May 7, 1957 S. C. EASTWOOD 2,791,544

METHOD OF USING A SINGLE REACTOR FOR A PLURALITY OF CONVERSIONS

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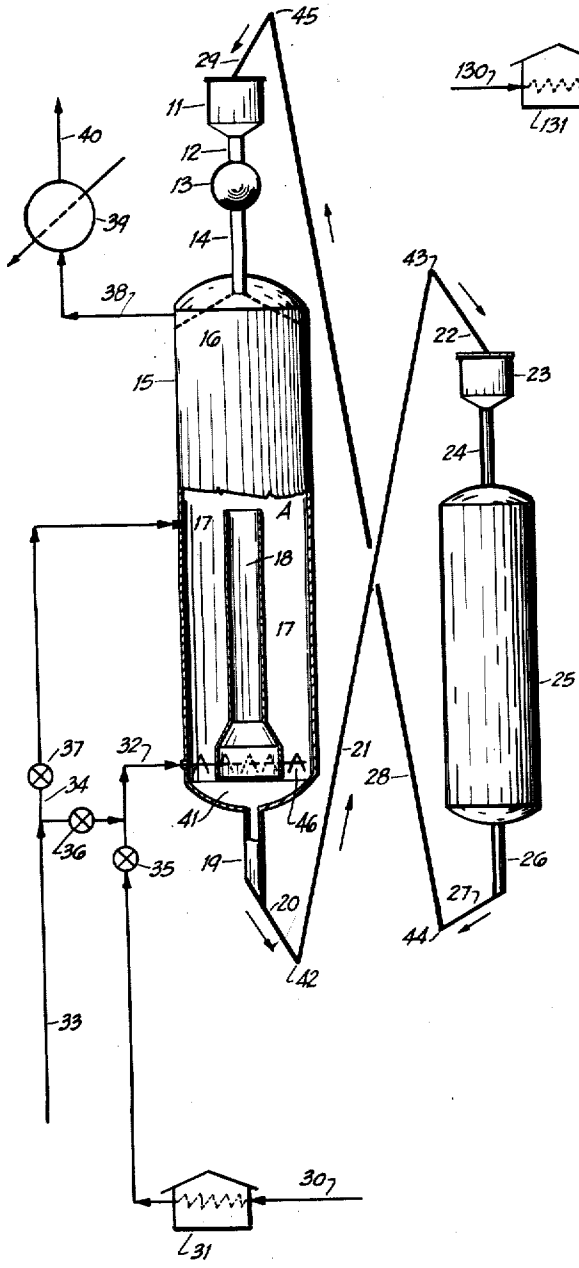


Fig. 1

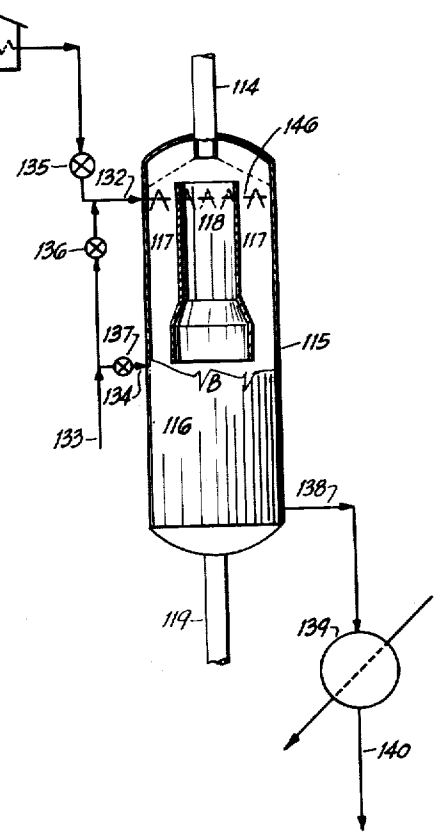


Fig. 2

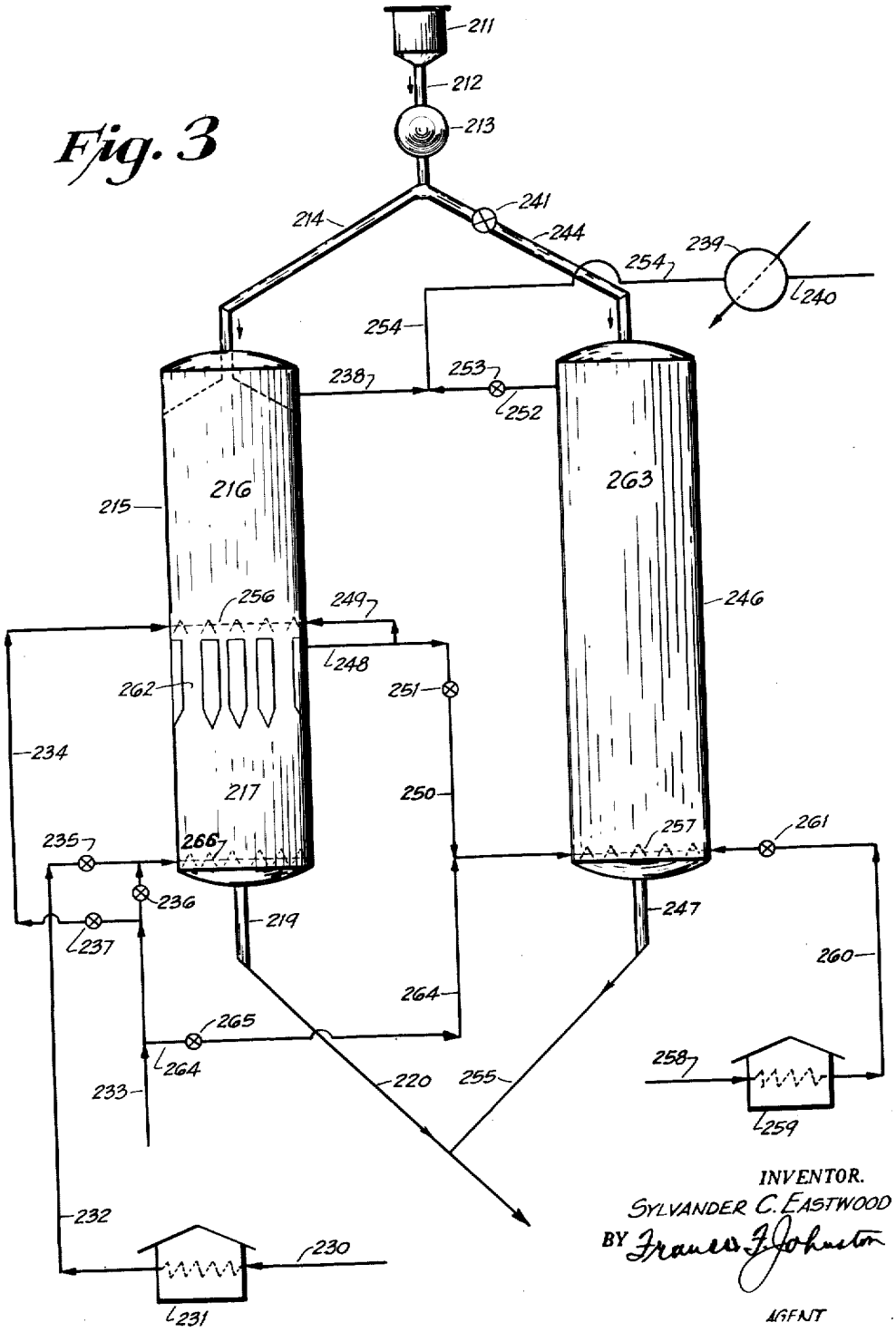
INVENTOR.
SYLVANDER C. EASTWOOD
BY Francis I. Johnston
AGENT

