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START-UP METHOD FOR A LOW-TEMPERATURE HYDROGENATION PROCESS

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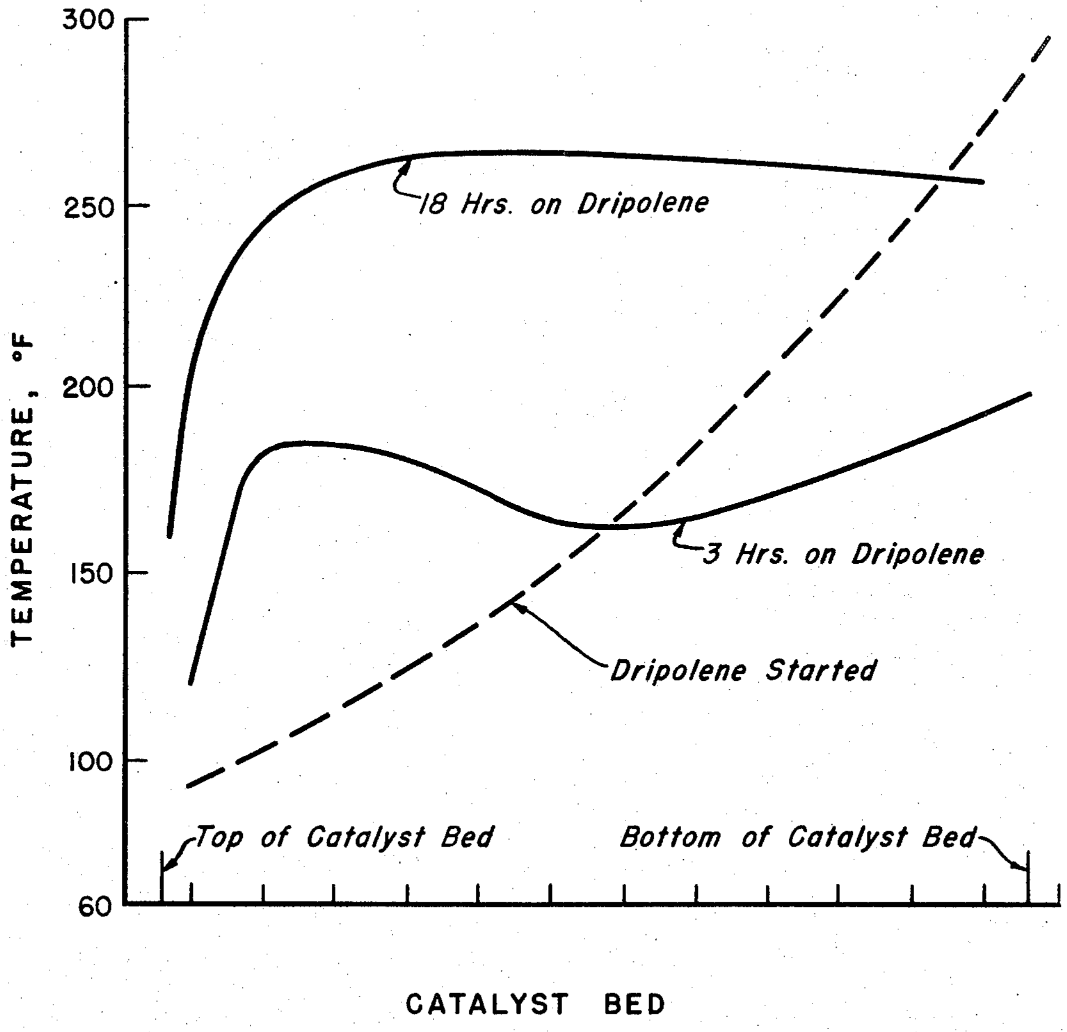

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START-UP METHOD FOR A LOW-TEMPERATURE HYDROGENATION PROCESS

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ABSTRACT OF THE DISCLOSURE

This method for starting up a process for the hydrogenation of dripolene comprises subjecting the catalyst to a deactivating treatment for temporarily deactivating the catalyst prior to its use as a catalyst for the hydrogenation of dripolene, said subjecting comprising contacting the catalyst with a deactivating medium under conditions which are suitable for the temporary deactivation of the catalyst in its entirety. An untreated virgin naphtha is a preferred deactivating medium.

