

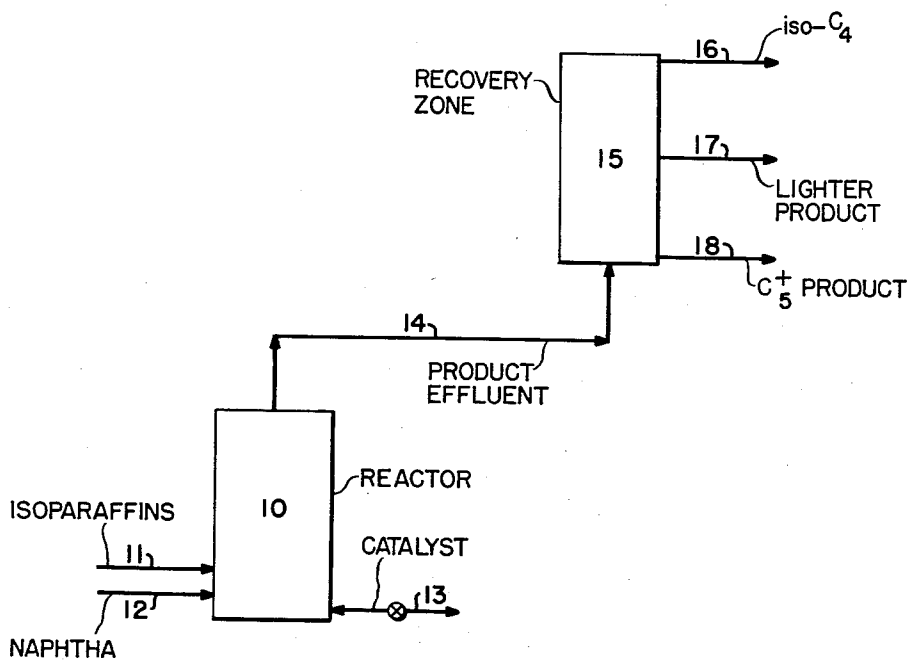
June 6, 1961

L. SPENADEL

2,987,561

METHOD FOR PRODUCING ISOPARAFFINS

Filed March 4, 1959



Lawrence Spenadel

Inventor

By *Robert J. Pearlman*

Agent

1

2,987,561

METHOD FOR PRODUCING ISOPARAFFINS

Lawrence Spenadel, Elizabeth, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Filed Mar. 4, 1959, Ser. No. 797,145

1 Claim. (Cl. 260—683.53)

The present invention is concerned with an improved method of upgrading paraffins to isoparaffins. More particularly, it deals with converting paraffins to isoparaffins to give good yields of desired products in the presence of substantial portions of aromatics.

The desire for obtaining high octane fuels has constantly increased with the development of engines of higher compression ratios. Thus the lowest grade gasolines of the present have a higher octane than the premium fuel of only a few short years ago. Among the ways advanced for securing requisite high octane constituents have been conversion processes designed to convert paraffin hydrocarbon, e.g. normal C_3 to C_{18} fractions, into isoparaffinic and branched chain molecules. It is well known that isoparaffins have substantially better octane characteristics than their normal paraffin counterparts. Additionally, the art recognizes that aromatics, such as benzene and toluene, also exhibit good octane qualities.

Among the processes heretofore advanced for the conversion of paraffins into more desirable isoparaffins is paraffin alkylation, sometimes termed paraffin disproportionation. Basically, this process involves contacting a normal paraffin hydrocarbon, preferably of from 6 to 18 carbon atoms, with an excess of isobutane and/or isopentane in the presence of a Friedel-Crafts catalyst, e.g. aluminum bromide. Among the products of the reaction will be a substantial portion of isoparaffin molecules having a number of carbon atoms intermediate to that of the normal paraffin and isobutane and/or isopentane feed. For example, reaction of normal heptane with isobutane will give isopentane and isohexane.

Normally, one of the most readily available feed materials for paraffin alkylation is a naphtha hydrocarbon fraction obtained by primary crude distillation of the paraffins left after removal of the aromatics from catalytically reformed or cracked naphtha. However, in addition to containing paraffins suitable for reaction, naphthas also contain substantial quantities, e.g. 1.0 to 40%, of aromatics. The aromatics are mostly benzene, toluene and xylene. In addition to naphthas, other feeds such as kerosenes and higher boiling hydrocarbons also contain aromatics.

