Diisopropyl from Isobutane-Ethylene Alkylation in Presence of BF_3-H_2O-HF Catalyst Systems

W. NELSON AXE AND WALTER A. SCHULZE

Phillips Petroleum Company, Bartlesville, Okla.

Because of the importance of diisopropyl as a high antiknock component of aviation gasoline, an investigation was undertaken of its production by direct alkylation of isobutane with ethylene in the presence of BF_3-H_2O-HF catalyst complex. The catalyst system resembles the $AlCl_3$-hydrocarbon complex in its ability to promote the juncture of isobutane and ethylene at temperatures of 100–135° F. and at pressures usually not higher than 200–250 pounds per square inch to yield alkylate containing from 50 to 70 volume % of diisopropyl (2,3-dimethylbutane). Since boron fluoride is more expensive than aluminum chloride, experimental work was mainly directed towards high alkylate yields with a minumum consumption of boron fluoride. Catalyst prepared by saturating 40 to 50% aqueous hydrogen fluoride with boron fluoride is capable of producing only about 8 to 10 volumes of alkylate per volume of catalyst at full activity. However, if the catalyst is continuously activated with boron fluoride, as much as 88 volumes may be produced before signs of failure become evident. In addition to activation, further extension of catalyst life may be effected by fortification of partially spent catalyst with anhydrous hydrogen fluoride, whereupon the system becomes once again responsive to boron fluoride activation. Results are reported showing the production of 195 volumes of alkylate per volume of catalyst. Additional experimental data are presented to show the effect of hydrogen fluoride concentration on catalyst activity, external isobutane-ethylene mole ratio and temperature on yield and quality of alkylate, and hydrocarbon impurities in the ethylene on alkylate quality.

IN RECENT years diisopropyl (2,3-dimethylbutane) has assumed considerable industrial importance as a blending agent in aviation gasoline because of its high antiknock rating, especially under supercharged rich-mixture conditions. Alden, Frey, Hepp, and McReynolds (*1*) recently described the commercial alkylation of isobutane with ethylene in the presence of an aluminum chloride catalyst to produce alkylate containing a major proportion of diisopropyl. The same authors also presented detailed information on the antiknock blending characteristics of pure diisopropyl and of the total alkylate.

The present paper is concerned with development work in the field of isobutane-ethylene alkylation utilizing the catalyst complex BF_3-H_2O-HF. A survey of the literature reveals that the only materials known to effect catalytically the interaction of isobutane and ethylene at moderate temperatures and pressures are aluminum halides and certain complex compounds of boron fluoride. Ipatieff and Grosse (*4*) alkylated isobutane with ethylene in the presence of BF_3-H_2O-Ni systems and obtained hexanes, octanes, and higher paraffins. However, the only boron fluoride complex thus far described that appears to be comparable with the aluminum halide catalysts for this reaction is the BF_3-H_2O-HF system wherein the BF_3 and H_2O are combined in a 1:1 mole ratio with the proportion of HF variable within certain limits. A catalyst of this nature was described for use in general alkylation reactions in the patent literature during the course of the present work (*6*). Incidental references to the possibility of use of catalysts of this nature are also found in a more recent patent (*3*). However, the technical and patent literature contains but little information of a detailed nature on ethylene-isobutane alkylation with the BF_3-H_2O-HF catalyst system.

THE CATALYST SYSTEM

Meinert (*5*) recommended the use of boron fluoride hydrate (saturated aqueous solutions of BF_3) as a catalyst for the alkylation of isoparaffins with mixtures of olefins containing ethylene. In the present work it was found that boron fluoride hydrate was capable of promoting isobutane-ethylene alkylation, but that ethylene conversion and active life were of a low order. A catalyst, however, prepared by saturating aqueous hydrofluoric acid with boron fluoride, exhibited a much higher order of activity but was found to fail rapidly after the production of 8 to 10 volumes of total alkylate per volume of initial catalyst charged. This catalyst was found to respond to intermittent or continuous activation with boron fluoride. In one laboratory scale test run using continuous BF_3 activation an alkylate production of 70 volumes of alkylate per volume of initial catalyst was realized. On incipient failure of the activated catalyst, fortification with a small amount of anhydrous hydrogen fluoride (approximately 5% of the original charge) was sufficient to restore full catalyst activity and to render the composition once again responsive to boron fluoride activation. In the small scale laboratory experiments the fortified catalyst appeared to have a life equivalent to new catalyst. Although a limited amount of work on a somewhat larger scale indicated the life of the fortified catalyst to be somewhat shorter than that of the new, the HF fortification could be repeated at least five times; thus the life of this expensive catalyst was extended considerably.

PREPARATION OF CATALYST. The catalyst is prepared by passing boron fluoride gas into aqueous hydrofluoric acid until no further gain in weight can be detected. The amount of boron fluoride absorbed corresponds to one mole of BF_3 per mole of water present in the solution. The final quantity of boron fluoride absorbed appears to be independent of the hydrogen fluoride concentration and the total pressure (Table I).

TABLE I. BORON FLUORIDE CONTENT OF BF_3-H_2O-HF CATALYSTS

System	BF_3/H_2O Mole Ratio	Pressure
$H_2O + BF_3$	0.980	Atm.
30% HF + BF_3	1.018	Atm.
40% HF + BF_3	0.965	Atm.
50% HF + BF_3[a]	1.002	Atm.
60% HF + BF_3	0.940	Atm.
50% HF + BF_3[b]	1.010	50 lb./sq. in. gage

[a] Average of a large number of preparations.
[b] Average of 4 preparations.