BACKGROUND OF THE INVENTION

The present invention relates to the catalytic hydrogenation of olefinic hydrocarbons. More particularly, the invention relates to a method for starting up a low-temperature process for the hydrogenation of olefinic hydrocarbons. Still more particularly, the present invention relates to a method of starting up a process for the hydrogenation of dripolene.

Dripolene is the normally liquid mixture of hydrocarbons that is obtained as a by-product in the high-temperature pyrolysis of butane and lighter hydrocarbons to produce ethylene and propylene. In this pyrolysis, such reactions as polymerization, alkylation, aromatization, and dehydrogenation occur. Dripolene contains virtually all classes of hydrocarbons; however, olefinic and aromatic compounds predominate. Benzene is present in large quantities. Dripolene may be blended into motor gasolines, where the high-octane numbers of its aromatic and olefinic components render dripolene a desirable blending stock. Moreover, dripolene may be fed to aromatic extraction units for the recovery of pure benzene. Dripolene may also be subjected to thermal polymerization to produce valuable resins.

Dripolene contains cyclic diolefins, which tend to form gum-like polymers in the presence of air, or upon heating. The presence of these cyclic diolefins in the liquid dripolene can cause the contamination of products and the fouling of process equipment. Therefore, these deleterious components must be saturated to prevent, or at least minimize, such undesirable side effects.

The dripolene may be hydrogenated in a low-temperature hydrogenation process wherein the troublesome unsaturated components will become saturated. One of the operating problems that is associated with a dripolene hydrogenation process is the inability to control satisfactorily the excessive temperature increases that result from the hydrogenation of the unsaturates when dripolene is initially contacted with the hydrogenation catalyst. It is not unusual to stop the dripolene being fed to the hydrogenation unit during the start-up a great number of times to prevent damage to the catalyst. Such cessations are necessitated by the excessive temperature increases. A typical start-up may have as many as 15 interruptions. The diolefins, in particular, hydrogenate readily and produce much heat during their hydrogenation.

Now there has been found a method for starting up a process for the hydrogenation of dripolene wherein the catalyst is temporarily deactivated prior to its use for the hydrogenation of dripolene. This method minimizes the number and scope of initial temperature increases occurring when dripolene contacts the catalyst. This method is the subject of the present invention.

SUMMARY OF THE INVENTION

Briefly, in accordance with the present invention, there is a method for starting up a process for the hydrogenation of dripolene wherein an active low-temperature hydrogenation catalyst is employed. This method comprises subjecting the catalyst to a deactivating treatment for temporarily deactivating the catalyst prior to its use as a catalyst for the hydrogenation of dripolene. This deactivating treatment comprises contacting the catalyst with a deactivating medium or agent under conditions which are suitable for the temporary deactivation of the catalyst in its entirety. Included in such conditions is a period of time for the contacting, which period of time is sufficient for the entire catalyst to have become temporarily deactivated. Such period of time must be sufficient to permit any temperature rise accompanying the contacting to pass through the entire bed of catalyst. An untreated virgin naphtha and dripolene containing a minor amount of carbon disulfide are suitable deactivating mediums. An untreated virgin naphtha having an end boiling point below 420° F. is preferred. The contacting of the catalyst is carried out in such a manner as to maintain the temperature of the catalyst below about 450° F.

ACCOMPANYING DRAWING

One figure accompanies this application. This figure is a simplified presentation of temperature profiles obtained from a hydrogenation catalyst bed during specific times of an experimental start-up of a dripolene-hydrogenation process as discussed in a subsequent example.

DISCUSSION AND SPECIFIC EMBODIMENTS

According to the present invention, the deactivating medium or agent is employed to temporarily deactivate the catalyst. An untreated virgin naphtha is a preferred deactivating medium. Such naphtha contains minor amounts of sulfur compounds and high-boiling polymers. Either of these components is believed to poison temporarily the catalyst; however, it is to be pointed out that the presentation of such theory herein is not intended to limit the scope of this invention. Dripolene containing added small amounts of at least one sulfur compound is another deactivating medium or agent. A typical sulfur compound that may be added to dripolene for this purpose is carbon disulfide.

