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HYDROGENATION PROCESS START-UP METHOD

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ABSTRACT OF THE DISCLOSURE

A start-up method for a process for the liquid phase selective non-destructive catalytic hydrogenation of α-methylstyrene in a mixed α-methylstyrene and cumene feed wherein upon the initial charging of hydrogen and α-methylstyrene to the hydrogenation zone containing a solid hydrogenation catalyst the concentration of hydrogen in the gases in said zone is maintained at not greater than 40 mole percent and the inlet temperature of the mixed feedstream is maintained at not greater than 160° F. until the hydrogenation reaction has commenced.

BACKGROUND OF THE INVENTION

The present invention relates to a hydrogenation process. More particularly, the present invention relates to a start-up method in a process for the selective non-destructive hydrogenation of alphamethyl styrene.

The selective hydrogenation of petroleum derived products in a non-destructive manner is well known and widely used throughout the oil and chemical industries. For example, selective hydrogenation is carried out to remove olefins and diolefins from aromatic feedstocks to prevent their polymerization and contamination of the products of later treatment processes and also to facilitate the separation of aromatic hydrocarbons from paraffinic hydrocarbons. Such selective hydrogenation processes are also employed to convert alkylene aromatic hydrocarbons to the more saturated alkyl aromatic hydrocarbons. In such a conversion the desire d product is the alkyl aromatic compound and the hydrogenation is carried out in a selective manner so as to avoid saturating the aromatic ring portion of the hydrocarbon.

The selective hydrogenation of alphamethyl styrene to cumene, or isopropylbenzene, is one such selective hydrogenation process wherein saturation of the aromatic ring is particularly to be avoided. This is true, not only because of the loss of desired cumene product occasioned by conversion of the cumene present to isopropylcyclohexane, but also the fact that such a saturated compound upon subsequent processing of the cumene product, for example by oxidation thereof, produces contaminants which not only lower the yield of the desired oxidation products but are very difficult to separate from those oxidation products. Consequently, particularly in the process for hydrogenation of alphamethyl styrene to cumene such hydrogenation of the aromatic ring is to be avoided whenever possible.

It has been found that in the initiation of a process for the selective hydrogenation of α-methylstyrene feeds, it frequently happens that when such feedstock and the hydrogen are first fed to a catalytic hydrogenation zone, there occurs a very rapid temperature rise resulting in conditions severe enough to cause hydrogenation of some of the aromatic rings present. This is particularly true in processes which employ feedstocks containing both α-methylstyrene and cumene as is a common practice in carrying out this process. This hydrogenation of the aromatic ring is an undesirable result inasmuch as it not only reduces the amount of cumene product recoverable, but also produces saturated cyclic compounds which contaminate the cumene product and products of its further reaction and treatment.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an improved process for the selective hydrogenation of α-methylstyrene in an α-methylstyrene and cumene feed.

Another object of the present invention is to provide a start-up method for a process for the selective non-destructive hydrogenation of an α-methylstyrene and cumene feed.

Still another object of the persent invention is to provide a start-up method for use in a process for the selective hydrogenation of an α-methylstyrene and cumene feed which prevents rapid temperature rises and hydrogenation of the aromatic rings contained in the feed.

These and other objects of the present invention will become apparent from the description below and the appended claims.

Basically, the process of the present invention provides a method whereby, in a selective hydrogenation of α-methylstyrene in an α-methylstyrene and cumene feed, hydrogenation of aromatic rings in the feed and temperature runaways are avoided on start-up of the process. According to the method, upon the initial introduction of hydrogen and the α-methylstyrene and cumene feed into a hydrogenation zone containing a solid hydrogenation catalyst the concentration of hydrogen in the gases present in said zone is maintained in a minor proportion of not greater than 40 mole percent and the temperature within the hydrogenation zone is maintained low by maintaining the inlet temperature of the feedstream at not greater than 160° F. until the hydrogenation reaction has commenced. After the onset of the hydrogenation reaction the concentration of hydrogen present and the inlet temperature of the feedstream are gradually increased along with increasing the feed rate of the α-methylstyrene and cumene feed until full rate steady state hydrogenation conditions are reached.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As explained above, the start-up method of the present invention is an improvement in the selective hydrogenation process used in the conversion to cumene of the α-methylstyrene present in an α-methylstyrene and cumene feedstream. The improvement provided by the present invention and the process of selective hydrogenation of α-methylstyrene will be described in general terms below. In the usual hydrogenation process, α-methylstyrene is generally present with cumene either by the nature of the source of the α-methylstyrene stream or by mixing such stream with recycled product cumene for the purpose of better temperature control in the hydrogenation reaction. Normally the α-methylstyrene and cumene feedstream will be comprised of from about 10 to about 60 percent α-methylstyrene, and preefrably from about 15 to about 35 percent thereof. If mixed with recycled product cumene the α-methylstyrene stream prior to mixing with the recycled cumene product normally has a composition within the following ranges:

