JOURNAL OF CATALYSIS 37, 120–126 (1975)

Temperature Effects on Conversion in the Catalytic Cracking of a Dewaxed Neutral Distillate

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Received April 30, 1974

The equations describing gas oil conversion in catalytic cracking are derived from fundamental considerations. In this way it is shown that the rate constant used in the time-on-stream theory is a complex quantity involving a number of parameters. Nonetheless, it has been found that this quantity which we propose to call "reactivity" obeys the Arrhenius equation and hence will yield an average activation energy for the cracking of gas oil constituents. This activation energy is found to be ~51 kcal/mole while the frequency factor is ~2 × 10^{18} sec^{-1}. The significance of these values is discussed in the light of the chemistry, kinetics and thermodynamics involved in catalytic cracking.

NOMENCLATURE

A	gas oil in cracking mechanism.
A_c	frequency factor for average cracking reaction, sec^{-1}.
A_j	*j*th species of gas oil.
A_0	frequency factor for k_0, sec^{-1}.
A_1	frequency factor for adsorption reaction, sec^{-1}.
A_{-1}	frequency factor for desorption reaction, sec^{-1}.
B	C_5 + gasoline in cracking mechanism.
C	coke + C_4-dry gas in cracking mechanism.
C_{A_0}	total concentration of gas oil initially.
C_A	total concentration of gas oil during reaction.
C_{A_j}	concentration of *j*th species in gas oil.
$C_{s_{A_j}}$	concentration of *j*th species-active site complex.
C_{so}	concentration of active sites initially.
C_s	concentration of active sites during reaction.
E_0	activation energy for k_0, kcal/g mole.
E_R	true activation energy for average cracking reaction, kcal/g mole.
E_1	activation energy for adsorption reaction, kcal/g mole.
E_{-1}	activation energy for desorption reaction, kcal/g mole.
G	rate constant parameter of the aging function, hr^{-1}.
K_{A_j}	adsorption equilibrium constant for *j*th species.
N	exponent of aging function.
P	cat/oil ratio (wt cat/wt feed).
W	refractoriness parameter.
X_A	instantaneous fraction of feed converted.
$\bar{X}_A$	time averaged fraction of feed converted.
X_{A_j}	mole fraction of *j*th species in gas oil.
$X_{A_{j_0}}$	initial mole fraction of *j*th species in gas oil.
b	catalyst/oil vapor density ratio ≈ 10^{-2}.
k_0	initial rate constant for cracking of gas oil.

k_{jq}	true rate constant for cracking of jth species of gas oil to product q.
l	total number of products formed.
m	order of decay rate expression.
t_f	catalyst time-on-stream, hr.
t	any intermediate time-on-stream during an experimental run, hr.
t_A	volume expansion correction term.

INTRODUCTION

Mathematical models based on catalyst time-on-stream have been successfully used to describe both conversion and selectivity in gas oil cracking (*1–4*). In all the above cases, however, lumped rate constants have been employed to account for the disappearance or appearance of a large number of molecular species which fall within certain boiling point ranges of interest. More specifically, one rate constant is used to describe the appearance of gasoline from gas oil, another to describe the appearance of coke and C_4^- gases from gas oil, and yet another to account for the recracking of gasoline to coke and C_4^- gases. The fact that satisfactory model fitting with such lumped constants has been possible suggests that this simplified procedure is fundamentally sound.

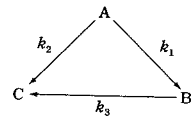
In this paper we investigate the detailed structure of the lumped rate constants both theoretically and through the use of experimental data from the cracking of an extracted and dewaxed neutral distillate.

THEORY

In a previous publication (*3*) a general equation was developed to describe catalytic cracking in a static bed reactor. The defining equation was shown to be

$$bk_0(1+Gt)^{-N}Pt_f = \int_0^{X_A}\left[\frac{1+\epsilon_A X_A}{1-X_A}\right]^{1+W} dX_A, \quad (1)$$

where b is a constant introduced by changing the space time variable, τ, using the relationship $\tau = bPt$, as outlined by Wojciechowski (*4*). Equation 1 was obtained from considerations involving the simplified gas oil cracking mechanism:



The values of X_A obtained from Eq. (1) are instantaneous fractional conversions for a catalyst age of t. In a static bed reactor, however, all measured values of conversion are the average values obtained at the end of an experimental run. In order to compare these experimental values with those predicted from the model, the calculated instantaneous conversions, X_A, must be time averaged from $t = 0$ to $t = t_f$ to yield $\bar{X}_A$, the time averaged conversion. The value of $\bar{X}_A$ is then compared with the experimental value of conversion for a given run.