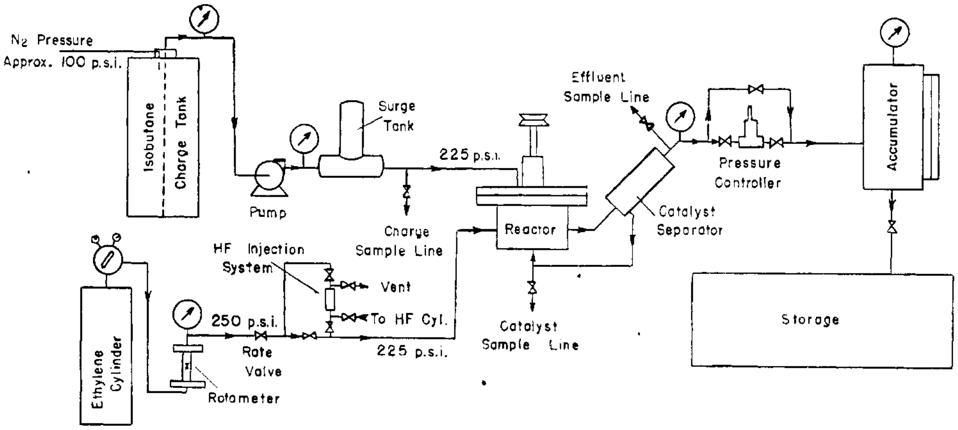

Figure 1. Flow Diagram of Pilot Plant for Isobutane-Ethylene Alkylation with BF_3-H_2O-HF Catalysts

Isobutane storage tank, approximately 15 gallons of isobutane-BF_3 blend; pump, Hills-McCanna UM2F chemical proportioning pump; surge tank, about 18 inches of 2-inch pipe, liquid charge capped with nitrogen; ethylene cylinder equipped with heated manifold and pressure regulator; reactor, turbo-mixer type (2600-cc. capacity) with brass lining, straight blades on stator, curved blades on 2.5-inch impeller; catalyst separator, brass tank (1200 cc.) mounted at about 45°; pressure controller, Fisher pressure relief valve; accumulator, 9-gallon tank with gage glass

The catalyst was prepared under pressure by charging the aqueous hydrofluoric acid to a copper- or brass-lined alkylation reactor and passing boron fluoride with agitation into the vessel from a tared cylinder until the reactor pressure reached 50 pounds per square inch gage, which indicated no further absorption of boron fluoride. The heat of reaction was dissipated by immersion of the reactor in a constant temperature water bath.

CHARACTERISTICS OF CATALYST. There is definite reason to believe that the hydrogen fluoride content of the catalyst enters into some sort of chemical union with the boron fluoride hydrate. Thus, it is virtually impossible to add anhydrous hydrogen fluoride to freshly prepared boron fluoride hydrate, even though both liquids are maintained below 32° F., because of the violent exothermic reaction. However, no such difficulties are involved on the addition of anhydrous hydrogen fluoride to spent catalyst as carried out in the fortification procedure. Catalyst compositions prepared from aqueous hydrogen fluoride solutions containing as much as 50% by weight of hydrogen fluoride have very little tendency to etch glass and do not exert any unusual toxic action on human skin. No benefit is derived in preparing catalyst from aqueous solutions containing more than 50% by weight of hydrogen fluoride. It would appear that maximum activity of this catalyst system is reached when the composition approaches one mole of hydrogen fluoride per mole of boron fluoride hydrate.

Catalyst prepared from 40 to 50% aqueous hydrogen fluoride is a clear, usually water-white, strongly fuming liquid having a specific gravity of about 1.75. The catalyst is exceedingly corrosive toward common alloy steels ordinarily used in refinery equipment, but copper and brass were sufficiently resistant to be used in the contacting and settling zones. The fact that the catalyst system does not etch glass appreciably permitted the use of gage glasses on the product accumulators.

As in the case of other acidic alkylation catalysts, the present catalyst forms acid-soluble oils which lower the specific gravity of the catalyst phase from 1.75 to about 1.3 during the course of its active life. Spent catalyst may have an oil content of as much as 35% by volume. Fresh catalyst dissolves considerable quantities of ethylene in the early stages of a run, and results in the apparently anomalous situation of good ethylene conversion but low yields based on ethylene.

ALKYLATION EQUIPMENT AND PROCEDURE

LABORATORY. The reactor employed in the laboratory alkylation runs consisted of a copper-plated steel vessel of 7.2-cm. inside diameter and 14-cm. depth. Agitation was provided by means of a vertically mounted $^1/_4$-horsepower motor-driven stirrer operating through a stuffing box at 1750 revolutions per minute. The stirring shaft was provided with two four-blade impellers working against fixed baffles on the wall of the reactor. The feed entrance to the reactor was located about midway between the top and bottom, while the effluent stream was discharged on the opposite side near the top of the reactor into a settling chamber. This latter vessel consisted of a vertically disposed brass tube 3.5 cm. in diameter and 22 cm. in height. Catalyst recirculation was accomplished through a $^1/_8$-inch brass pipe leading from the bottom of the separator to the bottom of the reactor.

The general technique used in the laboratory was such as to obviate the use of proportioning pumps. The isobutane-ethylene feed was preblended in cylinders having a nominal capacity of 4 gallons by passing gaseous ethylene into a known weight of isobutane precooled in a dry-ice bath, until the desired mole ratio of isobutane to ethylene had been attained. A constant pressure of ethylene equal to or slightly greater than the vapor pressure of the blend was applied to the vapor space above the liquid to provide a constant pressure head and to minimize changes in ethylene concentration as the feed stock was depleted. The flow rate of feed to the reactor was controlled by means of a needle valve at the outlet of the catalyst separator, and the rate of flow was determined by means of a calibrated gage glass on the low pressure product receiver. An internal thermocouple was used to measure the reaction temperature, which was controlled by means of a water bath. In most of the laboratory runs intermittent catalyst activation with boron fluoride was employed. This was accomplished by interrupting the flow of hydrocarbon and introducing gaseous BF_3 from a tared cylinder until an increase in pressure of the alkylation system indicated the catalyst to be fully saturated.

This small unit ordinarily operated at a liquid effluent rate of 1000 to 1400 cc. per hour to produce 200 to 400 cc. of debutanized alkylate per hour, depending on the mole ratio of isobutane to ethylene. Continuous runs of 50-hour duration producing about 4 gallons of debutanized alkylate have been realized from an initial charge of 200 cc. of catalyst. The principal factor limiting the length of laboratory runs was usually the life of the stuffing box.

PILOT PLANT. The pilot plant equipment for the study of isobutane-ethylene alkylation using the BF_3-H_2O-HF catalyst system was similar in many respects to that used in the laboratory. Certain modifications, however, were necessary to study the effect of continuous boron fluoride activation of the catalyst and in situ fortification of low activity catalyst with hydrogen fluoride. Boron fluoride is most conveniently introduced into the alkylation zone as a solution in the liquid isobutane feed. In order to avoid undesirable chemical reactions it was necessary to provide separate feed streams for the isobutane and ethylene, and means for proportioning these materials in order to maintain a reasonably constant external isobutane-ethylene mole ratio. These features, together with provision for periodic injection of known quantities of hydrogen fluoride into the system and the necessary number of pumps, flowmeters, and flow-control regulators, represent the main points of difference.