	Percent by wt.
α-Methylstyrene	63–83
Cumene	12–33
Other hydrocarbon and oxygenated derivatives	2–30

The recycled cumene product is generally mixed with the α-methylstyrene feedstream in the feed line leading to the hydrogenation reactor. In accordance with the procedure by which the process is normally operated, the mixed α-methylstyrene and cumene feed is introduced

into a hydrogenation reactor which contains a solid hydrogenation catalyst. This reactor may be operated in either an upflow or downflow manner, but it is generally preferred to operate the hydrogenation reactor as an upflow reactor. Within the hydrogenation reactor temperatue and pressure conditions are maintained such as to keep the α-methylstyrene and cumene feed in the liquid phase during its passage therethrough. Normal temperatures within the reactor will generally range from about 100° to 500° F. and preferably from 140° to 380° F., whereas pressures will be maintained within the range of 100 to 800 p.s.i.g. and more preferably from 150 to 400 p.s.i.g. The hydrogenation catalyst contained in the reactor will be one of the well-known solid hydrogenation catalysts such as a noble metal deposited on an alumina support.

Concurrently with the introduction of the mixed stream of α-methylstyrene and cumene, hydrogen is also introduced into the hydrogenation reactor. During normal operation of such process it is not necessary that the hydrogen stream introduced be pure hydrogen, but it is preferred for reasons of economy that it be a stream containing at least 75 mole percent hydrogen. The amount of hydrogen introduced into the reactor during normal operation varies somewhat depending on the hourly space velocity of the α-methylstyrene and cumene feed being introduced and the composition of such feed.

In the hydrogenation reactor the α-methylstyrene present in the mixed α-methylstyrene and cumene feed is selectively hydrogenated to cumene and a cumene product is removed from the reactor. Such product is removed overhead from the reactor in the case of upflow operation thereof. Some of the cumene product stream is recycled to the feed line to the hydrogenation reactor to supply recycled cumene thereto, and the remaining portion representing the cumene product is purified, stored, sold and/or forwarded to further treatment and reactions such as oxidation.

In the general process just described it has been found that upon start-up of the process, such as when the catalyst has been regenerated or replaced and the process is put back into operation or when the process is started up for the first time in a new installation, sharp temperature rises or "temperature runaways" are encountered in the reaction with the result that significant quantities of saturated cyclic compounds, chiefly isopropylcyclohexane, are produced by hydrogenation of the aromatic rings in the cumene either present in the feed stream or that produced by selective hydrogenation. As explained above not only is the yield of the desired cumene product thus reduced, but the undesirable saturated cyclic by-products cause difficulties in later processing of the cument product.

In accordance with the start-up method of the present invention, the hydrogenation reactor is first pressured with an inert gas prior to introduction of either the α-methylstyrene and cumene feed or hydrogen. This initial pressuring of the hydrogenation reactor serves two purposes. The pressuring with an inert gas serves as a safety measure to exclude air or oxygen from the reactor. Of much greater importance, the presence in the reactor of the inert gas serves to insure that the concentration is hydrogen in the gaseous phase in such reactor is maintained at a value of not greater than 40 mole percent until after the initiation of the hydrogenation reaction.

Pressures of an inert gas of between 10 and 200 p.s.i.g. in the reactor are generally sufficient both to insure that any air or oxygen has been displaced as well as to insure the necessary degree of dilution of the hydrogen initially introduced. Generally, a pressure of about 90 to 100 p.s.i.g. is preferred. The term "inert gas" as used herein refers to any gas which is unreactive under the conditions of the process, and more specifically refers to one of the gases commonly used for blanketing, purging, etc. Gases included in this group are the light hydrocarbon gases such as methane and ethane, nitrogen, argon, helium and the like. Practically any gas which does not react with the catalyst, the α-methylstyrene and cumene feed or the hydrogen can be used to pressurize the reactor in the present start-up method. Usually, because of its availability and economy, nitrogen is the inert gas chosen.