The hydrogenation of dripolene may be carried out in the presence of a platinum-containing catalyst. A used reforming catalyst is a suitable catalyst. Such used reforming catalyst may have seen hundreds of regenerations, often in excess of 500 regenerations. A typical reforming catalyst comprises platinum and a halogen supported on an active alumina catalyst base. A preferred halogen is chlorine. A suitable reforming catalyst would contain between about 0.1 weight percent and about 10 weight percent platinum and about 0.1 weight percent and about 3 weight percent chlorine on a gamma-alumina support. Prior to its use as a catalyst for the hydrogenation of dripolene, the used reforming catalyst must be reactivated. A typical reactivation process may comprise adjusting the halogen level to a level between about 0.6 weight percent and about 0.9 weight percent halogen, treating the catalyst with a gas containing up to 5 percent oxygen at a temperature as high as 800° F. to 1,000° F., a pressure within the range between about 200 p.s.i.g. and about 300 p.s.i.g., purging the catalyst with an inert gas, cooling the catalyst to a temperature of about 550° F. and treating the catalyst with a hydrogen-containing gas while cooling the catalyst from the 550° F. temperature to a temperature between ambient temperature and about 150° F.

The catalyst may be in the form of pellets, extrudates, spheres, or the like. Typically, pellets have a maximum dimension which does not exceed 1/4 inch; extrudates, a length which does not exceed 7/16 inch. A particularly suitable catalyst for the hydrogenation of dripolene is a catalyst which has been partially deactivated by continued use in a naphtha reforming process. A used reforming catalyst appears to be more stable and possess less tendency to hydrogenate aromatic compounds then fresh reforming catalysts. In addition, the used catalyst exhibits less tendency to cause wasteful hydrocracking of hydrocarbons, thus resulting in the recovery of larger yields of liquid products.

In the typical process for the hydrogenation of dripolene, the commingled feedstock and hydrogen-containing gas consists of a gas phase and a liquid phase wherein the liquid phase comprises substantially all of the charge stock. It is desired that at least 80 mole percent, and preferably at least 90 mole percent, of the dripolene charge contact the catalyst as a liquid. Desired pressures are within the range between about 100 p.s.i.g. and about 1,000 p.s.i.g. Preferred pressure fall within the range between about 300 p.s.i.g. and about 500 p.s.i.g. This latter range favors conditions at which the hydrogenation reaction occurs rapidly. Within the broad pressure range, the catalyst bed inlet temperature may be between 50° F. and about 200° F., more desirably between about 100° F. and about 150° F., and typically at 115° F. Generally, the temperature rise through an adiabatic bed is between about 300° F. and about 400° F. for complete olefinic saturation and provides an average reactor temperature between about 280° F. and about 340° F. This average temperature may be increased by providing more catalyst or it may be decreased by increasing the proportion of hydrogen-containing gas to charge stock. The hydrogen-containing gas is employed in an amount between about 500 standard cubic feet of gas per barrel of charge stock (s.c.f.b.) and about 10,000 s.c.f.b., typically between about 1,000 s.c.f.b. and about 4,000 s.c.f.b., and preferably between about 1,500 s.c.f.b. and about 3,000 s.c.f.b. The hydrogen-containing gas is composed preferably of at least 70 percent hydrogen and may be obtained from a naphtha reforming operation. This hydrogen-containing feed gas should contain no more than 5 p.p.m. of hydrogen sulfide. If the hydrogen-containing gas contains amounts of hydrogen sulfide in excess of 5 p.p.m., it must be chemically treated to maintain the low hydrogen sulfide level. Typically, the weight hourly space velocity is maintained between about 1 unit of dripolene per hour per unit of catalyst and about 3 units of dripolene per hour per unit of catalyst. Preferably, the weight hourly space velocity is held between about 1.5 units of dripolene per unit of catalyst and about 2 units of dripolene per unit of catalyst.

According to the invention, the preferred deactivating medium is an untreated virgin naphtha. Such virgin naphtha has an end boiling point which does not exceed 420° F.

The following examples are presented to enable the reader to more clearly understand the present invention. It is to be understood that these examples are presented for the purpose of illustration only and are not intended to limit the scope of the invention.

EXAMPLE I

A used commercial platinum-reforming catalyst was employed in this example. This catalyst contained 0.6 weight percent platinum on a gamma-alumina support. The catalyst, which had been subjected to more than 500 regenerations during its commercial use, was treated to contain about 1.0 weight percent chlorine.

