

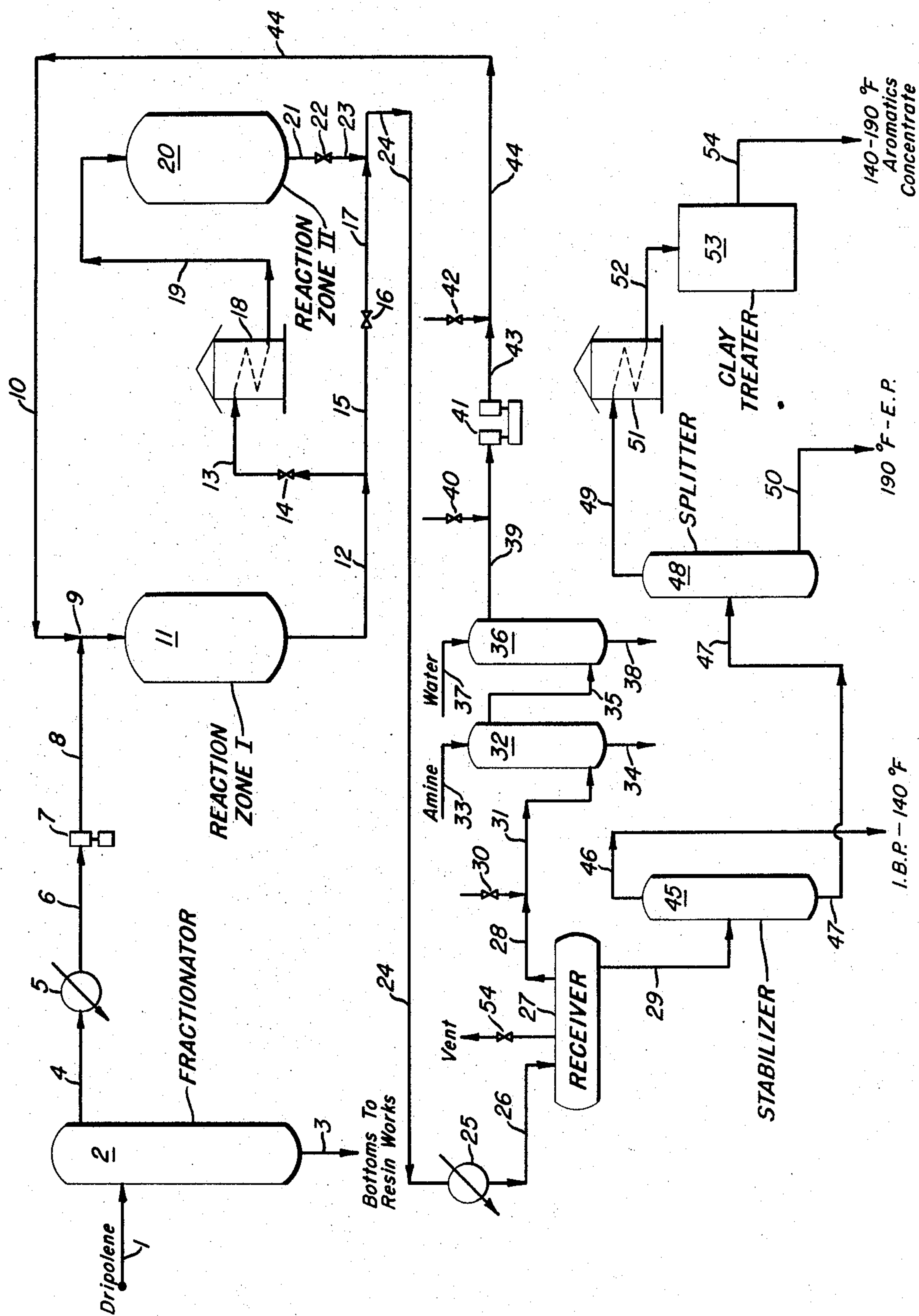
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CATALYTIC HYDROGENATION OF DRIPOLENE

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CATALYTIC HYDROGENATION OF DRIPOLENE

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This invention relates to the catalytic hydrogenation of olefinic hydrocarbons. More specifically the invention is concerned with an improved process for the catalytic hydrogenation of dripolene fractions, dripolene being the normally liquid mixture of hydrocarbons obtained as a byproduct in the high temperature pyrolysis of gaseous hydrocarbons.

