



US 20070293711A1

(19) **United States**(12) **Patent Application Publication**
Bakshi(10) **Pub. No.: US 2007/0293711 A1**(43) **Pub. Date: Dec. 20, 2007**(54) **LOW COST HIGH YIELD ISO-OCTENE/
ISOOCTANE PROCESS WITH CAPABILITY
TO REVAMP THE MTBE UNITS****Publication Classification**(51) **Int. Cl.**
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Technologies LLC, Katy, TX (US)**(21) **Appl. No.:** **11/454,044**(22) **Filed:** **Jun. 15, 2006**(57) **ABSTRACT**

This invention covers a process for dimerizing of isobutylene to Iso-octene and unique configuration is being disclosed, where the Feed is diluted to low level with recycle which has essentially no Iso-octene, dual catalyst system, new selectorator (IPA) and successive catalyst stages if needed to enhance the conversion. The process is very selective and provides higher isobutylene conversion.

Additionally the invention also covers the hydrogenation of olefins to Paraffin, Iso-octene to Iso-octane product under moderate conditions and with dual or single catalyst system.

RHT Iso-Octene Process

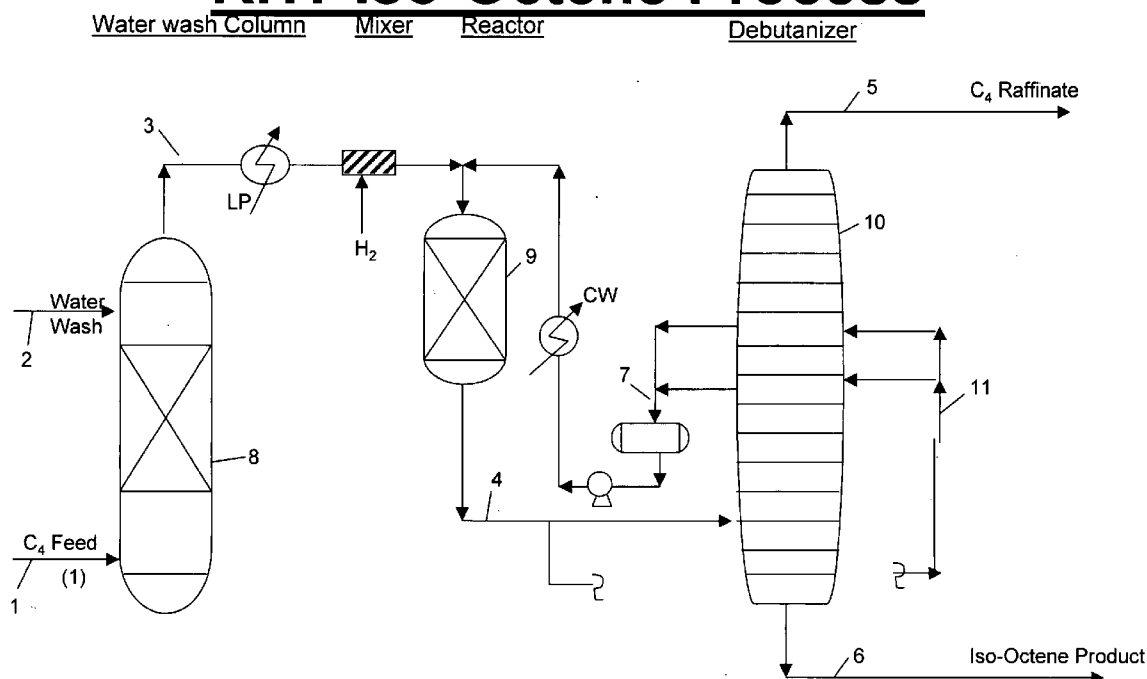