Heretofore it had been found to be necessary to reduce the aromatic concentration in the feed stream to no more than 0.1 wt. percent. It was found that higher concentrations of aromatics tended to destroy the catalytic activity of the prior art catalysts, e.g. aluminum chloride or iron chloride, giving poor yields as well as forming sludge and polymers. Thus conventional paraffin alkylation systems could not be operated to give desirable yields of branched chain products in the presence of substantial quantities of aromatics.

Consequently, it was previously necessary to subject paraffin alkylation feed to an aromatic removal step, generally a liquid extraction process. This aromatic removal step greatly adds to operating and investment costs of the overall system thereby adversely affecting its commercial attractiveness.

There therefore exists a demand for a paraffin alkylation system capable of giving good yields of desired products in the presence of substantial quantities of aromatics, e.g. 1 wt. percent or greater based on the total feed.

2

In accordance with the present invention, high concentrations of aromatics are readily tolerated in the reaction zone while obtaining exceedingly good yields of highly valued branched chain paraffins, such as isopentanes and isohexanes. More particularly, paraffin hydrocarbons are converted in the presence of a catalyst of aluminum chloride on a support containing iron chloride, silica and alumina. It has been found that aluminum chloride on this specific support shows exceptionally good catalytic properties in the presence of aromatics. In addition to the advantages indicated previously, by allowing reaction to take place in the presence of aromatics, the product stream will be a particularly good high octane material since aromatics as well as isoparaffins exhibit good octane properties. As will be shown later by way of experimental examples, the catalyst of the present invention is substantially superior to aluminum chloride alone or on alumina alone; aluminum chloride on silica-alumina alone; or simply ferric chloride on a base of silica-alumina. It is generally well known that $FeCl_3$ alone gives negligible activity in the presence of aromatics.

The paraffin-alkylation reaction may be conducted in the liquid or vapor state. Reaction temperatures of 200 to 300° F. are preferred. $AlCl_3$ rather than $AlBr_3$ is employed since it is less acidic and has less tendency to react with the basic aromatic constituents.

In order to clarify nomenclature, the term "paraffin feedstream" denotes the overall mixture of hydrocarbons (paraffins, isoparaffins and aromatic constituents) fed to the reaction zone regardless of whether the individual components be individually introduced or fed as a single stream.

The various aspects and modifications of the present invention will be made more clearly apparent by reference to the following description, specific embodiment and accompanying drawing.

Turning to the drawing, reactor 10 may be any one of a number of well known paraffin alkylation zones containing the catalyst of the present invention, i.e. aluminum chloride on a support of iron chloride, silica and alumina. It may operate in the liquid or vapor phase and under a wide range of pressures. The catalyst may be in the form of a fluid or moving fixed bed, fixed bed, liquid or gaseous suspension, etc. Numerous means for promoting good contact between reactant and catalyst, e.g. distribution grids, baffles, etc., may be employed.

In the specific embodiment presently described, reactor 10 serves principally to convert the normal heptane constituents of a naphtha fraction boiling in the range of 200 to 220° F. The naphtha contains about 15 wt. percent of aromatics based on C_6+ feed constituents and is introduced in reactor 10 by line 12. The aromatic constituents are primarily benzene and toluene. A relatively low molecular weight isoparaffin (as compared to the normal paraffin feed materials) is fed through line 11. In the present embodiment, the isoparaffin is isobutane. Generally, a molar excess of isobutane is employed, i.e. 1.1 to 10 moles per mole of normal heptane in the feed.

Reactor 10 is maintained at 200° F. and a pressure of 500 p.s.i.g., reaction taking place in the liquid phase. The catalyst comprises 40 wt. percent $AlCl_3$ (based on support). The support contains 4 wt. percent $FeCl_3$ and 95 wt. percent alumina-silica. The alumina/silica weight ratios are preferably about 10/90 to 30/70, e.g. 20/80. The reactants are introduced at an overall rate of 0.1–10 v./v./hr. based on total catalyst.