A quantity of 200 grams of this catalyst was charged to a small-scale automated test unit. The reactor of this unit was one-inch stainless-steel schedule-80 pipe. Its inside diameter was 0.957 inch. A 0.132-inch diameter thermowell was concentric with and extended down the reactor. An automated thermocouple was moved up and down in this thermowell and was used to measure the catalyst-bed-temperature profiles. The bottom and top sections of the reactor were packed with inactive alumina balls having a nominal diameter of 1/8 inch.

For this test, the unit was operated at a weight hourly space velocity of 1 gram of hydrocarbon feed per hour per gram of catalyst. The inlet temperature to the reactor was ambient temperature. The effluent from the reactor was passed to a high pressure separator which separated the liquid product from the hydrogen. No light hydrocarbons (C_2–C_4) were detected in the hydrogen stream off the separator.

The catalyst was regenerated in an oxygen-containing atmosphere at a temperature above 900° F., cooled to a temperature of 550° F., purged with nitrogen, contacted with hydrogen flowing at a rate of less than 0.2 of a standard cubic foot per hour (s.c.f.h.), and cooled to ambient temperature in the flowing hydrogen. Flowing hydrogen was continued until the catalyst has been subjected to the flowing hydrogen for about 56 hours. Then the unit was pressured in hydrogen to 300 p.s.i.g. and a dripolene fraction was charged to the reactor. The properties of this dripolene fraction, identified as feed number 1, are presented in Table I.

TABLE I.—DRIPOLENE FEEDSTOCK PROPERTIES

Feed number	1	2
Gravity, ° API	35.1	34.6
ASTM distillation, ° F.:		
IBP	116	120
10%	150	158
20%	160	166
30%	166	172
40%	172	176
50%	175	180
60%	178	186
70%	182	188
80%	186	196
90%	204	223
EBP	294	322
Sulfur, wt. percent	0.0017	0.0016
Chloride, p.p.m	5	10.2
Nitrogen, p.p.m	6	11
Metals, p.p.m.:		
Cu	0.1	1.0
Fe	0.1	1.0
Pb	0.1	1.0
As	1.0	---------
Bromine No., cg./gm	27	34.5
Benzene, vol. percent	70	62.2
Induction, min	15	30
Gum, mg./100 mg	163	50
Mav., mg./gm	72	---------

The initial contact of the dripolene with the catalyst resulted in extremely high localized temperatures. The temperatures rapidly rose about 600° F. and hydrogen consumption increased. The dripolene feed was stopped and the reactor was cooled. Two more attempts were made to charge the dripolene feed to the reactor, but in each case an excessive temperature was reached and the dripolene feed had to be stopped.

A virgin naphtha was then introduced into the reactor at a rate similar to that which was employed for the dripolene feed. The properties of this naphtha are presented in Table II.

TABLE II

Naphtha feedstock properties

Gravity, ° API	53.6
ASTM Distillation, ° F.:	
IBP	206
10%	229
20%	238
30%	248
40%	257
50%	268
60%	281
70%	297
80%	316
90%	341
EBP	394
Paraffins, vol. percent	45.0
Olefins, vol. percent	---
Naphthenes, vol. percent	40.7
Aromatics, vol. percent	14.3
Sulfur, weight percent	0.032
Nitrogen, p.p.m.	1.5
Research Octane No. (clear)	53.2
Motor Octane No. (clear)	51.2

It was found that a small reaction did occur when the naphtha was contacted with the catalyst and that if the bed temperatures were initially above 200° F., this reaction became uncontrollable. Since no light hydrocarbons were detected in the off gas, it was believed that this reaction comprised the hydrogenation of small amounts of aromatics and olefins rather than hydrocracking. The progress of the treatment of the catalyst was observed by following the movement of this temperature wave down the catalyst bed. Within 1.5 hours any associated temperature rise had passed through the catalyst bed and the virgin naphtha was stopped. The dripolene feed was again introduced into the reactor. No excessive temperature increase developed. This suggested that the catalyst was deactivated. During the subsequent 8 hours, the bed-temperature profile slowly rose to a steady-state level, which indicated that the catalyst had become slowly reactivated. It lined out at a steady-state level similar to that obtained with an active catalyst. At the steady-state level, the temperature profile progressed from ambient temperature at the top of the catalyst bed to a maximum temerature of about 255° F. at a point in the bed approximately ⅔ down the bed's length. This maximum temperature was then maintained in the remaining ⅓ of the bed. During the time that catalyst-bed-temperature profile was reaching a steady-state value, the dripolene product had an extremely dark hue. This color gradually cleared as the bed temperatures reached the steady-state level.

