

Temperature Effects on Gasoline Selectivity in the Cracking of a Neutral Distillate

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Received May 24, 1974

The selectivity for gasoline in catalytic cracking of a neutral distillate has been studied over a range of temperatures. We have found that the primary cracking reaction leading to undesirable products has an activation energy some 13 kcal/g mole higher than the parallel reaction leading to gasoline. This fact is the major reason for the decrease in gasoline yield at higher temperatures especially in view of the fact that the re cracking of gasoline has an activation energy very similar to that for its formation. On the other hand, the gasoline re cracking reaction shows a much lower frequency factor than its formation and this is the reason that the specific rate of re cracking of gasoline is much slower than the cracking of the feed.

INTRODUCTION

Commercially, the selectivity of a catalyst is regarded as its most important property. Nowhere is this aspect more thoroughly appreciated than in the petroleum industry where maximizing the production of desirable products from a barrel of crude is perhaps the primary operating criterion. Despite the importance of this phenomenon very little theoretical work has been published on the subject of selectivity in catalytic cracking.

In 1961 Froment and Bischoff (1) discussed the effect of various types of catalyst decay on the theoretical selectivity patterns in fixed bed reactors. Their analysis was successfully applied to a set of data obtained by the same authors (2). Unfortunately the approach proposed by Froment and Bischoff is experimentally cumbersome and as a result has not been widely used. The first attempt at applying a kinetic analysis based on time on stream to describe selectivity in gas oil cracking was that of Weekman in 1969 (3) where an ex-

ponential decay function was used to account for aging. In the same year Campbell and Wojciechowski (4) proposed an application of the time-on-stream theory of catalyst decay to describe theoretical patterns of selectivity in gas oil cracking in a fixed bed reactor. In 1970 Weekman and Nace (5) extended Weekman's fixed bed selectivity model to account for gas oil cracking in moving and fluid bed cat crackers and in 1971 Nace *et al.* (6) applied the model to the cracking of a wide variety of gas oil blends. More recently, Pachovsky *et al.* (7) have described a more general gas oil selectivity model while Pachovsky and Wojciechowski (8) have shown that this model can also be applied to gas oil selectivity over a diffusion limited catalyst.

In this paper we apply our selectivity model to data obtained from cracking a dewaxed neutral distillate in a static bed reactor over La-Y catalyst. We chose here to study a neutral distillate rather than a gas oil because its use simplifies experimental procedures without altering the fundamental aspects of the phenomena involved.

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THEORY

In previous publications (7,8) a model relating conversion and selectivity in a plug flow, static bed reactor to catalyst time on stream was presented. The defining model relationships are

$$\frac{dX_A}{d\tau} = (k_{10} + k_{20}) \left(\frac{1}{1 + Gt} \right)^N \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right)^{1+W}, \quad (1a)$$

$$\frac{dX_B}{d\tau} = \left(\frac{1}{1 + Gt} \right)^N \left\{ k_{10} \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right)^{1+W} - k_{30} \left(\frac{1}{1 + \epsilon_A X_A} \right) X_B \right\}, \quad (1b)$$

$$\frac{dX_C}{d\tau} = \left(\frac{1}{1 + Gt} \right)^N \left\{ k_{20} \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right)^{1+W} + k_{30} \left(\frac{1}{1 + \epsilon_A X_A} \right) X_B \right\}. \quad (1c)$$

Equations (1) were derived by assuming that the feed (A) may crack directly to gasoline (B) or to coke and light gases (C) and that gasoline (B) could re crack to C.

The catalyst decay in Eqs. (1) is described using the time-on-stream theory of Wojciechowski (9) which yields the expression

$$S = S_0 \left(\frac{1}{1 + (m-1)k_{md}t} \right)^{n/(m-1)} = S_0 (1 + Gt)^{-N}, \quad (2)$$

where S is the number of unpoisoned active sites at time t , m and n are orders of the decay and the cracking reactions, respectively, while k_{md} is the rate constant for the decay reaction (10).

The refractoriness of the feedstock (A) has been accounted for in Eqs. (1) according to the expression (7,10,11)

$$\frac{k}{k_0} = \left(\frac{C_A}{C_{A0}} \right)^W, \quad (3)$$

where k is the reactivity of the feed when reactant concentration has dropped to C_A

while k_0 is the reactivity of fresh feed when the concentration is C_{A0} .

