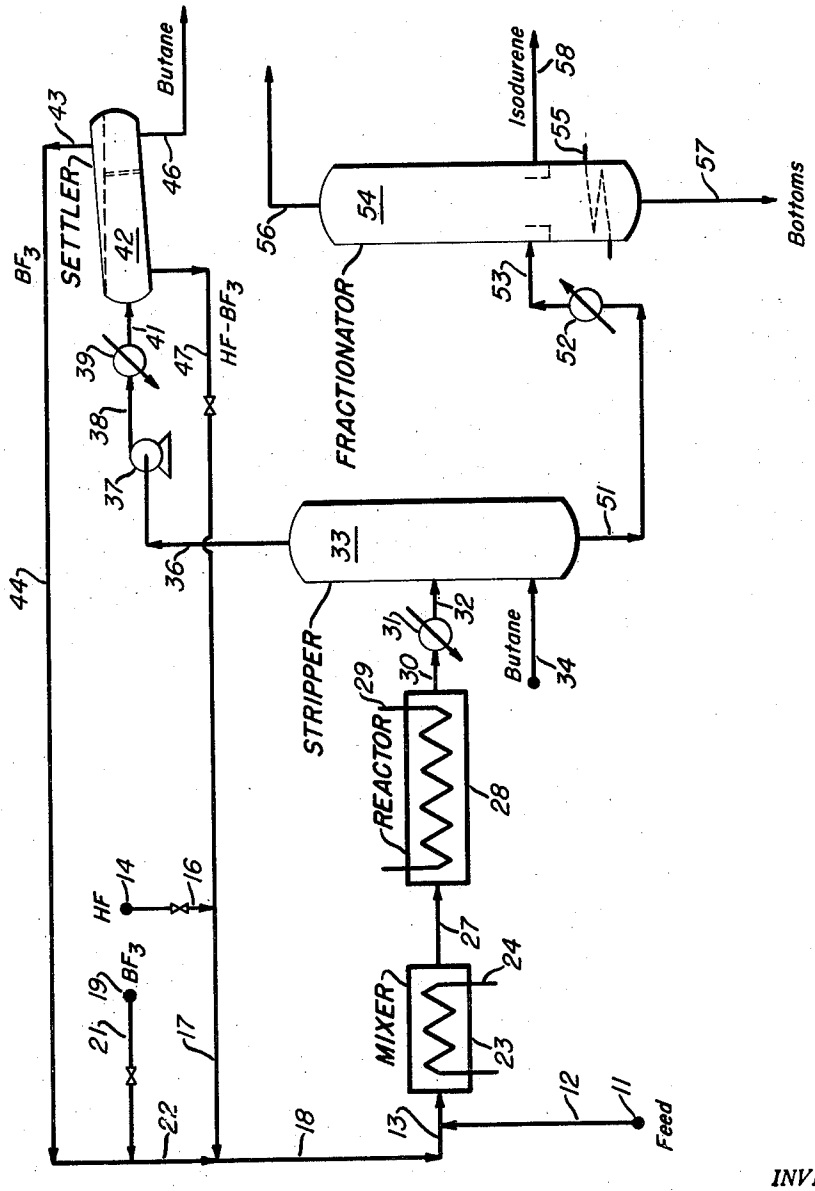
Nov. 17, 1953 A. P. LIEN ET AL 2,659,762

ISODURENE MANUFACTURE

Filed July 24, 1952



INVENTORS:
Arthur P. Lien
David A. McCaulay

BY Michael Dufinecz
ATTORNEY

Patented Nov. 17, 1953 2,659,762

UNITED STATES PATENT OFFICE

2,659,762

ISODURENE MANUFACTURE

Arthur P. Lien, Highland, Ind., and David A. McCaulay, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application July 24, 1952, Serial No. 300,652

9 Claims. (Cl. 260—668)

1

This invention relates to the isomerization of tetramethylbenzenes. Particularly it relates to the production of isodurene by the isomerization of prehnitene and/or durene.

The tetramethylbenzenes are valuable components of aviation safety fuels because of their very high octane numbers and high boiling points. However, the +80° C. freezing point of the durene (1,2,4,5-tetramethylbenzene) makes it undesirable as a high octane blending agent for aviation fuels. Although the −6° C. freezing point of prehnitene (1,2,3,4-tetramethylbenzene) is better than that of durene, it is still relatively poor for an aviation fuel blending agent. Isodurene (1,2,3,5-tetramethylbenzene) with its freezing point of −24° C. and the highest octane number of the tetramethylbenzenes is an exceptionally good blending agent for high octane aviation safety fuels.

