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HIGH CONVERSION HYDROGENATION

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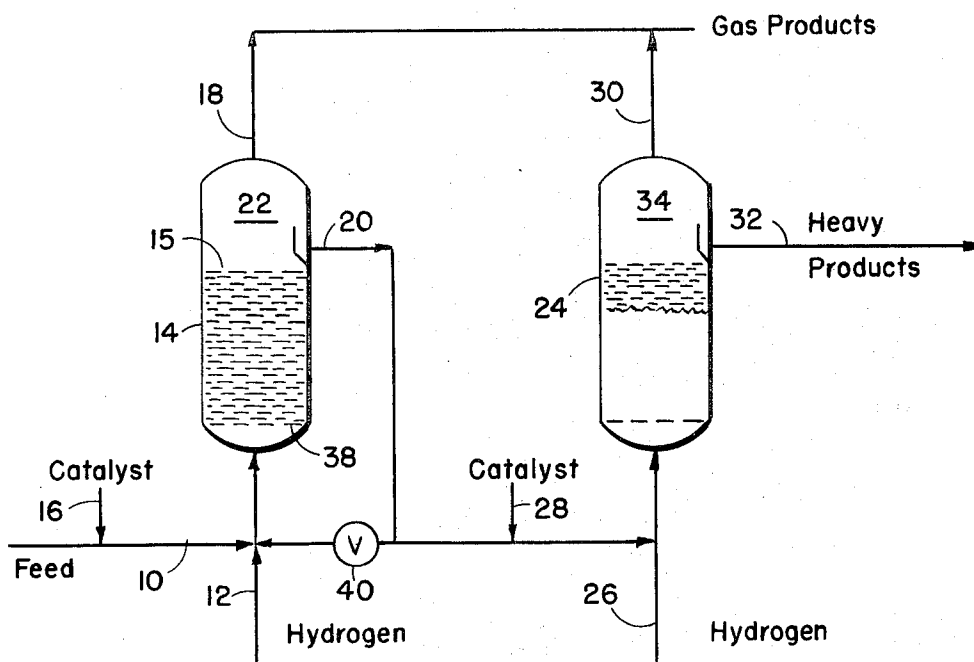
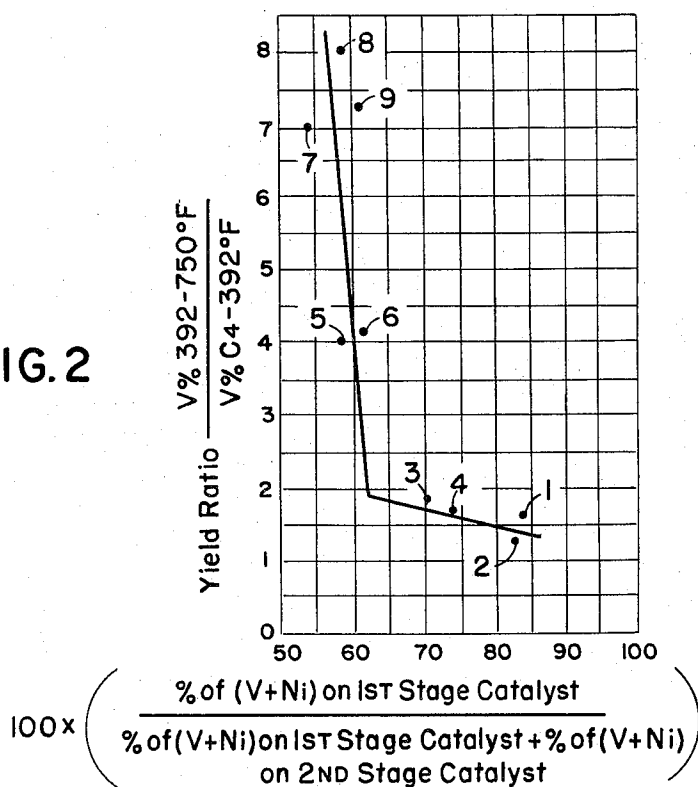


FIG. 1

FIG. 2



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HIGH CONVERSION HYDROGENATION

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4 Claims

ABSTRACT OF THE DISCLOSURE

A high conversion hydrogenation process for converting a petroleum residuum having at least 25 percent by volume boiling above 975° F. to material boiling below 975° F. takes place in a series of ebullated bed reactors. At least 65 percent of the metals in the residuum fed to the first reactor is deposited on the catalyst in the first reactor. The reactors are operated within 25° F. of one another to accomplish this. The ratio of the products boiling in the 392° to 750° F. range is maintained at less than twice that of the products boiling in the C₄ to 392° F. range.