Equations (1) are therefore kinetic rate expressions relating the rate of change of the weight fraction of A, B, and C to the age of the catalyst and the current weight fractions of A, B, and C present in the reacting mixture. The instantaneous values of fractional conversion (X_A) and of products produced (X_B , X_C) are related to the average values (\bar{X}_A , \bar{X}_B , \bar{X}_C) by

$$X = \frac{1}{t_f} \int_0^{t_f} X dt, \quad (4)$$

while the contact time is related to the time on stream by

$$\tau = bPt_f. \quad (5)$$

DISCUSSION

In a previous publication (12) we have discussed the effects of temperature on the conversion of this neutral distillate whose approximate mass spectral analysis is presented in Table 1. Fitting of the selectivity model reported above to the gasoline data from the neutral distillate resulted in the parameter values reported in Table 2. The results used are denoted by points; and the corresponding best fit curves, represented by solid lines, are shown in Figs. 1-3. Complete data used in these figures is presented in Table 3.

From Figs. 1-3 and from the F test results reported in Table 4 it is apparent that the selectivity model adequately describes the gasoline yield data at the 95% con-

TABLE I
MASS SPECTRAL ANALYSIS OF THE EXTRACTED AND DEWAXED NEUTRAL DISTILLATE USED IN THIS STUDY (CALLED A1W0)

Component	Approximate wt%
Saturate (paraffins and naphthenes)	84.5
Monoaromatics	15.5
Diaromatics	3.6
Higher aromatics	0.7

TABLE 2
PARAMETER VALUES FOR THE CRACKING OF AN
EXTRACTED AND DEWAXED NEUTRAL
DISTILLATE (CALLED A1W0)

Parameter	(°C): 482	503	524
k_0 (hr ⁻¹)	7.62×10^6	1.95×10^7	4.72×10^7
k_{10} (hr ⁻¹)	6.87×10^6	1.71×10^7	3.97×10^7
k_{20} (hr ⁻¹)	7.46×10^6	2.47×10^6	7.50×10^6
k_{30} (hr ⁻¹)	9.70×10^8	2.45×10^9	5.82×10^9
N	31.03	29.71	24.73
G (hr ⁻¹)	0.30	0.51	0.80
W	3.08	3.24	3.34
k_{10}/k_0	0.902	0.873	0.841
k_{30}/k_0	1.27×10^{-4}	1.25×10^{-4}	1.23×10^{-4}
GE at maximum gasoline yield	74.0	73.3	72.5
@ $\bar{X}_{A,max}$	0.78	0.76	0.73
b	7.10×10^{-3}	6.92×10^{-3}	6.72×10^{-3}

fidence level. Replotting the data shown in Figs. 1–3 against the corresponding conversion values reported in Table 3 produces the selectivity curves shown in Figs. 4–6.

The optimum performance envelope (OPE) is the upper bound of the selectivity plot and is such an important feature of the selectivity plot that it deserves special attention. It represents the maximum possible yield of gasoline that can be obtained

from a given feedstock at a specified conversion. Since it has been shown previously (4) that the optimum performance envelope is identical with the instantaneous selectivity curve (that is selectivity at a constant catalyst age, e.g., at age zero) it is a simple matter to solve Eqs. (1a) to (1c) to obtain the theoretical OPE. This theoretical OPE is shown in Figs. 4–6 by a solid line. Since it is the OPE which is observed in moving and fluidized bed reactors (14), and for this reason is important industrially, all further discussion concerning selectivity will deal with the OPE.

The initial slope of the OPE has been shown by Campbell and Wojciechowski (4) to be $k_{10}/(k_{10} + k_{20})$. This ratio is referred to as the ultimate gasoline efficiency (UGE) and is the fraction of feed converted to gasoline of the total feed converted under initial conditions. This ratio is important since it dictates the very best selectivity which can be expected for a given system at that temperature. As this selectivity only occurs at very low conversions, its practical utility is somewhat limited. Nevertheless, some interesting features arise from consideration of the UGE.

