The present invention relates to an improvement in hydroforming. More particularly, it relates to an improvement in hydroforming whereby in addition to naphtha reforming, increased amounts of light paraffins, particularly those with branched structures, such as isobutane, isopentane and L.P.G. (liquefied C4 and C5 hydrocarbons) are produced. Furthermore, the production of benzene and toluene in relation to heavier aromatics is maximized.

Hydroforming is now a matter of record and commercial practice in this country. Basically, the operation involves the contacting of a naphtha, either virgin, cracked, Fischer-Tropsch or any mixture thereof, with a solid catalytic material. The contacting takes place at elevated temperatures and pressures in the presence of added hydrogen. However, the process itself produces substantial amounts of hydrogen and in actuality this will almost always surpass the initial hydrogen which has been added to repress deactivation of the catalyst by carbon formation.

The reactions involved in hydroforming are: (1) dehydrogenation of naphthenes to the corresponding aromatic as where methylcyclohexane is dehydrogenated to form toluene, (2) isomerization of paraffins to form branched chain paraffins or isomerization of ring compounds, such as ethylcyclopentane to form methylcyclohexane, which latter compound is then dehydrogenated to form toluene, (3) dehydrocyclization of paraffins to aromatics such as n-heptane to form toluene, and (4) hydrocracking of the higher boiling constituents of the feed to form lower boiling constituents.

Hydroforming processes may be divided into two general classes, namely, the secondary and catalytic cycle. In the latter case, it is possible to use a separate reactor which is, itself, regenerable and may be substituted for any of the other reactors in the circuit while they are being regenerated. This would be obvious to one skilled in the art and, therefore, need not be considered at this time.

In many refinery situations, increased yields of liquefied petroleum gas (L.P.G.), isobutane and isopentane are desirable even at the expense of C4+ yield. This invention discloses a scheme to maximize L.P.G., isobutane, isopentane and lower boiling aromatic yields using a primary reaction zone or zones containing a conventional hydroforming catalyst followed by a secondary reaction zone containing a dehydrogenation activity-free acidic catalyst. The hydroformate from the primary reaction zone is passed through said secondary or catalytic cracking zone to produce the results just enumerated. By a dehydroformation activity-free catalyst is meant a catalyst having cracking activity but which does not contain any Group VIII transition metal such as platinum, palladium or nickel.

As a result of this treatment a variety of advantages may be realized. The yields of light isoparaffins can be increased beyond that normally obtained in hydroforming. Of particular importance is the fact that the ratio of the valuable isobutane and isopentane relative to the corresponding normal paraffins is markedly increased. A possible mechanism to explain this improved light isoparaffin yield is that the hydroformation activity blocks or minimizes the dual-functional isomerization catalytic reaction so that the isoparaffins formed from hydrocracking in much greater than equilibrium proportions do not isomerize to the corresponding normal paraffins. Thus, the ratio of isobutane and isopentane to their corresponding normal paraffins can exceed equilibrium. However, this invention is not contingent on the validity of this mechanism.

Furthermore, the use of a solid, acidic catalyst such as silica-alumina in the secondary reaction zone will result in a disproportionately higher benzene and toluene content in the hydroformer effluent. The increased lower boiling aromatic and isopentane content will result in a gasoline of improved overall research octane number and front end volatility. Furthermore, isopentane and benzene are particularly valuable in that they greatly improve the octane number of the lower boiling components of gasoline. This improved front end volatility coupled with the improved octane number of the lower boiling gasoline components is particularly significant in modern times for improving the fuel performance of low horsepower foreign designed cars which represent an increasing proportion of the car population.

Numerous areas in which L.P.G. plays an important role have sprung into prominence. Included among them is the whole area of alkylation. Bobutane is a valuable feed component for an alkylation plant and the production of such products is substantially increased by this invention.

Recent strides have also been made in the polymerization field, particularly in the production of polypropylene for plastics and 1,3-butadiene for rubber production. Butane and butene serve as the building blocks for these products.

Certain regions of the United States rely to town gas to heat homes and factories. Propane serves as an additive for this gas and greatly improves its heating value. The accompanying drawing diagrammatically illustrates a preferred embodiment of this invention. Many other modifications will be obvious to one skilled in the art and are intended to be within the scope of the invention.

Turning to the drawing, a desulfurized naphtha is introduced into absorber-debublerizer 11 and then through hydroformer 15. The hydroformed off-gas is removed through line 12; this consists mainly of hydrogen, hydrogen sulfide, water and C4+.