BACKGROUND OF THE INVENTION

When converting a residuum by destructive hydrogenation, the primary objective is to obtain as high a level of conversion of the fraction boiling above 975° F. (or other designated high boiling temperature) in the residuum feed as is compatible with an operable system.

The ultimate goal is, of course, to convert all of the charge stock boiling above 975° F. to lower boiling materials such as gasoline, kerosene, jet fuel, diesel oil and heavy gas oil with the complete elimination of the higher boiling liquids which have a lower value as products.

It is to be understood that many reactions proceed simultaneously when converting a residuum by destructive hydrogenation under the necessary high temperature and pressure conditions. These reactions include saturation, demetalization, cracking, desulfurization, denitrogenation, hydrogenation and similar reactions which take place at differing rates. The results are basically empirical and are functions of feedstock characteristics, temperature, pressure, space velocity, hydrogen feed rate, catalyst type, and catalyst activity.

The catalytic hydrogenation of residuum is well known and in the patent of Johnson, Re. 25,770, a process is disclosed wherein the reaction is accomplished in the liquid phase with the heated residuum and hydrogen passed upwardly through a bed of catalyst at such a rate as to force the particles into random motion in the fluids. This has become known as the ebullated bed technique.

In such a system, however, major factors remain which limit the degree to which any given feedstock can be converted. First, the chemical nature of the residuum itself with respect to the amount convertible under reactor conditions, limits the maximum conversion obtainable. Thus, one residuum feed might have a maximum conversion limitation of 60% while another could undergo over 80% conversion at the same reactor conditions. In practice, however, it is not possible to completely react all of this convertible material because of an existing second factor, which is the limitation on the maximum severity of the reaction conditions due to increasing coke forma-

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tion with increased reaction conditions. The fraction of a feed boiling above 975° F. can be converted either to lower boiling products or to coke. The latter product is undesirable because it produces an inoperable ebullated bed system. As the severity of the reaction conditions is increased, the production of lower boiling products from the fraction boiling above 975° F. increases. Unfortunately, conversion to coke also increases. Eventually, the reactor reaches a level of severity of conditions at which coke production is so great as to make the reactor inoperable. In this invention, a process has been found whereby a given feed material can be reacted at conditions more severe than could heretofore have been used on the feed thereby yielding a higher conversion of the fraction boiling above 975° F. to lower boiling products without the related increase in coke formation and subsequent inoperability of the reactor. The activity of the catalyst is important in the conversion of the fraction boiling over 975° F. The longer the activity of the catalyst is maintained at a high level throughout the reaction zones the higher the overall conversion of the residuum. Metals present in the residuum pose a problem as they deposit on the catalyst under reaction conditions thereby leading to a rapid deactivation of the catalyst and thereby reduces the conversion.

SUMMARY OF THE INVENTION

The present invention provides a high conversion hydrogenation method wherein more than 70% of the hydrocarbon feed material boiling above 975° F. is converted to products boiling below 975° F. This increased conversion capability is achieved by operating two or more reaction stages in series with removal of product vapors taking place between the stages at reaction conditions so as to maintain the ratio of products boiling in the range of 392° to 750° F. at less than twice that of the C₄ to 392° F. product yield. It has been found that this measure of reaction conditions is required in order to achieve the desired high conversion.

There are three major advantages in this invention which give rise to the unexpected result of increased levels in the conversion of the feed material boiling above 975° F. to products boiling below 975° F. These advantages are set forth hereinafter.

First, the presence of the naphtha in the liquid effluent fed to the catalyst caused precipitation of asphaltenes from the unconverted material fraction boiling above 975° F. By minimizing the presence of naphtha in the reaction zone, operating difficulties from line and reactor pluggage by asphaltene precipitation are avoided. By operating with one or more reaction stages in series and removal of reactor effluent vapors between stages, the concentration of C₄ to 392° F. naphtha in subsequent stages is minimized by removing the naphtha.