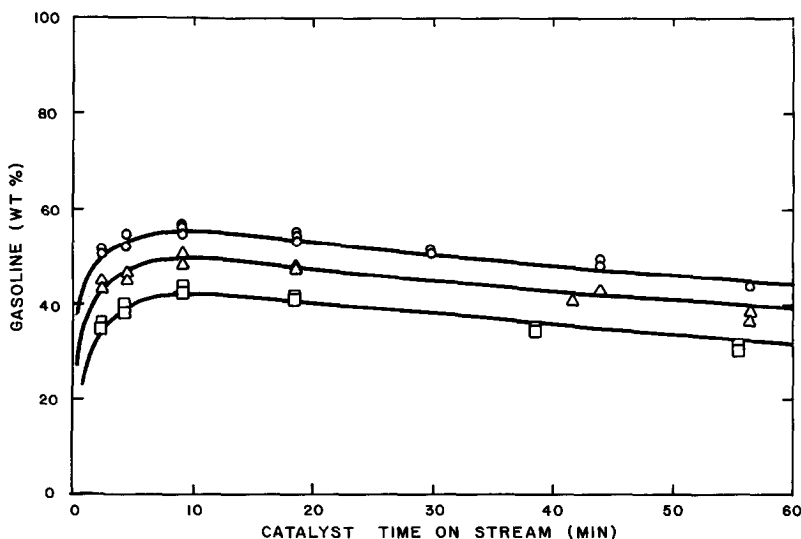


FIG. 1. Gasoline yield versus time on stream at 482°C. (—) Results predicted from the model. The experimental cat/oil ratios (wt/wt) are: (○) 0.25; (△) 0.05; (□) 0.01.

From Table 2 it is evident that the UGE is highest at the lowest temperature studied and decreases as the temperature is increased indicating that proportionally more feed will crack to products other than gasoline [i.e., butane, butene, and propylene (13)] as temperature is increased. It was shown in a previous publication

TABLE 3
EXTENSIVE DATA^a FOR THE CATALYTIC CRACKING OF A1W0 OVER LaY CATALYST

Temp (°C)	C/O ^b	TOS	\bar{X}_A	\bar{X}_B	Temp (°C)	C/O ^b	TOS	\bar{X}_A	\bar{X}_B	Temp (°C)	C/O ^b	TOS	\bar{X}_A	\bar{X}_B
482	0.25	2.37	64.95	50.78	503	0.25	2.38	68.18	47.78	524	0.25	4.55	73.93	57.60
		2.37	64.84	51.48			2.37	68.61	48.23			4.54	75.54	58.72
		4.54	70.82	54.58			4.55	71.95	54.30			9.02	79.13	58.39
		4.55	67.82	52.23			4.55	70.92	53.76			9.00	78.54	60.02
		9.01	73.48	55.86			9.04	73.20	58.27			18.51	75.60	51.94
		9.02	71.58	54.76			9.01	74.12	57.72			18.53	75.08	53.45
		9.04	74.46	56.18			9.04	74.98	58.70			39.92	65.01	40.68
		18.51	73.84	55.03			18.60	74.93	54.83			39.69	67.98	43.10
		18.51	71.16	54.68			18.72	73.34	51.65					
		18.67	72.21	53.68			18.74	75.05	55.69					
		30.00	70.25	50.45			44.26	65.54	41.88					
		30.41	70.63	51.00			57.47	61.78	34.17					
		43.93	69.09	48.76			57.47	62.09	36.77					
		56.67	65.61	44.47										
	0.05	2.37	55.37	45.56		0.05	2.38	54.50	43.89		0.05	2.37	66.98	52.75
		2.37	53.05	42.81			2.38	55.19	42.96			2.37	67.64	51.82
		4.53	56.77	46.09			4.55	59.01	47.25			4.54	69.82	54.57
		4.55	55.86	44.84			4.55	62.13	48.77			4.54	68.79	52.78
		9.01	60.18	48.30			9.03	65.44	50.84			9.01	70.78	54.00
		9.03	63.61	50.94			9.03	65.21	51.44			9.01	70.31	54.05
		18.55	61.10	48.10			18.51	64.05	47.71			9.00	67.24	51.68
		18.70	60.84	47.69			18.71	66.02	49.32			18.61	66.57	47.10
		43.99	57.81	43.10			18.74	64.08	49.07			18.44	66.28	48.84
		41.56	55.53	41.40			44.66	53.63	36.02			40.30	56.61	36.61
		55.79	50.42	35.69			57.13	48.02	29.39			39.44	52.67	37.01
		55.81	53.28	38.16			56.57	51.27	31.94			56.03	45.77	24.42
												55.07	45.23	24.42
	0.01	2.37	40.50	34.11		0.01	2.37	45.50	37.62		0.01	2.37	54.16	45.81
		2.37	39.36	34.08			2.36	47.79	39.90			4.54	58.55	48.23
		4.53	47.86	40.19			4.53	51.93	43.25			4.54	56.83	48.50
		4.53	46.12	38.81			4.55	50.56	41.49			9.02	59.64	46.86
		9.02	52.41	44.50			4.55	50.50	40.68			9.00	58.55	46.10
		9.04	50.56	42.89			9.01	52.47	42.85			9.02	60.87	46.06
		18.56	48.91	40.91			9.01	53.61	45.61			18.53	55.11	40.37
		18.53	49.82	41.82			18.53	51.91	42.15			18.38	53.29	42.71
		38.74	43.03	34.02			18.45	53.86	43.65			38.72	45.71	30.39
		38.41	45.12	35.21			38.87	44.30	32.42			38.43	41.92	30.01
		54.28	42.56	31.56			38.74	42.39	32.60			55.10	33.72	17.70
		53.88	40.76	30.30			54.95	37.32	24.32			54.63	34.40	18.00
							55.53	35.88	24.54					