A flow diagram of equipment assembly is given in Figure 1. The contactor and catalyst separator system was operated at 1.4 to 1.7 gallons per hour total throughput with reasonably good ethylene conversion and a minumum of catalyst carry-over. The average alkylate production from this plant amounted to about 0.5 gallon per hour with continuous on-stream times in the neighborhood of 70 hours.

PROCEDURE. Approximately 25% of the reactor volume was filled with catalyst, and the remainder of the vessel was filled with isobutane. Ethylene was then admitted, and the flow adjusted by means of a rotameter operating at 250 pounds per square inch to give the desired external isobutane-ethylene mole ratio. Pressure within the reactor was maintained at about 225 pounds per square inch by use of a pressure-release valve or a motor valve. The reaction temperature was controlled at 130–135° F. with an electrically heated water bath.

The constant delivery rate of the pump and calibration of the rotameter were relied on for control of the rate of production; however, all yield data are based on actual weight of materials taken from the charge tanks.

CONTROL TESTS AND PRODUCT EVALUATION. Since the commercial success of this process is predicated on the recovery and recycle of the boron fluoride used for catalyst activation, careful attention was paid to the boron fluoride balance. A weighed amount of boron fluoride was introduced into the isobutane charge tank to prepare a blend containing approximately 1.5% boron fluoride in isobutane. Since a certain amount of boron fluoride apparently reacted with scale on the inside of the tank, it was necessary to analyze this stream at frequent intervals to determine its actual boron fluoride content. This was accomplished by vaporizing weighed samples through absorption tubes filled with Ascarite and observing the weight of boron fluoride absorbed. A similar analysis was necessary on the reactor effluent stream, except that the analysis of this stream is complicated by the presence of nongaseous hydrocarbons. An all-glass Vigreux-type still was used for this purpose; it was fitted with a dry-ice cold finger to prevent the entrance ofalkylate into the absorption tube. The light gases were distilled from the sample and thence through an Ascarite absorber until the effluent vapors reached a temperature of about 65° F.; at that point all free boron fluoride had been boiled out of the sample. All samples were weighed; consequently an accurate material balance on the amount of recoverable boron fluoride was available.

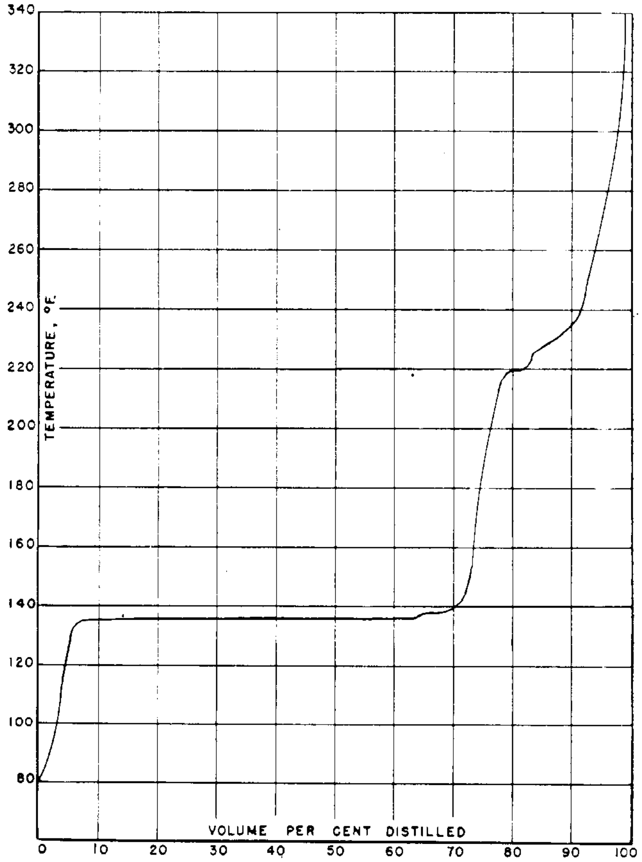

Figure 2. Distillation Characteristics of Isobutane-Ethylene Alkylate Derived from Ethylene Feed Containing 50 Mole % Propane

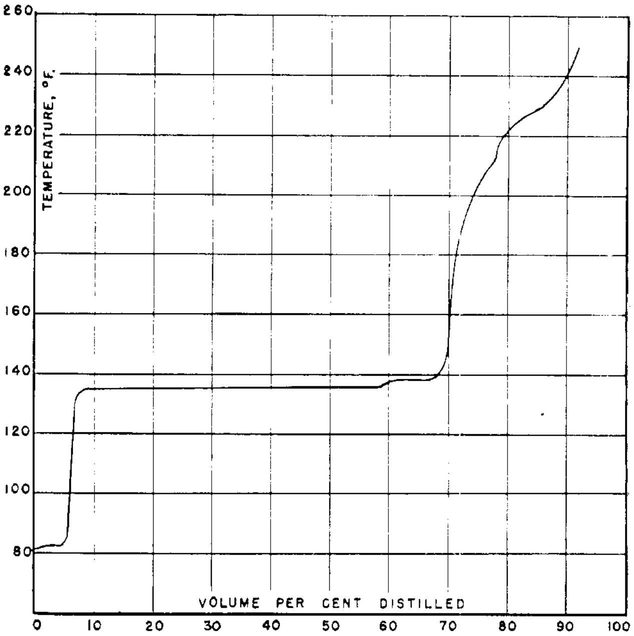

Figure 3. Distillation Characteristics of Typical Isobutane-Ethylene Alkylate

Pilot plant runs were divided into operating periods corresponding to a total hydrocarbon throughput of about 15 gallons. Analytical data were obtained on each period, so that complete evaluation of the process was available at various stages of catalyst life. Low temperature fractional analyses were carried out on the composite effluent from each period to give quantitative values for light components through isopentane. Composited samples of total alkylate were fractionated in 5-liter batches to determine diisopropyl content and to furnish material for antiknock rating. Other analytical tests included determination of the fluorine content of alkylate and the oil content of the catalyst.