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Fig. 3



INVENTOR.
SYLVANDER C. EASTWOOD
BY Frances F. Johnston
AGENT

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METHOD OF USING A SINGLE REACTOR FOR A PLURALITY OF CONVERSIONS

Sylvander Cecil Eastwood, Woodbury, N. J., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

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5 Claims. (Cl. 196—52)

The present invention relates to hydrocarbon conversions and, more particularly, to a means whereby one reactor can be used for the purpose of subjecting a hydrocarbon mixture to a plurality of conversions in the presence of the same particle-form catalyst under a plurality of operating conditions of different severities.

Thus, for example, it is well-known that in general it is usual to provide more severe conditions for reforming than for desulfurizing a mixture of hydrocarbons. In the past, reforming and desulfurizing of the same feed has been obtained employing the same catalyst but requiring two reactors or convertors. It has now been discovered that a plurality of conversions can be obtained in the same convertor or reactor by controlling the residence time and the reaction temperature.

It is an object of the present invention to provide a method of operating a single convertor to obtain desulfurization in one portion of the convertor and reforming in another portion of the convertor whilst passing the same particle-form solid contact material through both the reforming zone and the desulfurizing zone whilst maintaining sufficiently severe conditions in the one zone to obtain reforming of the hydrocarbon charge stock therein and less severe conditions in the desulfurizing zone to obtain practical desulfurization of the hydrocarbon charge stock therein. It is another object of the present invention to maintain the more severe conditions in the reforming zone by supplying the major or controlling portion of the heat required in that zone in the catalyst or particle-form solid contact material while maintaining less severe conditions in the desulfurizing zone by supplying the major or controlling portion of the heat required in the desulfurizing zone in the hydrocarbon charge stock. It is a further object of the present invention to facilitate the control of residence time and reaction temperature in the desulfurizing zone through bypassing effectively with respect to the hydrocarbon charge stock a portion of the catalyst entering the desulfurizing zone. It is also within the scope of the present invention to provide means for controlling the residence time and reactor temperature in a plurality of zones whereby a plurality of reactions in the presence of the particle-form catalyst can take place simultaneously. Other objects and advantages will become apparent from the following discussion taken in conjunction with the drawings in which,

Figure 1 is a schematic illustration of one embodiment of the present invention in which a portion of the particle-form solid-contact material or catalyst in one zone is by-passed with respect to the hydrocarbon charge stock; and

Figure 2 is a schematic illustration of another embodiment of the present invention in which a portion of the catalyst is by-passed in one zone;

Figure 3 is a schematic illustration of another embodiment of the present invention in which a portion of the

catalyst is not by-passed but reaction conditions are controlled by means of the catalyst-to-oil ratio.

It is generally accepted that the term "desulfurization" or "desulfurizing" means reducing the sulfur content of a hydrocarbon charge stock. One method known to the art is that of catalytic desulfurizing or catalytic desulfurization. In catalytic desulfurizing a hydrocarbon charge stock, the charge stock is contacted with a suitable desulfurizing catalyst of which many are known to the art at elevated temperatures in the presence or absence of hydrogen or hydrogen containing gas for a period of time sufficient at the temperature selected to reduce the sulfur content of the hydrocarbon mixture to a practical extent. A limitation upon the desulfurizing conditions is the practical requirement that the loss through decomposition be kept low while achieving a reduction of the sulfur content necessary to provide products which will meet specifications. Under such conditions, which relative to reforming conditions are relatively mild, the octane number of the charge stock is not raised effectively.

It is generally accepted that the term "reforming" or "aromatizing" or "cyclizing" is applied to a plurality of reactions occurring simultaneously or successively or both, in which a primarily aliphatic hydrocarbon charge stock is converted to a product having a higher octane number and a higher content of aromatic hydrocarbons than the charge stock.

For the desulfurizing conversion, the temperatures required are about 650° F. to about 900° F. and preferably about 700° F. to about 800° F. For the reforming conversion the temperatures required are about 825° F. to about 1025° F. and preferably about 875° F. to about 950° F.

The terms "desulfurizing" or "desulfurization" and, "reforming" or "aromatizing" or "cyclizing" are used herein in the sense briefly discussed hereinbefore.

In general, the present invention provides for a reforming zone and a desulfurizing zone in series relation through which the particle-form catalyst passes as a compact column. That is to say, the catalyst passes through one zone as a compact column, enters the other zone and passes therethrough as a compact column. However, since the conditions in the desulfurizing zone are much less severe than the conditions in the reforming zone, means must be provided for controlling the heat absorbed by the hydrocarbon charge stock in each zone to provide the severity of conditions necessary to maintain desulfurization without excessive loss and reforming without excessive loss.

