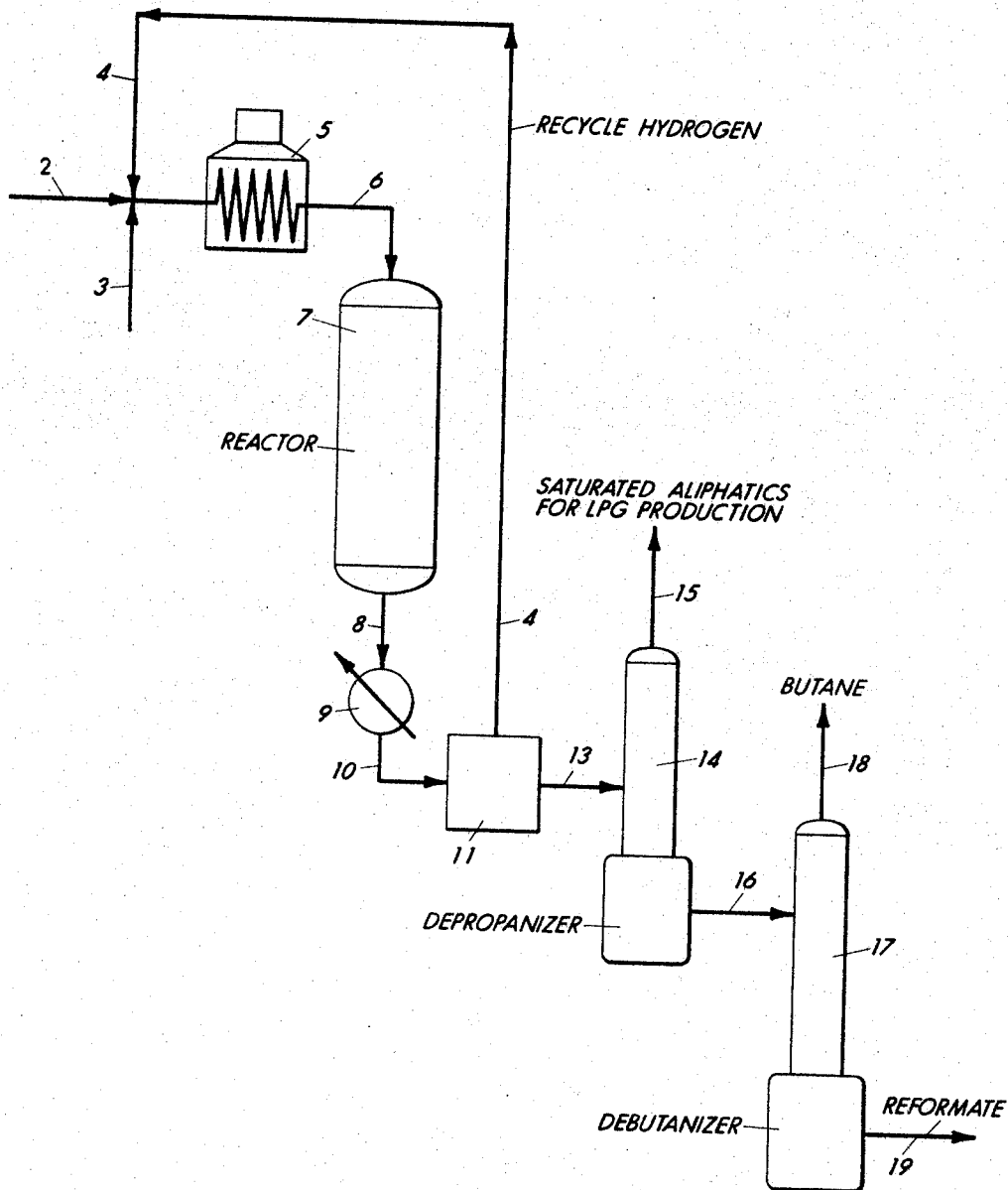


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HYDROGENATION DURING CATALYTIC REFORMING
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PRODUCTION OF LIQUEFIED PETROLEUM GAS FROM OLEFIN HYDROGENATION DURING CATALYTIC REFORMING

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ABSTRACT OF THE DISCLOSURE

Normally gaseous olefins can be saturated for liquefied petroleum gas production by injecting them directly into a catalytic reformer without decreasing the space velocity of the naphtha feed.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a method for producing liquefied petroleum gases by injecting normally gaseous olefins directly into a catalytic reformer with a conventional naphtha feed without decreasing the space velocity of the feed. The invention is thus related to the petroleum processing or petroleum refinery field.