^a Conversion and yields (wt%) are corrected for thermal reactions.

^b Cat/oil ratios are weight ratios.

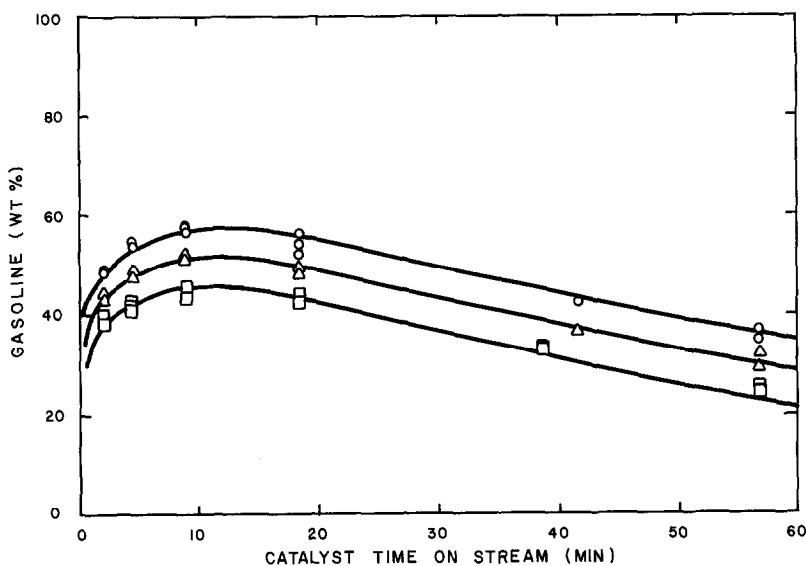


FIG. 2. Gasoline yield versus time on stream at 503°C. (—) Results predicted from the model. The experimental cat/oil ratios (wt/wt) are: (O) 0.25; (Δ) 0.05; (□) 0.01.

(12) that k_0 , the reactivity of the feed, has the form

$$k_0 = C_{s0} \sum_{j=1}^n \sum_{q=0}^{l_j} k_{jq} K_{Aj} X_{Ajo} \quad (6)$$

and further that in the case under consideration the above equation follows an Arrhenius relationship. Since k_0 is a sum of the two initial reactivities, k_{10} and k_{20} , Eq.