The catalyst leaves the kiln or regenerator at a temperature of about 1000° to about 1100° F., and preferably about 1000° to about 1050° F., and enters the first conversion zone at a temperature of about 975° to about 1075° F. and preferably at about 975° to about 1025° F. In accordance with the principles of the present invention, the reforming or desulfurizing temperature is obtained in the respective zones by regulating the rate of the hydrocarbon stream to make either the catalyst or the hydrocarbon stream controlling of the temperature. In other words, the ratio of catalyst to oil is controlling. Thus, the stock to be desulfurized and reformed can enter at the lower end or bottom of the reactor having a lower desulfurizing zone and an upper reforming zone and flows upward counter-current to downwardly flowing catalyst at a catalyst-to-oil ratio such that the oil inlet temperature controls the temperature of the zone. In the upper or reforming zone the catalyst-to-oil ratio is such that the catalyst inlet temperature is controlling.

In general, for producing reforming conditions, the catalyst-to-oil weight ratio, i. e., C/H, is about 4 to about

8 and preferably about 4 to about 6, and the space velocity is about 1.0 to about 3.0 and preferably about 1.5 to about 2.0 liquid volume of charge stock per unit volume of catalyst in the reforming zone.

In the desulfurizing zone the charge stock inlet temperature is about 650° to about 850° F. and preferably about 700° to about 800° F. The catalyst to oil weight ratio, i. e., C/H is about 1.0 to about 3.0 and preferably about 1.5 to about 2.0 and the space velocity is about 0.25 to about 1.0 and preferably about .50 to about 0.75 liquid volume of charge stock per unit volume of catalyst in the desulfurizing zone.

In general, the reaction temperature in the desulfurizing zone is about 650° to about 850° F., and preferably about 700° to about 800° F., while in the reforming zone the reaction temperature is about 825° to about 1025° F. and preferably about 875° to about 950° F.

Those skilled in the art will note that the catalyst-to-oil ratio in the desulfurizing zone is lower than in the reforming zones. To achieve these ends one can either contact a given volume of charge stock with a lesser volume of catalyst in the desulfurizing zone than in the reforming zone, or contact a lesser volume of hydrocarbons with a given volume of catalyst in the reforming zone than in the desulfurizing zone.

In the first alternative, a portion of the catalyst bypasses the desulfurizing zone. In the second alternative, an auxiliary reforming zone can be employed or the reforming zone can have a catalyst volume proportional to the catalyst volume of the desulfurizing zone. For practical reasons it is presently preferred to have the catalyst by-pass the desulfurizing zone.

Turning now to the drawings, the method of the present invention will be described first by following the course of the catalyst through the process, then by following the hydrocarbon charge through the process.

Referring to Figure 1 and using as an illustrative example of the plural treatment of a reactant in a single multi-zone reactor the desulfurizing and reforming of a mixture of hydrocarbons containing hydrocarbons capable of undergoing isomerization, and/or dehydrogenation and/or dehydrocyclization, all of which molecular changes are included generally in the designation, reforming, the course of the catalyst through a plurality of zones, i. e., a desulfurizing zone and a reforming zone will first be followed, and then the path of the mixture of hydrocarbons will be traced.

Active catalyst, for the purposes of the illustration—an alumina-silica cracking catalyst such as natural clays (fuller's earth), treated natural clays ("Super-Filtrol"), and synthetic associations of silica and alumina usually in gel form to which can be added other metals or metal compounds for special purposes, is placed in feed bin **11**. The catalyst can also be a group VI metal or metal compound associated with alumina or silica or in general any particle form catalyst which is suitable for producing any one or all of the molecular changes generally denominated, "isomerization," "dehydrogenation" and "dehydrocyclization."

The catalyst at a temperature of about 950° to about 1100° F. and preferably at about 975° to about 1025° F. when using a cracking catalyst, flows from feed bin **11** through conduit **12** into surge chamber **13**. From surge chamber **13** the hot active catalyst flows through conduit **14** into reactor **15** as a substantially compact column.

Reactor **15**, as illustrated, is divided into two zones, an upper reforming zone **16** and a lower, annular desulfurizing zone **17**. Zones **16** and **17** are preferably of correlated volumes whereby the residence time and/or the catalyst-to-oil ratio are correlated with the reaction temperatures in both zones to provide the more severe reforming conditions in reforming zone **16** as compared to the relatively mild desulfurizing conditions in annular desulfurizing zone **17**.

As illustrated in Figure 1, such correlated control is

provided by the catalyst by-pass **18**. That is to say, the hot catalyst flows as a substantially compact mass downwardly through reforming zone **16** to a point such as "A" where the catalyst is divided into two portions, to wit: a central stream which flows as a substantially compact column through by-pass **18** and, as illustrated, an outer annular substantially compact hollow column **17**.

By-pass **18** is of any suitable type whereby a portion of the catalyst mass is separated from the rest of the catalyst flowing through the reactor and maintained out of effective contact with the reactant to be treated in the desulfurizing zone.

In the drawing Figure 1, by-pass **18** is shown as a hollow, cylindrical column provided at its lower end with a flaring skirt. The cross-sectional area of the flared skirt is proportioned to the total cross-sectional area of the reactor or catalyst column to divert sufficient of the total catalyst column to provide in desulfurizing zone **17** the catalyst-to-reactant ratio required to provide the milder conditions necessary in zone **17**.

The catalyst to reactant ratio in zone **17** will be, as those skilled in the art know, dependent upon the temperature of the catalyst, the reaction temperature and the volume of reactant to be treated.

The by-passed catalyst flows as a substantially compact column through by-pass **18**. The balance of the catalyst flows as a substantially compact annular column through annular zone **17**. The two columns join in area **41** at the bottom of the reactor and flow as a single substantially compact column from the reactor through conduit **19** to chute **20**.

Generally, the catalyst in passing through the reactor becomes more or less inactivated. For economical reasons it is necessary to reactivate the catalyst. In many catalytic reactions the catalyst can be reactivated by combustion of the deactivating contaminant in a stream of combustion-supporting gas. Since the reforming and desulfurizing of a mixture of hydrocarbons results in the contamination of the catalyst with a carbonaceous deposit generally called coke, the reactivation of the catalyst has been illustrated in Figure 1 as taking place in a kiln or regenerator **25**. Accordingly, the deactivated catalyst flowing from reactor **15** through conduit **19** passes into chute **20** and thence to any suitable means for transferring the deactivated catalyst to the regenerator.