An object of this invention is the manufacture of a mixture of tetramethylbenzenes wherein isodurene is the predominant member. Another object is the manufacture of high purity isodurene by the isomerization of the other members of the isomeric tetramethylbenzenes. Yet another object is the treatment of a mixture of C_{10} aromatic hydrocarbons to produce a tetramethylbenzene fraction which consists essentially of isodurene.

These objects and other objects not specified are attained by contacting a feed comprising essentially prehnitene and/or durene, or a mixture of tetramethylbenzenes under substantially anhydrous conditions with a treating agent consisting essentially of between about 0.9 to 3 mols of BF_3 per mol of said feed tetramethylbenzene, and sufficient liquid HF to dissolve said feed to form a single phase solution of feed, liquid HF and BF_3, maintaining said solution at a temperature between about 20° and 100° C. for a time sufficient to reach an equilibrium composition and removing HF and BF_3 from the product hydrocarbons which are predominantly isodurene.

It has been found that the C_{10} aromatic hydrocarbons other than butylbenzene form complexes with BF_3 and HF, which complexes are stable in liquid HF solution. These complexes have differing dissociation constants, which dissociation constants appear to be a function of the position of the alkyl substituents on the benzene nucleus. It has been found that of the tetramethylbenzenes the most stable complex is formed by isodurene. The complex appears to contain for each mol of complex-forming C_{10} aromatic hydrocarbon at least 1 mol of HF and 1 mol of BF_3.