In the reaction zone, paraffin disproportionation takes place in the presence of large quantities of aromatics.

Product effluent is withdrawn through outlet 14 and consists primarily of isopentane and isohexane as well as unreacted feed materials. The product stream is passed to recovery zone 15 which may be any conventional recovery means such as a distillation or scrubbing zone. Generally unreacted isobutane is recovered through line 16 and may be recycled for further conversion. Typically, a C_5+ product may be recovered through line 18 and a lighter product fraction withdrawn by outlet 17. Means, not shown, may also be provided for recovery of any catalyst entrained in the product stream.

Catalyst may be periodically or continuously fed to, and/or withdrawn from, the reaction zone by line 13 in order to maintain the desired level of catalytic activity. If desired, a catalyst promoter such as a hydrogen halide may be introduced into the reaction zone although this will normally not be necessary.

In its broadest aspects, the present invention is applicable to isomerization reactions as well as paraffin alkylation systems. Isomerization reactions convert paraffin feed material into isomeric molecules of substantially the same carbon number as the feed, and are well known in the art, per se. No low molecular weight isoparaffin is required as a feed constituent. Appreciable quantities of aromatics were, heretofore, not compatible with securing desired isomerization yields. Thus, use of the present invention will greatly reduce or eliminate the problem of removing aromatics from the feed oil stream to the isomerization zone.

The following table presents a compilation of data illustrating the present catalyst system.

Table 1—Catalyst composition

	Broad Range	Preferred Range
Wt. Percent Aluminum Chloride Based on Total Support.....	25-90	40-60
Support:		
Wt. Percent Iron Chloride.....	5-50	10-15
Wt. Percent Silica-Alumina.....	95-50	90-85
Wt. Percent Silica present in the Silica-alumina.....	25-90	70-90

The unique nature of the present invention is illustrated by the experimental results described below.

It was desired to react a relatively high molecular weight paraffin, i.e. normal decane, and a relatively low molecular weight isoparaffin, i.e. isobutane, in the presence of high concentrations of aromatics (12.4% on total feed or 37 wt. percent toluene based on C_5+ feed). In the comparative runs, the hydrocarbons were reacted under identical temperature and pressure conditions, reaction being carried out in the liquid phase to substantial completion (4 hour period in each case). The experimental runs illustrate the use of catalyst systems employing (1) $AlCl_3$ alone, (2) $AlCl_3$ on a support consisting of silica and alumina without iron chloride, (3) iron chloride and silica-alumina without aluminum chloride and (4) the catalyst of the present invention, i.e. aluminum chloride on a support of iron chloride, silica and alumina. Additionally, the present catalyst is compared with $AlCl_3$ on gamma Al_2O_3 heretofore one of the few catalysts shown to have fair activity in the presence of aromatics.

The support for the present catalytic system was prepared by conventional techniques. A mixture of 6.7 parts by weight of silica to one part alumina (in this case a standard catalytic cracking catalyst sold under the trade name of DA-1) was calcined at 1200° F. for three hours. When cool, 9 parts of the mixture were slurried in an ether solution containing 1 part by weight of anhydrous $FeCl_3$ in approximately 10 volumes of dry ether. After 15 minutes of mixing, the ether was decanted and the catalyst support dried under vacuum. It was then heated under N_2 at 610° F. for 1 hour and at 1000° F. for 1 hour using a quartz dish covered with asbestos board. The support was then cooled and impregnated with $AlCl_3$ by mixing.

The finished catalyst was 50 wt. percent $AlCl_3$ (based on total support), the support being 10 wt. percent $FeCl_3$ and a 90 wt. percent mixture of silica and alumina in the weight ratio of 6.7:1.

The reaction conditions as well as product distribution are set forth in Table 2.