EFFECT OF HF CONCENTRATION ON CATALYST ACTIVITY AND LIFE

The precise optimum quantity of hydrogen fluoride required in the present catalyst system has not been determined. However, data derived from a large number of experiments indicate that the following molecular proportions should obtain: BF_3:H_2O:HF = 1:1:1. Since the BF_3-H_2O complex is a catalyst in itself, any addition of hydrogen fluoride to the system will be beneficial. On the other hand, evidence now available indicates that employ-

TABLE II. ISOBUTANE-ETHYLENE ALKYLATION WITH CATALYSTS OF VARIABLE HF CONTENT

	BF_3-H_2O	25% HF Satd. with BF_3	50% HF Satd. with BF_3
Mole ratio, isobutane/ethylene	2.60	2.75	2.84
Total isobutane, lb.	16.847	15.640	30.760
Total ethylene, lb.	3.148	2.718	5.226
Catalyst charge, cc.	200	250	250
Contact time, min.	35	18	19
Av. temperature, ° F.	135	137	133
Pressure, lb./sq. in. gage	230	225	225
Total alkylate, lb.	5.451	5.930	13.450
Yield, lb. alkylate/lb. ethylene	1.73	2.19	2.58

ment of quantities of hydrogen fluoride in excess of the given proportion results in inferior catalysts.

Laboratory experimental data are summarized in Table II to show the difference between catalysts made by saturating water, 25% aqueous hydrofluoric acid, and 50% aqueous hydrofluoric acid with boron fluoride.

The data presented in Table II are based on catalyst performance at full activity and bear no relation to catalyst life. Additional information on this point is available from pilot plant operations where the primary objective was to determine ultimate catalyst life. These latter alkylations were continued to the stage of definite catalyst failure. The following table gives data on the pilot plant alkylation with catalysts of variable HF content:

	30% HF Satd. with BF_3	40% HF Satd. with BF_3	60% HF Satd. with BF_3
Total alkylate produced, gal.	26.4	31.0	14.0
Vol. alkylate/vol. catalyst	134	195	84

EFFECT OF EXTERNAL MOLE RATIO AND TEMPERATURE

The value of maintaining a high isoparaffin-to-olefin ratio in acid alkylation is well recognized as a general and important reaction variable. Optimum temperature conditions, on the other hand, are often dependent on the nature of the catalyst system. This is exemplified in the low temperatures required in sulfuric acid alkylation as contrasted with the higher and more convenient temperatures employed in hydrofluoric acid alkylation. Since alkylation systems involving ethylene as the alkylating agent differ in many respects from other isoparaffin-olefin systems, a series of laboratory experiments was carried out (Table III) with catalyst activation at 2-hour intervals to ascertain the effect of varying the external isobutane-ethylene mole ratio and temperature on the yield and quality of alkylate. Each of the four runs was made using new catalyst prepared by saturating 50% aqueous hydrogen fluoride solution with boron fluoride.

From the information obtained in this limited number of experiments it may be concluded that high external isoparaffin-olefin mole ratios are not necessarily indicated for the isobutane-ethylene system using BF_3-H_2O-HF catalysts. With respect to alkylate quality as reflected by the antiknock ratings, the temperature effect appears to be more important than the isobutane-ethylene mole ratio. The only factor favoring the 4.15 mole ratio is the slightly greater percentage of isohexanes found in the total alkylate. However, this finding must be balanced against the evidence in favor of the 2.84 mole ratio, namely (*a*) higher ethylene conversion, (*b*) higher yields of alkylate based on ethylene charged, (*c*) higher octane ratings of the total alkylate, and (*d*) higher octane ratings of the diisopropyl concentrate.

The present data indicate that, although a more dilute feed with respect to ethylene favors somewhat higher yields of isohexanes, an increased formation of 2-methylpentane also results which is unavoidably included in the diisopropyl concentrate under ordinary conditions of fractionation. Ethylene conversion in a once-through operation is definitely influenced by the isobutane-ethylene mole ratio and is not merely a matter of a constant unreacted proportion of ethylene in the total effluent. In these experiments the weight of total effluent hydrocarbon material was approximately the same in all four instances, but the weight percentage of ethylene found by analyses for runs 1 and 3 amounted to 0.63 and 1.36 for the lower and higher mole ratios, respectively. In runs 2 and 4 at the lower reaction temperature the corresponding percentages were 0.88 and 1.41.

TABLE III. COMPARATIVE ISOBUTANE-ETHYLENE ALKYLATION RUNS AT DIFFERENT TEMPERATURES AND EXTERNAL ISOBUTANE-ETHYLENE MOLE RATIOS

	Run 1	Run 2	Run 3	Run 4
Isobutane/ethylene mole ratio	2.84	2.84	4.15	4.15
Av. temperature, ° F.	133	110	133	110
Alkylate composition, vol. %				
Pentanes	5.2	3.5	4.0	4.0
Hexanes	66.6	67.0	70.0	71.0
Heptanes	7.8	8.0	6.0	7.5
Octanes	13.0	14.5	13.0	11.5
Nonanes and heavier	7.4	7.0	7.0	6.0
Antiknock ratings				
Total alkylate				
A.S.T.M. (clear)	88.4	91.0	88.6	90.7
AN-VV-F-746	89.0	90.4	88.8	90.3
AN-VV-F-746 (4 cc T.E.L.)	107.6	109.4	106.8	108.0
Diisopropyl concentrate (135–140° F.), A.S.T.M. (clear)	91.8	92.5	90.5	91.9
C_7^+ alkylate (140–360° F.), A.S.T.M. (clear)	80.9	83.3	79.2	82.9
Yield data				
Total isobutane charged, lb.	30.760	29.675	31.520	30.600
Total ethylene charged, lb.	5.226	5.017	3.787	3.547
Total alkylate produced, lb.	13.450	12.500	7.960	7.980
Ethylene conversion, wt. %	95.7	93.3	87.0	86.5
Alkylate yield, lb./lb. ethylene charged	2.58	2.49	2.10	2.25
Diisopropyl concentrate (136–140° F.), vol. % of alkylate	62.5	63.5	66.0	67.5
Analytical data				
Alkylate gravity, ° A.P.I. at 60° F.	77.0	77.0	77.7	78.0
Reid vapor pressure of total alkylate, lb./sq. in.	6.65	6.30	6.75	6.80
Fluorine in total alkylate, wt. %	0.0026	....	0.0029	0.0038
Fluorine in diisopropyl concentrate, wt. %	0.0030	0.0027	0.0032	0.0037
Operating data				
Time on-stream, hr.	24.7	22.0	26.1	25.5
Pressure, lb./sq. in. gage	225	220	185	185
Effluent rate, cc./hr.	1150	1200	1000	1080
Contact time, min	19	18	22	20.5
Catalyst charged, cc.	200	200	200	200
Rate of alkylate production, cc./hr.	364	380	204	209