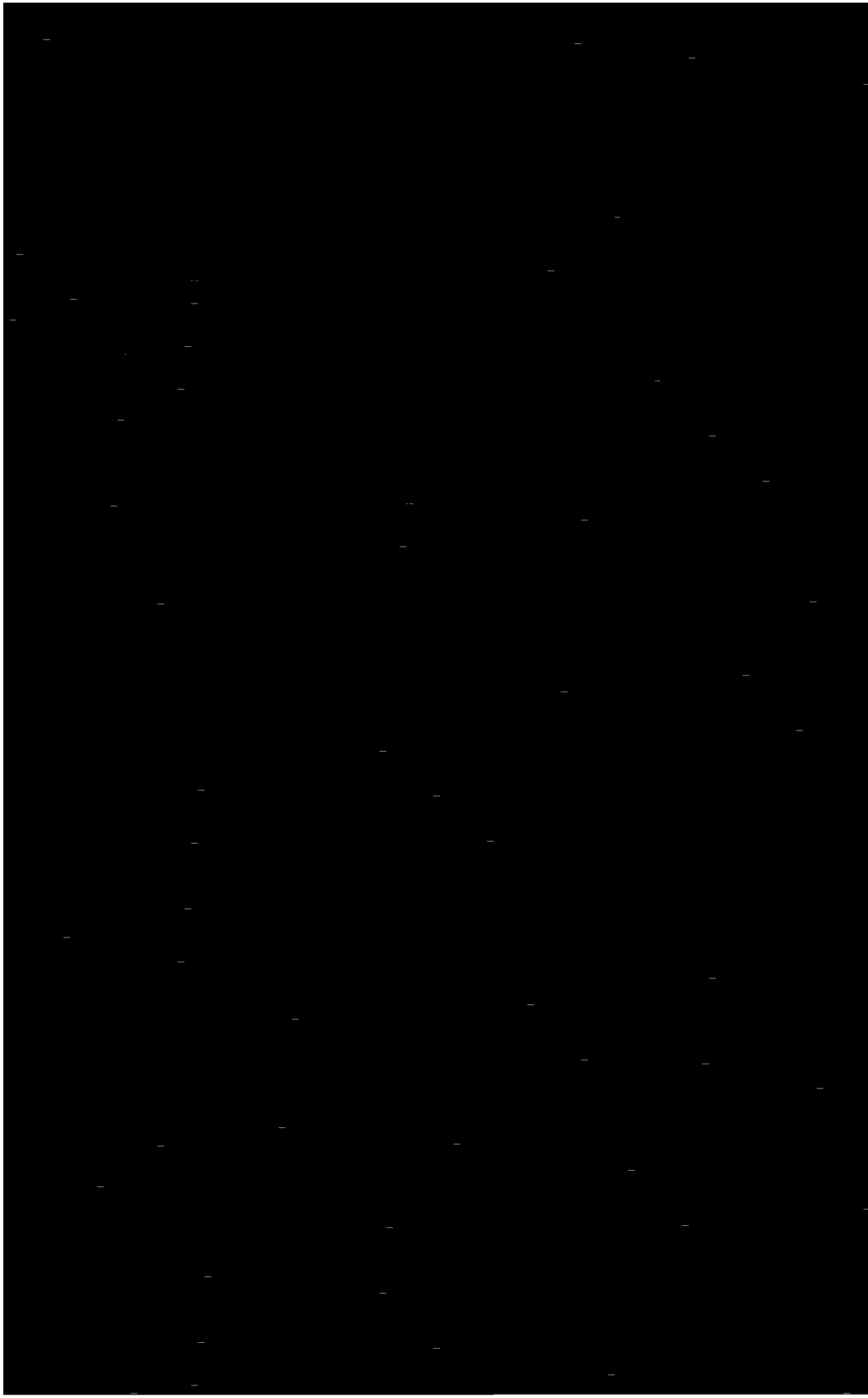
2

It has been found, under certain conditions of temperature and contacting time, that prehnitene and isodurene are isomerized in the presence of liquid HF and BF_3 to an equilibrium composition containing isodurene predominantly. Further, it has been found that the degree of isomerization can be carried to a point that substantially pure isodurene is the product of the reaction. Thus it is possible by the process of this invention to treat prehnitene and/or durene or a mixture of tetramethylbenzenes under conditions of temperature, contacting time, and composition of liquid HF—BF_3 treating agent to produce either a mixture of tetramethylbenzenes wherein isodurene is the predominant member, or a composition which consists essentially of isodurene, i. e., high purity isodurene.

It has also been found that a mixture of C_{10} aromatic hydrocarbons can be treated to produce a yield of isodurene greater than that theoretically obtainable by isomerizing the tetramethylbenzene content thereof. Apparently disproportionation, isomerization, and cracking reactions occur which result in the production of isodurene.

It has been found that sufficient liquid HF must be present to participate in the formation of the complex and also to dissolve the resulting complex. In general the amount of liquid HF used should be between about 2 mols and 50 mols or more for each mol of complex-forming aromatic hydrocarbon present in the feed. Preferably the amount of liquid HF should be between about 4 and 10 mols. More than 10 mols may be used, but little or no improvement in product quality is obtainable in most instances. The liquid HF used in this process should not contain more than about 2 or 3 weight percent of water, i. e., the process should be carried out under substantially anhydrous conditions.

It has been found that best results are obtainable when operating in a substantially single phase system. By single phase system it is to be understood that all the feed is dissolved in the liquid HF—BF_3 treating agent either in the form of a complex, or in physical solution. It has been found that the presence of complex in liquid HF markedly increases the solvent power of the liquid HF for non-complexed aromatic hydrocarbons and non-aromatic hydrocarbons. Thus it is possible to obtain a single phase system even though the feed to this process may contain appreciable amounts of non-complex forming aromatic hydrocarbons such as butylbenzene or non-aromatic hydrocarbons.



layer of butane is removed from settler 42 by way of line 46 and is recycled to line 34 by way of lines not shown. A bottom layer of liquid HF—BF_3 solution is withdrawn from settler 42 by way of valved line 47 and is recycled to the process by way of line 17.

The hydrocarbon product is withdrawn from the bottom of stripper 33 and is passed by way of line 51, heat exchanger 52 and line 53 into fractionator 54. Fractionator 54 is equipped with a reboiler 55 and is so constructed that a side stream of high purity isodurene may be removed therefrom. The minor amounts of C_9 aromatic hydrocarbons that are formed in the reaction are withdrawn from fractionator 54 by way of line 56 and are sent to storage not shown. A bottom fraction consisting of C_{11} and C_{12} aromatic hydrocarbons is withdrawn from fractionator 54 by way of line 57 and is sent to storage not shown. A high purity isodurene product is withdrawn as a side stream from fractionator 54 by way of line 58 and is sent to storage not shown.

When operating with a feed consisting of mixed C_{10} aromatic hydrocarbons about 7 mols of liquid HF and about 1.3 mols of BF_3 may be used per mol of C_{10} aromatic hydrocarbon. Operating conditions would otherwise be the same as described above except that the fractionation system would necessarily be more complex in order to separate isodurene from the numerous other aromatic hydrocarbons formed in the reaction zone, e. g. by disproportionation of alkylbenzenes containing ethyl groups and higher alkyl groups.