It should be noted that removal of the naphtha containing vapors between stages is readily accomplished by separating the vapor effluent from the liquid effluent at the top of the reaction zone under reactor conditions of temperature and pressure. Such practice is simple and inexpensive. However, in certain cases, it may be preferable to remove the total reactor effluent to another vessel wherein the separation can be made. In all cases, however, the separation is carried out substantially at reaction temperature and pressure.

Secondly, the use of multiple stages in series at individual conversion levels lower than a normal single stage operation allows a greater overall conversion to be obtained without the danger of coking. Separation of the catalyst into separate reactor zones protects the activity of the catalyst in the subsequent stages by reducing the amount of carbon put down on the catalyst surface. As will be shown by subsequent examples, the conversion level which can be attained with a single stage is limited to a lower level than is possible with multiple stages.

Finally, a heavy residuum oil contains certain metals chelated in the form of porphyrin compounds. As the various reactions and side reactions such as saturation, demetallization, cracking, desulfurization, denitrogenation, hydrogenation, etc. take place in the reactor, the metals of the porphyrin compounds are deposited on the catalyst and thereby deactivate the catalyst and decrease the ability of the catalyst to promote the desired reactions. It is most desirable, in a process where cracking and hydrogenation are the primary objectives, to keep the catalyst activity as high as possible for as long as possible. In this invention, it has been discovered that the majority of the metallic poisons are deposited in the first stage so that the catalyst activity and life in the second stage is significantly extended.

Metal deposition has been found to be directly proportional to temperature. It is, therefore, most desirable to operate the first stage reaction zone at a higher temperature than the temperature of the second stage. In practice, however, it becomes uneconomical to add the extra equipment required to maintain a significant temperature differential. It has been found that by operating the reaction zones of the disclosed hydrogenation conversion process within the 25° F. differential limit between stages, at least 65 percent of the total metals deposited are deposited on the first stage catalyst. This is especially significant in this process as such operating conditions insure the deeper hydrogenation which is desired in the second stage. By dividing the catalyst about equally into two or more reaction zones, the average catalyst activity for the zones is higher than the average which would result if the catalyst were in one reaction zone. As the amount of metal compounds present in the feed increases this effect becomes more important.

Thus, by using a staged operation with intermediate removal of vapor, difficulties due to reactor coking are avoided, catalyst activity and life are improved, and higher conversion levels than those obtained in either single stage or multiple stage without intermediate vapor removal can be effected.

It is a principal object of this invention to increase the conversion of the fraction of a residuum feed boiling above 975° F. to fractions boiling below 975° F. without increasing coking.

Another object of this invention is to operate a series multi-reaction zone hydrogenation unit so that the major portion of the metals deposition on the catalyst takes place in the first reaction zone.

A further object of this invention is to decrease the precipitation of asphaltenes in a hydrogenation system by removal of naphthas as a gaseous effluent between the stages.

Further objects of this invention will become apparent from the following detailed description.

DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic view in elevation of a multiple stage hydrogenation process.

FIG. 2 is a graph of the ratio of the volume percent in components boiling between 392° and 750° F. to the volume percent in components boiling between C₄ and 392° F. versus the percent of total metals deposited, which deposition occurs on the first stage catalyst.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the disclosed invention, a heavy hydrocarbon charge such as Kuwait residuum at 10, together with hydrogen at 12 is introduced into a reactor 14 of the type shown in the Johanson patent, Re. 25,770. Such a reactor will be suitably charged with a catalyst such as cobalt molybdenum oxide on alumina, the particles being of an average size between about 60 mesh and 270 mesh. A small makeup of fresh catalyst is combined with the feed at 16. Alternately, catalyst in the form of extrudates of 1/4 inch to 1/32 inch diameter may be used.

The liquid and gas upflow through the bed of catalyst should be such that it will tend to expand the catalyst bed at least 10% based on the bed volume without fluid flow, and such that the particles are all in a random motion in the liquid. Such conditions are described as "ebullated" in the aforementioned Johanson patent.

Under the preferred conditions of temperature, pressure, throughput and product composition as hereinafter set forth, a vapor effluent is removed at 18 and a liquid effluent is removed at 20 from the upper portion 22 of the reaction zone 14. The liquid is then conducted to the second stage reactor 24.