Figure 1
RHT Iso-Octene Process
Water wash Column Mixer Reactor Debutanizer

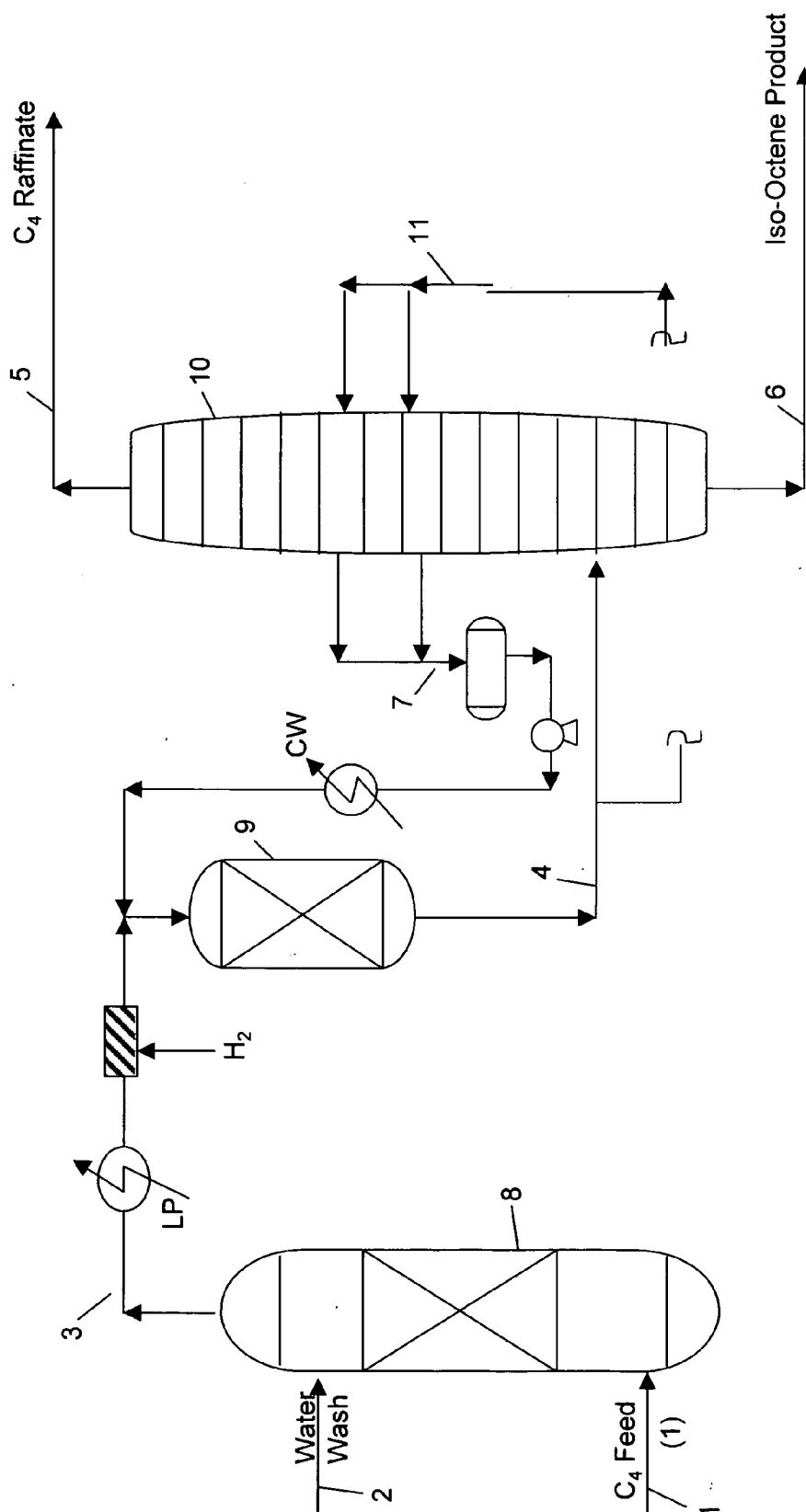


Figure 2

RHT Iso-Octene Process

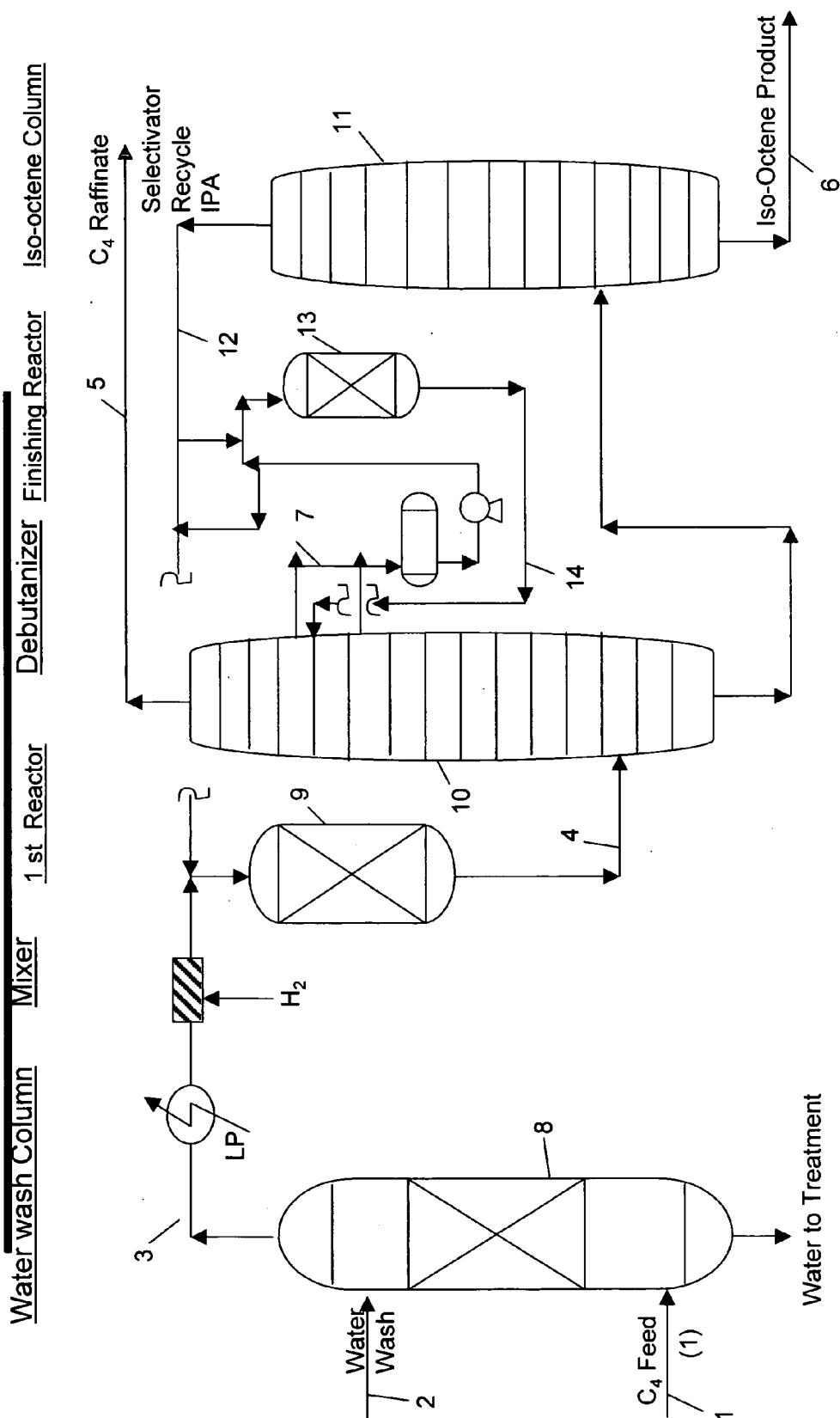


Figure 3

RHT Iso-Octene Process

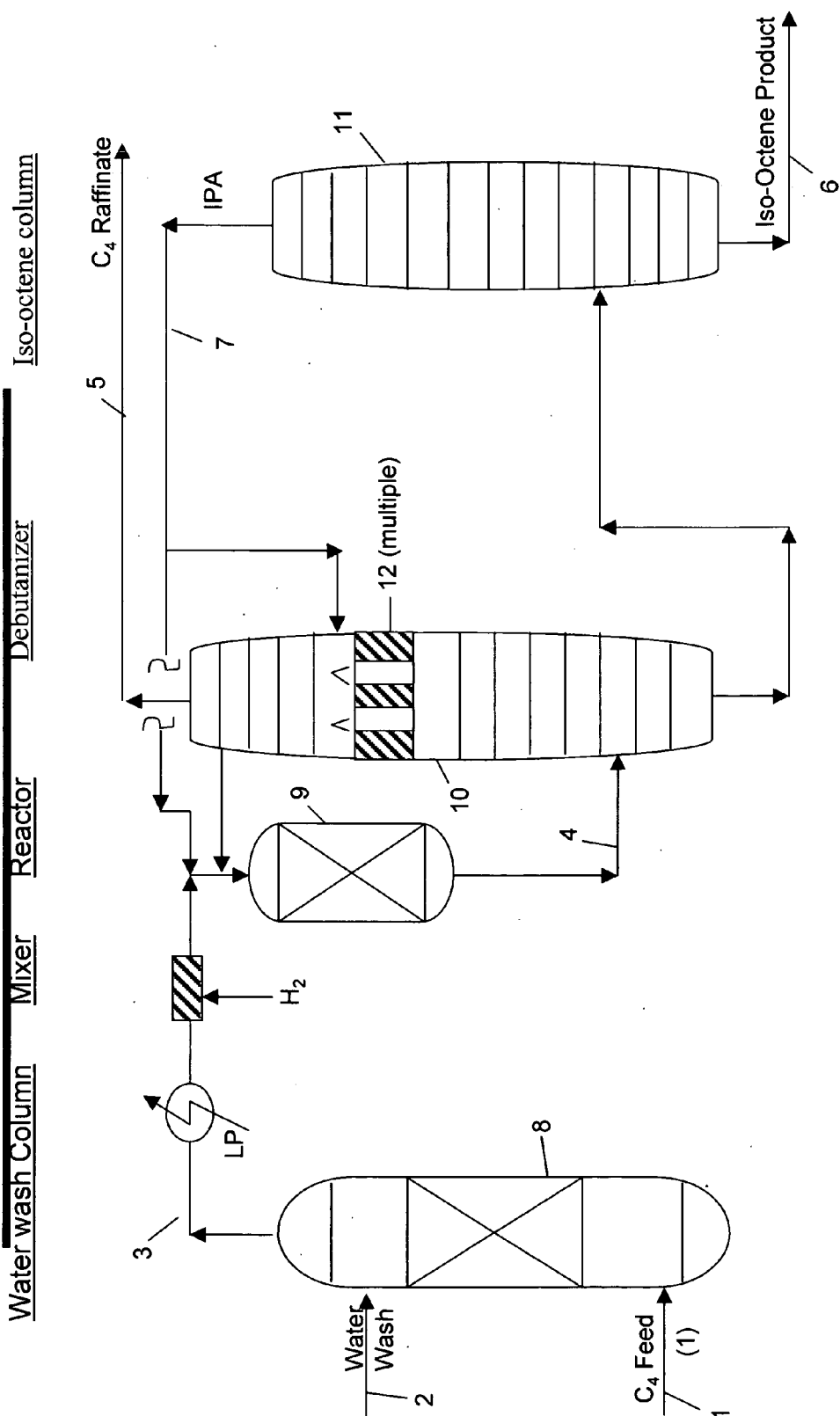


Figure 4

RHT Iso-Octene Process

Revamp of Conventional MTBE Unit

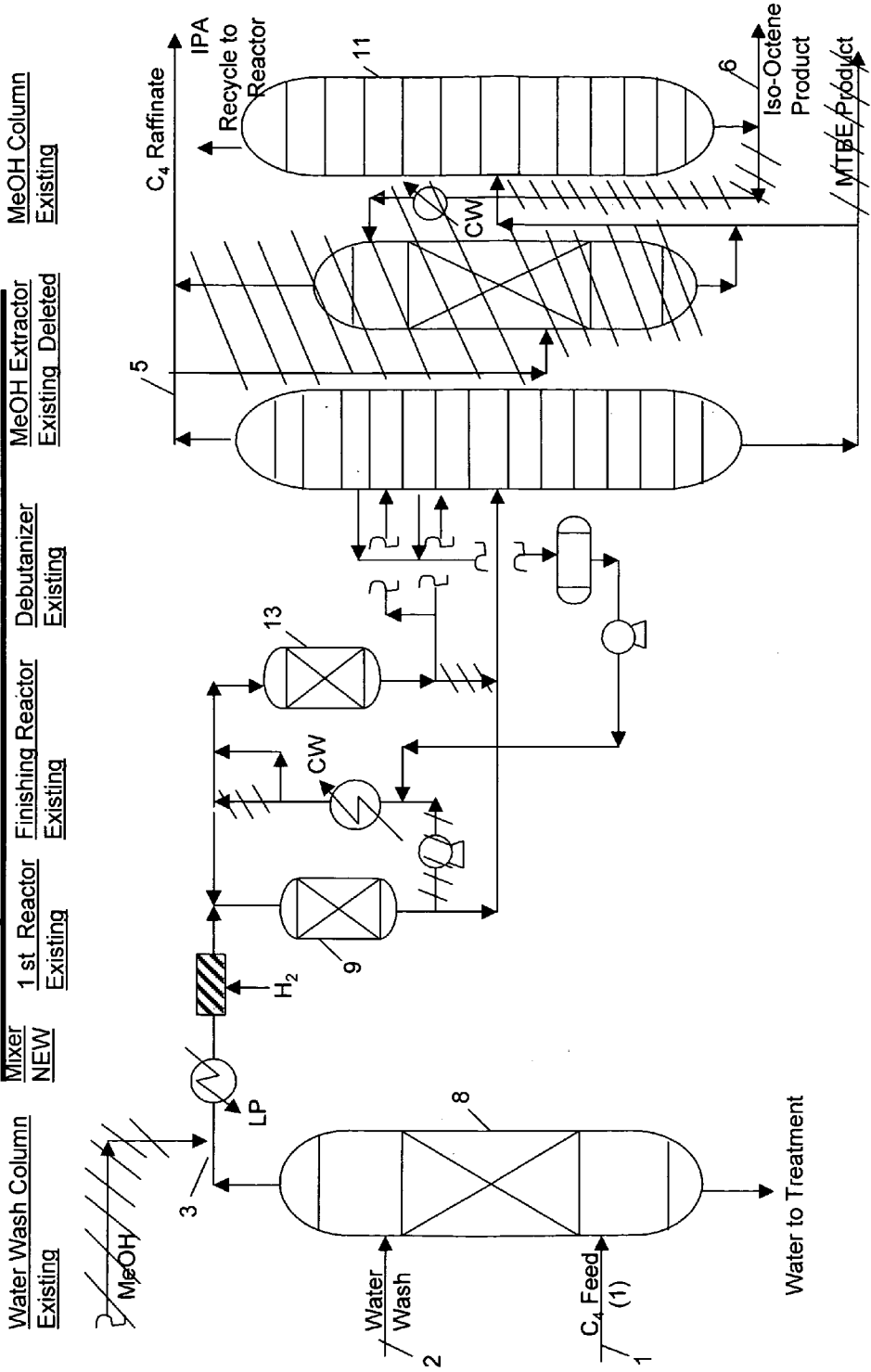


Figure 5

RHT Iso-Octene Process

Revamp of Reactive Distillation MTBE Unit

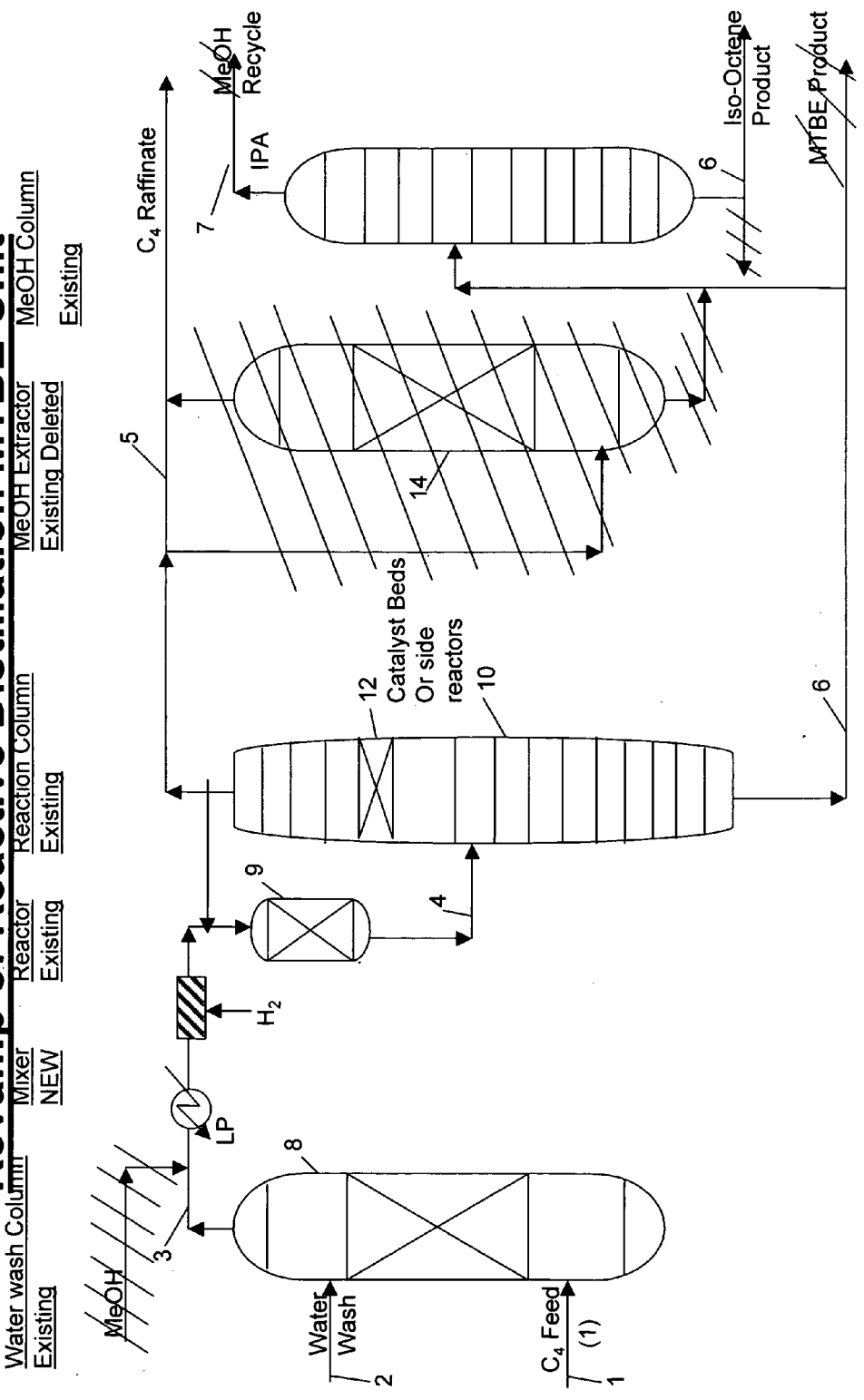
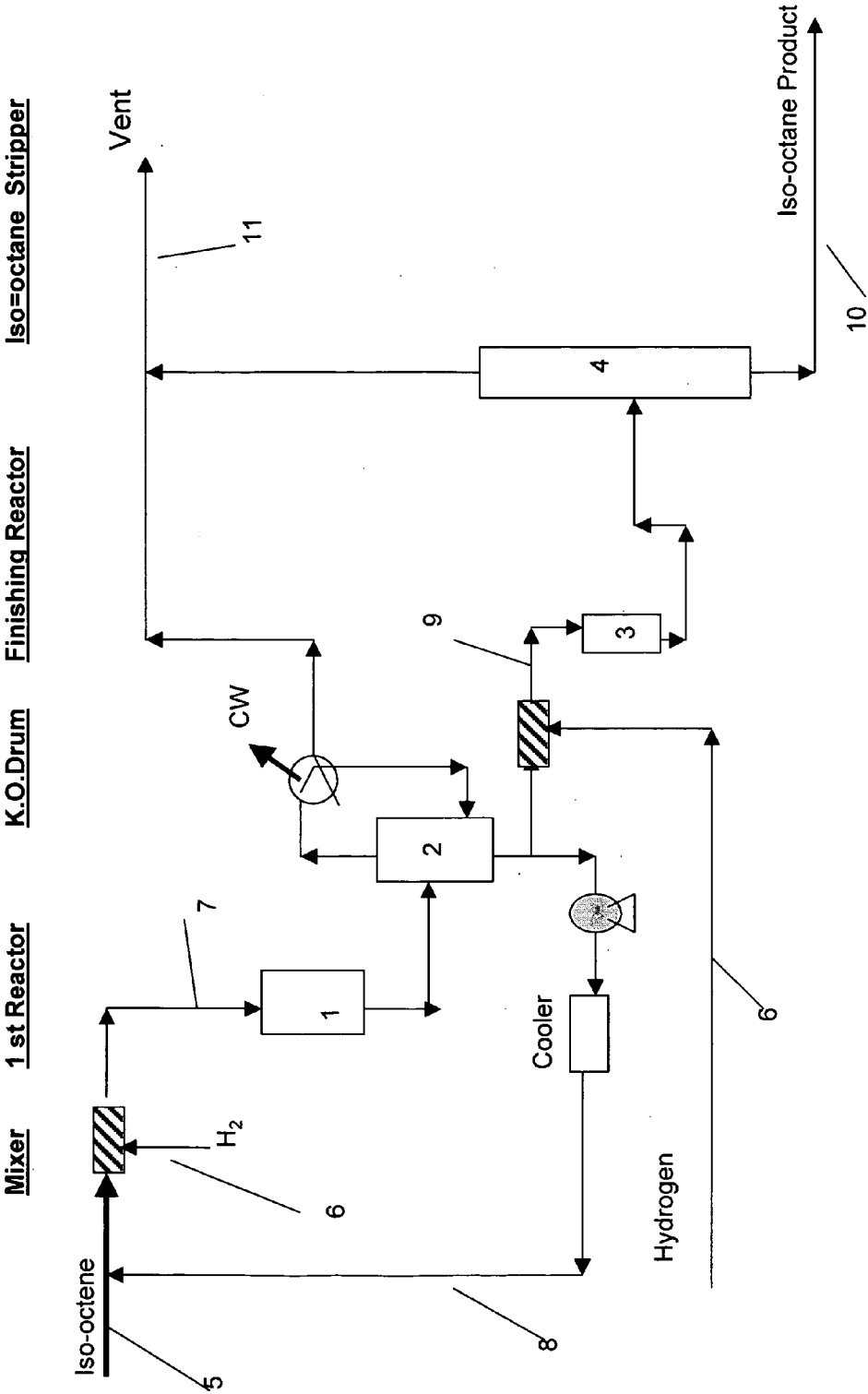