It is well known that the high temperature pyrolysis of gaseous hydrocarbons to prepare ethylene results in the by-production of a normally liquid mixture of hydrocarbons through reactions such as polymerization, alkylation, aromatization, dehydrogenation, and the like. The mixture is commonly termed "dripolene," and while it contains virtually all classes of hydrocarbons it predominates in olefinic and aromatic compounds, mainly benzene. As the demand for ethylene for the production of polyethylene and plastics and other petrochemicals rises, increasingly large supplies of dripolene are becoming available. Because of its benzene content, dripolene represents an exceedingly valuable material, and one which is steadily becoming more obtainable.

Thus far three large-volume usages have developed for dripolene. It is blended into motor gasolines, where the high octane numbers of its aromatic and olefinic components render dripolene a desirable blending stock. Dripolene may be fed to aromatics extraction units for the recovery of pure benzene. Finally, exceedingly valuable resins have been made by thermal or catalytic polymerization of high boiling dripolene fractions.

Dripolene however contains cyclic diolefins, and these give rise to problems which have somewhat restricted the quantity of dripolene blended into motor fuels or fed to aromatics extraction units. Cyclic diolefins tend to form gum-like polymers in the presence of air, or upon heating and for this reason only relatively small amounts of dripolene can be blended into premium motor fuels. And in aromatics extraction units, it is found that cyclic diolefins tend to concentrate in the aromatics extract, thereby complicating the preparation of pure aromatic compounds.

It has previously been disclosed in Oil and Gas Journal, volume 52, May 11, 1953, page 124, and in Haensel U.S. Patent Number 2,799,627 that a 130–360° F. ASTM distillation boiling range dripolene fraction may be treated in the presence of a platinum-alumina-halogen catalyst at elevated temperatures and pressures and in the presence of hydrogen gas to selectively hydrogenate monoolefins and diolefins without simultaneously hydrogenating the aromatic compounds to naphthenes. However, in attempting to utilize this process, we have found that an inordinate amount of a coke-like material forms throughout the charge stock preheater system and throughout the catalyst bed. In fact, with this process, after on-stream times of less than a week a solid coke-like matrix forms in the reactors which completely prevents further operations and necessitates shut-downs for coke and catalyst removal. It is therefore an object of the present invention to provide an improved method of conducting the

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catalytic hydrogenation of olefinic hydrocarbons in dripolene fractions which enables the process to be conducted for periods substantially in excess of those heretofore obtainable.

In accordance with the object above, we have now discovered a method of substantially reducing the formation of troublesome coke-like deposits. Briefly, we have discovered that coke formation is virtually eliminated if the dripolene fraction and a hydrogen-containing gas stream initially contact the platinum-alumina hydrogenation catalyst at conditions of temperature and pressure such that substantially all (i.e. about 80% or more, and preferably at least 90%) of the dripolene remains in the liquid phase, while maintaining a critically low hydrogen sulfide concentration in the hydrogen-containing gas stream. By means of our discovery it is possible to conduct the hydrogenation of dripolene in a convenient manner and with on-stream times of many weeks or months without the need for catalyst regeneration. Our system may be embodied in either of two variations, each of which has advantages under particular circumstances. In the first embodiment only one reaction zone is employed, and the commingled hydrogen-containing gas and liquid charge stock stream contacts a substantially adiabatic catalyst zone, and the exothermic heat of hydrogenation serves to increase the commingled stream temperature as it passes through the zone. In this embodiment the amount of catalyst, expressed as weight hourly space velocity (weight of charge stock per unit weight of catalyst per hour) is at least effective to hydrogenate olefinic hydrocarbons without the need for application of external heat. In the second embodiment, two reaction zones are employed, with interstage heating between the two. In the first zone, the dripolene charge stock is substantially in the liquid phase when the commingled stream of charge stock and hydrogen-containing gas contact the catalyst, and after partial hydrogenation an interstage heater raises the temperature between reaction zones in order to provide a higher temperature stream to the second zone and thus minimize the total amount of catalyst necessary. It will be noted that the single-zone embodiment requires no external heating facilities.

The amount of hydrogen sulfide that may be present in our process is quite critical, and accordingly we find it essential to provide to the reaction zone a hydrogen-containing gas stream containing less than 12 grains of hydrogen sulfide per 100 standard cubic feet of gas. If for example the level of sulfur in the hydrogen-containing gas exceeds 12 grains, both the catalyst activity and the catalyst life diminish rapidly, and if the level increases to as much as 57 grains per 100 s.c.f., the catalyst becomes completely deactivated in a matter of minutes. Fortunately however, the effect of either hydrogen sulfide gas or mercaptan sulfur in the dripolene feed on the hydrogenation process appears to be temporary with respect to its effect on product quality although periods of high sulfur do materially increase the amount of coke deposition.