The catalyst transfer means can be a gas-lift, an elevator or the like suitable for transferring particle form catalyst from the reactor to a regenerator. As shown in Figure 1 in a schematic manner, the catalyst transfer means is an elevator, preferably a bucket elevator. The design of such and other catalyst transfer devices are so well-known to those skilled in the art as to require no description particularly since the present invention is not concerned with the design of catalyst transfer means.

The deactivated catalyst passes through chute **20** to the boot **42** of elevator **21**. The deactivated catalyst is raised to head **43** of elevator **21** and discharged into chute **22** along which the deactivated catalyst flows to feed bin **23** of regenerator or kiln **25**.

Regenerator or kiln **25** is of any suitable design wherein the carbonaceous contaminant or coke can be burned off in a stream of combustion-supporting gas such as air. Since the present invention is not concerned with the design of such regenerators or kilns and since the design of such regenerators or kilns is well-known to those skilled in the art, the present invention is not limited to any particular regenerator.

The deactivated catalyst flows from regenerator feed bin **23** through conduit **24** into kiln **25** where, in a heated stream of combustion-supporting gas such as air, the coke is burned-off at a temperature below the damaging temperature at which the particular catalyst is deactivated in such a manner as to be practically useless as a catalyst for the reaction. For the catalysts of this illustration, the damaging temperature is in excess of 1400° F. Conse-

quently, the temperature in kiln or regenerator is not greater than about 1400° F. and can be as low as 950° F.

During passage through kiln **25** the coke deposit on the catalyst is burned-off and the catalyst reactivated. The hot reactivated catalyst flows from the kiln through conduit **26** into chute **27** and thence to any suitable catalyst transfer means whereby the reactivated catalyst is raised to reactor feed bin **11**. The catalyst transfer means can be a gas lift or the like, an elevator, etc. suitable for transferring catalyst from chute **27** to reactor feed bin **11**. As illustrated, the catalyst transfer means is a bucket elevator similar to that by which the deactivated catalyst is transferred from reactor **15** to kiln **25**. However, catalyst transfer means can be used to transfer the catalyst from the kiln to the reactor differing in type from that used to transfer the catalyst from the reactor to the kiln.

As shown, the catalyst flows along chute **27** to elevator boot **44** of bucket elevator **28** by which it is raised to head **45** of elevator **28**. From head **45** of elevator **28** the hot reactivated catalyst flows along chute **29** to reactor feed bin **11** ready to begin another cycle.

It will be noted that the operation illustrated in a schematic manner in Figure 1 is one in which the reaction takes place at substantially the same pressure as that at which the deactivated catalyst is regenerated. Those skilled in the art will recognize that when the reaction takes place at a pressure higher than that at which regeneration is carried out means must be provided to transfer the reactivated catalyst from a zone of lower pressure to the zone of higher pressure and to transfer the deactivated catalyst from the zone of higher pressure to the zone of lower pressure. For example, when the reactor is operated at super-atmospheric pressure and the regenerator at a lower pressure, a pressure lock is inserted between feed bin **11** and surge chamber **13** and between conduit **19** and chute **20**.

The reforming and desulfurizing operations illustrated schematically in Figure 1 provide for counter-current flow of catalyst and reactant. The catalyst flows downwardly through zones **16** and **17** while the reactant flows upwardly. Thus, a mixture of hydrocarbons containing hydrocarbons which can be isomerized and/or dehydrogenated and/or dehydrocyclicized in the presence of a particle-form catalyst, for example, a virgin naphtha is drawn from a source not shown and passed through line **30** into furnace **31**. In furnace **31** the naphtha to be desulfurized and reformed is heated to a temperature such that at a pre-determined catalyst-to-oil ratio and with the catalyst at a pre-determined temperature in zone **17**, desulfurizing of the naphtha takes place. For example, with the catalyst entering the desulfurizing zone at a temperature in the range of 850 to 950° F., the virgin naphtha is heated to about 650° to about 850° F. and preferably about 700° to about 800° F. in furnace **31**. The heated naphtha leaves furnace **31** through line **32** under control of valve **35**. The heated naphtha is distributed over the cross-section of annular desulfurizing zone **17** by a distributor **46** of any suitable design. By regulating the catalyst-to-oil ratio in annular zone **17**, the reaction temperature suitable for desulfurizing the naphtha with substantially no loss of naphtha is maintained at about 650° to about 850° F. and preferably, at about 700° to about 800° F.

The naphtha flows upwardly in annular zone **17** countercurrent to the downwardly flowing catalyst and during its contact with the catalyst is at least partially desulfurized upon entering reforming zone **16**.

Upon entering reforming zone **16**, the catalyst-to-oil ratio is changed because substantially all of the vapors of naphtha which contacted only the portion of the catalyst flowing through zone **17** now contacts the total volume of catalyst flowing through reforming zone **16**.

The catalyst entering reforming zone **16** generally will have a temperature of about 975° to about 1075° F. and preferably about 975° to about 1025° F. The catalyst entering desulfurizing zone **17** generally will have a temperature of about 850° to about 950° F. The naphtha or other mixture of hydrocarbons to be desulfurized and reformed entering zone **17** will have a temperature of about 650° to about 850° F. and preferably about 700° to about 800° F.

Under these conditions the catalyst-to-naphtha weight ratio, i. e., C/H, is about 4 to about 8 and preferably about 4 to about 6 in reforming zone **16** and about 1 to about 4 and preferably about 1.5 to about 2 in the desulfurizing zone. Accordingly, by-pass **18** is of such dimensions as to by-pass sufficient catalyst to provide the required catalyst-to-naphtha weight ratio. In other words, about 60 to about 75 percent and preferably about 65 to about 70 percent of the catalyst from the reforming zone passes through by-pass **18** while the balance, about 25 to 40 and preferably about 30 to about 35 percent of the catalyst, is in effective contact with the naphtha in desulfurizing zone **17**.

The at-least-partially desulfurized naphtha flows upwardly through reforming zone **16** where the molecular changes, generally classified as reforming, occur. The desulfurized and reformed naphtha flows from reforming zone **16** through outlet **38**, cooler **39** and line **40** to means for stabilizing and fractionating the effluent and subjecting the effluent to such after-treatment as is necessary.

