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On Identifying the Primary and Secondary Products of the Catalytic Cracking of Neutral Distillates

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It is shown that the catalytic cracking of an extracted neutral distillate results in the formation of C_5^+ gasoline, *n*-butane, butene and propylene as the sole primary products of cracking.

It is argued that branched chain aliphatics which arise in catalytic cracking are the products of secondary reactions involving product olefins as reactants. There is also reason to believe that, in general, a cracking event consists of the departure of an olefin followed immediately by neutralization and desorption of the residual carbonium ion.

NOMENCLATURE

k_{j0}	initial rate constant for formation of the *j*th product (hr^{-1})
k_0	initial rate constant for the conversion of A (hr^{-1})("reactivity")
X_A	instantaneous fractional conversion of A
X_B	instantaneous fractional production of B
$\bar{X}_j$	time averaged fractional product yield
t	instantaneous time-on-stream
t_f	total duration of experimental run
α_j	initial selectivity for formation of product *j* ("ultimate product efficiency," UPE)

INTRODUCTION

The catalytic cracking of hydrocarbons is a complex process, both because of the many reactions that can occur and because the activity of the cracking catalyst changes very rapidly during reaction.

Pioneer work in this field by Greensfelder and Voge (*1*) examined the cracking behavior of several pure hydrocarbons. Such studies showed that various hydrocarbons, in the presence of an acidic catalyst, crack to give preferentially fragments of three or more carbon atoms. These observations in turn resulted in theoretical considerations which attempt to explain the mode of action of the cracking catalyst. The application of these theoretical concepts to the prediction of product distributions from the catalytic cracking of *n*-hexadecane have generally shown good agreement for products containing between 3 and 13 carbon atoms. The major deviation from theory was evident for products with fewer than three carbon atoms. Greensfelder *et al.* (*2*) have ascribed the formation of these C_1 and C_2 hydrocarbons in the cracking of *n* C_{16} to "less favored types of cracking." Conversions in this study were 11 to 68% and it is now generally thought that the C_1's and C_2's originated in thermal reactions.

Data obtained by Greensfelder *et al.* (*2*) on the product distribution from cracking

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n-hexadecane in a fixed-bed reactor over Al_2O_3–ZrO_2–SiO_2 also indicated that even at the above conversion levels large amounts of isoparaffins were produced, presumably by secondary reactions. Voge (*3*), and more recently Nace (*4*), have proposed mechanisms to explain this result which is regarded as evidence that isoparaffins are primary reaction products. In the analysis of all the above data no extrapolations to zero conversion were attempted and data were obtained at conversion of about 30%. It has, however, been shown (*5*,*6*) that estimates of initial rates of formation of products can be obtained by extrapolation of the instantaneous selectivity plots to zero and this is the correct method of interpretation of the effects occurring in the absence of secondary reactions.

This paper presents a study of product distribution from a system that is subject to catalyst decay. The study is based on an experimental procedure suggested by the theoretical work of Campbell and Wojciechowski (*5*). A combination of this procedure and of the concept of initial selectivity is used to determine, in some detail, product distribution in catalytic cracking and to provide information about the reaction network through which catalytic cracking of petroleum distillates proceeds.

According to the technique of Campbell and Wojciechowski (*5*), the time-averaged yields are plotted against time-averaged conversions on a selectivity plot, with catalyst-to-oil ratio as a fixed parameter. In this way a system of constant cat/oil loops is generated and clearly indicates that at a given conversion it is possible to observe a variety of yields of a product depending on the conditions used in the experiment. This system of loops can be enveloped by a single curve which corresponds to the instantaneous selectivity curve for that product and has been called the optimum performance envelope (OPE) of the system. The OPE also describes the selectivity pattern of the same system if there had been no decay of catalyst activity. This condition is in practice approximated by runs at short times-on-stream when the effect of catalyst decay is small.