Suitable platinum-alumina hydrogenation catalysts are conveniently those catalysts which have been found eminently suitable for use in naphtha hydroforming processes. Generally, these catalysts contain from about 0.01 to about 10% by weight of platinum and may optionally from about 0.05 to about 3% by weight of a halogen, preferably chlorine and/or fluorine, on a high surface area alumina support such as the alumina described in Heard Reissue Patent Number 22,196. The catalysts may be in the form of pills, pellets, extrudates, spheres or the like, and conventionally have a size between about $\frac{1}{16}$ to $\frac{1}{4}$ " in maximum dimension. A particularly suitable catalyst is one which has been partially deactivated by continued use in a naphtha hydroforming process,

since it appears that catalysts previously used for hydroforming are more stable and have less tendency to hydrogenate aromatic compounds than fresh platinum-alumina catalysts. Furthermore, used catalysts exhibit less tendency to cause wasteful hydrocracking of hydrocarbons and thus result in higher yields of recoverable liquid product.

The conditions of pressure, temperature, liquid hourly space velocity and hydrogen-containing gas rate which are employed in the practice of the present invention are inter-related such that the commingled feedstock and hydrogen-containing gas, as it initially contacts the catalyst bed, 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 mol percent, and preferably at least 90 mol percent of the dripolene charge contact the catalyst as a liquid. Pressures within the range of 100 to 1000 p.s.i.g. are desired, with pressures from 300 to 500 p.s.i.g. preferred from a commercial standpoint as this latter range favors conditions at which the hydrogenation reaction occurs rapidly. Within the broad pressure range the bed inlet temperature may be between 50 and 200° F., most desirably between 100 and 150° F., typically 115° F. With most dripolene stocks the temperature rise through an adiabatic bed, for complete olefinic saturation, is on the order of 350–450° F. and provides an average reactor temperature of about 280–340° F. This average temperature may be increased by providing more catalyst or may be decreased by increasing the proportion of hydrogen-containing gas to charge stock. With respect to the hydrogen-containing gas, it is desirably employed in a proportion of 500 to 10,000 standard cubic feet per barrel of charge stock, preferably from 1000 to 4000 s.c.f./b., e.g. 1500 s.c.f./b. This gas preferably is composed of at least 70% hydrogen and may be derived from a naphtha hydroforming operation. Although the experimentally observed consumption of hydrogen varies between 600 and about 650 s.c.f./b., it is preferred to maintain a substantially larger amount in the reaction zone. This may be accomplished economically by recycling the excess hydrogen. The hydrogen-containing gas, if recycled, must be chemically treated to maintain the critically low hydrogen sulfide level therein.

Dripolene employed as the charging stock in our invention is a portion of the hydrocarbon liquid obtained by the high temperature pyrolysis of a normally gaseous hydrocarbon containing at least two carbon atoms in the molecule, or a mixture of such hydrocarbons. The normally gaseous hydrocarbon which is charged to the high temperature pyrolysis may be a byproduct refinery gas. In the preparation of dripolene, a gaseous hydrocarbon such as ethane, propane, propylene or a mixture of such hydrocarbons is preheated and passed through an alloy tube at a high space velocity and a pyrolysis temperature between about 1200° and 1800° F., preferably between about 1350° and 1550° F. Low pressures up to about 100 p.s.i.a. are ordinarily employed in this operation, a pressure below about 35 p.s.i.a. being satisfactory. The time of exposure to the high temperatures is usually about 0.05 to 5 seconds, contact times of 0.1 to 1 second being preferred.

The pyrolysis produces normally gaseous products containing unsaturated hydrocarbon such as ethylene, normally liquid hydrocarbons rich in unsaturated hydrocarbons including olefins and diolefins of varying boiling points and structural configuration, and various aromatic hydrocarbons, as well as tar. The unsaturated hydrocarbons such as ethylene which are contained in the normally gaseous product are usually the desired product of the pyrolysis process. The normally liquid hydrocarbons and tar which are obtained are considered to be byproducts of the pyrolysis operation. High temperature pyrolysis products are rapidly cooled, usually by quenching with water to a temperature of about 400° F. A viscous

tarry material condenses out of the gas during the quenching. The gases from the quenching operation are compressed and cooled and a liquid material which boils between about 100° and 400° F. condenses out of the gases during the compressing-cooling step. This liquid is dripolene. The amount of tar and dripolene produced is dependent upon the feed, temperature, contact time and pressure. The quantity of liquid hydrocarbons produced in this way is ordinarily about 3% by weight of the total quantity of gas charged to the pyrolysis reactor.