When it is desirable or necessary, the desulfurizing of the charge stock can take place in the presence of hydrogen. For this purpose hydrogen or preferably a hydrogen containing gas containing about 35 to about 95 percent hydrogen and the balance C_1 to C_6 hydrocarbons is drawn from a source not shown, heated in a furnace not shown to about 800° to about 1100° F. and preferably to about 900° to about 1000° F. and drawn through pipe **33** regulated by valve **36** and admixed with the charge stock in line **32**.

Similarly, when desired or required, the reforming reaction can take place, as is well-known, in the presence of hydrogen or a hydrogen containing gas drawn from a source not shown through lines **33** and **34** under control of valve **37**, and introduced into reforming zone **16** through one or more inlets and distributors not shown.

In the event that a recycle gas of low hydrogen content or devoid of hydrogen or any other gaseous reactant or heat carrier is to be used in conjunction with a liquid reactant, the gaseous reactant can be introduced into either or both zones by means of pipes **32** and **34**.

Figure 2 is a schematic illustration of an arrangement of a plurality of reaction zones in a single reactor or convertor through which a particle form catalyst flows successively wherein the reactant and catalyst flow concurrently and the first zone through which the catalyst flows is the zone of relative mild reaction conditions and the second zone of relatively severe reaction conditions in contrast to the converse as illustrated in Figure 1.

As in Figure 1, the course of the catalyst will be followed through the reactor and then a description of the path of the reactant or reactants through the reactor will be traced. For purposes of illustration, only the multizone single reactor is illustrated in Figure 2 since a reforming and desulfurizing operation will be used for illustrative purposes.

For purposes of illustration, a cracking and desulfurizing operation will be described in which desulfurizing takes place under relatively mild conditions in desulfurizing zone **117** and cracking takes place in cracking zone **116**.

Hot active catalyst from a feed bin such as **11** flows into a surge chamber such as **13** and thence through conduit **114** into desulfurizing zone **117** of reactor **115**. Desulfurizing zone **117** is preferably annular in cross-section while by-pass **118** is circular. The cross-sectional areas of desulfurizing zone **117** and by-pass **118** are propor-

tioned to provide a catalyst volume in zone **117** such that the catalyst-to-oil ratio is about 1 to 3, and preferably 1.5 to 2.0, and a space velocity of about .25 to 1.0 and preferably .5 to .75 when the catalyst enters the reactor at a temperature of about 975° to about 1075° F. and preferably about 975° to about 1025° F. and the oil to be desulfurized and cracked enters the desulfurizing zone at about 650° to about 850° F. and preferably about 700° to about 800° F. Under these conditions of reactant and catalyst inlet temperatures, catalyst-to-oil ratio and space velocity, the average reaction temperature in desulfurizing zone **117** is about 650° to about 850° F. and preferably about 700° to about 800° F.

In order to provide the catalyst-to-reactant ratio required in the desulfurizing zone **117**, about 60 to about 80, and preferably about 65 to about 70 percent of the catalyst stream entering reactor **115** flows through by-pass **118** and the balance, about 20 to about 40 and preferably about 30 to about 35 percent flows as a substantially compact annular column through desulfurizing zone **117**.

The two substantially compact columns, the cylindrical column flowing downwardly through by-pass **118** and the annular column flowing through desulfurizing zone **117** join at "B" and continue to flow downwardly as a single compact column through cracking zone **116**. When the catalyst reaches the bottom of reactor **115**, it is more or less deactivated with a carbonaceous contaminant generally called coke in the industry. The deactivated catalyst flows from the reactor through conduit **119** to suitable transfer means, and thence to a regenerator or kiln such as kiln **25** of Figure 1. The reactivated catalyst is then returned to the reactor feed bin ready for another cycle through the reaction zones and the regenerator.

A mixture of hydrocarbons suitable for cracking and requiring desulfurizing, such as a gas oil is drawn from a source not shown through line **130** and heated to at least a desulfurizing temperature in furnace **131**. A temperature of about 650° to about 850° F. and preferably about 700° to about 800° F. will usually provide satisfactory results. The heated oil is passed through line **132** under control of valve **135** to distributor **146** of any suitable design whereby the oil is distributed over the cross-section of annular desulfurizing zone **117**.

The oil enters the desulfurizing zone at a temperature of about 650° to about 850° F. and preferably about 700° to about 800° F. at such a rate to provide a catalyst-to-oil ratio in desulfurizing zone **117** of about 1 to about 4 and preferably about 1.5 to about 2.0 and a space velocity of about .25 to about 1.0 and preferably about .5 to about .75.

The oil flows concurrently downwardly with the substantially compact hollow cylinder or annulus of catalyst through desulfurizing zone **117**. During this contact the oil is at least partially desulfurized. The downwardly flowing catalyst and reactant flow from desulfurizing zone **117** into cracking zone **116** where the reactant contacts not only the catalyst from zone **117** but also the catalyst from by-pass **118**. However, since the volume of catalyst effectively contacted by the volume of reactant leaving desulfurizing zone **117** is appreciably greater, the catalyst-to-oil is increased and the temperature is increased. Consequently, the reaction conditions are more severe. In the cracking zone **116** the catalyst-to-oil ratio is about 4 to about 8 and preferably about 4 to about 6 and the space velocity is about 0.5 to about 4.0 and preferably about 1.0 to about 2.0.

The effluent from the desulfurizing zone flows concurrently downwardly with the substantially compact column of catalyst through cracking zone **116**. The catalyst leaves zone **116** via conduit **119** while the vaporous contents of zone **116** leave by way of line **138** to pass through cooler **139** and line **140** to after-treatment, stabilizing and fractionating equipment not shown.

When desirable or necessary, a gaseous heat carrier or a gaseous reactant can be mixed with the heated liquid reactant in line **132**. Such a gas can be drawn from a source not shown through line **133** under control of valve **136**. Furthermore, when necessary, a gaseous heat carrier or reactant can be introduced into cracking zone **116** through pipe **134** and its associated distributor not shown under control of valve **137**.