Figure 6

RHT Iso-octene to Iso-octane Hydro



**LOW COST HIGH YIELD ISO-OCTENE/
ISOOCTANE PROCESS WITH CAPABILITY
TO REVAMP THE MTBE UNITS**

FIELD OF THE INVENTION

[0001] The invention relates to producing dimer of Isobutylene especially but covers the dimerization of Isoamylenes as well. The Isobutylene dimerization provides a dimer but some of the normal butylenes' react with iso-butylene to produces some of isomers of these dimers. This dimer which is di-isobutylene is called commonly as Iso-octene is high octane compound similar to MTBE but without the environmental problems of MTBE. The major problem is this product is essentially olefinic and when there are specification as regards to olefin than it will have to be hydrogenated to Isooctane. Most of the MTBE plants can be converted to Iso-octene with little investment but one needs some higher capital investment for hydrogenation of Iso-octene to Iso-octane. Additional drawback is that the Isooctene yield compared to MTBE is reduced by about 70 percent. The art of this invention relates specifically to a new selectivator for the catalyst and also unique configuration so as to produce higher selectivity product and enhancing the yield as well. This will be explained fully in the Figures so as to make it more understandable to the individuals who are familiar with the art of catalytic reactions.

[0002] The invention also covers the hydrogenation of Iso-octene to Iso-octane (to 99% hydrogenation of olefins) in dual catalyst system at lower pressure than the competing technologies, reducing the cost.

BACKGROUND OF THE INVENTION

[0003] Low molecular weight unsymmetrical Ethers such as MTBE, ETBE are produced from iso-olefins and methanol/Ethanol reaction in the presence of acidic sulfonated ion exchange catalyst (e.g. Amberlyst 15 or 35 or equivalent) to produce ethers and are commonly added to the gasoline so as to reduce the pollution due to better burning qualities of these Ethers and Lower vapor pressure as well, which provide good burning gasoline, due to additional oxygen added through alcohol, and the combustion products have reduced CO in the combustion products. As this addition of Ethers was mandated by the Clean Air act of 1990 by EPA. These ethers have much higher octane and lower RVP of the gasoline blend that reduces the VOC's in the atmosphere. Addition of these compounds works as diluent also, which in turn reduce the other components of the gasoline blend like benzene, aromatics and olefins. In recent years due to leakage of MTBE from the gas stations storage tanks, some leaks from using it in water skis in lakes, and as solubility of the MTBE in water is high, it has created controversy as regards to suitability of the ethers in gasoline especially in USA. Some over 20 odd states in USA have banned Ether addition in gasoline, and other states might follow the trend, though it is still being used in RFG in some states in USA. In USA approximately 230,000 bbl/d of Ethers was being used in the gasoline, and if it is taken away as being suggested and is being forecasted, it will have at least about 70,000 bbl/d of shortfall of gasoline if Iso-octene is produced. Thus producing of Iso-octene via this route will be a low cost option. But if the Isobutylene can be alkylated with other normal olefins in the alkylation plant (which is normally being done for n-butenes if MTBE units are upstream)

and lot of the Alkylation plants will have revamped any way. The product will be higher than the Ethers but of lower octane. But one should note that alkylate is one of the most desirable component of the gasoline pool with reasonable high octane, no aromatics and no sulfur. But the alkylation plants need much higher investment and some cases would make economic sense to produce Iso-octene and/or iso-octane via dimerization route and then if need be hydrogenating the product to reduce the olefin content, and it all depends on the economics of each plant and the specification and the complexity of the refinery which produces the gasoline components.

[0004] The invention is in the field of dimerization of isobutylene in the presence sulfonated resin catalyst (e.g. Amberlyst 15 or 35 or equivalent), together with an trifunctional catalyst which is essentially resin catalyst doped into palladium (two bed approach in the reactor) and a new selectivator for solvating the catalyst which is Isopropyl alcohol. The configuration is provided to dilute the isobutylene in the feed to 5% or less by unique configuration and recycle of Iso-propyl alcohol and dual bed catalyst provides selective conversion of Isobutylene to dimer (Iso-octene), essentially 10 to 20% of the 1-butene plus 2-butenes also goes in the reaction to form codimers. In the reaction some trimer is also formed with small amount of tetramer and also some C8 Ethers as will be shown in the reaction Chemistry section of this patent. The palladium-doped resin catalyst selectively hydrogenates the butadiene and also stabilizes the olefins, which provide the longer catalyst life, as it does not polymerize on the catalyst.

[0005] The present disclosure and the art describes a process for producing Iso-octene and Iso-octane by dimerizing the isobutylene in C₄ stream in the fixed bed down flow reactor(s). In general, isobutylene dimerization process is done in the presence of similar acid catalysts that are used for etherification. We have selected a dual and different catalyst to do the dimerization to enhance the catalyst life. Essentially, the process uses an art of using a small amount of selectivator for solvating the catalyst that helps in the reactions sites to be available for the reaction. The catalyst pore size and properties are selected for enhancing the catalyst activity/life. The special catalyst have been listed in the later process description and are claims of the process so as to make dual catalyst beds an art claimed by this process together with the special selectivator/solvating agent.