The effect of reaction temperature on alkylate quality is obvious from the tabulated octane numbers. Both the total alkylate and the diisopropyl concentrate are definitely better at the 110° F. level than at the 133° F. level, regardless of the isobutane-ethylene mole ratio.

EFFECT OF POSSIBLE ETHYLENE IMPURITIES ON ALKYLATION SYSTEM

INERT PARAFFINS. Table IV presents data obtained in a laboratory run designed to simulate conditions where about 50 mole % of the olefin feed is made up of inert paraffinic hydrocarbons. The catalyst was prepared by saturating a 50% aqueous solution

TABLE IV. ISOBUTANE-ETHYLENE ALKYLATION IN PRESENCE OF PROPANE

Total on-stream time, hr.	27.5
Total isobutane charged, lb.	26.575
Total propane charged, lb.	5.520
Total ethylene charged, lb.	3.461
Av. mole ratio, isobutane/ethylene	3.72
Catalyst charged, cc.	200
Av. contact time, min.	22
Av. temp., ° F.	112
Pressure, lb./sq. in. gage	200
Total alkylate produced, lb.	7.180
Yield, lb. alkylate/lb. ethylene charged	2.08
Characteristics of alkylate	
Gravity, ° A.P.I. at 60° F.	77.6
A.S.T.M. octane No. of total alkylate	90.4
A.S.T.M. octane No. of diisopropyl concentrate	92.5

Table V. Alkylation of Isobutane with Mixed Olefin Feed

	Ethylene-Propylene	Ethylene-Isobutylene
Total isobutane charged, lb	20.740	15.280
Total ethylene charged, lb.	1.418	0.956
Total propylene charged, lb.	2.081	....
Total isobutylene charged, lb	....	1.930
Mole ratio, ethylene/propylene	1.0	....
Mole ratio, ethylene/isobutylene	...	1.03
Mole ratio, isobutane/total olefin	3.6	3.9
Av. temperature, ° F.	130	120
Pressure, lb./sq. in. gage	153	105
Contact time, min.	19	16
Total alkylate produced, lb.	7.301	5.627
Yield, % of theory	80[a]	82[b]
Yield, lb. alkylate/lb. total olefin	2.08	1.95
Characteristics of alkylate		
Gravity, ° A.P.I. at 60° F.	73.9	73.1
Bromine No., g./100 g.	0.0	0.0
A.S.T.M. octane No.	84.8	88.9
A.S.T.M. octane No. (1 cc. T.E.L.[c])	95.3	99.8

[a] Based on theoretical production of hexanes and heptanes.
[b] Based on theoretical production of hexanes and octanes.
[c] Tetraethyllead.

of hydrogen fluoride with boron fluoride. The distillation characteristics and composition of this alkylate are shown in Figure 2.

In general, the presence of an inert hydrocarbon in the alkylation system in quantities that might be present in refinery ethylene had no unusual adverse effect on the reaction; however, this experiment was not of sufficient duration to furnish any data on catalyst life. With an ethylene conversion of 91% by weight, the alkylate yield based on ethylene charged is lower than that usually found in undiluted systems. On the other hand, alkylate quality was found to be excellent. Comparison of Figure 2 with the typical alkylate of Figure 3 shows that a reduction in isopentane and isoheptanes and an increase in isohexanes have occurred. The production of heavy alkylate has been greatly reduced, since 99% of the total alkylate is distilled at 340° F. It may be concluded that inert light hydrocarbons in the ethylene feed will have no deleterious effect on alkylate quality.

Olefins. In commercial alkylation systems it is to be expected that the ethylene feed will be contaminated with appreciable quantities of other alkylating agents, particularly propylene. Two relatively short experiments were carried out according to the laboratory procedure to determine the effect of propylene and isobutylene, respectively. In these experiments 50 mole % of the olefin feed was ethylene; hence the added olefin could compete on an equal basis for the isobutane. The catalyst for each experiment was prepared by saturating a 50% aqueous solution of hydrogen fluoride with boron fluoride. A summary of the pertinent data from these runs is given in Table V.

Alkylate composition for the mixed-olefin alkylation runs may be derived from the distillation curves given in Figures 4 and 5. Inasmuch as propylene is assumed to be the most likely olefin contaminant, the relation of octane numbers to different portions of the distillation curve is shown in Figure 4.

The effect of propylene in the olefin feed is that of lowering the octane rating of the alkylate. As can be seen in Figure 4, the inferior quality is mainly due to hydrocarbons boiling in the range 212–340° F., which constitute 25.5 volume % of the total alkylate. On the other hand, the yield of isohexanes (mainly diisopropyl) amounts to 131% of the ethylene charged; this compares not too unfavorably with average values of about 140% for straight isobutane-ethylene alkylation. It may be inferred from this experiment that small percentages of propylene in the ethylene feed will not seriously affect the production of diisopropyl nor unduly degrade the quality of total alkylate.

As would be expected, alkylation with an equimolar mixture of ethylene and isobutylene did not materially reduce the octane rating of the alkylate, although the nature of the alkylate is considerably modified (Figure 5). In this experiment the isohexane fraction (mainly diisopropyl) made up 31 volume % of the total alkylate, with a yield of 175% based on ethylene charged. The isohexane yield on ethylene charged is considerably better than the 131% reported for the ethylene-propylene mixture and the 140% ordinarily expected from undiluted ethylene. This increase in isohexanes is undoubtedly the contribution of the isobutane-isobutylene system, since it normally gives a definite plateau in the diisopropyl boiling range of 8 to 10% of the total alkylate when liquid boron fluoride complex catalysts are employed. From this experiment it can be concluded that small proportions of olefins such as isobutylene will have no harmful effect on the quality of alkylate.