Similar operations are carried out in the second stage reactor. The liquid feed at 20 joins with additional hydrogen at 26 and passes upwardly through the same or a similar type of catalyst. Small amounts of additional makeup catalyst may also be added at 28. A gaseous effluent is removed at 30, and a liquid is removed at 32 from the upper portion 34 of the zone 24. The catalyst loading used in the second stage reactor 24 is about the same as that used in the first stage reactor 14.

A third reactor operating in essentially the same manner may also be employed.

Recycle of liquid effluent from above the catalyst interface 15 to below the distributor deck 38 is usually desirable to give proper temperature control and to establish a sufficient upflow velocity to assist in maintaining the catalyst in random motion in the case of catalyst in the form of 1/32 to 1/4 inch diameter extrudates. This recycle may be accomplished either externally utilizing valve 40, or internally as described in Johanson, supra.

In the case of a catalyst having a narrow size distribution in the range of 60 to 270 mesh, recycle is not necessary to maintain the catalyst in the ebullated state.

The distributor deck 38 is, of course, suitably perforated and may have bubble caps thereon as shown in U.S. Pat. 3,197,288.

The data from Table I is shown in FIG. 2. The graph demonstrates the variation of the percent of the total metals that are deposited on the catalyst, which percent is deposited on the first stage catalyst, with changes in vol. percent 392 to 750° F./vol. percent C₄ to 392° F. product ratio. The number adjacent to each point on the graph refers to the experiment number shown in Table I_A and I_B from which that point was obtained.

Table I_A and I_B list the properties of several typical heavy residuum oil feedstocks and the percentage yields obtained for each fraction following their conversion at the operating conditions as specified. They also list the relative loadings of the metal impurities, vanadium and nickel, on the first and second stage catalyst material.

TABLE I_A.—FEEDSTOCK PROPERTIES, YIELDS AND METAL DEPOSITS ON CATALYST

Example	Feedstock	Percent of feed boiling above 975° F.	Conversion of 975° F. feed	Yield, vol. percent based on feed		Ratio of 392 to 750° F./C ₄ to 392° F.	Percent (V+Ni) deposited on—	
				C ₄ to 392° F.	392°-750° F.		1st stage catalyst	2nd stage catalyst
1	Canadian Atmospheric Bottoms	57	85	26.0	43.0	1.65	20.0	3.6
2	Texas Residuum	70	70	33.5	46.5	1.39	5.19	1.02
3	West Texas Residuum	42	79	23.0	42.0	1.82	8.1	3.4
4	Lake Charles Vacuum Bottoms 72-63	89	71	16.5	28.5	1.72	2.6	0.9
5	Venezuelan Atmospheric Bottoms	51.5	56	10.0	35.0	3.5	10.32	7.31
6	Tia Juana Vacuum Bottoms	100	54	9.0	32.5	3.6	7.82	4.71
7	Tia Juana Atmospheric Bottoms 84-196	51	38	4	28	7.0	7.69	6.55
8	Khafji Atmospheric Bottoms 84-186	45	33	3	25	8.0	2.39	1.72
9	Khafji 84-199	45	37	4	29	7.25	9.47	6.02

TABLE I_B

Example	Percent of (V+Ni) which is on catalyst in—		Operating conditions				Feed properties			
	1st stage	2nd stage	° F., 1st stage	° F., 2nd stage	Pressure, p.s.i.g.	Space velocity overall, V _t /hr./V _r	Gravity, °API	Sulfur, weight percent	Vanadium, p.p.m.	Nickel, p.p.m.
1	84.5	15.5	835	835	2,350	0.5	10.1	4.2	107	80
2	83.5	16.5	840	840	2,250	0.35	3.8	4.3	38	29
3	70.5	29.5	850	850	2,250	0.9	16.8	2.5	28	11
4	74.5	25.5	840	830	3,000	1.1	13.1	1.37	23	17
5	58.5	41.5	790	790	2,000	0.5	11.0	2.8	424	71
6	62.3	37.7	835	835	2,250	0.90	8.0	2.73	570	89
7	53.8	46.2	810	810	2,000	1.5	17.1	2.2	364	54
8	58.2	41.8	780	780	2,400	1.0	13.4	4.45	77	28
9	61.1	38.9	790	790	2,400	1.0	13.4	4.45	77	28

From the experimental data disclosed in Table I_A and I_B, it was discovered that only by operating at the combination of process conditions, which conditions include maintaining the ratio of the 392° to 750° F. product to the C₄ to 392° F. product at less than 2:1 by volume, can at least 65 percent of the total metals deposited on the catalyst be deposited on the first stage catalyst. The criticality of this ratio is distinctly shown by the sharp change in slope of the line at the 2:1 ratio value in FIG. 2.