[0006] The Hydrogenation is designed either to use dual catalyst system, Nickel and followed by Palladium in the finishing reactor (one can use either of the catalyst in both the reactors if so desired). Provision is there to use Palladium Platinum catalyst in the finishing Reactor as an extension of this invention.

SUMMARY OF THE INVENTION

[0007] The process in this art claims that if feed has small amount of propylene (1 to 3%) which will be converted to isopropyl alcohol with small amount of water and iso-octene produced in the reactor which is taken as a bottom product in the debutanizer column. The Isopropyl alcohol will be recycled back to the reactor so as to have low requirement of propylene in the feed, propylene can be reduced to about 0.5% in the Feed, based on the losses in the process. The process in this art requires that IPA (isopropyl alcohol) be about 0.5% to 3.0% by wt in the C₄ feed to the reactor.

[0008] The Feed is water washed to remove the basic compounds in the feed and metal impurities especially acetonitrile which is well known catalyst poison for the etherification ion exchange catalyst. After the water wash, the Feed with slight amount of propylene is heated to the reaction temperature and is mixed with stoichiometric amount of hydrogen to hydrogenate the butadiene, and mixing it with recycle stream before sending it to the reactor. The feed is reacted to hydrogenate the butadiene with trifunctional catalyst and also forms the dimer in the down flow fixed bed reactor in both beds of catalyst. The recycle stream of Isopropyl alcohol (IPA) and the unreacted isobutylene with other C₄ components in the feed are recycled to the reactor so as to have low concentration of isobutylene in the reactor. This provides low conversion per pass in the reactor and it helps in having better selectivity. The 6 figures are herewith attached to describe the different configurations to provide the best catalyst activity, yield and selectivity.

[0009] The Isobutylene dimerizes and produces Iso-octene and also some side reactions takes place which produce the isomers of Iso-octene reacting with isobutylene and other straight chain olefins. The configurations, catalyst selection, operating conditions are chosen to give best results for selectivity and yield, together with enhancing the catalyst life. In the reaction some trimer and very small amount of tetramer are also formed, together with small amount of C₈ ethers.

[0010] Similar to the etherification process, once the reaction has taken place in the Fixed Bed Reactor or Reactors as shown in the Figures, the reactor effluent goes to the debutanizer column, where Iso-octene product is taken as bottom product and C₄ non reactive stream is separated as overhead product. The selectivator (IPA) and non-reactive C₄ stream can be taken as sidedraw and C₄ stream without IPA can be taken overhead. The overhead stream is normally sent to battery limit or alkylation unit. An alternate of this is that one can take the Isooctane and IPA in the bottom and send these to another column (existing methanol or alcohol column) and separate the IPA overhead and recycled to the reactor and bottom is Iso-octene product, this is very convenient in the case of revamp of MTBE unit. In the existing MTBE unit, Methanol recovery column is available to do this separation. The Methanol extractor can be used for any other use to enhance the yield and catalyst life or is available as idle equipment. As RHT flow sheets, show that unreacted reactants can be recycled from debutanizer with the selectivator, as a sidedraw, to a side reactor or bulk catalyst can be installed in the debutanizer as shown in the FIGS. 3 and 5, to enhance the conversion.

[0011] The advantages of the disclosed process are an art of improved catalyst system (dual catalyst beds Resin doped with palladium and resin catalyst Amberlyst 15 or 35 or equivalent), new process configuration, increased catalyst life due to selective hydrogenation butadiene and a new and improved selectivator IPA are at the heart of the process. Additionally it is much better option than the proprietary catalyst processes, which are expensive and use single source supplier, and provide lower conversion and selectivity (it as for MTBE). The RHT process has additional advantage of simple reactor design, no cumbersome catalyst loading requirements. The process has the advantage of changing the catalyst while the unit is in operation. The major breakthrough is that by recirculation of the some the side draw liquid the feed isobutylene concentration is

brought into range of one third to one fifth of the virgin feed concentration by dilution, which provides low conversion per pass and high selectivity. The product is sent back to the same location from where the sidedraw was taken out from column, so there is no effect on the debutanizer size. The reducing per pass conversion by dilution provides longer catalyst life and better yields and selectivity and new selectivator of Isopropyl Alcohol are the major claims and benefit of the process. As the boiling point difference of MTBE and Iso-octene are far apart (about 100 F), there is no problem in separation of C₄'s and the Iso-octene in the existing MTBE column if one returns the reactor effluent at the side draw location.

[0012] The invention covers the hydrogenation of iso-octene to iso-octane catalytically under milder conditions (lower pressure) and using a configuration which helps to enhance the hydrogenation due to dual catalyst system and is lower cost. The pressure and temperature in the reactor are in the range of 250 psig to 450 psig, (preferably closure to 250 psig) and temperatures are in the range of 200 to 500 F (preferably closure to 300 F) and hydrogen about 1.5 to 2.0 times the stoichiometric (closure to 1.30 times) are used in the process. The WHSV in the first reactor is in the range of 1 to 4 (preferably close to 2 to 3) and in the finishing reactor 3 to 6 (preferably closure to 4 to 5).

[0013] This unique feature will be apparent to one who is skilled in the art from the figures and claims and brief description of the figures.

BRIEF DESCRIPTION OF THE FIGURES

[0014] FIG. 1 is a simplified process flow diagram. The Feed stream 1 is washed in column 8 with water wash. The Feed stream 3 is heated to the reaction temperature and is mixed with hydrogen and is sent to the reactor item 9 which has dual catalyst. The feed to the reactor is mixed with as illustrated in the figure, with the selectivator and some of the side draw(s) or total draw(s) off stream 7, (which have some of unreacted isobutylene) taken from the debutanizer. This recycled stream to the reactor is provided so as to enhance the conversion, selectivity and product yield. The side draw quantity from the reactor is fed back to the column by stream 11 at the same location, hence this recycle products do not effect the column size. The recycled side draw streams to the reactor reduces the need for additional reactor and provides enhanced conversions and yields, and with proper design there is no effect on column and energy requirements. The C₄ are taken as stream 5 from the debutanizer item 10, and Iso-octene product is taken as stream 6. The reactor temperature is 100 to 120 F at the inlet and 140 to 150 F at the outlet of reactor and the pressure is kept at about 100 to 175 psig and it is essential that the reaction is done in liquid phase.

[0015] FIG. 2 is another mode of the simple process flow diagram where again Feed stream 1 is washed with water in column 8 and stream 3 after water wash is heated and mixed with hydrogen and is sent to the first Reactor item 9, which is mixed with stream 12 which is recycle IPA the selectivator and some of the draw off from stream 7. The Reactor effluent stream 4 is sent to debutanizer item 10 where C₄ and iso-octene is separated. Some of C₄ are taken as draw off from the debutanizer stream 7, which are recycled to first reactor and also to enhance the conversion are converted in the second Reactor Item 13 and the Reactor effluent stream a4 is sent back to the column for separation. The iso-octene

together with IPA are sent to the column where IPA is taken overhead and is recycled to both the Reactors via stream 12 and the Iso-octene is taken as bottom product as stream 6 and is sent to OSBL or for hydrogenation to produce Iso-octane as shown in FIG. 6. The configuration is similar to FIG. 1 except another reactor is added to enhance the conversion, selectivity and yield, (similar to FIG. 1), by taking a side draw(s) from the debutanizer and this stream is reacted in the side reactor in the presence of catalyst. The idea here is to do the reaction and conversion under controlled conditions so as to get the best yield and less catalyst deactivation. As in FIG. 1 the selector is distributed in both the reactors through stream 12. Additionally, the Iso-octene and the selector is taken in the second column overhead product and distributed into both the reactors. The C₄ stream is taken as overhead from the debutanizer column as stream 5 and is sent to alkylation or LPG system

[0016] FIG. 3 is another mode of configuration to enhance the yield and conversion and selectivity and most of the elements are similar to FIG. 1 up to the first Reactor and the backend after the debutanizer. The first reactor does the reaction same as in FIG. 1, there is always IPA selector used in all the configurations shown in all the Figures. To enhance the conversion bulk catalyst can be installed in the debutanizer item 12, so that the reflux liquid is converted to iso-octene, and the vapor is bypassed through the chimney trays. This bulk catalyst is installed on the Johnson Screen grid and hold down plate is used to keep the catalyst in the debutanizer. The design provides pressure balance in the chimney tray/trays by restricting the chimney flow so that slight liquid head is provided so as liquid to go through the catalyst in downflow manner as is the case normally. This restriction in chimney tray of the special nature is being claimed by the art of this invention. There could be multiple beds in the column but the bed height required is very small compared to the reactive distillation application. This is bulk catalyst, so the cost of catalyst is very low and is easy to install. Essentially the FIG. 3 configuration is similar to FIG. 1 except installing the bulk catalyst in the column. All the reaction is done in liquid phase. The Reactors, which use boiling in the reactor, are not efficient as some of the reactants go in vapor and the catalyst utilization is not optimum.

