as a representative commercial plasticizer. In the cases where Mooney viscosity was determined, the amates were equal or superior to the ester, and as the ester used is one of the best currently employed, the amates are therefore superior to it as plasticizers. In Table V the torsion test of Clash and Berg (2) was adopted as the chief diagnostic piece of evidence, coupled with heat loss at 100° C. Long-chain acids with long-chain alcohols and amines gave the best results.

When used in the poly(vinyl chloride) polymer, the plasticizers were compatible but in some cases did not soften the stock to a satisfactory degree. Low heat loss and low torsion test in the Clash and Berg (2) apparatus were sought. n-Butyl N,N-di-n-butyl azelamate gives 3.5% and −40° C., respectively, to hold first place. The corresponding sebacamate ranks second. The low temperature torsion test ranks the straight-chain dicarboxylic acids as the best, regardless of the substituent. Low heat loss seems best attained by use of large substituents on the ester and amide portions. Probably any compatible material of high molecular weight would be permanent.

The ultraviolet exposure test was run for a week as follows:
Strips, 1 × 5 inches, one half covered with aluminum foil, were mounted on a wooden disk. The disk, 30 inches in diameter and rotating at 5½ r.p.m., carried the specimens past a Hanovia Type 16200 mercury arc lamp at a distance of 6 inches. The exposure was about 2 seconds, thus subjecting the sample to some heat and ultraviolet light. It was thought that this alternating method might serve as a shock treatment and induce more rapid migration of the plasticizer to the surface. It seems to be effective, but no tests were made using a static situation for comparison.

Structure enters into the compatibility of the compound. For example, Campbell and Tryon (1) found that a long straight-chain acid or a mono-substituted amide tended to increase the difficulty of incorporation or prevent it altogether in Hycar OR-15. Benzyl N-2-ethylhexyl sebacamate, derived from sebacic acid, the esters of which are generally good plasticizers, does not function satisfactorily in natural rubber, Hycar OR-15, or Geon 101. It is fairly good in GR-S. These failures to plasticize adequately may be due to the benzyl group, but the author is inclined to place the blame on the mono-substituted amide, since the benzyl group does not appear to a disadvantage in the esters where it has been used.

Variation in structure appears again in iso-octyl N,N-di-n-butyl adipamate and 2-ethylhexyl N-2-ethylhexyl adipamate. In Hycar OR-15 the second compound is far superior; in natural rubber the first is much better, as it is in Geon 101.

It is evident that the effect of structure varies with the polymer. Commercial development depends upon the availability of low-cost secondary amines.

LITERATURE CITED

(1) Campbell, A. W., and Tryon, P. F., IND. ENG. CHEM., 45, 125 (1953).
(2) Clash, R. F., and Berg, R. M., Modern Plastics, July 1944, 35–40.
(3) Mooney, Melvin, IND. ENG. CHEM., ANAL. ED., 6, 147 (1934).
(4) Patterson, A. M., Capell, L. T., and Magill, M. A., C.A., 39, 5899 (1945).

Catalyst Activity in Cracking of Pure Hydrocarbons

D. E. NICHOLSON

Technical and Research Divisions, Humble Oil and Refining Co., Baytown, Tex.

THE importance of catalyst activity for conversion of gas oils to gasoline, gas, and coke has been dealt with in many publications in recent years. Numerous tests have been developed to define relative activity of catalysts, and an excellent survey of the major physical tests has been made by Ries (8). These determinations include measurements of surface area, pore volume, and pore radius from adsorption-desorption isotherms. In the case of catalysts of substantially uniform chemical composition, it is possible to estimate the activity by following a property such as heat of wetting with methanol, which gives an indication of the extent of surface accessible to reactant molecules (6). The most widely used method of measuring catalyst activity involves cracking a standard gas oil in a flow-type system at approximately 450° C., using 200 cc. of catalyst (1, 2). Products from the cracking reactions are often characterized as dry gas, liquid of lower boiling point than the initial boiling point of the feed, and coke. Many variations on the general method have been reported (9). All of these procedures are essentially the same, except for modifications in reporting data, choice of experimental operating conditions, and the physical form in which the catalyst is admitted to the cracking unit. Thus, workers have employed granular, pilled, and fluidized catalyst (3, 5).

The object of the present investigation was to study certain hydrocarbons of low molecular weight as potential starting materials in an activity test for rating cracking catalysts. The dealkylation of cumene has been recognized as suitable for screening catalysts (7, 10, 11). So far as is known, no work has been reported on the use of light paraffins for measuring catalytic activity. A more rapid test than the gas oil method would be advantageous. By utilizing compounds such as isobutane (2-methylpropane) or isopentane (2-methylbutane) it is possible to analyze the reaction products with a mass spectrometer rather than by distillation, effecting an appreciable saving in time.