Description of the prior art

Techniques of catalytic reforming in the presence of hydrogen are well known in the art. Such patents as Butler et al., U.S. 2,984,619, and Berger, U.S. 2,630,404, disclose the processes involved and the catalysts used.

"Hydroforming" is a process used to increase the octane number of hydrocarbon fractions boiling in the naphtha boiling range. "Hydroforming" has been defined as an operation conducted at elevated temperatures and pressures in which the naphtha feed is contacted with a solid catalytic material in the presence of hydrogen. The process is so operated that there is usually a net production of hydrogen. Hydrogen produced may be recycled. Hereafter the term "hydroforming" will be used to refer to the process of catalytic reforming in the presence of hydrogen.

At the present time, there are two principal methods of hydroforming. These methods are referred to as fixed bed hydroforming and fluid hydroforming. In the fixed bed method of hydroforming, the usual procedure is to pass a naphtha feed mixed with hydrogen rich gas successively through a bank or group of reactors with reheating of the reaction mixture between each reactor. Such a hydroforming system normally comprises three or four reactors operating in series and the system may be regenerative, semiregenerative, or nonregenerative. The fluid bed method of hydroforming consists of only one reactor zone or vessel and utilizes the fluid solids technique to maintain circulation of the finely divided catalyst particles between the reactor and regenerator. It is to be understood that the present invention may be utilized in either the fixed bed or fluid bed method of hydroforming.

The reforming of straight-run gasolines or naphthas is endothermic, but the degree of endothermicity depends primarily upon the extent of conversion, particularly the relevant amounts of hydrocracking, which is exothermic, and aromatization, which is endothermic. In a system applying adiabatic reactors, the over-all temperature drop can be as much as 200° F. or more.

While Berger discloses combining olefins boiling in the gasoline range with the naphtha feed to the reformer, he

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is interested in hydrogenating such olefins to the corresponding paraffins and then hydrocracking them to lower boiling paraffins with good antiknock qualities. The instant invention obtains a result that is different from that obtained by Berger by injecting normally gaseous olefins (olefins that are gases at ambient temperature and atmospheric pressure) into the reformer with the conventional naphtha feed and converting the normally gaseous olefins to saturated aliphatics for use as liquefied petroleum gases. The quality and quantity of the naphtha yield is also increased, while the normally gaseous olefins are almost completely converted to saturated aliphatics.

SUMMARY OF THE INVENTION

The object of this invention is to provide a method for producing saturated aliphatic hydrocarbons from normally gaseous olefins by injecting such olefins into a hydroforming zone together with the conventional hydroformer feed. The saturated aliphatic hydrocarbons so produced are suitable for use as liquefied petroleum gas.

It has been found that saturated aliphatic hydrocarbons may be produced by injecting normally gaseous olefins into the hydroformer or hydroforming zone with a conventional naphtha feed without a decrease in space velocity of the feed. Almost complete conversion of the normally gaseous olefins is obtained in this manner. The octane number of the reformate is increased even when the overall space velocity is increased. The heat from hydrogenation of the normally gaseous olefins compensates partly for the temperature drop caused by the dehydrogenation of naphthenes during reforming. Smaller furnaces may thus be used for reheating during the hydroforming process.

Singular features of this invention are the use of one conventional hydroforming catalyst to carry out two reactions in the hydroforming zone and the use of normally gaseous olefins, which the prior art taught were undesirable in the hydroformer process, to produce saturated aliphatics for LPG production with an increase in the quantity and quality of the naphtha yield.

This process enables a refiner to produce liquefied petroleum gases from normally gaseous olefin streams available in the refinery without large additional capital investment. The great demand for liquefied petroleum gases, usually a seasonal demand, can thus be met using existing streams in the refinery without the necessity for constructing special equipment for this process, since hydroforming is a process generally found in refineries today, especially refineries geared to the production of high octane gasolines. This invention is of special utility since an additional product can be produced with existing equipment with an actual increase in the efficiency of the normal hydroforming process.

BRIEF DESCRIPTION OF THE DRAWING

The process of the present invention may be more fully understood by referring to the accompanying drawing illustrating diagrammatically a flow plan of one embodiment of the same. It is to be understood that the reactor shown in the accompanying drawing may be either of the fixed bed type, the moving bed or the fluid bed type. It should also be understood that it is within the scope of the present invention to employ a group or bank of fixed bed reactors with furnaces between the reactors for reheating.

Reactor 7 will be referred to as a fixed bed type reactor, but this in no way limits the scope of the invention.