LABORATORY SCALE CATALYST LIFE

Early in the history of this work it was realized that catalyst compositions prepared from aqueous hydrogen fluoride solutions and boron fluoride exhibited short active life. Since the main catalyst ingredient, boron fluoride, is quite expensive, it was obvious that means for extension of this life should be sought. Experiments carried out under optimum conditions without the use of any activation technique showed that a given charge of new catalyst was capable of producing only 8 to 10 volumes of alkylate per volume of catalyst before serious evidence of failure became apparent. Intermittent treatment of the catalyst phase with boron fluoride will increase the alkylate production to 25–30 volumes per volume of initial catalyst charge. However, if activation is accomplished continuously—for example, by incorporating a small percentage of boron fluoride in the isobutane feed—the yield may be increased to 70 volumes of alkylate per volume of initial catalyst charge. At this latter point of incipient failure the addition of anhydrous hydrogen fluoride to the catalyst phase in amount equivalent to about 5% of the original catalyst charge

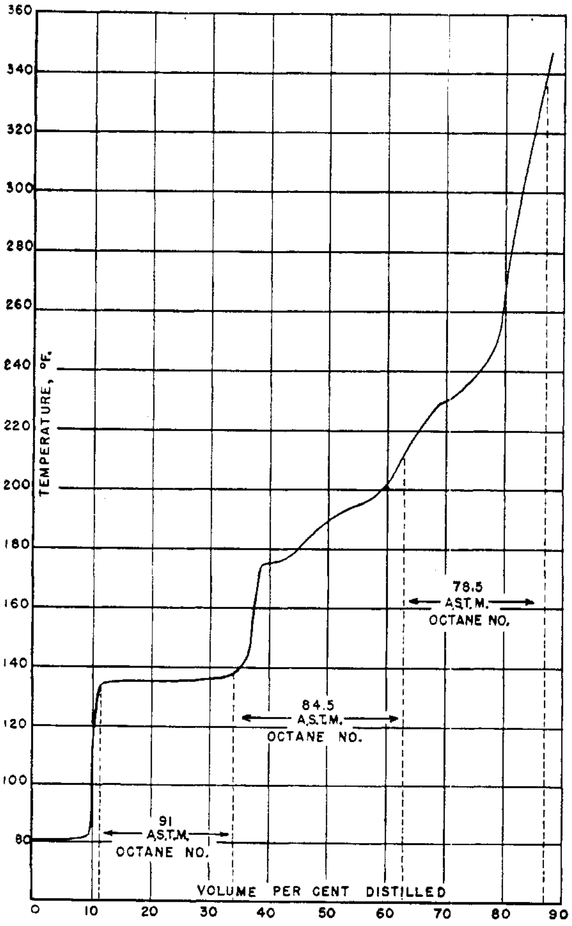

Figure 4. Distillation Characteristics of Product Derived from Alkylation of Isobutane with Mixed Ethylene-Propylene Feed of 1:1 Mole Ratio

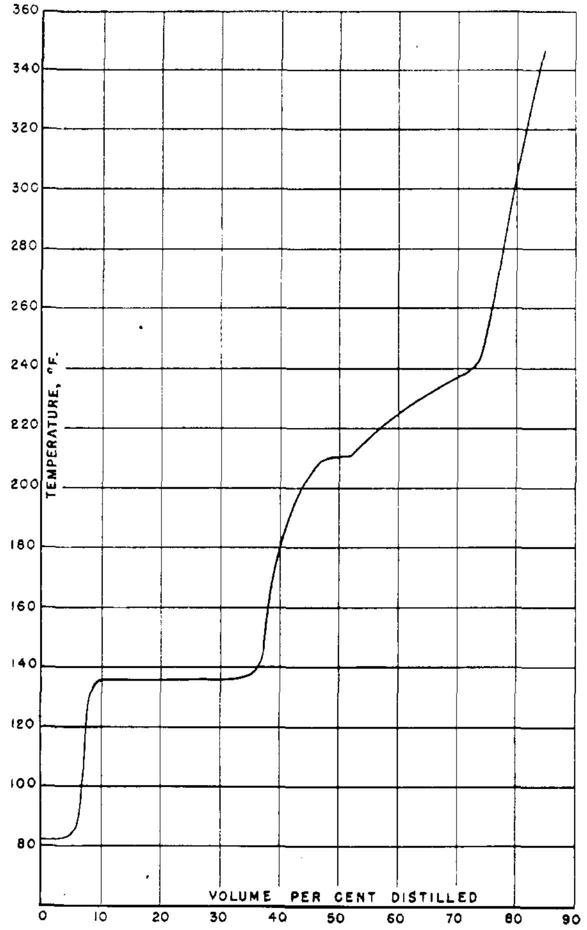

Figure 5. Distillation Characteristics of Product Derived from Alkylation of Isobutane with Mixed Ethylene-Isobutylene Feed of 1:1 Mole Ratio

will render the catalyst responsive to the boron fluoride activation treatment.

The efficacy of boron fluoride activation is illustrated by the data of Table VI. In this run the boron fluoride content of the isobutane varied between 1.07 to 1.69 weight %. Frequent analyses were carried out on the influent and effluent streams to check on the consumption of boron fluoride. The data of this run are additionally interesting because of the inadvertently low isobutane-ethylene mole ratio. As a result of this latter condition the quantity of heavy alkylate (nonanes and heavier) was increased, and the quality of alkylate thereby degraded. However, in spite of this departure, the validity of catalyst life data is not impaired.

The data of Table VI are indicative of the value of maintaining the BF_3-H_2O-HF catalyst system at full activity. On the assumption that free boron fluoride in the effluent stream can be recovered and recycled at a reasonable cost, the activation procedure would appear feasible. However, the alkylate production still amounts to only about 7 gallons per pound of total boron fluoride, assuming no recovery of boron fluoride from the catalyst phase. It is apparent, therefore, that additional means of extending the useful life of the inital catalyst charge are necessary. Revivification of a catalyst showing signs of decline in activity was found to be possible by fortification with a small quantity of anhydrous hydrogen fluoride. The data in Table VII were taken from a laboratory run wherein general catalyst activity was maintained by resaturating the catalyst phase with boron fluoride at intervals of 2 hours. While this method of activation is admittedly only about half as efficient as continuous activation, the response to hydrogen fluoride fortification is amply demonstrated.