A further argument for using simple compounds is that different batches of the standard gas oil prepared from time to time are not of identical composition. If a pure hydrocarbon would serve in the cracking test, the source of feed would not become unavailable in the future, the compound of interest being readily obtained in a state of high purity. Complete analysis of liquid products from the testing operation using gas oil is not possible because of the multitude of compounds present. More specifically, increased accuracy and precision are generally possible in an analysis of mixtures of a few components. The gas oil test for cracking catalyst activity as ordinarily performed does not detect conversion of molecules that are cracked but still boil at tempera-

tures higher than the initial boiling point of the original gas oil. With these ideas in mind, *n*-butane and isobutane were chosen as pure hydrocarbons to be cracked in the presence of catalysts of widely varying activities.

HYDROCARBONS

Experimental research grade isobutane and *n*-butane were obtained from the Phillips Petroleum Co. Determinations of the freezing point of representative samples showed the purities to be 99.87 mole % isobutane and 99.85 mole % *n*-butane. Samples were withdrawn from the liquid phase by inverting the cylinder, and were distilled twice in the vacuum line to remove traces of air prior to use in cracking experiments.

CATALYSTS

Silica-alumina catalysts contained as principal components 84.7% silica, 13.9% alumina, and 1.3% water, after drying for 2 hours at 110° C. This catalyst is of the type currently in wide use in fluid catalytic cracking units. Fresh catalyst had a surface area of 577 sq. meters per gram and a pore radius of 22 A. Heat and steam sintering applied in increasing severity lowered these initial values to yield five other samples (6, 7, 8, 9, and 10) of cracking catalyst covering the entire useful range of activity. The least active sample considered in this study showed a surface area of 69 sq. meters per gram. To check on the possibility of changes in surface area in the course of experiments, a small sample of a fresh catalyst was heat treated for periods up to 90 hours. During the first 18 hours of heat sintering in air at 500° C., the surface area of a sample dropped from an initial value of 521 to 461 sq. meters per gram. The sintering treatment was terminated after 90 hours, at the end of which time surface area has dropped to 433 sq. meters per gram. Four samples of catalysts exposed to gas oils have been included in the study. Powdered catalysts were compressed into cylindrical pellets of $^3/_{16}$-inch length and $^3/_{16}$-inch diameter with a rotary tablet machine.
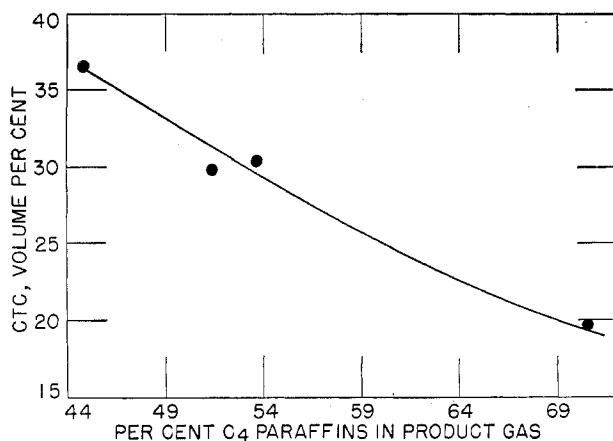

Figure 1. Catalyst activity in cracking *n*-butane

The four "equilibrium" catalysts, previously used in commercial fluid working units, were regenerated by calcining in air at 535° C. for 16 ± 2 hours before employment in the two activity tests. Such a treatment oxidizes quantitatively the coke deposited by the fluid cracking process. In the case of the six steam- and heat-deactivated catalysts, this step was not involved. These materials were loaded into the reactors, placed in the thermostat, and allowed 1.5 hours to reach thermal equilibrium while in contact with air. A 15-minute period of evacuation preceded each run.

APPARATUS AND PROCEDURE

Equipment was constructed of borosilicate glass throughout. The reactor, having a volume of 260 cc., was contained in a Hoskins muffle furnace fitted with a stainless steel block. Gaseous hydrocarbon, previously distilled twice in the vacuum line to separate trace amounts of air, was admitted to the reactor from one of several 2-liter storage bulbs. Three to 5 seconds were required for the evacuated reactor to fill completely. Pressure of hydrocarbon over the catalyst could be read on a mercury manometer to ±0.5 mm. Reaction times of 20 minutes, measured on a laboratory timer, were chosen for all experiments, at