Using the simplified scheme for catalytic cracking shown on Fig. 1, it can be shown that at the initial conditions of zero conversion and assuming all the reactions are of the same order

$$\frac{dX_B}{dX_A} = \frac{k_{10}}{k_{10} + k_{20}} = \alpha_1, \qquad (1)$$

where k_{10} and k_{20} represent initial rate constants for the formation of gasoline and the other primary products, respectively, and α_1 is the initial selectivity for the formation of gasoline (the ultimate gasoline efficiency). With the boundary condition of $X_A = 0$, $X_B = 0$, the solution of Eq. (1) becomes:

$$X_B = \frac{k_{10}}{k_{10} + k_{20}} X_A. \qquad (2)$$

The effect of the time-averaging process is obtained by integrating Eq. (2) over the time of the run and dividing the result by the final catalyst time-on-stream t_f. Thus,

$$\frac{1}{t_f}\int_0^{t_f} X_B \, dt = \frac{1}{t_f}\frac{k_{10}}{k_{10} + k_{20}}\int_0^{t_f} X_A \, dt, \qquad (3)$$

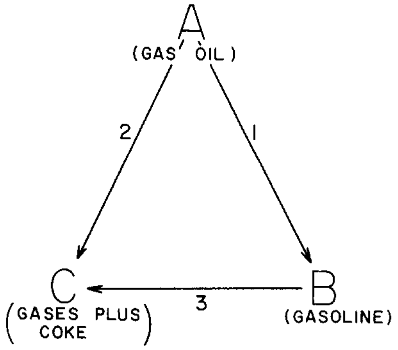


FIG. 1. Simplified cracking mechanism.

and hence

$$\bar{X}_B = \frac{k_{10}}{k_{10} + k_{20}} \bar{X}_A. \qquad (4)$$

This result shows that without considering the secondary process of gasoline cracking, the selectivity pattern which would result in the cracking of gas oil can be described by a straight line drawn through the origin of the selectivity plot with a slope $k_{10}/(k_{10} + k_{20})$. The line described by Eq. (4) is in fact the tangent to the observed optimum performance envelope at zero conversion and is called the "ultimate product efficiency" (UPE).

Previous studies (*5,7,8*) in this field have dealt only with gasoline selectivity and hence the above has been shown to apply in that case only. However, equations similar to Eq. (4) can be developed for all the products of a catalytic cracking reaction. Thus, for the *j*th reaction product, the ultimate product efficiency line on an $\bar{X}_j$ versus $\bar{X}_A$ plot has the slope

$$\bar{X}_j = \frac{k_{j_0}}{\sum_{j=1}^{n} k_{j_0}} \bar{X}_A = \frac{k_{j_0}}{k_0} \bar{X}_A = \frac{k_{j_0}}{k_{10} + k_{20}} \bar{X}_A, \qquad (5)$$

where k_{j_0} is the initial rate constant for the formation of the *j*th product and

$$k_0 = \sum_{j=1}^{n} k_{j_0} = k_{10} + k_{20}.$$

From the principle of conservation of matter it follows that

$$\sum_{j=1}^{n} \frac{k_{j_0}}{\sum_{j=1}^{n} k_{j_0}} = 1.0. \qquad (6)$$

This study is mainly concerned with the interpretation of cracking yields for various products on the basis of optimum performance envelopes and of the ultimate efficiencies of such products as represented by the slopes at the origin of their OPE's.

EXPERIMENTAL METHODS

Materials

The La-Y zeolite catalyst used in this study was prepared from Linde SK 40 molecular sieves. The sieves were contacted with an aqueous solution of $LaCl_3$ for 6 hr, filtered, and dried for 4 hr at 200°C. The exchange was repeated until further contacting did not lead to any significant reduction in the sodium content of the zeolite. The lanthanum exchanged powder was pelletized, crushed, and then steamed for 24 hr at atmospheric pressure to increase stability.

The feed stock was prepared from 150 raw neutral distillate. The treatment involved extracting the 150 raw neutral distillate with phenol to remove polycyclic aromatics and metallic contaminants. The raffinate, industrially known as 150 neutral solvent extract, is a highly paraffinic product with a pour point of 87°F and a wax content of 26.8 mole%. We will refer to this feed stock as AOWI. The composition of this feed is presented in Table 1.