The normally liquid mixtures of hydrocarbons which is termed dripolene has never been completely analyzed because of its complexity. A typical specimen of total dripolene was characterized as follows:

TABLE I

ASTM distillation range, ° F.:

Initial	100
10%	146
20	162
30	178
40	188
50	196
60	206
70	234
80	296
90	340
Final	360
Gravity, ° API at 60° F.	34.7
Bromine number, cg. Br ₂ /g.	104.1
Maleic anhydride value, mg. M.A./g.	79
Index of refraction, n_D^{25}	1.4830

A typical example of dripolene was analyzed by conventional techniques and was found to contain the following compounds in the amounts specified:

TABLE II

Analysis, volume—percent:

Propane and propylene	0.7
Isobutane	0.1
Isobutylene	0.8
1-butene	0.5
2-butene	0.6
n-butane	0.4
Butadiene	3.9
Pentadienes	7.7
Pentylenes	6.3
Other C ₅	0.4
Benzene	34.2
Toluene	7.8
Xylenes	1
Styrene	3
Dicyclopentadiene	5
"Other"	29.6

Our invention is particularly concerned with the fraction of dripolene boiling within the range of about 100–375° F., although it is not essential that the dripolene boil entirely within the range or that all of the dripolene fraction boil within the range. Our charging stock is obtained as an overhead or heartcut in the distillation of total dripolene to obtain about 70 to 90% of charge fraction, while the bottoms may be used to prepare resins by processes well known to the art.

To more fully describe the process of our invention and to illustrate the two embodiments thereof, attention is directed to the attached flowsheet showing a hydrogenation unit designed and adapted to produce from dripolene either an aromatic concentrate or a high octane motor fuel blending stock by either embodiment.

Dripolene liquid is withdrawn from external storage tanks and conducted through line 1 to fractionator 2 which is provided with corrosion resistant distillation trays or perforated pans, wherein an overhead dripolene charge stock fraction comprising about 80% of the total

dripolene is separated by distillation from about 20% of high boiling bottoms, which latter is sent via line 3 to the resins plant, not shown. The total dripolene fed to fractionator 2 has an analysis approximating the typical dripolene described previously. The 80% fractionator 2 overhead which is taken through line 4 has the following composition:

TABLE III

Charge analysis:

Gravity, ° API	32.4
RVP, p.s.i.a.	6.8
ASTM distillation, ° F.:	
IBP	134
10%	163
30%	179
50%	189
70%	202
90%	280
FBP	356

Light hydrocarbon analysis

Component:

C ₃	liquid vol. percent	0.1
iC ₄	do	0.3
1C ₄	do	0.2
2C ₄	do	0.2
nC ₄	do	0.2
C ₄ diolefin	do	1.6
C ₅ diolefin	do	6.6
C ₅ monoolefin	do	3.1
C ₅ paraffin	do	0.2
C ₆₊	do	87.5
Benzene	vol. percent	53
C ₆₊ gravity, ° API		28.0

The 80% dripolene charge fraction contains 70 parts per million sulfur and 29 parts per million organic chlorides, and has a bromine number of 48 (indicative of total olefins) and a maleic anhydride value (MAV, representing conjugated diolefins) of 47 mg./g. The bottoms withdrawn through line 3 has an ASTM distillation boiling range between about 200 and 400° F., preferably between about 230 and 375° F.

The dripolene charge is conducted through line 4, cooler 5, and line 6 to charge pump 7, which may be a multistage centrifugal pump adapted to pump the dripolene charge to the reactor system operating at a pressure of 325 pounds per square inch gage. The cooler 5 outlet temperature is about 80° F. The charge stock from pump 7 is sent through line 8 to juncture 9, where it is met by a stream of recycle hydrogen-containing gas from line 10 in the amount of 1350 standard cubic feet of total hydrogen-containing gas per barrel of charge. The gas has a composition of approximately 80% hydrogen, with the balance consisting primarily of methane, ethane, and some propane and propylene, together with less than the critical limit of 12 grains of H₂S per 100 standard cubic feet of total gas. It is highly preferred that this gas contain, if possible, less than 3 grains per 100 cubic feet of H₂S. The temperature of the commingled liquid and gas stream is 115° F., and at this temperature the commingled stream passes into reaction as employed, and is shown symbolically as a single bed or chamber 11, although it may comprise a plurality of serially or parallel-connected reaction chambers. At these operating conditions, 94 mol percent of the dripolene is in the liquid phase when the commingled stream initially contacts the catalyst.