After the hydrogenation reactor is pressured with the inert gas, there is established a flow of recycled cumene product which is heated to approximately 150° F. When the reactor has reached the temperature of the cumene feed, usually about 150° F. the inert gas pressure is raised to the normal operating level of about 165 to 220 p.s.i.g. Then a sufficient amount of hydrogen is charged to establish a hydrogen concentration in gaseous phase of approximately 30 to 35 mole percent, but such concentration is limited to no greater than 40 mole percent.

Thereafter the introduction of the α-methylstyrene is commenced by introduction thereof into the feed stream line together with the recycled cumene. During the start of the hydrogenation reaction, the temperature of the feed stream of α-methylstyrene and cumene is maintained at no greater than 160° F. and preferably at about 150° F.

Upon introduction of the α-methylstyrene stream and the resultant onset of hydrogenation, the concentration in the gaseous phase is maintained at no greater than 40 mole percent by introducing hydrogen into the recycled inert gas in sufficient quantity to maintain such concentration. The gas entering the reactor is sampled and analyzed to determine the amount of make-up hydrogen required. The hydrogen added to the recycled inert gas is generally a stream containing at least 75 mole percent and preferably about 90 mole percent of hydrogen.

The liquid hourly space velocity of the α-methylstyrene feed stream is initially held at a relatively low value of about from .027 to .134 per hour and preferably about .080 to .107 per hour while the recycled cumene flow rate is maintained at from a 5:1 to 6:1 ratio by volume to the α-methylstyrene feed stream. When employing the start-up method of the present invention, no temperature kick or exotherm is experienced and the onset of hydrogenation is accomplished under the relatively mild conditions initially established.

When the hydrogenation has been established and analysis of the product cumene demonstrates hydrogenation of essentially all the α-methylstyrene to cumene in the initial charge, the flows of α-methylstyrene, hydrogen and cumene are gradually increased up to full steady state rates. During such gradual increase, the temperature of the feed stream at the reactor inlet and the concentration of hydrogen in the gaseous phase are likewise gradually increased while the pressure in the reactor is maintained at approximately the level at which the hydrogenation was initiated, about 165 to 220 p.s.i.g. The rate of α-methylstyrene addition is increased at a LHSV rate of .080 to .107 per hour until it represents from 15 to 30 percent and preferably about 20 percent of the feed stream. Thereafter the flow rates of both the α-methylstyrene and cumene are increased up to full steady state rates so as to maintain this percentage composition of the feed stream. At the same time, the temperature of the feed stream at the reactor inlet is increased at a rate of not greater than 5° F. per hour and preferably 2 to 3° F. per hour until operating temperatures of about 190° to 205° F. but in no event in excess of 225° F. are established.

Likewise, during the period of gradual increase in rates, the concentration of hydrogen in the gaseous phase is graduaully increased at a rate of about 5 to 10 mole percent per hour and preferably at about 5 mole percent per hour until the inert gas is finally purged from the system and the hydrogen feed is charged at full purity of from 75 to 90 or more percent hydrogen as desired. At periods during the increase to full rate operation, the product cumene is sampled and analyzed to insure that essentially all the α-methylstyrene is hydrogenated to cumene. If the concentration of unreacted α-methylstyrene in the product stream is found to rise above the initial trace quantities,

then the hydrogen concentration and/or the feed stream inlet temperature can be raised by the next increment to secure essentially complete hydrogenation of such α-methylstyrene.

When carrying out the start-up procedure in the manner described above, analysis of the product cumene stream has established that only very small or virtually trace quantities of isopropylcyclohexane or other cyclic saturated compounds are produced compared to starting up with hydrogen of higher concentration or with a feed stream at higher reactor inlet temperatures.