TABLE VI. CONTINUOUS BF_3 ACTIVATION OF BF_3-H_2O-HF CATALYST

Total isobutane charged, lb.	28.871
Total ethylene charged, lb.	7.339
Mole ratio, isobutane/ethylene	1.9
Total alkylate[a] produced, lb.	15.530
Yield, lb. alkylate/lb. ethylene charged	2.12
Vol. alkylate/vol. of catalyst charge	70.0
Catalyst charged, cc.	150
BF_3 content of initial catalyst, lb.	0.387
Av. BF_3 content of isobutane feed, wt. %	1.37
Total BF_3 in isobutane charge, lb.	0.390
Total BF_3 in effluent hydrocarbon stream, lb.	0.339
Net consumption of BF_3, lb.	0.051
Gal. alkylate/lb. BF_3 (exclusive of catalyst)	61.5
Characteristics of alkylate	
Gravity, ° A.P.I. at 60° F.	75.3
A.S.T.M. octane No.	86.6
A.S.T.M. octane No. (1 cc. T.E.L.)	98.2

[a] Alkylate composition: C_5, 7.0%; C_6, 50%; C_7, 7.0%; C_8, 16.0%; C_{9+}, 20.0%.

The experiment was terminated with what appeared to be a fully active catalyst at the conclusion of period 15 (Table VII). The composite alkylate was of normal quality with the following composition: C_5, 6.5%; C_6, 63.7%; C_7, 5.5%; C_8, 16.1%; C_{9+}, 8.2%. The diisopropyl concentrate boiling between 136–140° F. with an A.S.T.M. octane rating of 92 constituted 60.3 volume % of the total alkylate.

If the efficiency of continuous boron fluoride activation can be combined with the demonstrated efficacy of hydrogen fluoride fortification, it may be deduced that 9.65 gallons of alkylate could have been produced instead of the 5.5 gallons actually obtained. Then, since 0.5 pound of BF_3 was used in preparing the catalyst, a yield of about 19 gallons of alkylate per pound of BF_3 consumed may be predicted. The cost of hydrogen fluoride in such speculation is neglected, since the quantities involved are not great and because its cost is only about one third that of the boron fluoride. Since it now appeared that the commercial use of this catalyst system was economically possible, further investigation on a larger scale was projected.

PILOT PLANT STUDY

In the preceding sections laboratory data were presented to show that continuous activation of the present catalyst system with boron fluoride is beneficial to catalyst life. It was also demonstrated that spent catalyst can be restored to a high degree of activity by periodic fortification with hydrogen fluoride. A thorough quantitative evaluation of these two methods of extending catalyst life, applied so as to complement each other, was undertaken. However, because of war emergency conditions it was not possible to carry this program to completion. It was possible, therefore, to carry out only three bona fide pilot plant runs, one

TABLE VII. HF FORTIFICATION OF BF_3-H_2O-HF CATALYST SYSTEM

Operating Period	Mole Ratio Isobutane/ Ethylene	Total Alkylate, Lb.	Yield, Wt. % on Ethylene Charge	Cumulative Yield	
				Lb.	Vol./vol. catalyst
1[a]	2.6	2.410	203	11.869	39.9
2	2.6	2.132	236		
3	2.6	2.229	245		
4	2.8	1.923	239		
5	3.1	1.750	186		
6	3.1	1.425	179		
7[b]	3.1	2.092	205	6.480	21.7
8	2.5	2.008	216		
9	2.8	2.380	242		
10[b]	2.8	2.750	246	9.210	31.0
11	2.8	2.410	247		
12	2.5	2.210	227		
13	3.0	1.840	234		
14[c]	3.0	2.480	248	3.556	11.9
15	3.0	1.076	233		

[a] Initial catalyst charge, 200 cc. (350 grams).
[b] 0.044 pound hydrogen fluoride added to catalyst.
[c] 0.031 pound hydrogen fluoride added to catalyst.