PROCEDURE

Experimental data for the cracking of a neutral distillate was obtained using a static bed reactor as described by John and Wojciechowski (*6*). Using a Burroughs 6700 computer, the model was fitted to the data to determine the parameters k_0, G, N, and W. The criterion of fit was the minimum sum of squares of residuals, a resid-

TABLE 1
Composition of AlWO

Component	Wt%
Paraffins	14.8
Non-condensed cycloparaffins	34.2
2 Ring condensed cycloparaffins	15.6
3+ Ring condensed cycloparaffins	19.8
Benzenes	4.4
Naphthyl benzenes	3.7
Dinaphthyl benzenes	3.1
Di-aromatics	3.6
Tri-aromatics	0.1
Tetra-aromatics	0.2
Penta-aromatics	0.2
Thiaphenes	0.2

ual being defined as the difference between experimental and calculated conversion. The charge stock used here was a dewaxed neutral distillate called AIWO and its composition is reported in Table 1.

DISCUSSION

The parameter $k_0 = (k_{10} + k_{20})$ has been previously defined as the initial rate constant for the cracking of gas oil. We will henceforth call it the feedstock "reactivity." This latter definition is preferred since we will show below that the application of the term "rate constant" to this quantity in the case of gas oil cracking is misleading. The ambiguity arises when one considers that k_0 is composed of a large variety of initial rate constants and other terms involved in the cracking of the various molecular constituents of the gas oil and therefore is not simply a pure rate constant even though it does have the units of a first order kinetic rate constant. The term "reactivity" on the other hand is more suitable since no absolute kinetic interpretation is implied while at the same time a comparison from a common base of the initial crackability of various charge stocks is made possible. The above considerations lead us to the conclusion that k_0 is a rather complex parameter; however in spite of this fact, a fundamentally correct expression for the reactivity can be derived from basic considerations.

If one considers the adsorption of some jth species of gas oil (A_j) on an active site (S) on the surface of the catalyst, then the adsorption equilibrium can be written as

$$A_j + \mathrm{S} \rightleftarrows \mathrm{S}A_j.$$

It has been shown by Kindl *et al.* (7) that adsorption sites on the surface of zeolites have a very narrow distribution of energies of adsorption and hence presumably will exhibit uniform activity. This fact implies that the Langmuir adsorption isotherm should be applicable in this case. The fraction of active sites occupied by the SA_jth complex is thus taken to be

$$\frac{C_{sA_j}}{C_s} = \frac{K_{A_j} C_{A_j}}{1 + \sum_{i=1}^{n} K_{A_i} C_{A_i}}, \qquad (2)$$

where n is the total number of adsorbed species, and K_{A_j} is the adsorption equilibrium constant for the jth species of the feed. The rate of disappearance of the jth species by a catalytic monomolecular reaction to give the product q can now be written as

$$V_{jq} = k_{jq} C_{s_{A_j}} = \frac{k_{jq} K_{A_j} C_A C_s}{1 + \sum_{i=1}^{n} K_{A_i} C_{A_i}}, \qquad (3)$$

where k_{jq} is the first order rate constant for the cracking of the jth adsorbed species to product q. The overall rate of reaction for the cracking of gas oil to give product q is then

$$\begin{aligned} V_{A_q} &= \sum_{j=1}^{n} V_{jq} \\ &= C_s \sum_{j=1}^{n} \left[\frac{k_{jq} K_{A_j} C_{A_j}}{1 + \sum_{i=1}^{n} K_{A_i} C_{A_i}} \right]. \end{aligned} \qquad (4)$$

Since each of the j species can crack to a variety of products, say l, then the overall rate of cracking of the n species of feed molecules to produce the l species of products is

$$\begin{aligned} V_{\mathrm{A}_q} &= \sum_{q=0}^{l} V_{A_q} \\ &= C_s \sum_{j=1}^{n} \sum_{q=0}^{l_j} \left[\frac{k_{jq} K_{A_j} C_{A_j}}{1 + \sum_{i=1}^{n} K_{A_i} C_{A_i}} \right]. \end{aligned} \qquad (5)$$