the end of which the reaction products were rapidly expanded into an evacuated receiver bulb, cooled by liquid nitrogen. The pressure in the reactor dropped to 3 to 10 mm. without appreciable delay after the appropriate stopcock was opened. Reaction products, including residual *n*-butane and isobutane, reached room temperature and could be transferred to small bulbs equipped with ground-glass joints suitable for connection to a mass spectrograph. Capillary tubing for manifolds maintained the volume of "dead" space negligible compared to the volume of the borosilicate glass reactor. The entire vacuum system of about 20-liter volume was easily reduced to a pressure of less than 1 micron via a two-stage mercury diffusion pump backed by a mechanical pump. Stopcocks of the high-vacuum type throughout the apparatus were lubricated with silicone grease.
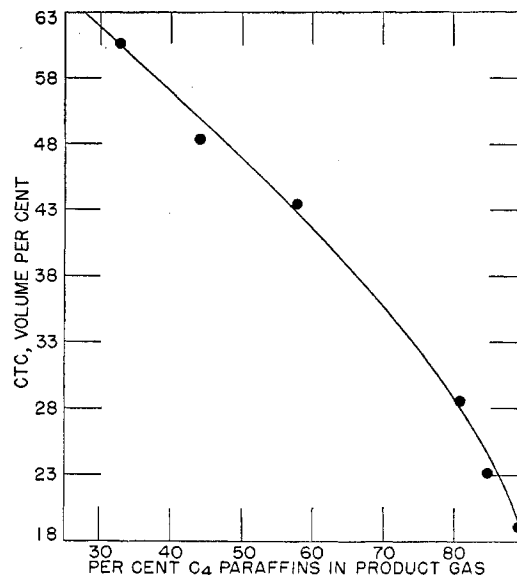

Figure 2. Catalyst activity in cracking isobutane

Temperature regulation was effected by means of a recorder-controller equipped with an iron-constantan thermocouple, calibrated against a 25-ohm platinum resistance thermometer in conjunction with a Mueller bridge circuit. The two parallel circuits in the original furnace were separated in order to provide primary and secondary heater control. With proper adjustment of supply voltages, temperature control to ±0.5° C. in the interval 350° to 550° C. was readily attained at a fixed point in the furnace. Gradients of ±2° C. were observed between the ends of the reactor. Care was taken to keep the orientation of both the thermocouple and reactor in the thermostat constant in the several experiments to minimize effects of existing thermal gradients.

DISCUSSION AND RESULTS

In contrast to the dealkylation of cumene, which has been described as a clean-cut reaction, the catalytic cracking of straight- and branched-chain paraffins is not a simple reaction. Appreciable quantities of hydrogen, methane, ethane, and propane are produced, concomitant with isomerization of the parent hydrocarbon. Even with these complications certain trends are evident from the experimental data, and the disappearance of starting material may be related to the conversion of gas oil in the standard test as customarily practiced (*2*). This condition seems especially true for the series of fresh and deactivated catalysts and, to a limited extent, for the equilibrium catalysts from commercial operations. Four samples of the latter, varying in catalyst testing conversion (CTC) values from 19.3 to 36.6, were used to promote decomposition of *n*-butane at 500° C. and a reaction time of 20 minutes in the one group of experiments. Catalyst testing conversion is defined as the volume per cent of gas oil cracked in the standard activity test. Table I includes activity and selectivity factors for the several catalysts, together

with analysis of products from cracking of n-butane under constant volume conditions. Initial pressures of 620 mm. of mercury and equal volumes of catalyst were employed for all runs.

Table I.   Equilibrium Catalyst Testing with n-Butane

Catalyst No.	1	2	3	4
Reactor temp., ° C.	500	500	500	500
Reaction time, min.	20	20	20	20
Product composition, vol. %				
Hydrogen	2.0	5.0	2.5	9.1
Methane	10.4	18.5	15.5	18.2
Ethane + ethylene	8.7	11.4	11.9	12.1
Propane + propylene	6.5	12.3	14.4	14.1
Isobutane	2.3	3.7	3.9	4.1
n-Butane	68.1	47.7	49.8	40.7
Butylenes	1.0	0.8	0.7	0.7
Heavier	0.7	0.5	1.0	0.7
Isobutane + n-butane	70.4	51.4	53.7	44.8
CTC, vol. %	19.3	29.7	30.6	36.6
Cu. ft. gas/barrel oil charged	141	198	152	231
Surface area, sq. m./g.	40	92	97	122

Approximately 30 to 60% of the starting material was cracked under conditions of the experiment. A plot of catalyst testing conversion vs. (per cent n-butane plus per cent isobutane in products) is shown in Figure 1. Blank runs in which catalyst in the reactor was replaced by quartz chips of surface area 1 sq. meter per gram indicated that about one half of the cracking was due to thermal reactions with the least active catalyst (No. 1). Table I shows that the percentage of hydrogen in reaction products bears no simple relation to activity of the catalysts. In other words, the effect apparently being detected here is not merely one of increasing hydrogen production as a result of higher conversion of n-butane; the cracking of n-butane is showing some selectivity. Further research will be required to establish this point with certainty.