Apparatus and Experimental Procedure

The experimental apparatus was similar to that previously described (*9*). In this

TABLE 1
COMPOSITION OF AOWI

Component	Wt%
Paraffins	25.8
Noncondensed cycloparaffins	36.2
2 Ring condensed cycloparaffins	12.9
3+ Ring condensed cycloparaffins	16.0
Benzenes	3.1
Naphthyl benzenes	2.6
Di-naphthyl benzenes	1.9
Di-aromatics	0.6
Tri-aromatics	0.1
Tetra-aromatics	0.1
Penta-aromatics	0.3
Thiaphenes	0.4

study the fixed-bed tubular reactor was constructed from a 1 in. diameter stainless steel pipe and the vaporizer-preheater section of the reactor was packed with 1/8 in. stainless steel balls. The whole unit was encased tightly in three pairs of 350 W ceramic furnaces. Temperature within the reactor bed was controlled to within ±2°C.

The experimental program was designed to generate the selectivity loops described earlier. To this end the reactor was packed with a known weight of dry catalyst and a measured volume of the liquid feed was pumped into the reactor at a constant rate by a syringe pump. The catalyst time-on-stream, t_f, was determined from the length of time required to pump a fixed volume of feed into the reactor. The catalyst time-on-stream was then varied by varying the feed rate. For each catalyst-to-oil ratio the catalyst time-on-stream was varied from 2 to 30 min. Four catalyst-to-oil ratios ranging from 0.0034 to 0.25 were investigated. Throughout the program a constant reactor volume of 50 cc was maintained by diluting the catalyst with clean Pyrex glass. Preliminary tests revealed that diluting the catalyst had no detectable effect on either the overall conversion or on product yields.

Analytical

The liquid product of the reactor was analyzed on a Tower's automatic standard distillation unit. Gasoline range hydrocarbons boiling up to 410°F were collected as the distillate. The bromine number and the olefin concentration of the gasoline were determined according to a procedure recommended by ASTM method D875 (*10*).

The gaseous products were quantitatively analyzed on a Pye temperature programmed chromatograph equipped with two 6 ft long, ¼ in. diameter columns packed with 60/80 mesh poropak Q and a thermal conductivity detector cell.

The yield of coke was determined from the weight of carbon dioxide produced during the regeneration of the catalyst.

RESULTS

The data presented here in graph form have been corrected for thermal reactions and are reported in full in Ref. (*11*). The need for this correction arises from the fact that, at catalytic cracking temperatures, homogeneous gas phase reactions are unavoidable. Thus the overall yield of any product is made up of two components: the thermal and the catalytic. In order to observe the catalytic yields, the thermal components have to be subtracted from the overall results.

Since the thermal conversion of the feed during a catalytic run cannot be determined experimentally, it was approximated by thermal conversion obtained during blank runs. It was assumed that at the same reaction conditions of temperature and time-on-stream, the conversion of the feed due to reactions in the gas phase is approximately the same in the catalytic runs as in the blank runs. The experimental procedure for the blank runs was identical in every respect to that used in the main experimental program. For the blank runs, however, the catalyst zone in the reactor was filled with clean crushed Pyrex glass and no catalyst.

At short times-on-stream (2–4 min) when the conversions obtained for blank runs are low compared with the overall conversions, the error in this approximation is least significant. Since all the conclusions drawn from this study are based on evidence from the OPE, the assumption that thermal conversion obtained during a blank run is approximately the same as thermal conversion during a catalytic reaction is valid within the experimental error.