Propane and butane are removed through line 13. The remaining product, boiling in the range of 125-450° F., is introduced into a series of hydroforming reactors through line 14. There are a series of three hydroformers, 15, 16 and 17, which constitute the primary reaction zone. Each of them contains a suitable hydroforming catalyst. Catalysts that may be used for hydroforming the feed are those containing 0.01-1.0 wt. percent platinum or 0.1-2.0 wt. percent palladium dispersed upon a highly pure alumina support such as is obtained from aluminum alcoholate, as per U.S. Patent No. 2,636,865 or from an alumina hydrosol prepared by hydrolyzing aluminum metal with dilute acetic acid in the presence of a very small catalytic amount of mercury. A suitable catalyst comprises about 0.2-0.8 wt. percent platinum widely dispersed upon alumina in the eta or gamma phase derived from a suitable aluminum alcoholate and having a surface area of about 50-300 square meters/gram.

Pressure in the three hydroformers, constituting the primary reaction zone, 15, 16 and 17 should be maintained at about 200-600 p.s.i.g. The feed is preheated to about 850-1000° F. in furnace 18 and is then passed to hydroformer 15 through line 15a. Within hydroformer 15 there is some cooling due to the reaction. Consequently, after the feed is removed from the hydroformer through line 19a it is then heated in furnace 19 through line 19c and introduced to hydroformer 16.
Within hydroformer 16 the feed is once again cooled somewhat by the reaction and, therefore, upon being removed from hydroformer 16 through line 20a it is introduced to reactor 20 where it is once again heated to temperature of about 850–1000° F. Finally, the feed passes through line 17a into hydroformer 17. Temperatures within the hydroformer catalyst bed vary from about 800–1000° F. Hydrogen or hydrogen-rich process or recycle gas is added to the powerformer feed through line 17b.

The hydrogen-rich or recycle gas normally contains about 65–90 mol. percent hydrogen with the remainder being light hydrocarbon gases. The exact composition of the recycle gas depends upon the hydroforming reaction conditions and upon the pressure and temperature at which the recycle gas is separated from the hydroformate. The amount of recycle gas employed may vary from 500–900 scf./bbl. and is preferably about 3000–7000 standard cubic feet/barrel of naphtha feed.

Under the reaction conditions maintained in hydroformers 15, 16 and 17 there is a tendency for carbon to form on the catalyst and it therefore becomes necessary to regenerate the catalyst. In order to do this and keep the unit in operation a swing reactor (not shown) is provided. The reactor is so manifolded that it may replace any other reactor. In this manner, hydroformers 15, 16 or 17 may be regenerated with no stoppage of operation. Placing this swing reactor would be obvious to one skilled in the art and need not be discussed at this time.

The catalyst is regenerated by burning the carbonaceous deposits from the catalyst. Regeneration is preferably effected with diluted air, or oxygen, as a facility of control of the temperature of regeneration. It is preferred to contact the regenerated or carbon-free catalyst with undiluted air or oxygen-enriched gas at temperatures of about 850–1100° F. for about 1–4 hours. It is also desirable to provide means for subjecting the regenerated catalyst, or a portion of it in continuous operation to reactivation with a halogen or halogen compound such as chlorine or hydrogen chloride. A free halogen such as chlorine is the preferred treating agent for reactivation.

Aside from the accumulation of poisons the deactivation of hydroforming catalysts proceeds by two mechanisms: (1) the loss of chlorine or other halogen which is normally present as part of the catalyst composition and that contributes substantially to the catalyst activity and (2) the agglomeration of the platinum metal into large or massive crystals having diameters in excess of about 50 Å. Units. Treatment of the catalyst with a halogen compound such as hydrogen chloride or the like is effective in restoring halogen content of the catalyst to the desired level and to this extent it is effective in restoring the activity of deactivated or partially deactivated catalyst. On the other hand, treatment of the catalyst with an elemental halogen, such as chlorine or the like, not only restores the catalyst halogen content to the desired level but also accomplishes the redispersal of the platinum metal by breaking up the large platinum crystallites.

Regeneration of the catalyst is effected as required by burning carbonaceous materials therefrom with oxygen-containing gas at temperatures of 800–1200° F., preferably at 900–1100° F. The pressure in the regeneration operation may be the same as during hydroforming or it may, if desired, be lowered to near atmospheric pressure. In burning off the carbonaceous deposits, a certain amount of water is formed by combustion of hydrogen in said deposits. This water is stripped from the catalyst and passes overhead with the flue gases and is removed from the system. Excess air is used for the regeneration to insure the complete removal of carbon or coke from the catalyst and to effect reactivation in admixture with chlorine. The regenerated or carbon-free catalyst can advantageously be treated with air at temperatures of 850–1100° F. for about 1–4 hours. The regenerated or carbon-free catalyst or the mixture of hydrogen gas or a mixture of chlorine gas and air in order to reactivate the catalyst, restore its chlorine content, and to distill or break up the large platinum crystallites that resulted during the use of the catalyst.