Referring specifically to the drawing, a hydrofined or low sulfur naphtha fraction, boiling in the range of 140°–400° F. is introduced into line 2. Simultaneously with

the introduction of the naphtha feed, hydrogen or hydrogen rich recycle gas is introduced into line 2 by means of line 4, and normally gaseous olefins are introduced into line 2 by means of line 3. This mixture passes through line 2 and enters furnace 5 where it is heated to a temperature of about 900 to about 1000° F.

From furnace 5, the heated mixture passes through line 6 to reactor 7 wherein the heated mixture contacts a fixed bed of platinum on alumina-based catalyst contained in the reactor. The temperature, pressure and other operating conditions in reactor 7, which will be hereinafter described, are adjusted to secure a hydroforming operation.

The hydroformed mixture leaves reactor 7 via line 8 and is cooled and partially condensed in cooler 9. From cooler 9, the hydroformate is introduced into separator 11 via line 10 where hydrogen containing gas which passes out the top is separated from the remaining mixture of liquid product. The hydrogen-containing gas passes out of separator 10 through line 4 and is recycled to line 2.

The liquid from separator 11 passes through line 13 to depropanizer 17 where the saturated aliphatic hydrocarbons and lighter materials suitable for liquefied petroleum gas manufacture are withdrawn overhead through line 15. The liquid material remaining in depropanizer 14 is passed via line 16 to debutanizer 17 where butanes are separated and withdrawn via line 18. The debutanized reformate is withdrawn via line 19.

The conditions necessary for hydroforming are set forth in tabular form below:

	Range	Preferred
Temperature, ° F.....	600-1,050	800-950
Pressure, p.s.i.g.....	Atmos.-1,500	50-800
Feed rate, w./hr./w.....	0.05-10	0.25-5
Recycle hydrogen rate, M s.c.f./b.....	0.1-20	1-10
Olefin rate, liq. Bbl./Bbl. Total reactor feed.....	0.001-0.5	0.01-0.3
Olefin/Naphtha mol ratio.....	0.001-2	0.01-1

The feedstock which is used in the present invention is a naphtha fraction boiling in the range of 140 to 400° F.

The naphtha fraction may be virgin naphtha, cracked naphtha or paraffinic naphtha. It is usually preferred that the feedstock be hydrofined or at least that the sulfur content of the feed to the hydroformer be kept at a level which does not poison the hydroformer catalyst.

The catalyst used in this invention is a platinum catalyst supported on an acidic alumina base. The acidity of the base of this catalyst is equivalent to from 0 to about 0.5 wt. percent chlorine based on the total catalyst composition. A commonly used composition of a catalyst used in normal hydroforming operation is one containing from 0.001 to 2.0 wt. percent platinum, 0.5 to 1.5 wt. percent chlorine and the remainder an absorptive alumina spacing agent or base. The catalyst may be made by methods known to the art. The process of the present invention may be more fully understood by the following examples illustrating the same.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Feeds consisting of approximately 25 vol. percent propylene (99 vol. percent C₃-) with 75 vol. percent of 190° F. to 330° F. hydrofined naphtha were hydroformed over fresh 0.3 wt. percent platinum, 0.5 wt. percent chlorine on alumina base catalyst at 250 p.s.i.g., 1.3 w./w./hr., 6M s.c.f./b. recycle gas at three temperature levels—895, 920 and 945° F. For comparison, runs were made on the naphtha feed alone at 1.0 w./w./hr. and recycle gas rate of 10M s.c.f./b. (identical to the conditions for the naphtha fraction of the combined feed). Since the unit was equipped with an isothermal reactor, data on the effect of propylene saturation on temperature drop in the catalyst bed could not be obtained. It was estimated, however, that for a feed containing 25 vol. per-

cent propylene, the heat released from saturating propylene approximately balances the heat adsorbed by the overall reforming reaction.

Table I summarizes the results. Regardless of operating temperature, whenever propylene was added, the bulk of it appeared as propane in the product. The C₅+ research octane number was increased even though the overall space velocity was increased with propylene addition. At constant clear RON, C₅+ reformate yields were significantly higher.