[0017] FIG. 4 is a MTBE unit process flow diagram, which is being converted to Iso-Octene process. The process flow diagram modification for revamp have been shown how to modify so as to be similar to FIG. 2, but it can be modified to be FIG. 1 or 3 easily if so required (based on the requirements of the process) to enhance the conversion and economics and capital investment requirements.

[0018] FIG. 5 is the similar process flow diagram to FIG. 1 to 4, which covers all the options. This FIG. 5 includes recycling the Feed to first reactor, and having bulk catalyst item 12 installed in the debutanizer column together with revamping of the Reactive distillation column of MTBE unit at low cost, having a higher conversions, better selectivity and catalyst life. In FIG. 4 and FIG. 5, alcohol extractor is deleted, but to save capital cost and to enhance the catalyst life it can be converted to iso-octene reactor and is being claimed by this art and patent claim.

[0019] FIG. 6 is the hydrogenation of iso-octene to iso-octane. The Iso-octene from the OSBL or directly from the debutanizer is pumped through line 5 to the reactor pressure, it is mixed with the recycle stream 8 which provides the

dilution and heat sink, mixed with hydrogen which is fed through line 6 and all are mixed by the inline Mixer before feeding to the Hydrogenation Reactor through line 7 at the reaction temperature and pressure. The Reactor product is flashed in Drum item 2, hydrocarbon vapor are condensed and sent back to drum. The vent is sent to fuel gas system. The Liquid from item 2 is fed to the Finishing Reactor item 3, after mixing with hydrogen by the inline Mixer. The Reactor effluent is fed to the Iso-octane Stripper item 4, to stabilize it. The Iso-octane product is taken as bottom product and cooled before sending it to storage.

DETAILED DESCRIPTION OF THE INVENTION

[0020] The major art and know how described here is a disclosure of producing Iso-octene by dimerizing isobutylene in the C₄ Stream from FCC, Steam Crackers, thermal crackers or on purpose dehydrogenation units. The reaction is performed in the presence of a new solvator/selector (IPA) which is helpful to keep the catalyst in solvated form, which stops the polymerization of olefins. The operating conditions and recycled streams are provided so that low conversion per pass is achieved due to dilution effect, and the total conversion of isobutylene is essentially kept to be optimum and is more than any other process. As reaction is pretty fast, one does not need too much of catalyst. The feed is washed for basic compounds that are poison for the catalyst similar to Etherification process. The present art provides a small amount of trifunctional catalyst so as to reduce any deactivation due to diolefins/butadiene. The dilution effect makes the process selective, due to low conversion per pass but the conversion is higher than the conventional processes on the fresh feed basis, the other straight chain olefins react to a lower degree with isobutylene under low per pass conversion, compared to other processes. The configuration provides reaction of the straight chain olefins lower compared to conventional scheme and the n-olefins are good feed stock for Alkylation. The codimers produced have lower octane than iso-octene. The catalyst used in this process is the same Ambryst 15, 35, 36 and CH10, K2431, K2621, K2629 or K2624 or equivalent. The resin catalyst doped with Pd (CH10 or K2624) or normal palladium or Nickel catalyst for hydrogenation is provided as dual layer bed, with WHSV with Pd doped catalyst. Pd or Nickel catalyst of 2 to 30, preferably in the range of 8 to 25 so as to selectively saturate the butadiene to olefin and also stabilize the olefins in the feed. As regards to other standard resin catalyst provided, WHSV is in the range 2 to 20, preferably in the range of 4 to 8.

[0021] The disclosed method and art can be understood by referring to the attached figures for the individuals who are familiar with the art, which are described in detail description of the figures herein. It should be understood that pipelines are in fact being designated when streams are identified and that stream are intended, if not stated when materials are mentioned. More over, flow control valves, temperature regulating and measuring devices, pumps, compressors, reboilers, condensers, coolers, heaters and drums and the like are understood as installed and operating in conventional relationships to the major items of equipment which are shown in the drawings and discussed hereinafter with reference to the continuously operating process of this invention and art there in. All of these valves, devices, pumps, and compressors, as well as heat exchangers, accu-

mulators, condensers and the like are included in the term auxiliary equipment. It is also understood that any of the equipment or reactors can be decoupled by installing a drum in between two equipment items, so as to operate the these equipment at different conditions. It is an ability of ordinary skill in the art to implement such auxiliary equipment, as needed, in view of the present disclosure.

[0022] FIG. 1 illustrates an embodiment of the disclosure process. Iso-olefin Feed 1 should have small amount of propylene so as to make Isopropyl alcohol (IPA) which works as a Solvator/Selectivator. It is normal practice to wash the feed with water or run it through adsorbent where all the impurities are removed which deactivate the catalyst. After the water wash, C₄ Feed through line 3, is mixed with hydrogen before it is sent to stand alone reactor 9, if dual function catalyst is being used. Stand alone reactor 9 can be fixed bed down flow, or upflow reactor and could have a recycle with cooler if required. If one uses single function catalyst like Amberlyst 35, then no hydrogen feed is required. Effluent 4 from the reactor is fed to the column 10. Heavy components like Iso-octene together with some of the IPA goes to the bottom of the column and are taken as product through line 6. The Lighter components e.g. other C₄'s and unreacted isobutylene together with IPA goes in the top section of the column 10. Partial draw off or total draw off is taken from one or multiple places through line 7 and after cooling is fed the first reactor for additional conversion. So as to optimize the column size, reactor effluent is distributed in the same proportion as was put in through lines 4 and 11. The dual function or single catalyst would be used so as to meet the catalyst life.

[0023] In the embodiment illustrated in the FIG. 1, reactants are exposed to the catalyst at low concentration due to recycle from the column, and in doing so the selectivity and conversion achieved are much better than the fresh Feed. If catalyst quantity provided is adequate to have WHSV of about 4 for the combined catalyst (dual function and single function) and the pressure and temperature are kept at 125 psig to 150 psig and temperature of 130 to 150 F is kept to provide optimum conversion and product quality. One has to see that minimum of 0.5 to 3% of IPA is in the reactor effluent which is being recycled with unconverted Feed through line 7. As shown in the FIG. 1 distillation is done to take the IPA with C₄'s in the draw off and that is being recycled. The non-reactive C₄ stream and normal olefins are taken overhead. In the normal feed very small amount of propylene in the Feed is required to make the additional IPA, which has been lost in the bottom and overhead streams.

[0024] FIG. 2 in this embodiment shows similar process flow diagram as FIG. 1, C₄ Feed is fed through line 1 and is washed in water wash Column (WWC). The C₄ Feed after washing, through line 3, is mixed with hydrogen before it is sent to stand alone reactor 9, if dual function catalyst is being used. Stand alone reactor 9 can be fixed bed down flow, or upflow reactor and could have a recycle with cooler if required. If one uses single function catalyst like Amberlyst 35, then no hydrogen feed is required. Effluent 4 from the reactor is fed to the column 10. Heavy components like Iso-octene together with the IPA goes to the bottom of the column and is fed to the Iso-octene column where product Iso-octene is taken through line 6. The lighter components in debutanizer e.g. other C₄'s and unreacted isobutylene is taken as overhead product, but some of the C₄'s are taken as side draw or multiple side draws through line 7 and are

isobutylene is converted to Iso-octene in side reactor(s) 13. The reaction product from the side reactor is sent to the column where they have withdrawn from or some other location where concentration is similar, but without increasing the Column diameter or duties. As shown that IPA is taken overhead in Iso-octene Column 11 as overhead product and is recycled to both the reactor's first reactor 9 and the sidedraw reactor 13. The dual function or single catalyst would be used so as to meet the catalyst life and is the claim of the invention. The operating pressure, temperature is in the same range as mentioned in FIG. 1 above.