In the first embodiment, a single reaction zone, reaction zone 1, operates essentially adiabatically, that is the commingled dripolene charge and hydrogen-containing gas stream are permitted to increase in temperature by the exothermic heat of monoolefin and diolefin hydrogenation on passage through the catalyst bed. The catalyst employed is spent Ultraforming catalyst obtained

after more than one year's use in a regenerative naphtha hydroforming unit and has an activity for hydroforming of substantially less than that of fresh Ultraforming catalyst, but is very nearly as active for hydrogenation as is fresh catalyst. The catalyst in Reaction Zone I, i.e. chamber 11, is in the form of pellets having an average length and diameter approximating 1/8" and is disposed so as to permit downflow passage of the commingled stream. A weight hourly space velocity of 2 is employed. In passage through Reaction Zone I the dripolene plus hydrogen stream temperature is increased to 625° F., which provides an average reaction temperature of 370° F. In this zone, 625 standard cubic feet per barrel of hydrogen is consumed by olefin hydrogenation, a quantity which compares closely with the theoretical hydrogen consumption based on the observed experimental heat of reaction, 280 B.t.u./lb. The quantity of catalyst in Reaction Zone I is that which provides a weight hourly space velocity of 2.0, i.e. 2.0 pounds of dripolene charged per hour for each pound of catalyst in Zone I. The hydrogenated stream leaving chamber 11 passes through line 12, line 15, valve 16, line 17, and line 24 to cooler 25, and then through line 26 to receiver 27. Valves 14 and 22 are closed, thus blanking off heater 18 and reactor 20 which are not used.

As an alternate embodiment to the use of a single Reaction Zone I, a modification may be employed wherein the necessary quantity of catalyst can be reduced substantially. In this second embodiment, the catalyst is loaded in adiabatic Reaction Zone I to provide a weight hourly space velocity of from say 4 to 20 (less than half the loading as in the previous embodiment), and the product stream leaving chamber 11 through line 12, instead of passing through by-pass line 15, a valve 16 and line 17, passes through heater 18 and a second adiabatic reaction zone, Reaction Zone II. This latter zone is represented symbolically by chamber 20 which also may be a plurality of serially or parallel-connected reaction chambers. Reaction Zone II also has a catalyst loading to provide a weight hourly space velocity of from 4 to 20, but not necessarily the same loading as in Zone I. In this two-zone embodiment, only a fraction of the olefin hydrogenation is completed in Reaction Zone I, and as a consequence the partially hydrogenated stream is reheated by heater 18 after passage through line 12, valve 14, and line 13, to a temperature within the range of about 200 to 500° F. Thereafter, it is passed through line 19 to Reaction Zone II and thence via line 21, valve 22, line 23, and line 24 to cooler 25 and receiver 27. For this operation, valve 16 is closed. Thus, by providing a higher temperature in Reaction Zone II and consequently a more rapid reaction rate, olefin hydrogenation proceeds more rapidly with a consequently reduced catalyst requirement while still retaining the benefits of the invention in having liquid phase hydrogenation occurring in Reaction Zone I. Thus, the coke deposition of prior art processes is substantially reduced by the elimination of preheaters and by commencing hydrogenation while most of the dripolene charge is in the liquid phase.

In either alternative, the hydrogenated product stream comprising partially hydrogenated dripolene in vapor form together with excess hydrogen-containing gas is cooled in cooler 25 wherein the hydrogenated dripolene fraction condenses as a liquid which is sent, along with the noncondensable hydrogen-containing gas, to receiver 27. At receiver 27, the hydrogen-containing gas is separated and withdrawn through line 28 and conducted via line 31 to amine scrubber 32, where a descending stream of diethanolamine or other agent effective to absorb H₂S is employed to remove hydrogen sulfide gas formed by the destructive hydrogenation of sulfur compounds in the dripolene charge. The amine is withdrawn from line 34 and heated in a stripper, not shown, for the purpose of releasing absorbed hydrogen sulfide.

Since hydrogenation results in a net consumption of hydrogen on the order of 600–650 standard cubic feet per barrel, it is necessary to replenish this by the addition of hydrogen from an external source, conveniently a naphtha hydroforming unit. Depending upon the pressure and hydrogen sulfide concentration of the hydroformer hydrogen-containing gas, it may be added at either valved line 30, valved line 40 or valved line 42. Briefly, if the hydroformer gas is relatively high in hydrogen sulfide, irrespective of its pressure, it is conducted into the system through valved line 31 where it can pass into the amine scrubber 32 for hydrogen sulfide removal. However, where the hydroformer gas is relatively low in hydrogen sulfide, it may be added to the system either through valved line 40 if at low pressure or valved line 42 if at high. The composition of hydroformer gas varies with the operation of the hydroformer and may range for example from 70–95% hydrogen, the balance being saturated light hydrocarbons such as methane, ethane and propane. If this gas is of a purity below about 80% it may be desirable to vent a portion of the gas from receiver 27 through valved vent line 54 so as to prevent a build-up of noncondensable methane, ethane and propane within the recycle gas system. Where large quantities of hydroformer gas are available, the present recycle gas system may be eliminated in favor of a once-through hydrogen flow.

