.53	10000
720	2	0.81	9700	0.81	9700
585	2	26.80	9800	27.50	9800
System B					
1000	1	0.14	9000	0.14	9000
800	1	4.2	11000	4.26	11000
1000	2	3.00	12500	4.67	9000
800	2	4.66	11000	3.00	11000
System C					
2000	1	2.10	10000	2.10	10000
1600	1	7.40	13000	7.80	10000
1150	1	8.70	10000	12.00	13000
2000	2	2.20	10000	5.80	10000
1600	2	8.50	13000	8.20	13000
1150	2	13.80	10000	13.80	13000
System D					
1597	1	4.8	12500	4.80	12500
1418	1	5	13500	5.30	13500
1188***	1	10	10000	5.00	9940
1597	2	5.9	12500	6.10	12500
1418	2	5.3	13500	5.40	13500
1188	2	13	10000	11.50	9000

Appendix E: Statistics for A_d and E_d Values

Definitions

1. Coefficient of Determination $= r^2 = 1 - (SSE / SSM)$

$$SSE = \sum w_i * (y_i - y'_i)^2 \text{ (from } n \text{ to } i, n = 1)$$

Where w_i is weight, y_i is the y data value and y'_i is the predicted y value.

$$SSM = \sum w_i * (y_i - y''_i)^2 \text{ (from } n \text{ to } i, n = 1)$$

Where y''_i is the measure of y values

2. Degree of Freedom Adjusted $r^2 = \text{DOF Adj } r^2 = 1 - \frac{[SSE * (n - 1)]}{[SSM * (DOF - 1)]}$

$$\text{DOF} = n - m$$

m = number of coefficients fitted

3. Fit Standard Error (Root MSE) $= S_t = (\text{MSE})^{0.5}$

4. F-Statistic $= \text{MSR} / \text{MSE} = [(SSM - SSE) / (m - 1)] / [SSE / \text{DOF}]$

$$\text{MSR} = (SSM - SSE) / (m - 1)$$

Table E1. Statistic Results for A_d and E_d from Equation 17

System A					
Pressure	Reaction Order	r^2	DF Adj r^2	Fit Std Err	F-stat
900	1	0.9992	0.9991	0.0233	194761
900	2	0.9995	0.9995	0.0171	360362
720	1	0.9998	0.9998	0.0080	152169
720	2	0.9999	0.9999	0.0049	403284
585	1	0.9919	0.9908	0.8000	1949
585	1.3	0.9998	0.9998	0.1087	106431
585	1.6	0.9972	0.9968	0.4675	5738
585	2	0.9877	0.9861	0.9834	1284
System B					
1000	1	0.9986	0.9986	0.0146	85437
1000	2	0.9993	0.9993	0.0100	181691
800	1	0.9992	0.9991	0.0439	40412
800	2	0.9994	0.9993	0.0380	53942
System C					
2000	1	0.9911	0.9898	0.1060	1662
2000	2	0.9917	0.9906	0.1019	1801
1600	1	0.9998	0.9998	0.0112	102343
1600	2	0.9994	0.9993	0.0380	53942
1150	0.9	0.9547	0.9511	3.3524	548
1150	1	0.9611	0.9580	3.1077	642
1150	1.1	0.9501	0.9461	3.5186	495
1150	1.3	0.9272	0.9214	4.2507	331
1150	2	0.8423	0.8297	6.2572	139
System D					
1597	0	0.9964	0.9964	0.2703	77826
1597	0	0.9963	0.9963	0.2751	75133
1418	0	0.9988	0.9987	0.0228	53315
1418	0	0.9999	0.9999	0.0062	731384
1188	0.9	0.9231	0.9038	1.7067	108
1188	1	0.9272	0.9091	1.6597	115
1188	1.3	0.9131	0.8914	1.8139	95
1188	1.6	0.8997	0.8746	1.9487	81
1188	2	0.8831	0.8539	2.1035	68

Appendix F: System A 650 psia at $(n) = 1.3$ and $(n) = 1.6$

Figure F1. Plot of the Temperature against Time obtained at 650 psia with System A. The solid line was calculated from Equation 11 using $n=1.3$.

Figure F2. Plot of the Temperature against Time obtained at 650 psia with System A. The solid line was calculated from Equation 11 using $n = 1.6$.

Figure F2. Plot of the Temperature against Time obtained at 650 psia with System A. The solid line was calculated from Equation 11 using $n = 1.6$.

Figure G2. Plot of the Temperature against Time obtained at 1150 psia with System C.
The solid line was calculated from Equation 11 using $n = 1.3$.

January 8, 2003

To Whomsoever It May Concern:

Mr. Phil Alemania has my permission to use the information contained in my paper entitled "Analysis of Temperature-Time Data for Deactivating Catalysts", Ind. Eng. Chem., Process Des. Dev., 18, 399 (1979).

Signed,

A handwritten signature in black ink, appearing to read 'A. S. Krishna', written in a cursive style.

A. S. Krishna

(formerly known as S. Krishnaswamy)