Since, for purposes of illustration, the desulfurizing and cracking of a gas oil has been described, those skilled in the art will understand that the catalyst can be any suitable cracking catalyst such as natural clays, such as fuller's earth, treated clays such as "Super-Filtrol," synthetic associations of alumina and silica usually in gel form with or without other metals or metal compounds added for special purposes and the like.

Figure 3 provides a schematic illustration of a means for carrying out two reactions with the same catalyst under different conditions of severity wherein the capacity of the zone in which the less severe conditions prevail is appreciably greater than the capacity of the zone wherein the more severe conditions prevail. As before, the course of the catalyst through reactor **215** and auxiliary reactor **246** will be followed and then the course of the vaporous reactants through reactor **215** and auxiliary reactor **246** will be traced.

Hot active catalyst in bin **211** flows through conduit **212** into surge chamber **213**. From surge chamber **213** hot active catalyst flows into conduits **214** and **244**. In the event that the capacity of zone **216** is sufficient to handle the total reactant from zone **217** of reactor **215**, conduit **244** is provided with a suitable shut-off valve **241**.

The hot active catalyst, for the purpose of illustration and description a cracking catalyst having reforming characteristics, flows as a compact column along conduits **214** and **244** to reactors **215** and **246** respectively. The hot active catalyst flows downwardly as a substantially compact column through both reactors **215** and **246** counter-current to vaporous reactant flowing upwardly.

The catalyst flows downwardly in reforming zone **216** of reactor **215** where the temperature of the catalyst is about 825° to about 1025° F. and preferably about 875° to about 950° F.

In order to obtain a reforming reaction, the space velocity of the vaporous reactant entering reforming zones **216** and **263** is about 1.0 to about 3.0 preferably about 1.5 to about 2.0 and the catalyst-to-liquid reactant weight ratio is about 4 to about 8 and preferably about 4 to about 6.

The total catalyst in reforming zone **216** passes through seal legs **262** into desulfurizing zone **217** wherein the space velocity is about .25 to about 1.0 and preferably about .5 to about .75 and the catalyst-to-liquid reactant weight ratio is about 1 to about 4 and preferably about 1.5 to about 2.0. Under these conditions, the average reaction temperature in desulfurizing zone **217** is about 650° to about 850° F. and preferably about 700° to about 800° F.

The total catalyst flowing into reforming zone **263** flows downwardly as a substantially compact column through reforming zone **263** of reactor **246** to leave the reactor via conduit **247** and chute **255** to a catalyst transfer means.

The total catalyst flowing through zone **217** leaves reactor **215** by conduit **219** and thence along chute **220** to any suitable catalyst transfer means whereby the deactivated catalyst is transferred to a regenerator or kiln such as kiln **25** of Figure 1. Such a catalyst transfer means can be an elevator, gas-lift or the like.

The catalyst from both reactors **215** and **246** is transferred by a suitable catalyst transfer means, not shown, to a regenerator, not shown, reactivated and returned to feed bin **211** in any suitable manner.

A mixture of hydrocarbons suitable for reforming and requiring desulfurizing, such as a mixture of hydrocarbons capable of isomerization and/or dehydrogenation and/or dehydrocyclization, for example—a virgin naph-

tha, is drawn from a source, not shown, through line **230**, heated in furnace **231** and the heated oil discharged into desulfurizing zone **217** of reactor **215** through line **232** and associated distributor **266** under control of valve **235**.

Distributor **266** is of any suitable type whereby the heated reactant, naphtha, can be distributed over the cross-section of desulfurizing zone **217**.

The naphtha is heated to a temperature of about 650° to about 850° F. and preferably to about 700° to about 800° F. in furnace **231** and enters desulfurizing zone **217** at about the temperature at which it leaves furnace **231**.

The heated naphtha flows upwardly counter-current to the downwardly flowing substantially compact column of catalyst at a catalyst-to-oil weight ratio of about 1.0 to about 4.0 and preferably about 1.5 to about 2.0 and at a space velocity of about 0.25 to about 1.0 and preferably of about 0.50 to about 0.75. During contact with the catalyst at an average temperature of about 650° to about 850° F. and preferably about 700° to about 800° F. produced by correlation of catalyst temperature, naphtha temperature, catalyst-to-naphtha weight ratio and space velocity, the naphtha is at least partially desulfurized.

The desulfurized naphtha leaves desulfurizing zone **217** by line **248**. When the entire effluent from desulfurizing zone **217** can be adequately treated in reforming zone **216**, the entire effluent passes through lines **248** and **249** (with valve **251** closed) to distributor **256** which is of any suitable type whereby the effluent can be distributed over the cross-section of reforming zone **216**.

When the entire effluent from desulfurizing zone **217** cannot be adequately treated in reforming zone **216**, a portion is diverted through valve **251** and line **250** to reforming zone **263** of reactor **246**. When the quantity so diverted is insufficient to be efficiently reformed in reforming zone **263** additional low sulphur naphtha such as a cracked naphtha can be drawn from a source not shown through line **258** heated to a reforming temperature in furnace **259**, discharged therefrom through line **260** under control of valve **261** into distributor **257** where it is mixed with the portion of effluent from desulfurizing zone **217** which enters distributor **257** from line **250**.

The effluent from desulfurizing zone **217** is introduced into reforming zone **216** and the effluent or effluent and additional naphtha is introduced into reforming zone **263** at a rate such that the catalyst-to-naphtha ratio is about 4 to about 8 and preferably about 4 to about 6 and the space velocity is about 1.0 to about 3.0 and preferably about 1.5 to about 2.0.

The vaporous reactants flow upwardly from distributors **256** and **257** through reforming zones **216** and **263** counter-current to a downwardly flowing substantially compact column of catalyst in each reforming zone.

The effluent from reforming zone **216** passes through line **238** to line **254**. The effluent from reforming zone **263** passes through line **252** to line **254**. The mixed effluents then pass through cooler **239** and line **240** to after-treatment, stabilization and fractionation.

When the capacity of reforming zone **216** is such as to adequately treat the total effluent from desulfurizing zone **217** and reactor **246** is not in operation valve **253** is closed.