(6) can be expanded to

$$k_0 = k_{10} + k_{20}$$

$$= \left[\sum_{j=1}^m \sum_{q=0}^{l_j} k_{jq} K_{Aj} X_{Ajo} + \sum_{i=1}^n \sum_{q=0}^{l_i} k_{iq} K_{Ai} X_{Aio} \right] \quad (7a)$$

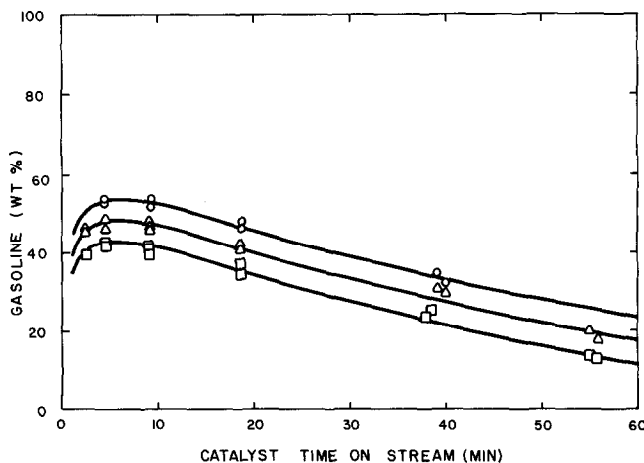


FIG. 3. Gasoline yield versus time on stream at 524°C. (—) Results predicted from the model. The experimental cat/oil ratios (wt/wt) are: (O) 0.25; (Δ) 0.05; (□) 0.01.

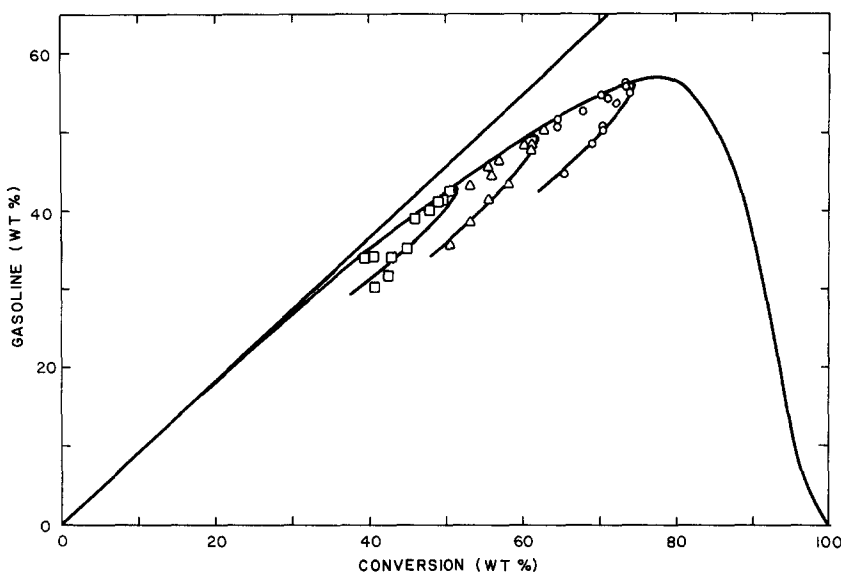


FIG. 4. Gasoline selectivity at 482°C. (—) Results predicted from the model. The experimental cat/oil ratios (wt/wt) are: (○) 0.25; (△) 0.05; (□) 0.01.

or

$$k_{10} = C_{s_0} \sum_{j=1}^n \sum_{q=0}^{l_j} k_{jq} K_{Aj} X_{A_{j_0}}, \quad (7b)$$

$$k_{20} = C_{s_0} \sum_{i=1}^n \sum_{q=0}^{l_i} k_{iq} K_{Ai} X_{A_{i_0}}, \quad (7c)$$

where the interval j to m corresponds to reactants which crack to produce gasoline while the reactants i to n crack to produce undesirable products. It is evident in comparing Eqs. (7b) and (7c) with Eq. (6) that k_{10} and k_{20} should behave in a manner analogous to k_0 ; that is, both k_{10} and k_{20} are ex-