This increase on and control over the percent of total metals that are deposited on the catalyst in the first stage is highly advantageous as it enhances the depth of hydrogenation that can be expected in the second stage.

Having thus described the invention in general terms, reference is now made to the specific examples which have been carried out in accordance with the techniques of the present invention and which should not be construed as unduly limiting thereof.

EXAMPLE I

It is found experimentally that the conversion of Mid Continent East Texas Residuum is limited to about 75% in a single stage reactor pilot plant. At conditions which give conversion levels exceeding about 75% the reactor becomes coked. However, when a two stage reactor system is employed in which the liquid effluent from the first stage is processed in a second stage the ultimate conversion which is attainable is about 90%. The experimental data is summarized in Table II.

The lighter and more valuable product structure is indicative of the greater desirability of the two stage operation.

TABLE II.—COMPARISON OF SINGLE STAGE AND TWO STAGE PROCESSING OF MID CONTINENT EAST TEXAS VACUUM RESIDUUM

	Feed	One stage	Two stage
Catalyst—100-200 mesh cobalt molybdate on alumina:			
Catalyst loading, gm. catalyst/reactor volume			
.....	0.4	0.4	0.4
Pressure, p.s.i.g.	1,500	1,500	1,500
Temperature, ° F.	858	858	858
Space velocity, V _t /hr./V _r	0.57	0.75	0.75
H ₂ s.c.f./bbl. fresh feed	7,000	7,000	7,000
Yields:			
C ₁ -C ₃ wt. percent	4.0	3.0	3.0
H ₂ S, NH ₃ , wt. percent	1.0	0.9	0.9
C ₄ -392° F. vol. percent	23.5	16.9	16.9
392-750° F. vol. percent	42.0	36.7	36.7
750-975° F. vol. percent	31.6	29.4	29.4
975° F., vol. percent	100	10.3	22.5
C ₄ +liquids, vol. percent	107.4	105.5	105.5
° API	14.9		
C ₄ +	31.0	27.3	27.3
C ₄ -392° F.	64.4	64.5	64.5
392-750° F.	32.8	33.1	33.1
750-975° F.	21.0	21.8	21.8
975° F.	1.2	8.5	8.5
Percent S	1.05		
C ₄ +	0.13	0.19	0.19
C ₄ -392° F.	<0.07	<0.07	<0.07
392-750° F.	<0.07	<0.07	<0.07
750-975° F.	0.15	0.24	0.24
975° F.	0.31	0.48	0.48

EXAMPLE II

In order to understand the effect of staging in retaining the hydrogenation activity of the catalyst where deep cracking takes place the following experiment is performed at a conversion of 90% with a charge stock consisting of a Canadian oil containing 107 p.p.m. of vanadium and 80 p.p.m. of nickel present in the form of porphyrin type compounds.

Utilizing two stage processing, summarized in Table III, the second stage catalyst is prevented from becoming poisoned by large deposits of vanadium and nickel.

TABLE III

Stage	First	Second	Overall
Catalyst	(1)	(1)	
Catalyst loading, gm. catalyst/cc. reactor	0.45	0.45	0.45
Pressure, p.s.i.g.	2,350	2,350	2,350
Temperature, °F.	830	830	830
Space velocity, $V_1/hr./V_r$	1.0	1.0	0.5
H_2 , s.c.f./bbl. fresh feed	6,000	6,000	10,000
Yield, percent on feed:			
H_2S , NH_3 , wt. percent			3.9
C_1-C_3 , wt. percent			5.8
$C_4-392^\circ F.$, vol. percent			36.5
$392-750^\circ F.$, vol. percent			50.2
$750-975^\circ F.$, vol. percent			15.1
$975^\circ F.$ +, vol. percent			9.0

¹ $\frac{1}{32}$ " dia. Como ext.