As noted above, the catalyst contained in the reactor can be any of the well known solid hydrogenation catalysts. Although not required, it is generally preferred that porous, particle form supports be employed for the catalyst to adquately disperse and increase the surface area of the actual catalytic agent. Such porous supports may comprise natural or treated clays, such as kaolin or bentonite; clay-like materials, such as Celite or Sil-O-Cel; and synthetic materials, such as magnesium oxide, silica gel, alumina gel, zeolites, activated carbon or diatomaceous earth and the like. Activated alumina, which is the well known crystalline alpha alumina monohydrate, or chi alumina are quite satisfactory and preferred as porous catalyst supports. The catalytic agent employed can be any of the noble metals in Group VIII of the Periodic Table with atomic numbers of at least 27, such as rhodium, palladium and platinum; and also cobalt, nickel, either supported or unsupported, and the like. Because of their high hydrogenation activity at low temperatures, the preferred catalylst are palladium or platinum on alumina supports, with palladium on activated alumina support the most desirable catalyst. When the catalyst comprises one of the noble metals on a support, the noble metal will generally be present within the range of 0.1 to 5% and preferably 0.2 to 1% by weight of the catalyst.

The following examples will serve to illustrate the present invention and demonstrate the utility of the present start-up method.

The examples were carried out with an α-methylstyrene stream of the following approximate composition which, in normal operation, is mixed in a ratio of 1:3 with a stream of recycled cumene.

	Percent by wt.
α-Methylstyrene	75.6
Cumene	17.3
Mesityl oxide	2.0
Acetophenone	1.9

with traces of other unidentified compounds.

Example I

Using a system such as that described above, a reactor containing a solid hydrogenation catalyst comprised of an alumina support and containing 0.3 weight percent of palladium was utilized for hydrogenation of α-methylstyrene employing the start-up procedure as described. The reactor was pressured with nitrogen to approximately 100 p.s.i.g. At this point, a stream of recycled cumene product at 150° F. was admitted to the reactor. Following this additional nitrogen was admitted to the reactor in an amount to increase the reactor pressure to 175 p.s.i.g. Hydrogen was then admitted to establish a hydrogen concentration of approximately 26 mole percent as determined by analysis of the gas. Thereupon, introduction of a stream of α-methylstyrene was begun and hydrogenation initiated. No temperature rises were noted upon commencing hydrogenation or the subsequent gradual increases in feed rates of α-methylstyrene, cumene and hydrogen and increases in the feed stream inlet temperature and hydrogen concentration. The feed rates, temperatures and concentration of hydrogen as the reaction was brought to steady state conditions are set out in Table 1 below. Analysis of the cumene product stream for unreacted α-methylstyrene and isopropylcyclohexane as well as of the gas for hydrogen concentration established that substantially complete hydrogenation of the α - methylstyrene charged was accomplished with substantially no hydrogenation of the aromatic rings in the feed as indicated by the presence of isopropylcyclohexane in the product. The result of such analyses are set out in Table 2 below.

TABLE 1

Hours	Cumene/AMS streams, by vol.	AMS LHSV/hr.	Temp., °F.	Pressure, p.s.i.g.	Percent H_2
0	7.5	.054	150	175	25.6
4	5.0	.080	156	175	35
8	3.15	.107	160	175	45
12	3.0	.134	160	175	55
16	3.0	.147	160	175	55
24	3.0	.147	160	175	65
32	3.0	.161	165	175	65
40	3.08	.174	170	178	65
48	3.0	.187	170	178	70
80	3.1	.228	175	176	75
96	3.0	.254	175	176	----
104	3.0	.255	175	176	----
112	3.0	.254	175	176	----
120	3.0	.254	175	176	----
128	3.0	.268	175	175	----
136	3.0	.281	175	180	----
144	3.0	.294	175	180	----
152	3.0	.308	175	180	----
160	3.0	.308	175	180	----
168	3.0	.321	185	180	----
176	3.0	.335	190	180	----
184	3.0	.348	195	180	----

TABLE 2

Hours	Percent IPC	Percent AMS	Percent H_2
2			25.6
4	0.56	0.01	35
6	0.71	0.01	40
8	0.98	0.01	45
26	1.81	0.22	65
30	1.80	0.57	----
38	1.76	0.30	----
44	N.A.	0.11	----
50	1.50	0.07	70
56	1.38	0.08	----
74	1.25	0.08	75
98	1.08	0.10	----
162	0.94	0.79	----
170	0.96	0.11	----
178	0.90	0.14	----

In contrast to the above results, it was found that upon start-up of the same reactor system containing fresh catalyst for hydrogenation of α-methylstyrene at gradually increased feed rates, but with the inlet temperature of the α-methylstyrene and cumene feed initially at 225° F. and the concentration of hydrogen in the reactor gas phase at 70 to 80 mole percent there was produced a cumene product stream containing approximately 12 percent by weight of isopropylcyclohexane over the first 24 hours of such start-up. Likewise, when a similar start-up of fresh catalyst in the same reactor was carried out with the initial inlet temperature of the α-methylstyrene and cumene feed at about 195° F. and the hydrogen concentration at approximately 70 mole percent there was produced approximately 6 percent by weight of isopropylcyclohexane in the cumene product stream over the first 24 hours of operation.