If we change the notation by taking

$$\sum_{j=1}^{n} C_{A_j} = C_{\mathrm{A}} \quad \text{and} \quad X_{A_j} = \frac{C_{A_j}}{C_{\mathrm{A}}},$$

where C_A is the concentration of total unconverted feed, then Eq. (5) becomes

$$V_A = C_s C_A \sum_{j=1}^{n} \sum_{q=0}^{l} \left[\frac{k_{jq} K_{A_j} X_{A_j}}{1 + C_A \sum_{i=1}^{n} K_{A_i} X_{A_i}} \right]. \tag{6}$$

The denominator of this expression can be simplified by considering the consequences on Eq. (6) of the term $C_A \sum_{i=1}^{n} K_{A_i} X_{A_i}$ being dominant. Clearly in this case, the overall rate of cracking would become zero order with respect to feed concentration. This order, however, has not been observed in gas oil cracking by any previous worker (*1,3,8*). Hence it must be concluded that

$$C_A \sum_{i=1}^{n} K_{A_i} X_{A_i} \ll 1. \tag{7}$$

The inequality (7) implies that at reaction conditions, active sites are sparsely covered by carbonium ions. Using this approximation, Eq. (6) can now be simplified to

$$V_A = C_s C_A \sum_{j=1}^{n} \sum_{q=0}^{l_j} k_{jq} K_A X_{,A}. \tag{8}$$

Under initial conditions Eq. (8) becomes

$$\begin{aligned} V_{A\,\text{initial}} &= C_{s_0} C_{A_0} \sum_{j=1}^{n} \sum_{q=0}^{l_j} k_{jq} K_{A_j} X_{A_j} \\ &= k'_0 C_{s_0} C_{A_0}. \end{aligned} \tag{9}$$

Using this definition of k'_0, the overall cracking rate expression becomes

$$V_A = k_0 \theta C_A \sum_{j=1}^{n} \sum_{q=0}^{l_j} k_{jq_0} K_{A_j} X_{A_j}, \tag{10}$$

where $k_0 = k'_0 C_{s_0}$ and $k_{jq_0} = k_{jq}/k'_0$. θ is the fraction of original active sites remaining ($= C_s/C_{s_0}$) and is obtained from the decay function of the time-on-stream theory. In Eq. (10) the term $\sum_{j=1}^{n} \sum_{q=0}^{l_j} k_{jq_0} K_{A_j} X_{A_j}$ accounts for the refractoriness of the feedstock (*9*) and Kemp and Wojciechowski (*10*) have shown that it is usually well approximated by the function $(C_A/C_{A_0})^W$.

Because of the complexity of the expression for the reactivity, k_0, it is not immediately apparent whether this parameter will follow an Arrhenius type of temperature dependence, however, an examination of the individual terms of the k_0 expression provides a partial answer to this question. Since C_{s_0} is a concentration and is independent of temperature, it need not be considered further. On the other hand k_{jq} is the rate constant for the monomolecular cracking of the *j*th adsorbed species of the feedstock and should obey the Arrhenius law. The adsorption equilibrium constant, K_{A_j} will likewise obey the Arrhenius law regardless of whether the adsorption–desorption reaction is exothermic or endothermic. The product of these two terms will therefore display Arrhenius behavior. A large sum of such Arrhenius dependent terms modified by fractional concentrations $X_{A_{j_0}}$, can be shown by computer simulation to exhibit an Arrhenius relationship over fairly wide ranges of temperature.

Figure 1 shows that in fact the experimental values of k_0 do show an Arrhenius temperature dependence. If it is now assumed that some average value of the product, $\overline{k_A K_A}$, can be used to represent each of the *n* species of the feed, we can write

$$k_0 = C_{s_0} \sum_{j=1}^{n} \sum_{q=0}^{l_j} k_{jq} K_{A_j} X_{A_{j_0}}$$

n

$$= C_{s_0} \overline{k_A K_A} \sum_{j=1}^{n} X_{A_{j_0}} = C_{s_0} \overline{k_A K_A} \tag{11}$$

For such an average value it is then possible to consider the activation energies and the frequency factors for the cracking and adsorption constants in turn. From Fig. 1, the activation energy for k_0 is found to be 51.4 kcal/g mole and the frequency factor is 2.26×10^{18} sec^{-1}.