Table 2

Runs	(1) $AlCl_3$ with no support	(2) $AlCl_3$ on support of Silica-Alumina ¹	(3) 10 wt. percent $FeCl_3$ and 90 wt. % Silica-Alumina (No $AlCl_3$)	(4) $AlCl_3$ on 10% $FeCl_3$ and 90% Silica-Alumina	(5) $AlCl_3$ on γAl_2O_3
Feed, grams:					
$10C_{10}$			90.7		
nC_{10}			29.2		
Toluene.....			17.2		
Conditions:					
Temperature, ° F.....			250		
Time, Hrs.....			4		
Pressure, p.s.i.g.....			700		
Analysis of C_5+ Product—Wt. percent:					
$10C_{10}$	2.6	1.1	negligible	17.7	6.8
nC_{10}	0.5	0.2	do.	1.6	0.5
Total C_{10}	3.1	1.3	do.	19.3	7.3
2,2 Dimethyl butane.....	0.2	0.1	do.	0.8	0.3
2 methylpentane, 2,3 dimethylbutane and cyclopentane.....	1.1	0.4	do.	7.5	5.3
3 methylpentane, cyclohexane.....	0.5	0.1	do.	3.5	2.3
nC_{11}	0.1	0	do.	0.8	0.5
$C_{11}H_{24}$	9.7	1.0	do.	9.4	6.5
Total C_{11}	11.6	1.6	do.	22.0	14.9
Total C_{11} and C_{12}	14.7	2.9	do.	41.3	22.2
2,2 Dimethylpentane, 2,4 methylpentane methylcyclopentane.....	0.3	0	do.	0.2	0.2
2,3 Dimethylpentane, 3,3 dimethylpentane.....	0.1	0	do.	0.6	1.1
nC_{12}	0	0	do.	0.1	0
$C_{12}H_{26}$	21.7	37.2	do.	18.0	18.4
Total C_{12}	22.0	37.2	do.	18.9	19.7
Total $C_{11}+$	63.3	59.9	100	59.8	58.1

¹ 50 wt. percent $AlCl_3$ based on support, 6.7 parts silica per part alumina, based on weight.

5

The weight percentage of C_5 and C_6 products, particularly the branched materials, is the true index of the yields of desired products since they are the principal high octane components desired from the paraffin alkylation reaction. Additionally, the rest of the product stream is principally unreacted feed constituents. Comparing the present catalyst (Run 4) with Runs 1, 2 and 3 ($AlCl_3$ alone or on a support consisting of silica-alumina, or iron chloride on silica-alumina), it is seen that aluminum chloride on a support of iron chloride, silica and alumina gives many fold higher yields of desired C_5 and C_6 products in the presence of aromatics. Even when compared to the catalyst of Run 5, which heretofore was considered to be a fairly good catalyst for effecting reaction in the presence of large quantities of aromatics, the present invention gives yields twice as large.

It is to be further noted that it is the combination of constituents found in the present invention, rather than any individual component, which is responsible for the greatly increased yields.

The above experiments are set forth by way of illustration, rather than limitation, of the present invention.

Summarily, by operating in accordance with the present invention, paraffins can now be successively converted to good yields of isoparaffins without requiring aromatics removal from the paraffin feedstock. Both operational and investment costs of the overall system are thereby greatly reduced.

Having described the present invention, that which is

6

sought to be protected is set forth in the appended claim.

What is claimed is:

- A process for converting paraffins into isoparaffins which comprises passing a feed stream containing relatively high molecular weight normal paraffins and relatively low molecular weight isoparaffins into a reaction zone maintained at reaction temperature, there being present in said feed stream about 15 to 37 wt. percent aromatics based on C_5+ feed constituents, and contacting said feed stream in said reaction zone with a catalyst comprising aluminum chloride on a support, the amount of said aluminum chloride being in the range of about 25 to 90 wt. percent based on total support and said support consisting essentially of iron chloride, silica and alumina, said iron chloride representing from about 5 to 50 wt. percent of said support.

References Cited in the file of this patent

UNITED STATES PATENTS

- | | | | |
|----|-----------|-----------------------|---------------|
| 20 | 2,349,458 | Owen et al. ----- | May 23, 1944 |
| | 2,393,104 | Crosse et al ----- | Jan. 15, 1946 |
| | 2,476,416 | Ipatieff et al. ----- | July 19, 1949 |
| | 2,695,325 | Stoops ----- | Nov. 23, 1954 |

OTHER REFERENCES

Thorpe: "Dictionary of Applied Chemistry," vol. I, pp. 560-561, and vol. IV, p. 392, Longmans, Green and Co., 1921.