After treatment in amine scrubber 32, the essentially hydrogen-sulfide-free hydrogen-containing gas (i.e. containing less than 12 grains of H₂S per 100 standard cubic feet) is conducted via line 35 to water scrubber 36 where a descending stream of water from line 37 scrubs entrained or vaporized amine from the gas. The rich water stream is withdrawn through line 38 and is concentrated for amine recovery in a distillation column, not shown. If desired, water vapor removal facilities such as a glycol scrubbing tower or a silica gel or alumina drier may follow water scrubber 36 in line 39.

The treated gas passes from water scrubber 36 through line 39 to the suction of recycle gas compressor 41. Compressor 41 recycles the gas through lines 43, 44 and 10 back to the juncture 9 with dripolene charge line 8 and thence to Reaction Zone I.

Returning now to receiver 27, hydrogenated dripolene as a liquid condensate passes through line 29 to stabilizer 45. The unstabilized hydrogenated dripolene, obtained from hydrogenation in a single Reaction Zone I, has the following analysis:

TABLE IV

Gravity, °API	34.4
Reid vapor pressure, p.s.i.	6.0
ASTM distillation, ° F.:	
IBP	126
10%	162
30%	178
50%	188
70%	202
90%	296
FBP	412
F-1 octane, clear (research)	100.2
F-2 octane, clear (motor)	88.5
C ₅ + gravity, °API	33.0
C ₆ + gravity, °API	30.1

Light hydrocarbon analysis

Component:	
iC ₄	Liquid volume percent
nC ₄	do
iC ₅	do
nC ₅	do
C ₆ +	do
Bromine No., cg./g.	5
MAV, mg./g.	0.2

The product yields by catalytic hydrogenation are set forth below. The increase in volume and in weight percent recoveries is primarily due to an increase in volume and weight produced by the hydrogenation.

TABLE V

Product Yields. ¹	Yields, Wt. Percent	Yields, Vol. Percent
C ₁	0.2	
C ₂	0.1	
C ₃	0.1	
iC ₃	0.1	0.2
nC ₄	1.9	2.8
iC ₄	1.3	1.9
nC ₅	3.7	5.0
C ₆ +	93.7	92.1
Total	101.1	102.0
Benzene	53	
Unstabilized Product	101.4	

¹ Yields are based on dripolene overhead charged.

In stabilizer 45, the fraction boiling from the initial boiling point to 140° F. is taken overhead through line 46 while the stabilized product is withdrawn as a bottoms through line 47 and conducted to splitter 48 where it is rerun to distill a 140–190° F. aromatics concentrate as an overhead and a 190° F.-E.P. fraction as a bottoms. The respective properties of the IBP-140° F. fraction from line 46, the 140–190° F. fraction from line 49, and the 190° F.-E.P. fraction from line 50 are set forth below.

TABLE VI

Properties of hydrogenated dripolene overhead fractions

	IBP-140° F. Fraction	140-190° F. Fraction	190° F. plus Fraction
Weight Percent of Charge	9.6	61.8	28.6
Composition of Fraction:			
Total C ₄ Olefins	2.8		
nC ₄	8.5		
C ₅ Olefins	19.7		
iC ₅	14.7		
nC ₅	54.3		
Bromine No.	26.8	1.9	5.2
MAV	0.6	0.5	1.5
Benzene In Fraction, Vol. Percent		90.6	
Aromatics, Vol. Percent			78.2
Olefins, Vol. Percent			5.8
Saturates, Vol. Percent			16.0
Corrosion, ASTM Copper Strip Doctor		OK	
H ₂ S		passes	
RSH		0.0001	
SO ₂		passes	
Acidity		nil	
Thiophene Sulfur		6 p.p.m.	
Jet Sulfur		6 p.p.m.	
Research Octane, Clear			98.5
Research Octane, +1.0 cc. TEL			101.6
Research Octane, +3.0 cc. TEL			104.3
RVP, p.s.i.			0.6
Gravity, °API			28.2
ASTM Distillation:			
IBP			230
10%			242
30%			254
50%			270
70%			306
90%			390
FBP			410

It may be noted from the above that the 140–190° F. aromatics-rich fraction contains 90.6 volume percent benzene, is non-corrosive under the ASTM copper strip test, and has sulfur contents which are entirely satisfactory for all commercial purposes. However it does contain a trace of olefinic and diolefinic material as indicated by the 1.9 bromine number and the 0.5 maleic anhydride value, and therefore prior to extraction to remove a 100% pure benzene fraction it is desirable to pass the 140–190° F. fraction from line 49 through heater 51, line 52, and clay treater 53 at about 50 p.s.i.g. pressure and at the boiling point of the fraction at this pressure for the purpose of polymerizing diolefins. Alternatively, sulfuric acid or maleic anhydride may be used for this treatment.