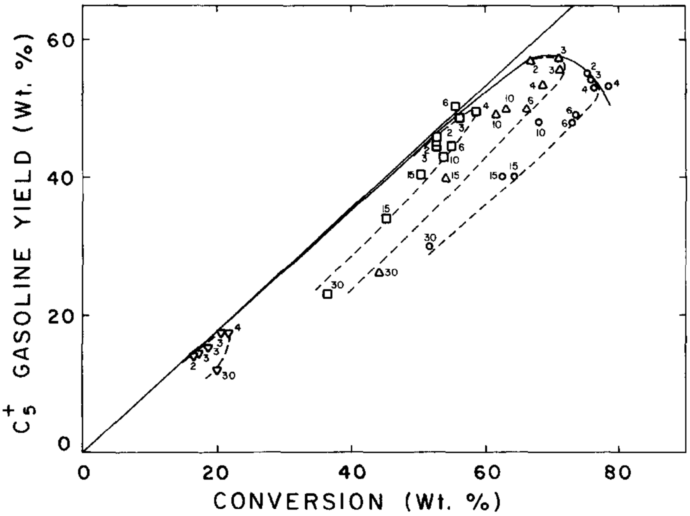


FIG. 2. Gasoline selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental condition: Reaction temperature = 503°C, feedstock = AOW1; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

Selectivity Behavior for Fixed-Bed Reactors

The time-averaged selectivity behavior of gasoline is characterized by loops, which show that at any given conversion level it is possible to obtain many different gasoline yields. This is illustrated in Fig. 2. It is evident that the system of loops can be contained in an enveloping curve, the OPE. The experimental runs performed at short times-on-stream lie on the OPE.

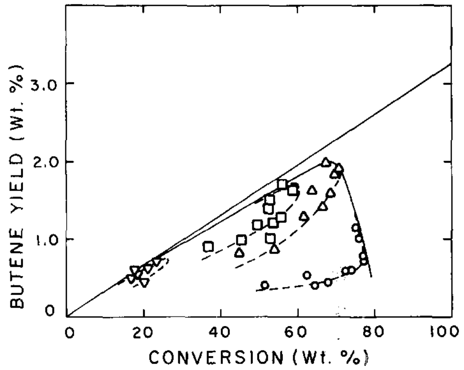


FIG. 3. Butene selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental condition: Reaction temperature = 503° C, feedstock = AOW1; cat/oil: (○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

Figure 2 also shows that the gasoline OPE exhibits a maximum at about 68% conversion level. Both the time averaged and instantaneous selectivity patterns observed in the case of gasoline range compounds were also observed for butene (Fig. 3). As in the case of gasoline, there is a maximum in butene yield as conversion is increased.

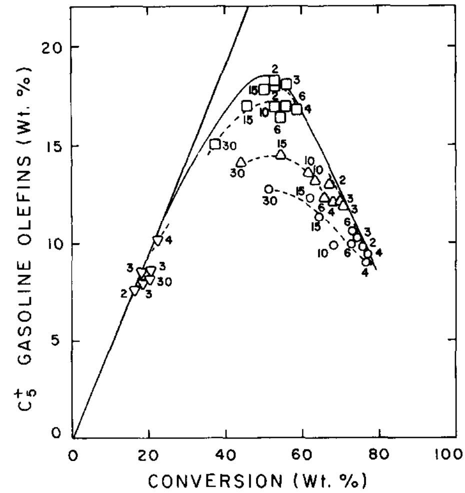


FIG. 4. C_5^+ Gasoline olefins selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOW1; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

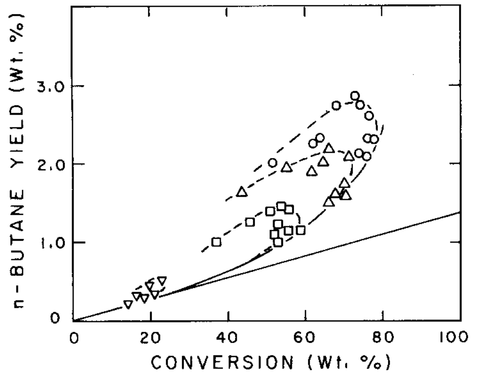


FIG. 5. n-Butane selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOW1; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

The trend in the yield of butene appears to be characteristic of all olefins in the C_5, 410°F gasoline boiling range. Figure 4 shows the selectivity behavior of such gasoline range olefins.