[0025] FIG. 3 is another variation of FIGS. 1 and 2, C₄ Feed is fed through line 1 and is washed in water wash Column (WWC). The C₄ Feed after washing, through line 3, is mixed with hydrogen before it is sent to stand alone reactor 9, if dual function catalyst is being used. Stand alone reactor 9 can be fixed bed down flow, or upflow reactor and could have a recycle with cooler if required. If one uses single function catalyst like Amberlyst 35, then no hydrogen feed is required. Effluent 4 from the reactor is fed to the column 10. Heavy components like Iso-octene together with the IPA goes to the bottom of the column and is fed to the Iso-Octene column where product Iso-octene is taken through line 6. The lighter components in debutanizer e.g. other C₄'s and unreacted isobutylene are taken as overhead product. With the reflux some of isobutylene is reacted in the column bulk catalyst shown as 12 (can have multiple beds). IPA is taken as overhead product in Iso-octene Column 11, where IPA is recycled to the first stand alone reactor 9 and also to Column bulk catalyst section 12. These details of operating conditions and WHSV will be illustrated in a separate section. The debutanizer catalyst 12 is provided as bulk catalyst on the grating and Johnson screen is used to see that catalyst does not pass through to bottom of the column. The catalyst in the column enhances the conversion. Instead of bulk catalyst one can provide side reactor the other conditions remain the same as for FIGS. 1 and 2.

[0026] FIG. 4 is an embodiment in which it is shown how to revamp the existing MTBE unit. The hatched lines and equipment are to be deleted. Additional reactor in parallel may be required but might not be necessary. So most of the equipment is available and some piping modifications might be necessary. It is possible that all the instruments are adequate. So revamp cost are very low. Operating conditions and catalyst requirements are as for FIG. 1, 2 and 3. In FIG. 4, C₄ Feed is fed through line 1 and is washed in water wash Column (WWC). The C₄ Feed after washing, through line 3, is mixed with hydrogen before it is sent to stand alone reactor 9, if dual function catalyst is being used. Stand alone reactor 9 can be fixed bed down flow, or upflow reactor and could have a recycle with cooler if required. If one uses single function catalyst like Amberlyst 35, then no hydrogen feed is required. Effluent 4 from the reactor is fed to the column 10. Heavy components like Iso-octene together with the IPA goes to the bottom of the column and is fed to the Existing Methanol recovery column (Iso-octene column) where product Iso-octene is taken through line 6. The lighter components in debutanizer e.g. other C₄'s and unreacted isobutylene is taken as overhead product through line 5, but some of the C₄'s are taken as side draw or multiple side draws through line 12 and isobutylene is converted to Iso-octene in side reactor(s) 13 which is existing finishing MTBE reactor but has to be repiped. The reaction product from the side reactor is sent to the column where they have

withdrawn from or some other location where concentration is similar, but without increasing the Column diameter or duties. As shown that IPA is taken overhead in Iso-octene Column 11 as overhead product through line 7, and is recycled to both the reactors, first reactor 9 and the side draw reactor 13 through line 14. The dual function or single catalyst would be used so as to meet the catalyst life and is the claim of the invention. The operating pressure, temperature is in the same range as mentioned in FIG. 1 above. Naturally the Methanol feed system and the methanol Extractor 15 can be used for alternate use in the unit to enhance yield and catalyst life.

[0027] FIG. 5 is illustrates an embodiment in which it is shown how to revamp the Reactive distillation MTBE unit to Iso-octene unit. The hatched lines and equipment are to be deleted. Additional reactor in parallel may be required but might not be necessary. So most of the equipment is available and some piping modifications might be necessary. It is possible that all the instruments are adequate. So revamp cost are very low. Operating conditions and catalyst requirements are similar to as for FIGS. 1, 2 and 3. In FIG. 4, C_4 Feed is fed through line 1 and is washed in water wash Column (WWC). The C_4 Feed after washing, through line 3, is mixed with hydrogen before it is sent to stand alone reactor 9, if dual function catalyst is being used. Stand alone reactor 9 can be fixed bed down flow, or upflow reactor and could have a recycle with cooler if required. If one uses single function catalyst like Amberlyst 35, then no hydrogen feed is required. Reactor effluent through line 4 is fed to the column 10. Heavy components like Iso-octene together with of the IPA goes to the bottom of the column and is fed to the Existing Methanol recovery column (Iso-octene column) where product Iso-octene is taken through line 6. The lighter components in debutanizer e.g. other C_4 's and unreacted isobutylene is taken as overhead product through line 5, but some of the C_4 's are taken as side draw or multiple side draws (not shown) and are recycled to the first reactor to reduce the conversion per pass, enhancing isobutylene conversion to Iso-octene in side reactor 9 which is existing first MTBE reactor but has to be repiped. The reflux in the column can be converted by installing bulk catalyst in the column as suggested in FIG. 3 or can be repiped as side reactors as shown in FIG. 2. Reaction product from the side reactor is sent to the column where they have withdrawn from or some other location where concentration is similar, but without increasing the Column diameter or duties. As shown that IPA is taken overhead in Iso-octene Column 11 as overhead product through line 7 and is recycled to both the reactor s first reactor 9 and the side Draw reactors through line 15 and some to the bulk catalyst in the column, reaction zone if required, though this might not be required. The dual function or single function catalyst would be used so as to enhance the catalyst life and is one of the claims of the invention. The operating pressure, temperature is in the same range as mentioned in FIG. 1 above. Naturally the Methanol feed system and the methanol Extractor 14, can be used for alternate use in the unit to enhance yield and catalyst life.

[0028] Individuals familiar with the skill in the art do understand the importance of removing the basic compounds by Feed water wash system. After water wash, the second major art in Iso-octene Technology is to have), 0.05 to 2.5% of Solvator/selectivator in catalyst (alcohol) with the Feed to provide good catalyst life and low polymeriza-

tion. Here selectivator being used is Isopropyl Alcohol, and any other compound if they are boiling in that range will also recycle which can not be helped. The third art in this embodiment is being used is to have tri-functional catalyst at a very high WHSV (15 to 25), so as to see that the diolefins do not polymerize on catalyst. The other major art in the embodiment is reduce the conversion per pass in the reactor, which enhances the catalyst life and selectivity. The art has already been described so as to be able to use the existing column size by putting the recycle stream flows to at the same location from where these were so that there is no effect on debutanizer design compared to conventional processes. As C_4 and C_8 separation is pretty easy there is no problem in achieving this concept. The last but not the least is the selection of right catalyst and we will here suggest catalyst, which we claim, will provide optimum conversion and yield.

[0029] One of the major skill in the art is to have the clean feed devoid of basic compounds, right catalyst selection, selectivator and per pass conversion to be reduced. The process is for dimerizing the Isobutylene, but it also reacts with some straight chain olefins, which provides isomers with slightly lower octane. The reaction products are sent to the debutanizer where Iso-octane is separated from C_4 stream. Iso octene with other byproducts is sent to existing Methanol recovery column or new column to separate the selectivator and recycle it to the reactor. The bottom product is Iso octene with very good octane and can be hydrogenated to provide Iso-octane, which will provide the product, which will reduce the olefins, concentration in the gasoline pool.

[0030] All the figures show that unreacted feed can be recycled to the first reactor and isobutylene there in would be converted to iso-octene or codimers. It will be diluted as well so the conversion per pass will go down and quality will be good. No doubt the selectivator will be recycled either from this debutanizer or after separating in a second column. The other Option is by putting the side reactors conversion can be enhanced, but the recycle to the first reactor be still kept so as to have low per pass conversion, this is one of the major claim of the process. The column size will not be effected, as the products will be fed at the same location from where they are withdrawn. C_4 and iso-octene separations not difficult so there is no problem in separation and keeping the per pass conversion low in the reactor which provides better selectivity and catalyst life as well.