It is to be understood that the above embodiment is illustrative only and many items of process equipment have been omitted. Many variations of this process may be readily devised by those skilled in the art. All such variations are intended to come within the scope of the invention.

The results obtainable by this process are illustrated below.

The apparatus used in the illustrative test was a 1570 ml. carbon steel autoclave feed with a 1725 R. P. M. mechanical stirrer. The desired amount of feed was charged to the reactor. The substantially anhydrous liquid HF was then added. The BF_3 was then added to the reactor and the contents of the reactor were raised to the desired temperature and agitated for the desired contacting time. At the end of the contacting time the stirrer was stopped and the contents were allowed to settle for 10 minutes.

The contents of the reactor were withdrawn into a flask containing about 700 ml. of ice. The flask and its contents were allowed to warm to room temperature under a hood. The decomposition of the complex by the water resulted in the separation of an oil phase and an aqueous HF—BF_3 phase. The aqueous phase was discarded. The oil phase was withdrawn and washed with ammonium hydroxide to remove traces of HF and BF_3. The oil product was fractionated through a column containing about 30 theoretical plates. The close-boiling fractions from this distillation were then analyzed by ultraviolet and infrared absorption methods.

RUN 1

The feed to this run was substantially pure durene. This run was carried out using 33 mols of liquid HF and 1.3 mols of BF_3 per mol of durene. The contents of the reactor were agitated for 30 minutes at a temperature of 60° C.

The product oil consisted of, on a mole basis, C_9 aromatic hydrocarbons, 4%; C_{10} aromatic hydrocarbons, 86%; and C_{11}—C_{12} aromatic hydrocarbons, 10%. The C_{10} aromatic fraction was found to consist within experimental error only of isodurene.

RUN 2

In this test the feed consisted of durene. The treating agent consisted of, per mol of durene, 17 mols of liquid HF and 1.4 mols of BF_3. The contents of the reactor were agitated for 60 minutes at 0° C. Analysis showed that about 4 mol % of durene had been converted to C_9 and C_{11} aromatic hydrocarbons. The C_{10} aromatic hydrocarbon fraction in the product oil contained about 4% of isodurene and the remainder durene. This run shows that at this low temperature no appreciable isomerization occurs.

Thus having described the invention, what is claimed is:

1. A process for the production of isodurene from the other isomeric tetramethylbenzenes, which process comprises contacting under substantially anhydrous conditions a feed comprising essentially at least one other tetramethylbenzene with from about 0.9 to 3 mols of BF_3 per mol of said tetramethylbenzene, and with sufficient liquid HF to dissolve said feed and associated BF_3, maintaining said solution at a temperature between about 20° and 100° C. for a time sufficient to reach an equilibrium composition, and removing HF and BF_3 from the isodurene-enriched product hydrocarbons.

2. The process of claim 1 wherein said feed consists essentially of a mixture of tetramethylbenzenes.

3. The process of chain 1 wherein said feed consists essentially of durene.

4. The process of claim 1 wherein the amount of liquid HF is between about 2 and 50 mols per mol of said tetramethylbenzene.

5. The process of claim 1 wherein the contacting time is between about 2 minutes and 60 minutes and wherein the longer times correspond to lower temperatures of contacting.

6. A process for the production of high purity isodurene from the other isomeric tetramethylbenzenes, which process comprises contacting under substantially anhydrous conditions a feed comprising essentially at least one other tetramethylbenzene with between about 1 and 1.5 mols of BF_3 per mol of said tetramethylbenzene, and with between about 4 and 10 mols of liquid HF per mol and said tetramethylbenzenes, maintaining said contacting at a temperature between about 40° and 80° C. for a time sufficient to convert said feed tetramethylbenzene essentially to isodurene, separating HF and BF_3 from the product hydrocarbons, and separating high purity isodurene from said product hydrocarbons.

7. The process of claim 6 wherein the feed to the process consists essentially of a mixture of C_{10} aromatic hydrocarbons and the BF_3 usage and the liquid HF usage is based on total C_{10} aromatic hydrocarbon content therein.

8. The process of claim 6 wherein the contacting time is between about 10 and 40 minutes and wherein the longer times correspond to higher temperatures of contacting.

9. The process of claim 6 wherein the feed consists essentially of durene.

ARTHUR P. LIEN.
DAVID A. McCAULAY.

No references cited.