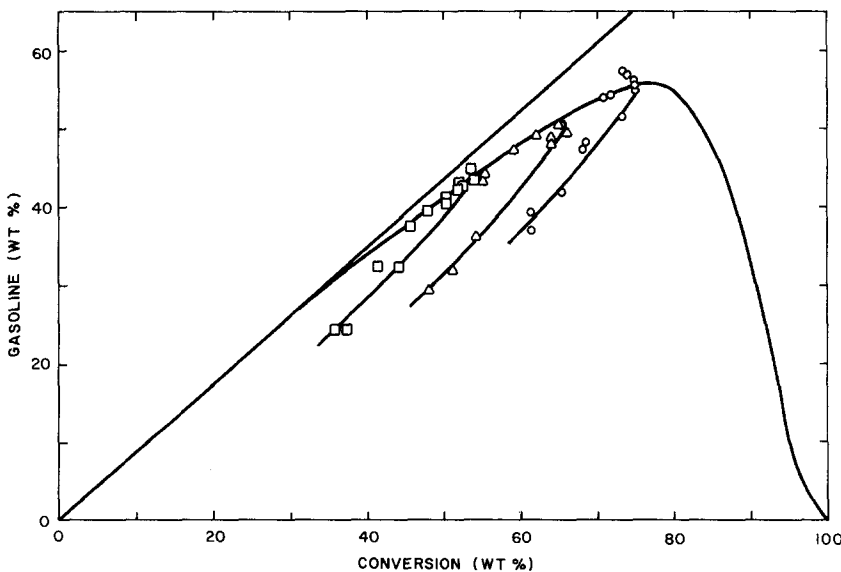


FIG. 5. Gasoline selectivity at 503°C. (—) Results predicted from the model. The experimental cat/oil ratios (wt/wt) are: (○) 0.25; (△) 0.05; (□) 0.01.

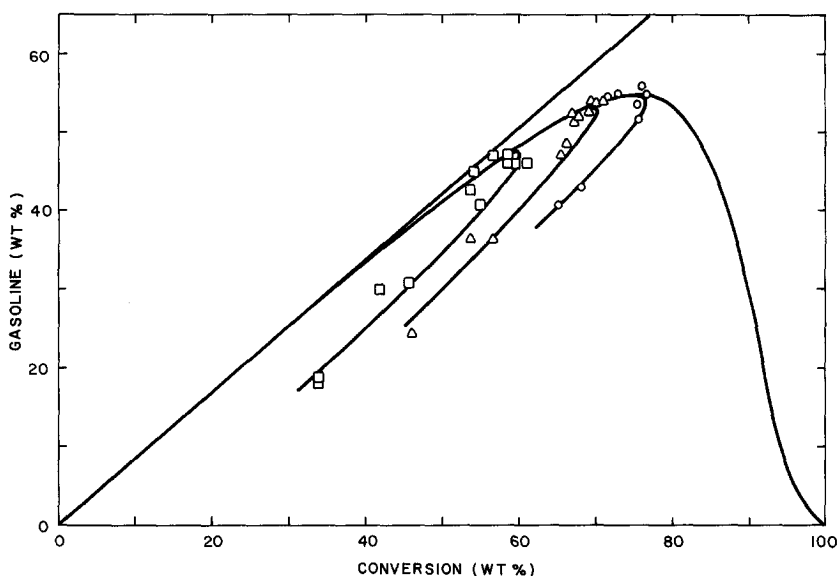


FIG. 6. Gasoline selectivity at 524°C. (—) Results predicted from the model. The experimental cat/oil ratios (wt/wt) are: (O) 0.25; (Δ) 0.05; (\square) 0.01.