The chloride partial pressure in the reaction vessel may be in the range of from 0.001–2 atmospheres, preferably 0.01–1 atmosphere. The quantity of chlorine supplied may be in the range of 0.1–2.0 wt. percent, preferably about 0.5 wt. percent based on the catalyst. The chlorine treatment may be carried out for periods of from about 15 seconds to 1 hour, preferably about 1–15 minutes. While the chlorine-treated catalyst may be subjected to air-stripping to remove excess chlorine, it is usually preferred to avoid stripping chlorine from the reactivated catalyst since the chlorine content governs the hydrocracking activity of the catalyst which in turn controls the volatility of the hydroformate.

The amount of chlorine desirable is to remain on the stripped catalyst is related to the platinum content of the catalyst. With high platinum content catalysts, a relatively high chlorine content is desirable and a correspondingly lower chlorine content is desirable for lower platinum content catalysts. In general, the total amount of chlorine (i.e., both chlorine combined with chlorinated and adsorbed) remaining on the catalyst, when employing a catalyst of 0.6 wt. percent platinum content, may be in the range of about 0.2–1.25 wt. percent and is preferably about 0.5–1.0 wt. percent.

The effluent from the primary reaction zone is removed from hydroformer reactor 17 through line 23 and heat exchanger 23a, valve 30a, and is introduced into the secondary reaction zone, reactor 24. This reactor may contain any one of a great variety of fixed bed solid catalysts which are dehydration activity-free and are of the acidic type. Among those which are applicable are those produced by the Filtrol Corp. and are known as Filtrol 38 SR and Catalyst 11. Furthermore, catalysts which are composed of mixtures of alumina and silica, as well as silica and magnesia are applicable. Within this group of catalysts is the catalyst comprising about 15% alumina and 87% silica. Cracking catalysts made of silica and alumina and containing up to 30% alumina may be used. Other cracking catalysts such as used in catalytic cracking of oils also may be used.

Temperatures within the secondary reaction zone zone 24 are about 1100° F. and preferably would be near the temperature of the effluent from the primary reaction zone since this eliminates the need for large scale heating or cooling between the two zones.

The pressure in the secondary reaction zone is nominally the same as in the primary reaction zone. The hydrogen generated in the primary reaction zone together with that contained in the recycle gas tend to suppress carbon formation in the secondary reaction zone 24. The secondary reaction zone can be contained in the tail reactor in a cyclic or semicyclic hydroformer, or the secondary reaction zone could be contained in a separate reactor used in conjunction with a hydroformer. For maximum economy available hydroformer regeneration facilities may be used to regenerate the secondary reaction zone.

Continuous use of the secondary reaction zone 24 may be obtained by providing an alternate secondary reaction zone reactor 24a to be placed in service while regenerating reactor 24 after carbonaceous deposits are built up to an undesirable high level. When regenerating reactor 24, valve 30a must be closed. The hydrogen feed after passing through heat exchanger 23a would then pass into line 31a. Along line 31a is valve 32a which would open when alternate cracking catalyst reactor 24a is in use, and closed when reactor 24a is being regenerated.
The conditions in alternate cracking catalyst reactor 24a are identical to those used in cracking catalyst reactor 24. Hydroformy natural gas 4a is removed through line 25a and passes through valved line 25 into flash drum 26. Alternately, the function of the secondary reaction zone may be obtained by using a fluid bed catalytic cracker. The secondary reaction zone can be regenerated with an oxygen-containing gas at temperatures between 800–1520 °F.

As a result of this treatment in the secondary reaction zone, the hydroformed product is substantially altered. The product removed from secondary reaction zone 24 is considerably different from that which entered the zone. The product was a silica-alumina cracking catalyst containing 13% silica and 15% Al₂O₃. The catalyst is in a bed form with a diameter of 0.7 m/s/g surface area. The secondary reaction zone 24 is maintained at a temperature of about 940 °F and a pressure of about 600 psig. Effluent from the secondary reaction zone 24 is then introduced into the back end fractionation unit 31.

From the fractionator about 140,000 s.c.f./d. of off-gas containing C₃ and C₄ hydrocarbons and hydrogen are recovered through line 32. About 850 barrels/day of propane and butane are recovered through line 33. About 7000 barrels/day of C₅–C₇ hydrocarbons are recovered through line 34 and passed into fractionator 35. Additionally, about 7000 barrels/day of C₅–C₇ hydrocarbons are recovered through line 35 and passed into fractionator 36. In this manner iso and normal pentane are separated, about 445 barrels/day of isopentane are mixed with the C₅–C₇ hydrocarbons from line 36 to produce gasoline. The remaining n-pentane is recycled through line 40 and combined with the hydroformed feed transported through line 14.