As shown by this example, treatment of the catalyst with the virgin naphtha before the dripolene feed was charged to the reactior temporarily deactivated the catalyst and prevented excessive temperatures from occurring when the dripolene feed was charged subsequently to the reactor.

EXAMPLE II

A fresh platinum-reforming catalyst was charged to the test unit described in Example I. This catalyst contained 0.8 weight percent platinum and 0.76 weight percent chlorine on a gamma-alumina support.

A 200-gram charge of the catalyst was placed in the reactor. The unit was pressured in nitrogen and purged. The hydrogen at a flow rate of 6 s.c.f.h. and a pressure of 300 p.s.i.g. was introduced into the reactor. The catalyst was then heated to 550° F. in this hydrogen and then permitted to cool in hydrogen to ambient temperature.

Initially, naptha was charged to the hydrogen-pressurized reactor. Properties of this naphtha are presented in Table II. Operating conditions similar to those employed in Example I were employed in this test. After 4.5 hours, it was believed that the entire bed of catalyst has been deactivated and the virgin naphtha was stopped. Then a dripolene fraction was charged to the unit. This dripolene fraction was designated as feed No. 2. The properties of this dripolene fraction are presented in Table I. Very shortly after the introduction of the dripolene into the reactor excessive temperatures were reached. The dripolene feed was stopped immediately and the reactor was cooled. Subsequently, the virgin naphtha was charged to the reactor for an additional ½ hour at the same weight hourly space velocity. Then the dripolene feed was again introduced into the reactor. Excessive temperatures were not exhibited; the catalyst was deactivated. The catalyst was slowly reactivated as the dripolene feed was processed. Temperature profiles of the catalyst bed are presented in the accompanying figure. A temperature profile obtained immediately after the dripolene feed had been started is presented. Also presented is a temperature profile obtained after the catalyst had been treated with dripolene for 3 hours. Moreover, a temperature profile obtained after the catalyst had been treated with the dripolene feed for 18 hours is presented. The 3-hour bed temperature profile depicts the slow reactivation of the catalyst. During this period of reactivation the product obtained from the hydrogenaton process had a dark hue. After the 18 hours of dripolene feed, a fully-developed temperature profile was being employed.

This example shows that an adequate pretreat of the hydrogenation catalyst with the virgin naphtha prior to the use of the catalyst to hydrogenate dripolene deactivates the catalyst sufficiently to prevent the formation of subsequent high temperatures. It shows that such deactivation is only temporary and that reactivation of the catalyst can be achieved over a short period of time.

The above two examples, providing specific embodiments of the present invention, show that a hydrogenation catalyst to be used for the hydrogenation of dripolene can be effectively treated according to the present invention to prevent the formation of excessive temperatures during the initial stages of the hydrogenation run.

What is claimed is:

1. A method for starting up a process for the hydrogenation of dripolene wherein an active low-temperature hydrogenation catalyst comprising a platinum-on-alumina reforming catalyst is employed, which method comprises subjecting said catalyst to a deactivating treament for temporarily deactivating said catalyst prior to its use as a catalyst for the hydrogenation of dripolene, said subjecting said catalyst to a deactivating treament comprising contacting said catalyst with a deactivating medium for a period of time that is sufficient for the entire catalyst to have become temporarily deactivated, said deactivating medium being an untreated virgin naphtha which has an end boiling point that is below 420° F.

2. The method of claim **1** wherein said contacting is carried out in such a manner as to maintain the temperature of said catalyst below about 450° F.

3. The method of claim **1** wherein said contacting is carried out at a pressure between about 100 p.s.i.g. and about 1,000 p.s.i.g. and a weight hourly spaced velocity between about 1 and about 3 units of deactivating medium per hour per unit of catalyst.

4. The method of claim **2** wherein said contacting is carried out at a pressure between about 100 p.s.i.g. and about 1,000 p.s.i.g. and a weight hourly space velocity between about 1 and about 3 units of deactivating medium per hour per unit of catalyst.

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