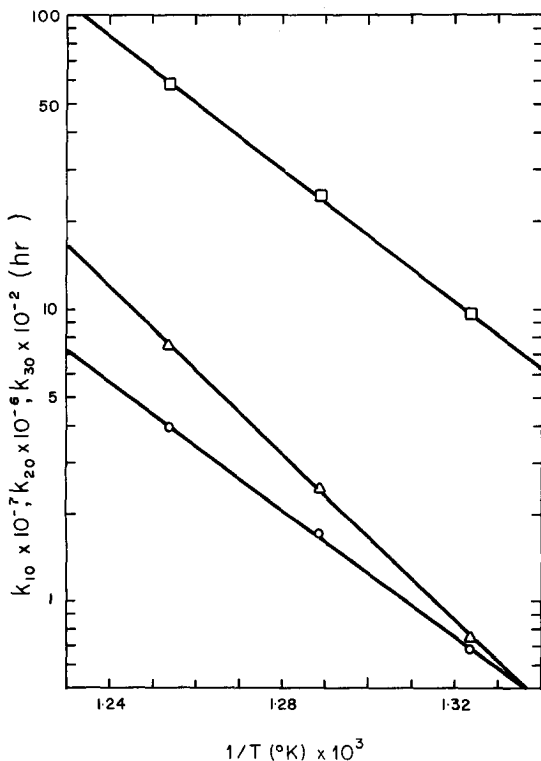


FIG. 7. Arrhenius plot for k_{10} , k_{20} and k_{30} . The experimental data are for the parameters: (O) k_{10} ; (Δ) k_{20} ; (\square) k_{30} .

pected to follow an Arrhenius relationship. That this is true is shown in Fig. 7. Since k_{30} is not directly related to the feed an expression similar to Eq. (6) cannot be written for k_{30} . However, Fig. 7 shows that this constant also follows an Arrhenius temperature dependence. Although no verification is given here, it is believed that k_{30} is related to the olefin concentration in the gasoline and hence an expression similar to Eq. (6) but based on the olefin concentration may be applicable. This question will be discussed in a future publication.

From Fig. 7 we are able to compute the activation energies and frequency factors for the rate constants and these are reported in Table 5. As in the case of k_0 reported earlier (12) we find that the activation energies for k_{10} , k_{20} and k_{30} are considerably higher than those reported previously for catalytic cracking rate constants. These high values for the activation energy can be justified in a manner similar to that previously (12) applied to explain the activation energy for k_0 . Comparing the activation energies of k_{10} and k_{20} shows

TABLE 4
TEST FOR ADEQUACY OF SELECTIVITY MODEL BY F TEST AND 95% CONFIDENCE LEVEL

Temp (°C)	Estimate of pure error variance	No. of data points	SS _{<i>t</i>}	F values	
				Tabulated	Calculated
482	0.000300	38	0.00589	$F(\cdot 95, 13, 19) = 2.11$	1.51
503	0.000273	38	0.00404	$F(\cdot 95, 12, 20) = 2.28$	1.23
524	0.000574	33	0.00798	$F(\cdot 95, 10, 17) = 2.45$	1.39

that the one for k_{20} is some 13 kcal/g mole higher. This fact explains the decrease in the UGE as temperature is increased. The overcracking rate parameter, k_{30} , on the other hand, has been found to have an activation energy which is almost identical to that of k_{10} . Previously (5) it had been reported that for a gas oil the activation energy for the over-cracking rate parameter is almost twice as large as that for the reactivity. We feel that the values of k_{30} found here are so small in comparison to k_{10} and k_{20} that we should be careful with our conclusions regarding the behavior of re-cracking. It appears from our results that there is not a great difference between the activation energies of primary and secondary reactions.

It is also evident from Table 5 that the frequency factors for k_{10} and k_{20} are higher than expected with k_{20} having a slightly higher value. The excess in the frequency factor (that is the quantity above 10^{13} , the normal frequency factor) has been attributed to the entropy of adsorption (12). By assuming $C_{s_0} \approx 10^{-4}$ moles/cc and using the b values reported in Table 2, we can calculate entropies of adsorption

TABLE 5
THERMODYNAMIC VALUES FOR RATE CONSTANTS
IN THE CRACKING OF A1W0 ON La-Y

	k_{10}	k_{20}	k_{30}
E_0 (kcal/g mole)	50.2	64.1	57.2
A_0 (sec ⁻¹)	5.57×10^{17}	2.20×10^{21}	1.98×10^{14}
ΔS (cal/g mole °C)	40.2	56.8	24.2

from the expression for A_0 , the observed frequency factor.

$$A_0 = A_c \cdot e^{\Delta S/R} \cdot C_{s_0} \cdot b.$$

These are reported for the three rate constants in Table 5. The differences in the ΔS values are interesting and on further analysis may be able to tell us something about the differences in the chemistry of the reactions leading to gasoline and to the by-products. At this point however we are only prepared to say that on the basis of the values reported in Table 5 it appears that in the case of neutral distillates, an increase in cracking temperature decreases selectivity due only to an increase in undesirable primary reactions of the feed and not due to increased re-cracking of gasoline and that the re-cracking reaction is slower than the primary reaction mainly due to a much lower frequency factor.