When it is desired or necessary, both reactions can be carried out in the presence of a gas. Thus, for example, the desulfurizing can be carried out in the presence of hydrogen or a hydrogen-containing gas. Similarly, the reforming reaction can be carried out in the presence of hydrogen or a hydrogen-containing gas. Furthermore, for some purposes it can be desirable to supply heat to either or both zones by means of a gaseous or vaporous carrier. For such purposes, a suitable gas can be drawn from a source not shown through pipe **233** and passed into pipe **232** under control of valve **236** and thence into desulfurizing zone **217**. Similarly, a gas can be passed from pipe **233** through pipe **234** under control of valve **237** to reforming zone **216**. Likewise, a gas can be passed from pipe **233** through pipe **264** under control of valve **265** into reforming zone **263**.

Thus, for example, in accordance with the principles of the present invention, a blend of 50 volume percent coker gasoline and 50 volume percent straight run heavy naphtha having a boiling range of 128° to 433° F. was treated as described hereinbefore. The effluent of the desulfurizing zone at various desulfurizing temperatures produced with an oil inlet temperature of 629° to 962° F. at the space velocities indicated was obtained in yields noted and with the sulfur content and octane numbers listed in Table I.

TABLE I

Run No.	1	2	3	4	5	6
Average Desulfurizing Temperature, °F	929	825	765	690	972	997
Sulfur percent weight, Desulfurizing Zone Effluent	0.18	0.17	0.17	0.21	0.26	0.29
Yield of Effluent, percent volume	77.9	90	93	95	77.8	82.3
Space Velocity	0.5	0.5	0.5	0.5	0.1	2.0
Catalyst-to-naphtha weight ratio	4.1	4.2	4.2	4.3	4.1	4.2
Octane number of Effluent [1] from Desulfurizing zone	75.0	69	61.5	60	74.8	74.6
Octance number of Effluent [2] + 3 cc. TEL	86.4	81	75.5	74.5	86.0	85.6
Percent Sulfur Removed	66	68	68	60	51	45

Sulfur content of feed-to-desulfurizing zone 0.53 weight percent. Research octane rating of the feed was 61.5 clear and 72.0 with 3 cc. TEL.

[1] Research.

[2] Research +3 cc. TEL.

It will be noted that runs numbers 2, 3 and 4 were made at desulfurization temperatures of 690° to 825° F. and at relatively low space velocities while runs Nos. 1, 5 and 6 were made at desulfurization temperatures in excess of 900° F. at space velocities of 0.5, 1.0 and 2.0. Nevertheless, the yield of desulfurized oil of comparable grade was far greater, i. e., in excess of 90 volume percent in the runs made at low temperatures and low space velocities than the yield of desulfurized oil in the runs made at high temperatures and low space velocities or high temperatures and high space velocities. Accordingly, it is preferred to operate at temperatures of about 700° to about 800° F. in the desulfurizing zone.

When the afore-described effluents are then reformed as described hereinbefore, the finished products are obtained in the yields and with the octane numbers indicated in Table II.

TABLE II

	Run No. 4
Average reforming temperature °F	970
Yield reformate, volume percent on charge of desulfurizing zone effluent	80.0
Space velocity	1.5
Catalyst-to-oil weight ratio	4.5
Octane number of reformate [1]	75.0
Octane number of reformate+3 cc. TEL [2]	87.0

[1] Research.

[2] Research +3 cc. TEL.

Those skilled in the art will understand that the auxiliary reforming zone **263** can have a capacity just sufficient to treat the portion of effluent from desulfurizing zone **217** in excess of that which can be treated in reforming zone **216** or reforming zone **263** can have a capacity such as to treat an additional low sulfur naphtha or the like as well as or simultaneously with the effluent from desulfurizing zone in excess of that which can be treated in reforming zone **217**.

In view of the foregoing description and discussion, it is believed apparent to those skilled in the art that the present invention provides a means for carrying out a plurality of reactions at different reaction conditions of temperature and residence time in a plurality of zones in a reactor through which a single catalyst or a mixture of catalysts flows successively as a substantially compact

column and that the reaction condition in the different zones are controlled, regulated and maintained by controlling the catalyst-to-reactant weight ratio, the space velocity and correlating the aforesaid with the catalyst and reactant temperatures to provide different reaction temperatures in each zone. Specifically, the present invention provides for desulfurizing and reforming a mixture of hydrocarbons under relatively severe reforming conditions in one zone and desulfurizing the same mixture of hydrocarbons under relatively less severe conditions in a second zone by controlling, regulating and maintaining a different catalyst-to-reactant weight ratio and a different space velocity in each zone. Thus, for example, a reforming catalyst, for example, a chromia-alumina or a molybdena-alumina reforming catalyst, can be used at reforming temperatures and pressures of about 850°–1080° F., preferably about 875° to 1060° F., and about 25–600, preferably about 100 to 300 p. s. i. a. in the presence of about 1–15, preferably about 4–10 mols of recycle gas per mol of naphtha or about 1–8, preferably about 2–5 mols of hydrogen at a space velocity of about 0.1–6.0, preferably about 0.5–2.0, volumes of liquid charge stock per volume of catalyst in the reforming zone. The charge stock is desulfurized at a temperature of about 650°–850° F., preferably about 700° to about 800° F. in the presence of the reforming catalyst used in the reforming zone.

I claim:

1. A process for desulfurizing and reforming a hydrocarbon mixture in a single multi-zone reactor which comprises introducing active particle-form catalyst, said catalyst combining activity for reforming with activity for hydrogenation of organically combined sulfur in a hydrocarbon mixture to hydrogen sulfide, at a temperature of about 950° F. to about 1100° F. into a single multi-zone reactor, flowing said catalyst through a reforming zone, flowing a portion of said catalyst from said reforming zone to and through a by-pass zone, flowing the balance of said catalyst through a desulfurization zone, introducing a hydrocarbon mixture to be desulfurized and reformed into said desulfurization zone at a temperature of about 650° F. to about 850° F., flowing said hydrocarbon mixture at a liquid space velocity of about 0.25–1.0 v./v./hr. through said desulfurization zone in contact with said balance of said catalyst to at least partially desulfurize said hydrocarbon mixture and to lay down a carbonaceous deposit on said catalyst, flowing at least partially desulfurized hydrocarbon mixture from said desulfurizing zone into and through said reforming zone at a space velocity of about 1.0–3.0 v./v./hr. in contact with said catalyst to reform said at least partially desulfurized hydrocarbon mixture and to lay down a carbonaceous deposit on said catalyst, withdrawing reformed and desulfurized hydrocarbon mixture from said reforming zone, withdrawing catalyst contaminated with carbonaceous deposit from said desulfurizing zone and from said by-pass zone, regenerating and heating said withdrawn catalyst to a temperature of about 950° F. to about 1100° F. by combustion of said carbonaceous deposit, regulating the flow of catalyst and at least partially desulfurized hydrocarbon mixture through said reforming zone to provide a catalyst to oil ratio of about 4 to 8 to maintain a reaction temperature of about 825° F. to about 1025° F. in said reforming zone, and regulating the flow of catalyst and hydrocarbon mixture through said desulfurizing zone to provide a catalyst to oil ratio different to the aforesaid catalyst to oil ratio and about 1 to 4 to maintain a reaction temperature of about 650° F. to about 850° F. in said desulfurizing zone.