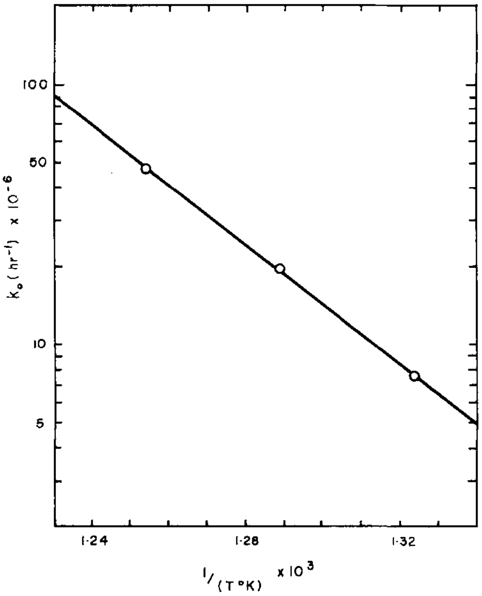


FIG. 1. Arrhenius plot of reactivity, k_0, for a wax-free neutral distillate called AIWO.

The experimental value for the frequency factor appears at first sight to be larger than expected. The explanation for this lies in the fact that from Eq. (11) we see that the frequency factor, A_0, is of the form

$$A_0 = A_c \cdot \frac{A_1}{A_{-1}} \cdot C_{s_0} \cdot b,$$

where A_c is the frequency factor for the average monomolecular cracking reaction while A_1 and A_{-1} are the average frequency factors for the adsorption and desorption rate constants, respectively, C_{s_0} is the original concentration of active sites on the catalyst and b results from the fitting procedure used in Eq. (1) and reported previously (*3*) and has a value of about 10^{-2}. The ratio A_1/A_{-1} can also be written as $e^{\Delta S/R}$, where $\Delta S = S_{\substack{\text{adsorbed}\\\text{species}}} - S_{\text{reactants}}$. Since A_c is the frequency factor associated with a true unimolecular rate constant for the average cracking reaction, it should not have a value greater than 10^{13} sec^{-1}, the value of the universal frequency factor. A_0 is, however, of the order 10^{15} which implies that $bC_{s_0}e^{\Delta S/R} \geqslant 10^2$ and hence if $b \approx 10^{-2}$ and $C_{s_0} \approx 10^{-4}$ moles/cc, $e^{\Delta S/R} \geqslant 10^8$ or $\Delta S \geqslant 46$ cal/g mole °K. A positive ΔS indicates that the entropy of the adsorbed species must be higher than the entropy of the gas phase reactants. This in turn may be due to the relatively large number of configurations which a molecule may assume upon adsorption while losing only three translational and three rotational degrees of freedom (*11*).

The large value of the observed frequency factor can also be considered from another point of view. The ratio A_c/A_{-1} can be thought of as the ratio of the probability of an energized carbonium ion cracking to the probability of its desorbing without reaction. If we assume that $A_1 \approx 10^{13}$ (g mole)$^{-1}$ sec^{-1}, the ratio A_c/A_{-1} becomes 10^8. Thus it appears that A_{-1} is much smaller than A_c and that an energized carbonium ion is much more likely to crack than it is to desorb.

The measured activation energy, E_0, is seen from Eq. (10) to be the energy required to raise an average gas phase molecular species to the activated state. That is

$$E_0 = E_c + E_1 - E_{-1},$$

where E_1 and E_{-1} are the activation energies for the adsorption and desorption reactions, respectively.

Assuming that the average carbon number for the feedstock is 25, and from determining the changes in enthalpy for a variety of C_{25} compounds cracking to a variety of products, it has been found that a likely average value for ΔE is 36 kcal/g mole. The above results are summarized in the form of an energy diagram in Fig. 2. Since it is not possible to calculate E_1 or E_{-1} from the work performed here, nor are there any independent data concerning these energies, a value for E_c cannot be obtained from our results. To evaluate E_c, it would be necessary to perform cracking runs at high pressure where

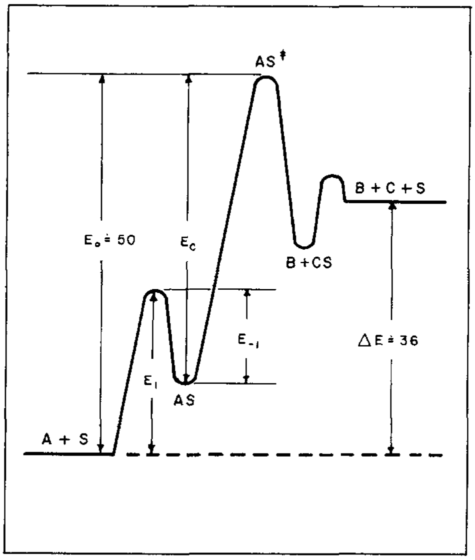


FIG. 2. Energy diagram for the catalytic cracking of a wax-free neutral distillate. E_c is the true activation energy for an average feed molecule. All numerical values have units kcal/g mole.

the overall reaction rate is zero order with respect to feed.