TABLE VIII. PILOT PLANT ISOBUTANE-ETHYLENE ALKYLATION DATA

Operating period	1	2	3	4	5	6	7	8	9	10	Total or Average
Operating data											
On-stream time, hr.	7.25	7.00	7.00	8.00	6.50	8.25	6.50	7.00	7.50	4.50	69.5
Mole ratio, isobutane/ethylene	2.67	2.84	2.60	2.86	2.48	2.19	2.60	2.75	2.47	2.26	2.58
Effluent rate, gal./hr.	1.64	1.69	1.66	1.43	1.56	1.43	1.35	1.60	1.52	1.40	1.53
Alkylate production, gal./hr.	0.498	0.509	0.514	0.410	0.538	0.390	0.390	0.355	0.431	0.430	0.448
Reactor pressure, lb./sq. in. gage	225	225	225	225	225	230	225	225	220	225	225
Av. reactor temperature, ° F.	135	135	133	135	134	134	140	130	132	135	134
Material balance											
Ethylene charged, lb.	9.12	8.56	8.95	8.49	8.63	10.81	6.59	8.37	9.32	5.31	84.14
Iso-C_4 + BF_3 charged, lb.	51.35	51.28	48.69	51.33	44.97	49.97	37.04	48.78	48.49	25.41	457.31
Total feed charged, lb.	60.47	59.84	57.64	59.82	53.60	60.78	43.63	57.15	57.81	30.72	541.45
Av. BF_3 in iso-C_4 feed, wt. %	1.70	1.57	1.46	1.79	1.53	1.75	1.67	1.90	1.86	2.11	1.71
Isobutane charged, lb.	50.48	50.48	47.98	50.43	44.28	49.10	36.42	47.86	47.59	24.88	449.50
BF_3 charged, lb.	0.87	0.81	0.71	0.90	0.69	0.87	0.62	0.92	0.90	0.53	7.81
Total effluent recovered, lb.	59.04	58.81	57.67	57.02	50.40	58.91	43.63	55.95	56.39	31.46	529.28
BF_3 in effluent, wt. %	1.43	1.53	1.18	1.64	1.08	1.37	1.35	1.50	1.43	1.58	1.39
BF_3 in effluent, lb.	0.84	0.90	0.68	0.93	0.55	0.81	0.59	0.84	0.81	0.50	7.45
BF_3 lost or consumed, lb.	0.03	−0.10	0.03	−0.03	0.14	0.06	0.03	0.08	0.09	0.03	0.36
Over-all material recovery, wt. %	98.0	98.4	100.0	95.4	94.2	97.0	100.0	98.2	97.6	102.5	97.8
Compn. of total effluent (BF_3-free), wt. %											
Ethylene	0.48	0.45	1.82	2.66	0.80	3.46	2.52	2.90	2.28	1.59	1.90
Propane	0.35	0.29	0.20	0.26	0.10	0.32	0.35	0.36	0.48	0.30	0.30
Ethyl fluoride	0.29	0.12	0.10	0.10	0.12	0.12	0.59	0.34	0.83	1.07	0.32
Isobutane	64.49	64.86	62.00	65.14	61.46	65.65	66.52	71.35	64.21	60.62	64.74
Isopentane	3.49	3.39	2.92	2.79	3.04	2.92	2.31	2.36	3.28	3.67	3.03
Hexanes and heavier	30.90	30.89	33.00	29.05	34.48	27.56	27.21	22.69	29.00	32.75	29.76
Yield data											
Total alkylate, lb.	20.52	20.21	20.40	18.65	19.85	18.25	14.35	14.12	18.35	11.02	175.72
Ethylene converted, wt. %	96.8	96.8	88.0	81.5	95.2	80.8	83.8	80.5	77.2	89.1	88.2
Isobutane converted, wt. %	24.0	24.0	26.5	24.0	26.6	20.0	21.5	16.2	23.4	26.5	23.4
Yield on ethylene charged, wt. %	225	239	228	220	230	169	218	169	197	215	209
Yield on ethylene converted, wt. %	232	244	258	270	241	208	260	209	228	230	237
Yield on isobutane converted, wt. %	171	167	161	155	167	185	184	182	165	167	167
HF consumption											
HF added, lb.	0.294	0	0	0	0.237	0	0.244	0.239	0.244	0.158	1.416
HF to ethyl fluoride, lb.	0.071	0.029	0.024	0.024	0.025	0.029	0.107	0.079	0.191	0.140	0.719

of which was designed to translate laboratory findings to a firmer quantitative basis, whereas the other two were concerned with catalyst composition. The results of the former run, the first exhaustive catalyst life test using the equipment of Figure 1, are presented in Table VIII to show the potentialities of the present catalyst system. The procedure employed was the one previously described.

PILOT PLANT DATA. During the course of the run, 449.5 pounds of isobutane and 84.1 pounds of ethylene were charged to the reactor to produce 175.7 pounds (31 gallons) of total alkylate. This production amounts to 195 volumes of alkylate per volume of initial catalyst charge. The initial catalyst activity was in line with the laboratory results, as is evidenced by the production of about 88 volumes of alkylate per volume of catalyst before the first fortification with anhydrous hydrogen fluoride. However, the activity of the fortified catalyst phase was more transitory than expected. It is suspected that a great improvement in yield and catalyst life could be effected with the attainment of more uniform operating conditions. Thus there is no reason to believe that the low over-all ethylene conversion of 88.2 weight % is an inherent characteristic of this alkylation system, in view of a large number of laboratory runs showing conversions of 95% or better. Subsequent to the termination of this work it was discovered that the impeller was not providing adequate mixing in the reactor. This factor alone could account for both low ethylene conversion and foreshortened catalyst life.

TABLE IX. ALKYLATE PRODUCTION AND CATALYST CONSUMPTION

	Lb.	Gal. Alkylate/Lb.
Catalyst components in initial catalyst charge		
Boron fluoride	1.60	19.4
Hydrogen fluoride	0.294	105.0
Water	0.440	...
Catalyst components consumed in activation and fortification		
Boron fluoride	0.36	76.0
Hydrogen fluoride	1.122	27.7
Total		
Boron fluoride	1.96	15.8
Hydrogen fluoride	1.416	21.9

Table IX summarizes the relation between alkylate production and catalyst consumption. It will be noted that 15.8 gallons of alkylate were produced per pound of boron fluoride consumed, assuming no recovery of BF_3 from the catalyst phase. Since these data were obtained under conditions not conforming to good operating conditions, it is concluded that a production of over 20 gallons of alkylate per pound of boron fluoride consumed could be achieved without much difficulty.

RECOVERY OF BORON FLUORIDE

One of the primary problems connected with the use of the BF_3-H_2O-HF catalyst system in commercial alkylation reactions is the reduction of catalyst cost. In Table IX 1.96 pounds of boron fluoride have been charged against the alkylate production, whereas in Table VIII 7.81 pounds of boron fluoride were included in the isobutane feed to the reactor for activation of the catalyst. Since virtually all of this activation boron fluoride appears in the effluent stream, it is proposed to recover this physically dissolved boron fluoride by the process described by Axe (*2*), in which the effluent hydrocarbons boiling lower than isobutane are subjected to gas-liquid extraction with solvents such as β,β'-dichloroethyl ether, phenetole, and anisole. These solvents are capable of absorbing up to one mole of boron fluoride per mole of solvent in the form of thermally decomposable liquid complex compounds, and are resistant to the polymerizing action of the boron fluoride during repeated absorption and decomposition cycles.

LITERATURE CITED

(1) Alden, R. C., Frey, F. E., Hepp, H. J., and McReynolds, L. A., *Oil Gas J.*, 44, No. 40, 70 (1946).
(2) Axe, W. N., U. S. Patent 2,377,396 (June 5, 1945).
(3) Bruner, F. H., Clarke, L. A., and Sawyer, R. L., *Ibid.*, 2,345,095 (March 28, 1944).
(4) Ipatieff, V. N., and Grosse, A. V., *J. Am. Chem. Soc.*, **57**, 1616 (1935).
(5) Meinert, R. N., U. S. Patent 2,348,637 (May 9, 1944).
(6) Slotterbeck, O. C., *Ibid.*, 2,296,370 (Sept. 22, 1942).

REPORT No. 559-46R of the Phillips Petroleum Company Research Department.