After diolefin removal the 140-190° F. fraction is passed through line 54 and conducted to an aromatics extraction unit employing known selective solvents such as diethylene glycol-water, diethylene glycol-triethylene glycol-water, phenol, sulfur dioxide, or Pourx or a silica gel chromatographic adsorbent.

Returning to stabilizer 45, the IBP-140° F. fraction containing almost 90% pentanes and pentenes is highly useful as a gasoline blending component to provide front end volatility properties. Similarly, the 190° F.-E.P. fraction taken as a bottoms through line 50 splitter 48 is composed of about 78% aromatics, largely boiling within the toluene and xylene range, and as shown has an exceedingly valuable high octane rating, making it a desirable blending component for motor fuels. Its research octane clear is 98.5, and with 3 ccs. of tetraethyllead per gallon is 104.3.

Thus it is evident that our process is eminently suitable for hydrogenating olefinic hydrocarbons in a low boiling dripolene fraction. Of particular interest is the fact that benzene comprises 53 volume percent of the dripolene charged to Reaction Zone I, and also is 53 volume percent of the total liquid product obtained at receiver 27. This indicates that substantially none of the benzene is hydrogenated under our reaction conditions, although about 90% or more of the monoolefins and the diolefins are saturated. The above run was conducted for a total of 280 hours and during this time the maleic anhydride value of the total product remained below 2 while the bromine number remained below 14.

While there exists a very important limit with respect to the maximum tolerable hydrogen sulfide level in the hydrogen-containing gas, it has been found that organic sulfur compounds in the dripolene charge have a far lesser effect on the process and do not lead to coke formation. For example, when the normal 70 p.p.m. sulfur content of dripolene was increased four hundred fold by the addition of butyl mercaptan, the product maleic anhydride value remained unchanged. However at the same time the product bromine number increased from 4 to 16. When butyl mercaptan addition was discontinued the bromine number returned to 4. These indicate that organic sulfur does not affect hydrogenation of diolefins but does alter the catalyst's activity for monoolefin hydrogenation. Thus when it is desired to employ the total hydrogenated dripolene as a motor fuel blendstock, organic sulfur compounds can be added to the charge for the purpose of retaining high-octane monoolefin in the product while selectively hydrogenating polymer-forming diolefins.

Where, however, the dripolene charge contains excessive sulfur, or when it is desired to produce a very high purity product, mercaptan removal facilities may be installed. Sodium or potassium hydroxide, caustic-methanol or similar extraction facilities, placed preferably before fractionator 2 can remove any dissolved hydrogen sulfide and most of the lower molecular weight mercaptans before the charge is hydrogenated. In addition, and more for the purpose of eliminating corrosion in product stabilizer 45 and splitter 48, hydrogen sulfide may be extracted from the unstabilized dripolene passing through line 29 by suitable basic materials, of which mention may be made of sodium or potassium hydroxide, monoethanolamine-water, diethanolamine-water, or solid sodium carbonate.

Numerous other modifications may be made to the two principal embodiments described above, with the obtention of improved or equivalent results. For example, a portion of the hydrogen-containing recycle gas may be heated out of the presence of the dripolene, and may be added to the effluent leaving Reaction Zone I and before passage into Reaction Zone II. Thus the low-catalyst requirements of the two-zone embodiment is achieved while any possibility of coking up heater 18 because of residual diolefins is of course obviated entirely.

From the discussion and the examples above, it is evident that our process is an extremely valuable improvement in the catalytic hydrogenation of olefinic hydrocarbons in dripolene fractions. By employing our invention and contacting the dripolene with a platinum-alumina catalyst in the presence of low H_2S content hydrogen gas while the dripolene is initially substantially entirely in the liquid phase, it is possible to minimize or reduce almost entirely the quantity of coke formation heretofore experienced under the prior art processes. Our discovery may be used either in the form of a single adiabatic reaction zone employing a low space velocity or may have two or more adiabatic zones with interstage heating whereby substantial economies are achieved in respect to the necessary quantity of catalyst.