FEED.—Canadian Residuum of 10° API, 4% sulfur, 57 vol. percent boiling higher than 975° F.

INSPECTION ON CATALYST

TABLE IV

	First stage	Second stage
As charged at beginning of run:		
Cat. diameter, inches	$\frac{1}{32}$	$\frac{1}{32}$
Chemical analyses:		
Percent CoO	3.6	3.6
Percent MoO ₃	13.33	13.3
Percent Fe	0.02	0.02
Base	Al_2O_3	Al_2O_3
As dumped from reactor at end of run:		
Percent vanadium	10.8	2.1
Percent nickel	9.2	1.5
Percent carbon	20.0	23.9

Table IV summarizes the inspections on the catalyst as charged at the start of the operation. The unexpected result here is the sharp gradient in the deposition of porphyrins which tend to poison the catalyst. This point is illustrated by analyses made on the catalyst at the end of the run after 897 hours on stream.

While the foregoing represents the preferred embodiment, it is conceived that the invention will be carried out within the following ranges of operating conditions:

Pressure, (total): 1000–3000 p.s.i.g.

Hydrogen partial pressure: 1000–2000 p.s.i.

Temperature: 1st stage 800–900° F., 2nd stage $\pm 25^\circ F.$ of first stage.

Space velocity: 0.25 $V_1/hr./V_r$

Hydrogen rate: 4000–6000 s.c.f./bbl.

Modifications of the invention will occur to those skilled in the art upon consideration of this disclosure without departing from the spirit or scope thereof and accordingly only such limitations should be imposed on the invention as are set forth in the appended claims.

We claim:

1. A multi-zone method for converting material boiling above 975° F. in a crude petroleum charge containing at least 25 vol. percent of components boiling above 975° F. to material boiling below 975° F. wherein the charge, in liquid phase, is passed upwardly through a first reaction zone containing a hydrodesulfurization catalyst and a hydrogen rich gas under conditions in which the catalyst is maintained in random motion in the liquid, and wherein the temperature in the reaction zone is maintained in the range of 800° to 900° F. and the total pressure is in the range of 1,000 to 3,000 p.s.i.g., the improvement which comprises:

(a) separating a gaseous effluent from the total effluent from said reaction zone without substantial temperature or pressure change to minimize naphtha concentration in a subsequent reaction zone and avoid precipitation of converted material boiling above 975° F.;

(b) passing the liquid effluent, without substantial reduction in temperature, to a subsequent reaction zone also containing some of said hydrodesulfurization catalyst;

(c) maintaining reaction conditions in the subsequent reaction zone substantially at the same pressure as in the first zone with a maximum hydrogen rate of 6000 s.c.f./barrel in each reaction zone and with a temperature difference between the reaction zones not to exceed 25° F. and wherein at least 65 percent of the metals deposited on the catalyst are deposited in the first stage;

(d) maintaining a total space velocity for the several reaction zones of at least 0.25 $V_1/hr./V_r$;

(e) separating the gaseous effluent from the liquid effluent from the effluent of the subsequent reaction zone;

(f) converting at least 70% of the feed boiling above 975° F. to product boiling below 975° F.;

(g) and recovering from the total effluent of the respective reaction zones a liquid component, which liquid component on fractionation yields a fraction of a boiling range of about 392 to 750° F. and a fraction of a boiling range of about C_4 to 392° F. wherein the ratio of the 392 to 750° F. material to the C_4 to 392° F. material is less than 2 to 1 by volume based on product yield.

2. A method of converting a crude petroleum charge as claimed in claim 1, wherein the catalyst particles are in the size range of from 60 to 270 mesh Tyler and the velocities of the liquid and gas passing upwardly through said reaction zones are sufficient to expand the catalyst particles in said reaction zones at least 10% over their settled volume.

3. A method of converting a crude petroleum charge as claimed in claim 1, wherein the catalyst particles are in the size range of $\frac{1}{4}$ " to $\frac{1}{32}$ " in major diameter, the velocities of liquid and gas sufficient to expand the body of catalyst particles at least 10% over its settled volume, and a part of the reactor liquid effluent is recycled to the lower part of said reaction zones without substantial cooling.

4. A method of converting a crude petroleum charge as claimed in claim 1 wherein the catalyst loading is the same in the reaction zones.

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