The necessity for maintaining the concentration of hydrogen at a value not greater than 40 mole percent as well as maintaining a relatively low initial inlet temperature of the feed stream in order to realize the advantages of present start-up procedure is demonstrated by the following example.

Example II

The same general start-up procedure as described above in Example I employing a fresh charge of the same catalyst as used therein was carried out. However, in this instance the initial temperature of the α-methylstyrene and cumene feed was at about 185° F., although it was rapidly decreased to about 160° F. In addition, the hydrogen concentration at the initiation of hydrogenation was greater than 80 mole percent. This was indicated by the fact that after only 18 hours of operation the analysis

of the off gases showed a hydrogen concentration of 85.5 mole percent. As a consequence, the cumen product stream contained up to 10.6 percent of isopropylcyclohexane during the first 24 hours of operation and from about 1.6 to 6.3 percent thereof during the second 24 hours of operation. After this initial period, however, the production of isopropylcyclohexane by the hydrogenation of the aromatic ring was controlled to less than 1.0 percent.

The analyses of the product stream from the reactor and the hydrogen concentration in the gas are set out in Table 3 below.

TABLE 3

	Percent		
Hours	IPC	AMS	H_2
3		.01	
6	10.41	.01	
10		.02	
16	10.58	.03	
18	9.77		85.5
22	7.60	.05	
23			91.7
26	6.27	.06	91.9
34	4.29	.01	80.2
42	3.45	.08	58.1
50	1.63	.05	
74	0.84	.35	
100	0.82	.05	
140	0.62	.05	
148	0.74	.11	

What is claimed is:

1. In a process for the selective non-destructive hydrogenation of α-methylstyrene in an α-methylstyrene and cumene feed wherein said α-methylstyrene and cumene feed in the liquid phase and hydrogen are introduced into a hydrogenation zone containing a solid hydrogenation catalyst, selected from the group comprising a noble metal of Group VIII of the Periodic Table having an atomic number of at least 27, cobalt or nickel, the improvement whereby saturation of aromatic rings in said feed and excessive temperatures are prevented in the initiation of said process, said improvement comprising

(a) pressuring said hydrogenation zone with an inert gas unreactive under the conditions of the process, prior to introduction of hydrogen thereto,

(b) maintaining the concentration of hydrogen to inert gas in said hydrogenation zone at not greater than 40 mole percent until after the initiation of the hydrogenation of α-methylstyrene, and

(c) maintaining the inlet temperature of said feed stream at not greater than 160° F. until after the initiation of the hydrogenation of α-methylstyrene.

2. The process of claim 1 wherein said catalyst comprises from 0.1 to 5 percent by weight of palladium or platinum supported on alumina.

3. The process of claim 1 wherein said α-methylstyrene and cumene feed comprises from 10 to 60 percent by weight α-methylstyrene.

4. The process of claim 1 wherein said inert gas is nitrogen.

5. The process of claim 1 wherein said α-methylstyrene and cumene feed and said hydrogen are maintained in contact with said catalyst at a temperature of from about 100° to about 500° F. and at a pressure of from about 100 to 800 p.s.i.g.

6. The process of claim 1 wherein said concentration of hydrogen in inert gas in maintained at about 30 mole percent until after initiation of hydrogenation.

7. The process of claim 1 wherein said inlet temperature is maintained at about 150° F. until after initiation of hydrogenation.

8. The process of claim 1 wherein said α-methylstyrene and cumene feed and said hydrogen are maintained in contact with said catalyst at a temperature of from 140° to 380° F. and at a pressure of from 150 to 400 p.s.i.g.

9. The process of claim 1 wherein after the initiation of hydrogenation of α-methylstyrene the concentration of hydrogen in said hydrogenation zone is increased at a rate of not greater than 5 mole percent per hour until such concentration is at least 75 mole percent and the said inlet temperature of the said α-methylstyrene and cumene feed is increased at a rate of not greater than 5° F. per hour to an inlet temperature of at least 190° F.

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