2. A process for catalytically cracking and desulfurizing a hydrocarbon mixture in a single multi-zone reactor which comprises introducing hot active particle form solid catalyst which combines activity for converting hydrocarbons boiling above the gasoline range into hydrocarbons boiling in the gasoline range with activity for hydrogenating organically combined sulfur in said hydrocarbon mixture to hydrogen sulfide at a temperature of about 975° F. to about 1075° F. into a multi-zone reactor, flowing a portion of said catalyst through a by-pass zone, flowing the balance of said catalyst through a desulfurizing zone, flowing a stream of catalyst from said by-pass zone, flowing a stream of catalyst from said desulfurizing zone, combining said flowing streams of catalyst, introducing said combined flowing streams of catalyst into a catalytic cracking zone, introducing hydrocarbon mixture to be desulfurized and catalytically cracked into said desulfurizing zone at a temperature of about 650° F. to 850° F., flowing said hydrocarbon mixture at a liquid space velocity of about 0.25 to 1.0 v./v./hr. through said desulfurizing zone in contact with said catalyst to produce an at least partially desulfurized hydrocarbon mixture and to lay down a carbonaceous deposit on said catalyst, flowing said at least partially desulfurized hydrocarbon mixture through said cracking zone at a liquid space velocity of about 0.5 to 4.0 v./v./hr. to produce a catalytically cracked and at least partially desulfurized hydrocarbon mixture and to deposit on said catalyst a carbonaceous deposit, withdrawing cracked and at least partially desulfurized hydrocarbon mixture from said catalytic cracking zone, withdrawing catalyst contaminated with carbonaceous deposit from said catalytic cracking zone, regenerating and heating said catalyst to a temperature of at least about 975° F. to about 1075° F. by combustion of said carbonaceous deposit, regulating the flow of said balance of catalyst through said desulfurizing zone to provide a catalyst to oil ratio of about 1 to 4 to maintain said desulfurizing zone reaction temperature at about 650° to about 850° F. and regulating the flow of the combined streams of catalyst from desulfurizing zone and said by-pass zone through said cracking zone to provide a catalyst to oil ratio different to the aforesaid catalyst to oil ratio and about 4 to 8 to maintain said cracking zone reaction temperature.

3 A process for reforming and desulfurizing a hydrocarbon mixture which comprises introducing active particle-form solid catalyst at a temperature of about 825° F. to about 1075° F. into two reforming zones A and B, said catalyst combining activity for reforming hydrocarbons with activity for hydrogenating organically combined sulfur in a hydrocarbon mixture to hydrogen sulfide, flowing said catalyst through said reforming zones, flowing catalyst from said reforming zone A only into and through a desulfurizing zone, introducing a hydrocarbon mixture at about 650° to about 850° F. into said desulfurizing zone, flowing said hydrocarbon mixture through said desulfurizing zone in contact with said catalyst to provide an at least partially desulfurized hydrocarbon mixture and to produce a carbonaceous deposit on said catalyst, regulating the flow of said hydrocarbon mixture through said desulfurizing zone to provide a liquid space velocity of 0.25 to 1.0 v./v./hr. and to provide a catalyst to oil ratio of about 1–4 to maintain a reaction temperature of about 650° F. to about 850° F., introducing said at least partially desulfurized hydrocarbon mixture into said reforming zones A and B, proportioning the feed of at least partially desulfurized hydrocarbon mixture to said reforming zones A and B to provide a liquid space velocity of about 1 to about 3 v./v./hr. in each of said reforming zones while providing a catalyst to oil ratio in each of said zones A and B different to the aforesaid catalyst to oil ratio and about 4 to about 8 to maintain a reaction temperature of about 825° to about 1025° F., flowing said partially desulfurized hydrocarbon mixture through said reforming zones in contact with said catalyst to produce a reformed desulfurized hydrocarbon mixture and to produce a carbonaceous deposit on said catalyst, withdrawing reformed desulfurized hydrocarbon mixture from said reforming zones, withdrawing catalyst contaminated with carbonaceous deposit from said reforming zone B, withdrawing catalyst contaminated with carbonaceous deposit from said desulfurizing zone,

combining said withdrawn catalyst, regenerating and heating said catalyst to a temperature of about 825° F. to about 1075° F. by combustion of said carbonaceous deposit, and recycling said heated catalyst to said reforming zones.

4. In the method for subjecting hydrocarbon mixtures to at least two different conversions in a plurality of reaction zones, one of said reaction zones being at a higher temperature than the other which comprises introducing a given quantity particle-form catalytic material catalyzing the reaction in all reaction zones at at least said higher temperature into one of a plurality of reaction zones, flowing said given quantity of particle-form catalytic material through all of said reaction zones, contacting all of said given quantity of particle-form catalytic material with reactant in each of said reaction zones, regulating the flow of reactant to each of said reaction zones and regulating said given quantity of particle-form catalytic material to establish relatively mild reaction conditions in one of said reaction zones and relatively severe

reaction conditions in the others of said reaction zones, the improvement which comprises contacting only a part of said given quantity of particle-form catalytic material with reactant in the reaction zone under relatively mild reaction conditions.

5. The improvement in the process of claim 4 wherein the reactant contacts only about 60 to about 80 percent of the given quantity of catalytic material in the zone under relatively mild reaction conditions.

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