Each of the four mass spectrometric analyses reported represents the average of determinations run in triplicate on different days; the reproducibility and accuracy of the instrument for gas analysis were checked from time to time with standard samples of known composition. For a major component (n-butane) present in amounts of 20 to 80 mole % the accuracy was usually within ±0.5 mole %. The reproducibility in analysis was often better— i.e., ±0.1 to 0.2%. Each item of data from the gas oil test in Table I represents an average of four or more determinations.

After the preliminary experiments were completed, the series of six silica-alumina catalysts described above was studied by cracking isobutane. In the temperature range 450° to 500° C. isobutane is decomposed catalytically at a rate approximately four times that of n-butane, but the rates of thermal cracking for the two compounds are substantially equal. Therefore, isobutane was selected as a second compound for consideration in efforts to minimize competitive thermal reactions. The results from the studies with isobutane are given in Table II and Figure 2.

A good correlation is obtained between catalyst testing conversion and the volume per cent of C4 paraffins in the reaction products. Surface area of these catalysts also correlates with activity as expressed by catalyst testing conversion. It is obvious

Table II.   Fresh Catalyst Testing with Isobutane

Catalyst No.	5	6	7	8	9	10
Reactor temp., ° C.	450	450	450	450	450	450
Reaction time, min.	20	20	20	20	20	20
Product composition, vol.%						
Hydrogen	7.9	1.0	1.1	1.2	3.6	5.4
Methane	27.4	1.4	1.7	1.9	4.3	5.7
Ethane + ethylene	9.7	0.8	0.6	0.8	2.4	2.9
Propane + propylene	19.4	3.9	8.1	9.3	25.2	35.6
Isobutane	22.8	85.5	80.0	75.3	46.1	30.4
n-Butane	10.0	3.5	4.9	5.3	11.7	13.8
Heavier	2.7	2.8	3.7	4.7	7.4	5.2
Isobutane + n-butane	32.8	89.0	84.9	80.6	57.8	44.2
CTC, vol. %	61.5	15.8	23.1	28.6	43.4	48.3
Cu. ft. gas/barrel oil charged	461	92	105	111	237	283
Surface area, sq. m./g.	577	69	84	122	224	264

that surface area alone does not adequately depict catalytic cracking behavior; many substances of high surface area, such as silica gel, will not even promote the cracking process.

Data in Table II are based on two determinations from different loadings of the reactor. Duplicate runs agreed to within 0.5 mole % isobutane content, this variation being of the magnitude of reproducibility of mass spectrometric analyses.

Effect of adsorbed water on catalyst activity was qualitatively in agreement with the findings of Hansford—viz., heating of catalyst at 450° C. under vacuum for 24 hours lowered conversion as measured by n-butane decomposition (4). The decrease in activity noted in this investigation corresponded to approximately 25% relative change in amount of n-butane disappearing. Precautions were taken to expose the series of equilibrium and deactivated catalysts to uniform pretreatment to maintain samples on a consistent basis.

CONCLUSIONS

Light hydrocarbons such as the butanes appear useful in measurement of cracking activity of catalysts. Assuming that a mass spectrometer is available, a technique of the type outlined requires somewhat less expensive and smaller equipment than tests employing gas oils.

LITERATURE CITED

(1) Alexander, T., and Shrimp, H. G., Natl. Petroleum News, **36**, No. 31, R-537 (1944).
(2) Conn, M. E., and Connolly, G. C., IND. ENG. CHEM., **39**, 1138 (1947).
(3) Grote, H. W., Hoekstna, T., and Tobiasson, G. T., Ibid., **43**, 545 (1951).
(4) Hansford, R. C., Ibid., **39**, 849 (1947).
(5) McReynolds, H., Proc. Am. Petroleum Inst., **27** (III), 57 (1947).
(6) Mills, I. W., Oil Gas J., **46**, No. 28, 237 (1947).
(7) Plank, C. J., and Nace, D. M., Divisions of Petroleum and Physical and Inorganic Chemistry, Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions, 125th meeting, ACS, Kansas City, Mo.
(8) Ries, H. E., Jr., Advances in Catalysis, 4, 88 (1952).
(9) Shankland, R. V., and Schmitkons, G. E., Proc. Am. Petroleum Inst., **27** (III), 57 (1947).
(10) Stright, P., and Danforth, J. D., J. Phys. Chem., **57**, 448 (1953).
(11) Tamele, M. W., Discussions Faraday Soc., No. 8, 270 (1950).