TABLE I.—SUMMARY OF RESULTS

		Test No.					
		I	II	III			
15	Hours on Oil.....	8-13	14-19	20-25	26-31	32-37	38-43
	Wt. percent, C ₃ - in feed.....	18.9	22.4	22.4	22.4	22.4	18.8
	Vol. percent, C ₃ - in feed.....	25.2	29.5	29.5	29.5	29.5	25.1
	Olefin/Naphtha Mol Ratio.....	0.61	0.61	0.75	0.75	0.60	0.60
	Temperature, ° F.....	895	895	920	920	945	945
	W./w./Hr. Total Feed.....	1.36	0.95	0.98	1.29	1.01	1.25
	C ₅ + RON-Cl.....	99.5	96.3	101.3	103.5	103.2	104.1
20	Yields on Total Feed:						
	H ₂ Wt. percent.....	0.65	1.73	1.75	0.54	1.52	0.50
	C ₂ Wt. percent.....	19.1	3.0	4.5	23.3	5.0	21.0
	C ₃ + Vol. percent on Naphtha:						
	At actual RON-Cl.....	83.3	82.8	77.9	80.2	74.6	74.3
	At 95 RON-Cl.....	89.4	84.2	86.7	93.5	86.3	87.9

TABLE II.—PROPYLENE BALANCE

		Test No.		
		I	II	III
		Temperature		
		895	920	945
Propane Yield, Wt. Percent:				
	From Naphtha.....	2.4	3.5	4.1
	From Propylene.....	16.7	19.8	16.9
	Total.....	19.1	23.3	21.0
35	C ₃ added to feed ¹	19.8	23.5	19.7
Propylene Balance, Wt. Percent:				
	Hydrogenated to C ₃	84	84	86
	Gain in C ₃ + Yield.....	7	11	2
	Gain in C ₄ Yield.....	6	6	6
	Gain in C ₁ +C ₂ Yield.....	3	-2	6
	Unaccounted.....	1		

¹ Converted to equivalent wt. percent of propane.

Table II shows a propylene balance for the three operating temperatures assuming that the addition of propylene did not change the C₃ yield from virgin naphtha. About 85 wt. percent of the propylene was recovered as propane. The remainder could be attributed to increase in C₁, C₂, C₄ and C₅+ reformate.

TABLE III.—HYDROGEN CONSUMPTION

		Test No.		
		I	II	III
H ₂ Balance, Wt. Percent on Naphtha:				
	Yield, No C ₃ - added.....	1.73	1.75	1.52
	Yield, C ₃ - added.....	0.80	0.70	0.62
	H ₂ used to saturate C ₃ -.....	0.93	1.05	0.90
55	Calculated H ₂ requirement based on propane recovered.....	0.94	1.17	0.95

Table III presents a hydrogen balance. As expected, the addition of propylene reduced the hydrogen yield. The measured decrease in hydrogen yield agreed well with the calculated amount of hydrogen required to saturate the portion of propylene that was recovered as propane.

While the invention contemplates the use of normally gaseous olefins and mixtures thereof, olefins in the C₂-C₅ range are preferred, since the best quality LPG's are most efficiently produced from the saturated aliphatics produced from such olefins.

In brief, this invention shows a method of converting normally gaseous olefins to saturated aliphatic hydrocarbons which can then be converted to liquefied petroleum gases. This invention requires no additional capital expenditure in the normal refinery and enables desirable liquefied petroleum gas products to be produced without adversely affecting yields of high octane gasoline. By in-

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jecting normally gaseous olefins into the hydroformer with the naphtha feed unexpected and unobvious results consisting of excellent yields, higher octane product and low cost conversion of normally gaseous olefins to saturated aliphatic hydrocarbons are obtained.

It is understood that the 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.

Other olefins such as ethylene and butylenes may be employed. The purity of the gaseous olefin is not critical. Mixtures of olefins which may also contain paraffins can also be processed by this invention.

What is claimed is:

1. A process for converting normally gaseous olefins to the corresponding saturated aliphatic hydrocarbons which comprises injecting a feedstream comprising said olefins and naphtha into a hydroforming zone under hydroforming conditions in the presence of a hydroforming catalyst to convert the olefins to said saturated aliphatic hydrocarbons, and then separating said saturated aliphatic hydrocarbons from the hydroformate produced in the hydroforming zone.

2. The process of claim 1 wherein the normally gaseous olefins are olefins having 2 to 5 carbon atoms and mixtures thereof.

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3. The process of claim 1 wherein the hydroforming conditions comprise a temperature of from about 600 to about 950° F. and a pressure of from about atmospheric to about 1500 p.s.i.g.

4. The process of claim 1 wherein the normally gaseous olefin is propylene.

5. The process of claim 2 wherein the feed rate is from about 0.25 to about 5 w./hr./w., the temperature from about 800 to about 950° F. and the pressure from about 50 to about 800 p.s.i.g. and the catalyst comprises a platinum on alumina hydroforming catalyst.

6. The process of claim 5 wherein the normally gaseous olefin is propylene.

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