As emphasized in the introduction, gasoline production plays a very important role in governing the economics of catalytic cracking. In view of this, it is desirable to maximize the gasoline yield per barrel of feed cracked. We know that this maximum gasoline yield per pass will occur when

$$\frac{d\bar{X}_B}{d\bar{X}_A} = 0.$$

Since the OPE for the time-averaged conversion and time-averaged gasoline yield is also the instantaneous selectivity pattern, then

$$\frac{d\bar{X}_B}{d\bar{X}_A} = \frac{dX_B}{dX_A} = 0.$$

Thus dividing Eq. (1b) by (1a) and equating the result to zero gives

$$\frac{dX_B}{dX_A} = \frac{k_{10}[(1 - X_{A_{\max}})/(1 + \epsilon_A X_{A_{\max}})]^{1+W} - k_{30}[1/(1 + \epsilon_A X_A)]X_{B_{\max}}}{(k_{10} + k_{20})[(1 - X_{A_{\max}})/(1 + \epsilon_A X_{A_{\max}})]^{1+W}} = 0, \quad (8)$$

where the quantities $X_{A_{\max}}$ and $X_{B_{\max}}$ refer to the conversion required for maximum gasoline yield and the resultant yield, respectively. Equation (8) reduces to

$$X_{B_{\max}} = \frac{k_{10}}{k_{30}} \frac{(1 - X_{A_{\max}})^{1+W}}{(1 + \epsilon_A X_{A_{\max}})^W} = \bar{X}_{B_{\max}}. \quad (9)$$

Equation (9) is perfectly general and will apply to gas oils as well as to neutral distillates.

Using Eq. (9) maximum gasoline yields and the corresponding gasoline efficiencies have been calculated for the three temperatures studied here and are reported together with corresponding values for MCGO (8) in Table 6. It is interesting to note that despite the large differences between the rate constants for A1W0 at the three temperatures, the OPE's remain almost identical as shown in Figs. 4, 5, and 6. Furthermore, the OPE for MCGO (7) is not vastly different from those for A1W0 even though the rate constants and refractoriness for the two feedstocks are greatly different. Similarly comparison of the gasoline efficiencies at the maximum gasoline yields $[(GE)_{\max}]$ in Table 6 shows that these values do not differ greatly for the 30/60 REHX and La-Y catalysts even though these two systems differ greatly in both catalyst and feed. On

the other hand, the $(GE)_{\max}$ for the diffusion limited catalyst is considerably

lower than those for the diffusion free catalysts and the reason for this has been discussed in detail previously (8). It is also apparent that for the neutral distillate increasing temperature causes a decrease in $(GE)_{\max}$ although the dependence is not very strong.

In general therefore it appears that in the cracking of the extracted and dewaxed neutral distillate (A1W0) over La-Y catalyst the major effect of temperature on selectivity can be ascribed to a difference in the activation energies of the primary cracking reactions leading to gasoline on one hand and those leading to butane, butene and propylene on the other.

CONCLUSIONS

In our work we have found little evidence that would substantiate the claim that neutral distillates constitute a class of optimal cracking feedstocks. In fact based on gasoline selectivity considerations alone they are inferior to gas oils such as MCGO. Their reputation as desirable cracking stocks no doubt stems from the fact that at common testing conditions they give a higher conversion and hence more gasoline than do commercial feedstocks.

We have found that the decrease in gas-

TABLE 6
COMPARISON OF MAXIMUM GASOLINE YIELDS

System	Catalyst mesh size	Temp (°C)	$(GE)_{\max}$	$\bar{X}_{A_{\max}}$	$\bar{X}_{B_{\max}}$ (wt%)
A1W0/La-Y	35/45	482	74.0	78.0	57.5
		503	73.3	76.3	56.0
		524	72.5	73.1	53.2
MCGO/REHX	30/60	482	72.8	81.0	59.0
MCGO/REHX	4/10	482	61.2	84.8	51.9

oline yield at any given conversion as temperature is increased is mainly due to the higher activation energy for primary cracking reactions leading to undesirable products and not to a disproportionate increase in the rate of re cracking of gasoline.

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