Having described the invention, we claim:

1. In a process for the catalytic selective hydrogenation of olefinic hydrocarbons in a low-boiling fraction of dripolene, said dripolene being the normally liquid mixture of hydrocarbons obtained in the pyrolysis of normally gaseous hydrocarbons having at least two carbon atoms in the molecule at a temperature between about 1200 and 1800° F. and a contact time between about 0.05 and 5 seconds, the improved method of operation whereby conversion of olefins to coke is substantially reduced which comprises commingling said dripolene fraction with a hydrogen containing gas, said hydrogen containing gas having less than 12 grains of hydrogen sulfide per 100 standard cubic feet, and passing said commingled dripolene fraction and hydrogen-containing gas stream, while said dripolene fraction is initially substantially in the liquid phase and at a temperature between 100 and 150° F., into at least one fixed substantially-adiabatic bed of platinum-alumina hydrogenation catalyst, whereby monoolefins and diolefins in said dripolene fraction are hydrogenated and wherein said stream temperature is increased by the exothermic heat of hydrogenation to vaporize said dripolene fraction.

2. Process of claim 1 wherein said hydrogen-containing gas stream is employed in a proportion of between about 500 and 10,000 standard cubic feet per barrel of dripolene fraction, and the total bed inlet pressure is within the range of 100 to 1000 p.s.i.g.

3. Process of claim 1 wherein the hydrogen-containing gas stream is employed within a proportion of between about 1000 and 4000 standard cubic feet per barrel of dripolene fraction, and the total bed inlet pressure is within the range of 300 to 500 p.s.i.g.

4. Process of claim 1 wherein the platinum-alumina hydrogenation catalyst is spent hydroforming catalyst.

5. In a process for the catalytic selective hydrogenation of olefinic hydrocarbons in a low-boiling fraction of dripolene, said dripolene being the normally liquid mixture of hydrocarbons obtained in the pyrolysis of normally gaseous hydrocarbons having at least two carbon atoms in the molecule at a temperature between about 1200-1800° F. and a contact time between about 0.05 and 5 seconds, the improved method of operation whereby conversion of olefins to coke is substantially reduced which comprises commingling said dripolene fraction with a hydrogen-containing gas, said gas having less than 12 grains of hydrogen sulfide per 100 standard cubic feet, passing said commingled dripolene fraction and hydrogen-containing gas while said dripolene fraction is initially substantially in the liquid phase and at a temperature between 100 and 150° F. into a first fixed substantially-adiabatic bed of platinum-alumina hydrogenation catalyst, wherein monoolefins and diolefins in said dripolene fraction are at least partially hydrogenated and wherein said stream temperature is increased by the exothermic heat of hydrogenation to at least partially vaporize said dripolene fraction, withdrawing said commingled stream from the first bed and heating said stream to a temperature within the range of about 300° F. to about 600° F., and passing the heated commingled stream into at least

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one additional fixed substantially-adiabatic bed of platinum-alumina hydrogenation catalyst for additional hydrogenation of monoolefins and diolefins.

6. Process of claim 5 wherein the hydrogen-containing gas stream is employed in a proportion between about 500 and 10,000 standard cubic feet per barrel of dripolene fraction, and the commingled dripolene fraction and hydrogen-containing gas stream initially contacts the bed of hydrogenation catalyst at a total bed inlet pressure within the range of 100 to 1000 p.s.i.g.

7. Process of claim 5 wherein the hydrogen-containing gas stream is employed in a proportion of between about 1000 and 4000 standard cubic feet per barrel of dripolene fraction, and the commingled dripolene fraction and hydrogen-containing gas stream contacts the first bed of hydrogenation catalyst at a total bed inlet pressure within the range of 300 to 500 p.s.i.g.

8. Process of claim 5 wherein the product stream after

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the last bed of hydrogenation catalyst is cooled to separate a liquid product from a normal gaseous material, and the liquid product is thereafter fractionally distilled to separate a relatively low-boiling fraction for aromatics extraction from a relatively high boiling fraction for use as a motor fuel component.

9. Process of claim 5 wherein the platinum-alumina hydrogenation catalyst is spent hydroforming catalyst.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,953,612

September 20, 1960

Manford R. Haxton et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 62, after "charge" insert -- stock --;
column 10, line 44, for the claim reference numeral "1"
read -- 2 --.

Signed and sealed this 4th day of April 1961.

(SEAL)

Attest: ERNEST W. SWIDER

~~XXXXXXXXXX~~
~~KARL H. AXLINE~~
Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents