PRODUCTION OF XYLIDINE AND TOLUENE

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By Attorney
The present invention relates to improvements in the art of producing aviation gasoline, and more particularly, it relates to a combination process in which naphtha is reformed and simultaneously nitro aromatics are hydrogenated to form amino aromatics, the reforming reaction and the hydrogenation taking place simultaneously in a single reaction zone employing the same catalyst.

The development of aviation fuel in the last few years has been directed toward improving its rich mixture performance, that is, to say, its performance when the ratio of a fuel to air in the cylinders of an airplane motor is larger or greater than normal. It has been found that fuels which contain certain additives have a superior rich mixture performance. Thus, the addition of compounds such as cumene to aviation gasoline greatly increases its capacity for power output in a supercharged engine, that is, where the engine employs rich mixture conditions. The rich mixture performance of aviation fuel is very important from the standpoint of take-off and acceleration. It is readily understandable that the performance of, for example, a pursuit army airplane during the period of take-off from the ground and its ability to rapidly gain speed in flight is a factor of considerable importance. Since the discovery that aviation fuels do not always perform the same when used in both lean and rich mixture, it has caused the industry to carefully investigate the properties of fuels in supercharged engines, that is, to say, when the mixture of fuel and air is such that the fuel content is proportionately high. As previously stated, it has been found that a number of aromatics, and particularly substituted aromatics, greatly increase the anti-detonation qualities of a fuel operating under rich mixture conditions. To evaluate or forecast the probable or expected performance of an unknown fuel, there has been devised a test known as the 3-C blending value test (Army-Navy test AN-VV-F-748) which is especially designed to evaluate the fuel characteristics of an unknown aviation gasoline with various fuel-air weight ratios to determine power output. The indicated mean effective pressure (I.M.E.P.) determined in lbs. per sq. inch is an indication of the potential capacity of the fuel from the standpoint of power output.

The present invention has to do with a combination process in which, as previously indicated, an aviation base stock and an aviation gasoline additive are formed simultaneously, and an important feature of the invention is that the reaction forming on the one hand and hydrogenation of a nitro aromatic on the other, which latter is the additive, are thermally opposing reactions inasmuch as the reforming is endothermic while the hydrogenation is exothermic and advantage is taken of this condition to utilize the heat evolved in the process and to control temperature conditions in the reaction zone.

The main object of the present invention, therefore, is to produce an aviation gasoline and an aviation additive effective in increasing the power output of an aviation fuel employed in a supercharged engine. Other and further objects of my invention will appear more fully from the following description and claims.

In the accompanying drawing I have indicated diagrammatically a flow plan which illustrates a preferred modification of my invention.

Referring in detail to the drawing, a petroleum naphtha fraction containing substantial quantities of naphthenes, that is to say, containing at least 30 volume percent naphthenes, and preferably up to 60-70% naphthenes, is charged to the present system through line 1, thence heated in a fired coil 3, withdrawn through line 5 and discharged into a reactor 10 containing a reforming catalyst.

Simultaneously hydrogen from some source is introduced to the present system through line 6, heated in a fired coil 8 and thence discharged into line 8 where it mixes with the preheated naphtha and passes with it into reactor 10. Reactor 10 contains, as stated, a reforming catalyst. A good catalyst is one which consists of 5-12 weight percent of molybdenum oxide, and the balance "activated alumina," that is to say, aluminum oxide substantially free of alkali metal oxides, water, and other contaminants and prepared in known manner. The "activated alumina" acts as a support or spacing agent. Other catalysts may be used. For example, good results are obtained by using from 15-40 weight percent chromium oxide on alumina or using a mixture of nickel and tungsten sulfides, or, in fact, the oxides of the H, V, and W group metals of the periodic system give good results, and these may be supported on activated alumina, magnesia, or the like. I may also use platinum supported on activated carbon.

As to operating conditions within the reactor 10, the temperature should be within the range of from 800 to 925° F., with temperatures around 875° F. preferred. The pressure existing within reactor 10 should vary from 100 to 1000 lbs./sq. in. or higher, but I prefer to operate at around 200
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3 to 300 lbs./sq.in. gauge pressure and the feed rate of naphtha to the reaction zone should be from \( \frac{1}{2} \) to 2 volumes of oil per volume of catalyst per hour on a cold oil basis, with a feed rate of about 1.2 volumes of oil per volume of catalyst per hour preferred. The amount of hydrogen charged to the reactor 10 should vary from 2000 to 4000 cu. ft. of hydrogen per barrel of oil.

I have described generally the reforming conditions, and it is pointed out that these were known prior to my invention. Subsequently it will appear that as a result of the reforming of the naphtha, xylene streams and those nitrated in line 20 to line 8 and these are passed into reactor 10 where they undergo hydrogenation to form xylylene. As previously indicated, the reforming reaction and the hydrogenation of the nitroneylene are opposing reactions from the standpoint of thermodynamics and at least a portion of the heat absorbed by the endothermic reaction of reforming which is essentially a dehydrogenation reaction, although isomerization, polymerization, and perhaps some cracking also takes place, may be supplied by the exothermic heat released during the hydrogenation of the nitroneylene to form the amino aromatics. Consequently, it is possible to operate my process at least after operations have been initiated and the system is at reaction temperature in such a manner as to require very little, if any, preheating of the naphtha and the hydrogen in fired coils 3 and 8, respectively. In other words, by properly proportioning the nitroneylene feed with respect to the naphtha feed to reactor 10, the reaction therein taking place may be made self-sustaining with respect to heat requirements. In order to assist in causing uniform flow of the gases and/or vapors passing through reactor 10, the entering gases and vapors are forced through a foraminous member 12 which serves as a support for the catalyst C, which catalyst is in the physical form of lumps, granules, pills, pellets, and the like.

The reaction products are withdrawn through a line 27, quenched with oil or the like at 23 to cause cooling to 600°F. or lower, and then they are discharged into a high pressure separator 25 where the hydrogen or gases rich in hydrogen are withdrawn through line 38 and recycled to line 5 for further use in the process. Since the recycle stream 38 will normally contain hydrocarbons such as methane, ethane, ethylene, propylene, etc., it may be desirable to enrich hydrogen recycled to line 5 to cause the recycle stream to pass through an oil scrubber, which I have shown merely diagrammatically, since this type of equipment is well known to the art, wherein the hydrocarbons are dissolved out of the gaseous mixture by means of a solvent oil, such as a naphtha, and then the hydrogen-enriched gas is recycled to line 8 as previously indicated. A portion of the recycle stream in line 38 may be withdrawn from the present system through line 34. The reaction products freed from the hydrogen and withdrawn through line 40 carrying pressure reducing valve 42 and thence passed to a fractionator 45 where they are fractionated under a pressure of 100 lbs./sq.in. As shown in the drawing, however, it may be desirable to first discharge the products in line 40 into a depropanizer 48 from which propane and lighter hydrocarbons may be rejected from the system through line 49.

Referring again to fractionator 45, a good method for fractionating the products is to take off three fractions as follows: first, a crude benzene fraction is taken off overhead through line 50, second, an intermediate fraction comprising crude toluene is taken off through line 52; and third, a fraction comprising crude xylene is taken off through line 55. The various fractions which are withdrawn from fractionator 45, as indicated, are, of course, impure, that is to say, they are not pure aromatics but are associated with paraffins and olefins of comparable boiling range. The customary procedure is to solvent treat these crude fractions and they are desired in pure form, as where, for example, toluene of nitratable grade is desired. The purification of benzene and toluene forms no part of my present invention and these may be treated in any suitable manner to produce desired products.

The xylene product, on the other hand, according to my present invention is in whole or in part nitrated in nitrator 60, by withdrawing through line 55 the xylene fraction and passing it into a nitrator 60 where it is nitrated under known conditions to form mono-nitroxylene. The details of nitrating aromatics, such as xylene, are well known to those skilled in this art and per se it does not form part of my present invention. The nitrated xylene is then passed through line 20 into line 5 and treated as hereinbefore described. The ratio of nitroxylenol to naphtha feed to the reactor 10 may vary from 2 to 10 parts by weight of naphtha per part of nitroxylenol. In runs which I conducted at 950° and 850°F, I obtained yields of about 50% xyylene, based on the nitroxylenol charged. Of course the fractionator contains, as a result of the hydrogenation of the nitroxylenol, xylene and lighter hydrocarbons may be rejected from the system through line 49. A portion of the xylene may be withdrawn from the system through line 67.

It is pointed out that xyylene has a blending value as determined by 1% blends in a 100 number base gasoline of around 1500 lbs./sq.in. (indicated mean effective pressure, APFD-3C rich method), and it is obvious that this material is an excellent additive to aviation gasoline for the purpose of enhancing its rich mixture performance.

I have thus described an operation in which I simultaneously produce in an integrated operation aromatics and amino aromatics and specifically, xyldine. It may be desirable to carry out the reactions in reactor 10 at somewhat lower temperatures than those previously indicated (around 900°F.). say at around 600°F. and at pressure of 0 to 100 lbs./sq.in. gauge, but in order to accomplish reforming under these conditions, it is necessary to employ a very active reforming catalyst such as platinum supported on activated charcoal. However, when operating at the higher temperatures and pressures, the naphtha undergoing reforming serves to temper the reduction of the nitro compound. Also it is desirable to quench the reaction products by means of an oil such as a naphtha or other quenching medium at 23 in the passage of the reaction mixture of the products including the amine as quickly as possible, to prevent decomposition of the amine.

I have found that a highly desirable activator for the reduction of the nitro aromatics in reactor 10 is a sulfide, particularly carbon disulfide, and I prefer to feed a small quantity, say 1% or so, through line 35 in the recycle stream or at some
other convenient point, for as indicated, I have found that the addition of this material increases the production of the amine.

In the process which I have previously described, I consider the main advantage to be that contrary to prior methods of producing amines from the corresponding nitro derivatives of aromatics, I may operate continuously and in vapor phase and use the heat released to supply the endothermic heat of a reforming reaction taking place in the same zone as the hydrogenation of the nitro aromatics. Heretofore, as far as I am aware, the reduction of nitro aromatics to the corresponding amines was accomplished in liquid phase using hydrochloric acid and tin or iron. Also, this latter process is much more cumbersome than the one I have described.

It will be apparent to those skilled in the art that numerous modifications falling within the spirit thereof will readily suggest themselves to those familiar with this art.

What I claim is:

1. The continuous process of simultaneously producing toluene and xylidine which comprises charging a naphthenic naphtha containing between 60 and 70% of naphthenes including methyl cyclohexane to a reforming zone together with hydrogen and nitroxylene, permitting the mixture to contact a reforming catalyst at temperatures between 850° and 950° F. and under a pressure between 200 and 300 lbs. p. s. i. g. and pressure whereby the methyl cyclohexane is converted to toluene and the nitroxylene is converted to xylidine, withdrawing the reaction products from reaction zone, fractionally distilling the products to recover toluene, xylene and xylidine, separately conducting a portion of the xylene to a reaction zone where it is subjected to nitration, and recycling the thus nitrated xylene to the reforming zone.

2. The process set forth in claim 1 in which benzene, toluene and xylene are recovered from the fractional distillation zone.

3. The method set forth in claim 1 in which the amount of nitroxylene charged to the reforming zone with respect to the naphthenic naphtha similarly charged to said zone is such as to provide a substantial portion of the total heat required for the endothermic reaction of reforming.

RALPH M. HILL.

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