In previous work (*12*) we have shown that for the extracted and dewaxed neutral distillate used in this work, the catalyst is adequately described by an exponential decay function. This is because N, the aging exponent, is very large for this feedstock and hence m, the order of the decay reaction with respect to active sites, given by

$$m = 1 + \frac{1}{N}$$

is very near unity. It is apparent from Table 2 that temperature causes N to decrease slowly indicating that the mechanism of decay is slowly changing toward a greater involvement of two site decay reactions. At the same time k_{md}, the decay rate constant, increases with temperature as shown on an Arrhenius plot in Fig. 3. These phenomena will be discussed elsewhere.

TABLE 2
PARAMETER VALUES FOR THE NEUTRAL DISTILLATE AT THREE TEMPERATURES

Parameter	Temp (°C) 482	503	524
$b\ k_0$ (hr^{-1})	5.41×10^4	1.35×10^5	3.17×10^5
k_0 (hr^{-1})	7.62×10^6	1.95×10^7	4.72×10^7
N	31.03	29.71	24.73
G (hr^{-1})	0.30	0.51	0.80
W	3.08	3.24	3.34
k_{md} (hr^{-1})	9.01	10.40	15.58
b	7.10×10^{-3}	6.92×10^{-3}	6.72×10^{-3}

It is also found that W, the parameter which describes the feedstock refractoriness, increases with temperature. This in turn means that the overall order $(1 + W)$ of the gas oil cracking reaction increases with temperature. Since both the reactivity and the order of reaction increase with temperature, we have a compensation occurring with the result that conversion in gas oil cracking does not increase as rapidly with temperature as one would expect based on the activation energy of the reactivity alone. Failure to recognize this temperature dependent nature of the order of reaction would lead one to predict a lower energy of activation for reactivity than that reported here. This

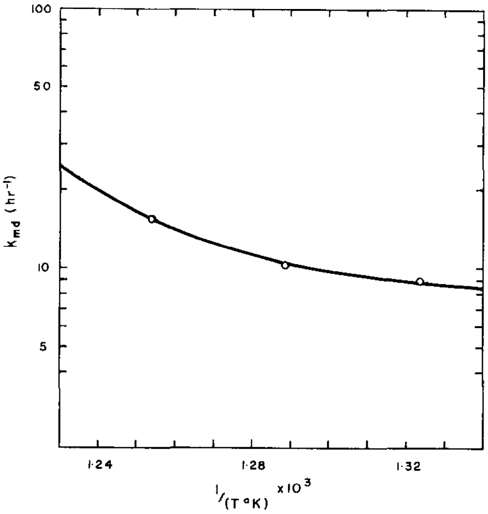


FIG. 3. Arrhenius plot of mth order decay rate constant.

is no doubt the major reason why most previous gas oil cracking studies (*13*) have reported energies of activation in the order of 30 kcal/g mole. We feel, however, that our value is more representative of the energy of activation for the average cracking reactions and will be of greater value in fundamental thermodynamic and kinetic arguments.

CONCLUSIONS

A derivation has been presented which shows the theoretical foundations for the gas oil reactivity, k_0. It is seen that this parameter is in actuality a rather complex quantity. Despite its complexity the theoretical expression for k_0 is shown to generally follow an Arrhenius temperature dependence. The theoretical arguments are supported by experimental evidence which shows that the experimental values for k_0 reported here do follow an Arrhenius behavior with an activation energy of 51.4 kcal/g mole and a frequency factor of 2.26×10^{18} sec^{-1}.

It is found that an increase in temperature causes the mechanism of decay to change slowly toward a greater involvement of two site decay reactions. At the same time, the decay rate constant, k_{md}, does not follow an Arrhenius temperature dependence but does increase with temperature.

The refractoriness of the feedstock, W, is found to be temperature dependent and hence the overall order of cracking reaction $(1 + W)$, is also temperature dependent. The compensation effect produced by the increase both in the reactivity and in the overall order of the cracking reaction results in a temperature effect on conversion which is smaller than would be expected on the basis of the activation energy of the reactivity parameter alone.

The set of self-consistent values of the various parameters reported here will hopefully be of some help to those engaged in reactor optimization studies and will help to introduce realism to the conclusions thus derived.

ACKNOWLEDGMENTS

We thank Imperial Oil of Canada Limited for the feedstock and its analysis. We also thank the National Research Council of Canada for financial support.

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