In this manner a gasoline was produced with a C₈+ yield of 78.9 vol. percent and a research octane of 88.7. This gasoline has exceptionally good front end volatility. This is to say, the lightier boiling components have a high octane rating. Consequently, cars will start more quickly and there will be less of a tendency for knock within the engine.
9100 barrels/day of C5+ hydroformate are recovered through line 34 and passed into depentanizer 35. 8800 barrels/day of C5+ hydroformate are recovered through line 36 including 860 barrels/day of toluene and 50 barrels/day of benzene; about 260 barrels/day of normal and isopentane are removed through line 37 and introduced into superfractionation zone 38. In this manner iso and normal pentane are separated, about 175 barrels/day of isopentane are mixed with and directed along with the C5+ hydroformate to form gasoline. The remaining n-pentane is recycled through line 40 and combined with hydrogen feed transported through line 14.

In this manner a gasoline was produced with a C5+ yield of 91.5 vol. percent and the C3+ research octane was 82.2.

Thus, the following improvements in Example 1 with respect to Example 2 are to be noted.

The C5+ research octane level was increased by 6.5. Propane was increased by 4.9 wt. percent. Total L.P.G. yield was increased by 8.3 wt. percent, isopentane yield by 2.7 vol. percent, isobutane yield by 3.2 vol. percent, benzene by 1.6 vol. percent and toluene by 3.7 vol. percent.

It is understood that this invention is not limited to the specific examples which have been offered merely as illustrations and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for increasing the isopentane and benzene contents of hydroformed gasoline and for producing maximum L.P.G., which comprises introducing a naphtha into a catalytic hydroforming zone maintained under hydroforming conditions, passing the total effluent containing hydrogen from said hydroforming zone into a catalytic hydrocracking zone containing a dehydrogenation activity-free acid type cracking catalyst under hydrocracking conditions to produce a hydrocracked product containing a maximum of benzene, isopentane and L.P.G., passing the hydrocracked product to a flash zone to separate hydrogen-rich gases from hydrocracked liquid, recycling said gases to said hydroforming zone, fractionating said hydrocracked liquid into separate streams of gas, propane and butane, and C3+ hydrocarbons, passing the C3+ hydrocarbons into a depentanizing zone whereby a C5+ hydrocarbon fraction and a C5 hydrocarbon fraction are separated, passing the said C5 fraction into a second fractionation zone whereby separate streams of iso C5 and normal C5 hydrocarbons are recovered, recycling said normal C5 hydrocarbons to said hydroforming zone and adding the said iso C5 fraction to the C5+ fraction to produce a high octane gasoline.

2. The method of claim 1 in which the said cracking catalyst is silica-alumina.

3. The process of claim 1 wherein the said C5+ hydroformate is passed into an aromatics recovery zone whereby separate streams of C5, benzene, toluene and a heavier fraction are recovered, and said heavier fraction is mixed with the said hydroformate feed.

4. A process according to claim 1 wherein said hydroforming zone is maintained at a temperature of 800-1000° F. and a pressure of 200-600 p.s.i.g. and said recycle gas rate is from 500-9000 standard cubic feet of hydrogen/barrel of oil and said hydrocracking zone is maintained at a temperature of 900-1000° F. and a pressure of 200-600 p.s.i.g.

5. A process for increasing the isopentane and benzene contents of hydroformed gasoline and for producing maximum L.P.G., which comprises introducing a hydroformate feed into a catalytic hydroforming zone to produce a hydroformed product, passing the total hydroformed product into a catalytic cracking zone containing a dehydrogenation activity-free acid type cracking catalyst wherein a maximum of benzene, isopentane and L.P.G. are produced, recovering a cracked product, removing hydrogen-rich recycle gas from said cracked product to separate a liquid cracked product, recycling said gas to said hydroforming zone, fractionating said liquid cracked product to recover separate streams of off-gas, propane and butane and C3+ hydrocarbons, passing said C3+ hydrocarbons into a depentanizing zone whereby a C5+ fraction and a C5 hydrocarbon fraction are separated, passing the said C5 hydrocarbon fraction into a second fractionation zone whereby separate streams of iso C5 and normal C5 hydrocarbons are recovered, recycling said normal C5 hydrocarbons to said hydroforming zone, adding the said iso C5 hydrocarbon fraction to the C5+ hydrocarbon fraction and thereby producing a high octane gasoline.

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