Figures 5 and 6 show that the selectivity pattern of n-butane and propylene are also characterized by loops contained within optimum performance envelopes. However, whereas in the case of gasoline and butene the OPE defined the upper limits of the product yield at any given conversion, in the case of n-butane and propylene they define the lower limits of yield. This difference is apparent from the behavior of the individual loops. In this case the experimental runs at high space velocities (short t_f) form the lower part of the loops coincident with the OPE. As the space velocity is decreased at a given cat/oil, more n-butane is formed until a maximum is reached. Further decrease in the space velocity causes a drop in the yield. Thus, the loops approach the origin in an anticlockwise direction. The optimum performance envelopes formed when the loops are enclosed do not show a maximum within the conversion range investigated. This is taken as evidence that unlike butene and the C_5^+ gasoline fraction, neither n-butane nor propylene react further to a significant extent at the cracking conditions used here. The upward curvature of the loops away from their initial slope constitutes evidence that these compounds are formed from both the feedstock and the primary products.

The selectivity behavior of isobutane, propane, ethane, ethylene, methane and coke (Figs. 7–12) is similar to that de-

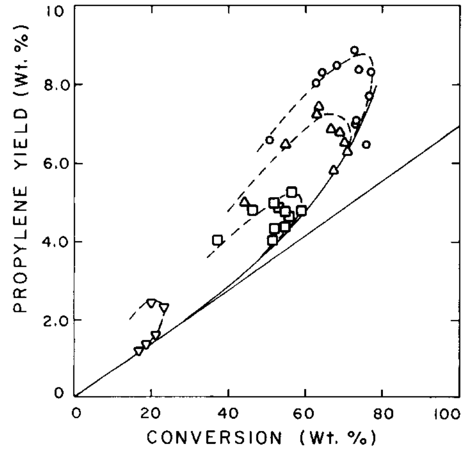


FIG. 6. Propylene selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOWI; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

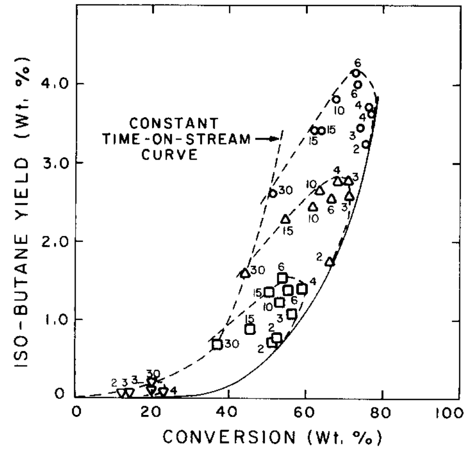


FIG. 7. Isobutane selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOW1; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

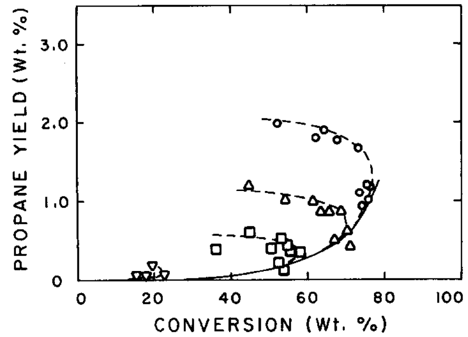


FIG. 8. Propane selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOWI; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

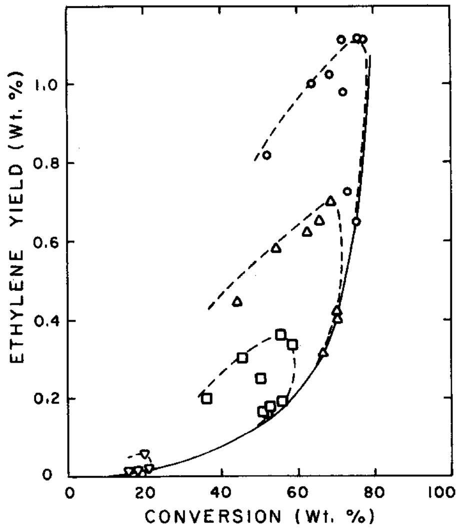


FIG. 10. Ethylene selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOW1; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

scribed for *n*-butane and propylene. The significant difference lies in the fact that the optimum performance envelopes for *n*-butane and propylene follow a trend indicating a finite slope at the origin. This means that these compounds are products of the primary cracking reaction. The gasoline and butane optimum performance envelopes also show nonzero slopes at the origin of the selectivity plot. On the other hand, the optimum performance envelopes of all the other products including isobutane and coke follow a trend indicating zero slopes at the origin. Therefore, these compounds are not produced in the initial cracking step and are clearly secondary reaction products. According to Eq. (6) the sum of all the initial selectivities (UPE's) should be equal to one. Table 2 shows that this condition is approximately fulfilled in

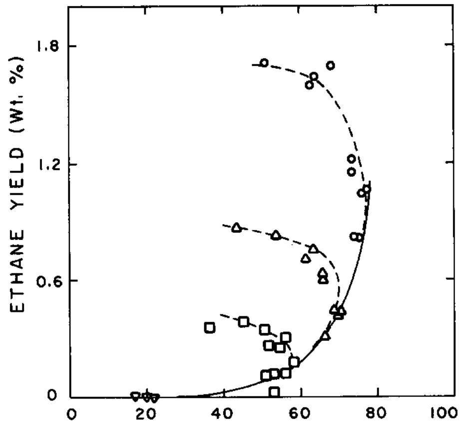


FIG. 9. Ethane selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOWI; cat/oil:(○); 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

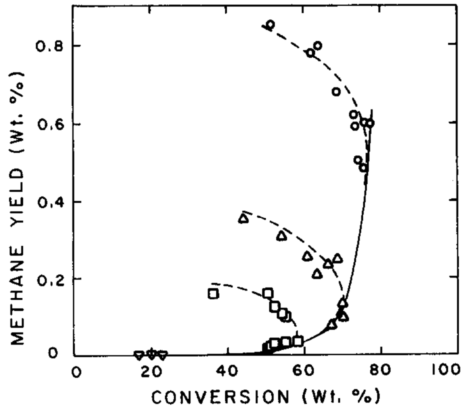


FIG. 11. Methane selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOWI; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

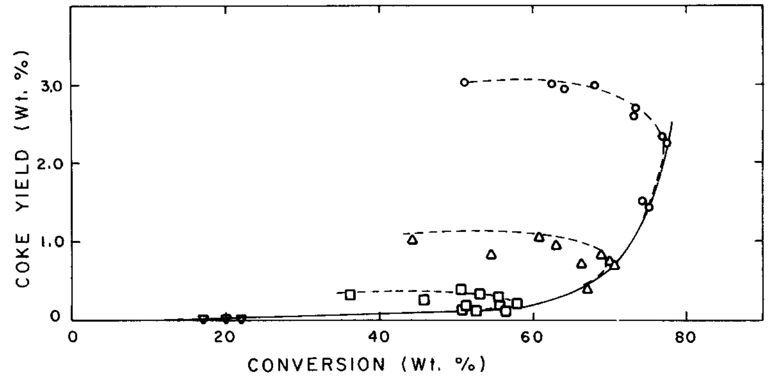


FIG. 12. Coke selectivity behavior of a fixed-bed reactor with decaying catalyst. Experimental conditions: Reaction temperature = 503°C, feedstock = AOWI; cat/oil:(○) 0.25, (△) 0.05, (□) 0.01, (▽) 0.0034.

this case leaving no doubt that all the primary products have been accounted for.

DISCUSSION

In a fixed-bed reactor experiencing catalyst decay, all the reactants fed into the system do not crack at the same level of catalytic activity. The first molecules to come in contact with the fresh catalyst are cracked at a level of activity equal to the initial activity of the catalyst. Subsequent molecules are cracked by a progressively less active catalyst. As a result, the observed yield from a fixed-bed reactor is a time-averaged value, and the cumulative selectivity which is defined as yield/conversion becomes a function of the catalyst time-on-stream. When experimental runs are carried out at short times-on-stream, the difference between cumulative selectivity and instantaneous selectivity is very slight. Therefore, data obtained under these conditions tend to lie on the optimum performance envelope, which represents instantaneous yield values. As the time-on-stream is increased, the time averaged yields show increasing departure from the instantaneous yield behavior.

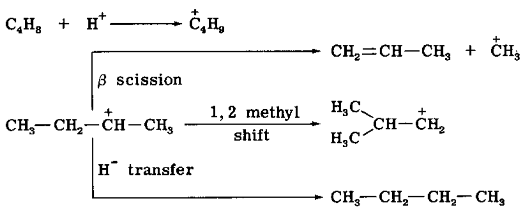
TABLE 2

SUMMARY OF INITIAL SELECTIVITIES OF REACTION PRODUCTS FROM CATALYTIC CRACKING OF THE EXTRACTED NEUTRAL DISTILLATE (AOWI)

Product	Initial product selectivity at 503°C
Gasoline	0.880
n-Butane	0.013
Isobutane	0.000
Butene	0.033
Propylene	0.070
Propane	0.000
Ethylene	0.000
Ethane	0.000
Methane	0.000
Coke	0.000
Σ	0.996

In the case of the primary unstable products of catalytic cracking (butene and gasoline range hydrocarbons), the time-averaged yields are lower than the instantaneous yields. On the other hand, the time-averaged yields are higher than the instantaneous yields in the case of the stable primary or stable secondary products as evidenced by the behavior of the loops in Figs. 5–12. This phenomenon no doubt accounts for the unexpectedly high yield of isobutene and isopentane obtained by Greensfelder *et al.* (*2*) when they cracked hexadecane in a fixed-bed reactor at a time-on-stream of 60 min. This was regarded as evidence that the isomerized components are products of primary cracking. Any study designed to demonstrate the action of a cracking catalyst must be based on the behavior of the optimum performance envelopes in order to avoid such misconceptions. In Fig. 7 it is shown that it is possible to arrive at two different conclusions regarding isobutane formation depending on how data from a fixed-bed reactor is analyzed. Since the constant 30 min time-on-stream curve in Fig. 7 has a definite slope at the origin of the selectivity plot, the conclusion would be drawn that isobutane is formed as a primary reaction product (*3*). On the other hand, the trend of the OPE shows clearly that isobutane is formed only in secondary reactions.

The work of Greensfelder and Voge (*1*) with pure hydrocarbons has indicated that olefins isomerize more readily than paraffins. For instance butene was reported to react readily to isobutane while the cracking of *n*-butane did not yield any detectable amount of isobutane. Franklin and Nicholson (*12*) and Brouwer and Hogeveen (*13*) have also reported that *n*-butane does not isomerize to isobutane on acidic catalysts. The inert nature of *n*-butane at catalytic cracking conditions is indicated here by the OPE shown in Fig. 5 which shows that as conversion is increased, the yield of *n*-butane increases without reaching a maximum. The existence of a maximum in the selectivity curves of butene and of the gasoline fraction on the other hand suggests that these compounds react readily by secondary reactions. Butene for instance can react according to the following scheme:



These reactions account for the formation of isobutane and some of the methane formed in secondary reactions.

The isomerization and hydride ion transfer reactions of gasoline range olefins will not affect the yield of gasoline since the boiling points of the products are within the gasoline boiling range. However, catalytic cracking of the gasoline range compounds inevitably leads to the formation of lower boiling materials. For example, the cracking of pentane will yield propylene and ethane. We believe the C_1 and C_2 fractions probably arise from the β scission of carbonium ions formed from short chain olefins, produced in the primary reaction.

In the formation of carbonium ions by hydride ion abstraction from components of the feed, the reported C–H bond energies (*14*) suggest that the hydrogen on the terminal carbon is more difficult to abstract than the other hydrogens. It is concluded from this that the formation of primary carbonium ions is energetically much less favorable than the formation of secondary or tertiary carbonium ions. Cracking of a secondary carbonium ion by β scission must lead to the formation of an olefin with at least three carbon atoms in the molecule as long as we admit that internal CC bonds crack more readily than the CC bonds near the ends of the chain. An examination of the results reported here shows that propylene is indeed the smallest compound formed in the primary cracking step. We are unable at present to explain the conflict posed by the presence of *n*-butane and the absence of propane among the initial products.

Estimates of the initial selectivities of olefin formation obtained from Figs. 3, 4, and 6 show that olefins constitute 58 wt% of the products formed in the initial cracking step. This result implies that there are slightly more moles of olefins formed initially than there are of saturates. In the gasoline fraction, however, it appears that equal amounts of olefins and of saturates are formed. If the feedstock had been composed of pure straight chain aliphatics, a similar result would have indicated that the initial cracking event on an average takes place close to the center of the hydrocarbon chain or alternately that the carbonium ion can be formed on any carbon in a chain with equal probability. Furthermore, this data indicates that the carbonium ion left on the surface of the catalyst after the olefin is cracked off abstracts a hydride ion and is in most cases promptly desorbed rather than cracking further. It must be pointed out that these arguments rest on the assumption that there is a similar distribution of molecular weights between the olefins and the saturated products of the primary cracking reactions. This has not been tested but appears to be a reasonable assumption to make.

The fact that coke is not formed in the primary reaction step might have been expected in view of the work of Blue and Engle (*15*) which suggested that the presence of olefins in the reacting medium is essential for coke formation. The exact role of olefins in the coke forming process has not been determined, but according to Blue and Engle (*15*) and Thomas (*16*) olefins play an important role as acceptors of hydrogen from species which remain adsorbed on the catalyst to form a hydrogen deficient material. Voge (*3*) and Appleby *et al.* (*17*) subscribe to the hypothesis that coke is formed via condensation reactions involving aromatics and olefins. In our case olefins were not present in the neutral distillates used as feed and the absence of coke as a primary product lends strong support to the view that olefins are essential for coke formation.

From the patterns of selectivity and other considerations discussed here we propose that the catalytic cracking of gas oils proceeds via a complex reaction network in which we have ascertained the following facts:

1. C_5^+ gasoline and butene are unstable primary products.
2. Propylene and *n*-butane are stable products formed from both the feedstock and the unstable primary products.
3. Isobutane, propane, ethylene, ethane, methane and coke are stable secondary reaction products which arise from the unstable primary products.

From these we can construct a more detailed mechanism of catalytic cracking as shown in Fig. 13. In this scheme reactions 2*i* sum up to give reaction 2 in the simplified scheme shown in Fig. 1 while reactions 3*i* correspond to reaction 3 of the simplified mechanism shown on Fig. 1.

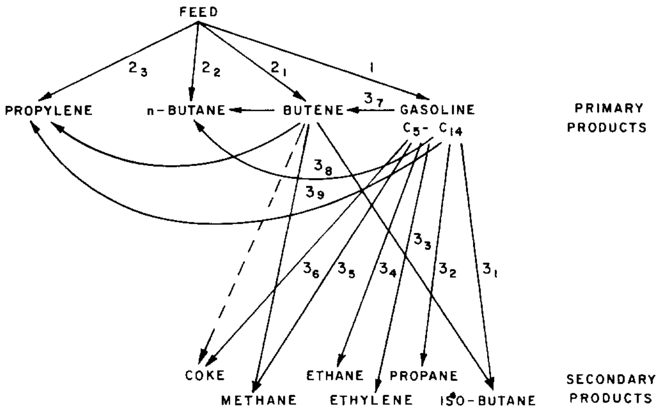


FIG. 13. Extended cracking mechanism.

CONCLUSION

Our theoretical and experimental work shows that fundamental studies on catalytic cracking using a decaying catalyst can best be conducted in a fixed-bed reactor. We have shown that a study of product distributions from a fixed-bed cracker on the basis of the OPE's provides a means of understanding the details of the action of the cracking catalyst. For instance primary and secondary reaction products can be identified by noting the initial product selectivity. From this information we can establish the reaction network through which catalytic cracking of gas oils proceeds.

Here we have shown that gasoline, propylene, *n*-butane and butene are the only primary products of catalytic cracking of gas oil while all other products arise by secondary reactions. We have also shown that isomerized products probably arise from secondary reactions, presumably those of olefins produced in the initial cracking event. There is also good reason to believe that the initial cracking event consists of the cracking off of an olefin followed immediately by hydride ion transfer and desorption of the remaining moiety.

ACKNOWLEDGMENTS

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