[0031] Alternatively, the catalyst can be installed in the column as bulk catalyst on a grating with Johnson Screen and a holddown grid, with chimneys for by passing the vapor. There could be more than single bed (multiple beds) and similarly the side reactor can be more than one to enhance the conversion, only major requirement is to keep the conversion low in the reactors and that enough selectivator is there so as to provide the catalyst solvated. Reactions stages can be as desired but normally in this application, two reaction stages will provide the economical conversion of about 95 to 99 wt % isobutylene.

[0032] In this patent, selectivator/solvator which is being used is Isopropyl Alcohol and any other compounds which boil at the same or close boiling compounds will automatically go with IPA and will be recycled to the reactor. The single pass conversion is to kept low so as to get the best selectivity.

[0033] The reaction is done around 100 degrees F. to 160 degrees F. and the reactor pressures are kept at around 95 to

150 psig. The catalyst used is Amberlyst CH10 (palladium or Nickel catalyst for selective hydrogenation, plus Amberlyst 35 or 36, or one can use Lewatit K 2624 plus K 2431 or SP 112-H or equivalent Catalyst in resin family or zeolyte family but not limited to these catalyst or any catalyst which provides acidity for the reaction and the proper properties is acceptable and will be used. The dual catalyst system is claimed by the art in this process as selective hydrogenation is mandatory for the process to enhance the catalyst life, but if one is prepare to sacrifice the catalyst, than one can operate the unit without selective hydrogenation.

[0034] Examples of suitable selector/solvents could be any alcohol which boils below the Iso-octene so that it can be recycled to the reactor. Here RHT process has come up with an IPA selector, which is formed by hydration of propylene in Feed and small quantity of water, which are normally available in the feed with the same resin or acidic catalyst.

[0035] The first reactor operates at about 95 to 175 psig and 100 degrees F. to 190 degrees F. in the presence of above mentioned catalyst, together with selector and dilution so as to reduce the per pass conversion. The iso-olefin (isobutylene) in the Feed can be say from 7% to 60 percent in the C₄ feed stream. The high concentration feeds need careful consideration but the advantages is that some of these Feeds don't have basic compounds and also other olefins are in small quantity so the catalyst life and selectivity can be maintained if heat of reaction or per pass reaction is properly controlled.

[0036] 95 to 99 wt % isobutylene conversions can be easily achieved with a reasonably high Octane product. The selectivity can be kept good so that boiling range of the product is similar to the gasoline boiling range. It is expected that 97 to 99 percent isobutylene is converted, and normal butylenes are converted from 10 to 25%. The product is expected to be about 80 to 90% C₈ olefins and 10 to 20% of C₁₂ Olefins with 0.1 to 1.0% of C₁₆ olefins. But selectivity is much better than most of the processes available in the market due to reduced per pass conversion and lower temperature. Higher temperature and vapor in the reactor provides lower selectivity and conversion so reactor is operated in liquid phase as desired by the reaction kinetics.

[0037] In the embodiment of this patent, art is illustrated that one can get high conversions with one reactor, side reactors, by installing catalyst in the column, and there are advantages of each configuration to keep the conversion low by diluting the feed with recycle which provides high selectivity. For the most of cases, where this application will be applied be first to the existing MTBE units after that one will consider the on purpose MTBE merchant units and there is real advantage in realizing this once the MTBE is phased out. As shown in the FIG. 4 and 5, RHT process with very little additional Capital cost can revamp the conventional or reactive distillation MTBE units.

[0038] The major invention in this embodiment is that using the IPA selector. Dual catalyst to stabilize the feed and reduce the butadiene by selective hydrogenation of the feed, provide dilution to reduce the conversion per pass which improves the selectivity and catalyst life and reduces the exotherm in the reactor, provide side reactors to enhance the conversion or by installing bulk catalyst in the column by

providing vapor bypass of the bed with chimney trays. These are the major claims of this invention for producing Iso-octene.

EXAMPLES

[0039] The following example illustrates the feeds which could be used for making Iso-octene. These could be from multiple sources FCC C₄ Stream, Steam Cracker C₄ Stream and on purpose Isobutane Dehydrogenation units, which can provide good feed for Iso-octene production. The higher concentration feeds need is well suited to this configuration.

C ₄ Feed from the FCC unit:	
Component	wt %
Propane	1.2
Propylene	0.7
Isobutane	23.9
Isobutylene	17.8
1-Butene	13.7
c-2-butene	12.6
t-2-butene	14.3
n-butane	15.3
C ₃ 's	0.5
Total	100.00
<u>Iso-octene Product</u>	
C ₈ olefins	90 to 92%
C ₁₂ Olefins	7.5 to 9.0%
Other byproducts	0.5 to 2.0%
<u>Iso-octane Product</u>	
C ₈ Paraffins	91 to 93%
C ₁₂ Paraffins	7 to 8.5%
Other impurities	0.5 to 2.0%

[0040] The following reaction conditions and yields can be expected from this unit:

Based on the configuration and feed compositions following conditions will be required for the first and Side reactors configuration:

[0041] Inlet Temp (F) 100 to 180 (100 to 130 F preferable)

[0042] Pressure (psig) 100 to 175

[0043] LHSV (hr)⁻¹ 3 to 6

[0044] Iso-olefin Conversion (%) 97 to 99% (overall)

[0045] n-olefin Conversion: Minimize the olefin conversion to Codimers

[0046] Reaction Chemistry

Iso-octene Reactions:

[0047] 2 Isobutylene→Iso-octene

[0048] Isobutylene+n-butykene→Codimers

[0049] Isobutylene+iso-octene→C₁₂ olefins

[0050] Iso-octene+Iso-octene→C₁₆ olefins

[0051] Alcohol+olefins→C₈ Ethers

Iso-octane Reactions:

[0052] C₈ olefins+H₂→C₈ Paraffin

[0053] C₁₂ olefins+H₂→C₁₂ Paraffin

[0054] C₁₆ olefins+H₂→C₁₆ Paraffin

What RHT iso-octene/iso-octane process claims is:

1. A Process for producing Iso-octene Comprising:

A) Dimerizing the isobutylene in the FC C, Steam Cracker, Thermal Cracker or on purpose dehydrogena-

- tion streams, in the presence of sulfonated resin catalyst Amberlyst 15, 35 or 36 or equivalent at moderate temperatures as defined in the process invention. The process uses a top bed of catalyst which is for selective hydrogenation e.g. Palladium, Nickel, Resin doped Palladium, Nickel/Mo, Co/Mo, Ni/W or Pd/Pt etc. but not limited to, so as perform selective hydrogenation of diolefins in the Feed, followed by normal resin catalysts Amberlyst 15, 35, 35 or equivalent. The WHSV is 5 to 15 for first catalyst bed, which is hydrogenation catalyst, and 3 to 6 for the resin catalyst, on fresh Feed basis. The temperature is in the range of 100 to 160 F, and pressure is 100 to 175 psig at the reactor inlet.
- B) Taking total sidedraws or partial sidedraws from the debutanizer after the Iso-octene and heavy's have gone down the column, and recycling it to the 1st Reactor to reduce the concentration of the isobutylene in the reactor. This recycle reduces the isobutylene concentration to half to one fifth compared to fresh Feed isobutylene concentration.
- C) Providing small amount of propylene in the feed so that it is hydrated and makes Isopropyl alcohol (IPA), which is used as solvator/Selectivator to enhance the catalyst activity. This is recycled in the system with the C₄ stream so as to make very small amount of IPA.
- D) To enhance the conversion part of the recycle stream is sent to the side Reactor which enhances the conversion and selectivity. It is claimed that the liquid is returned at the same location from where the sidedraw was taken or at a suitable location, so as to have no effect on size of the debutanizer column design.
- E) The special art in the configuration is being used in the process so as to recycle sidedraw's which provide the dilution and some of unconverted isobutylene is recycled in turn, new selectivator (IPA) to get the best results in conversion to solvate the catalyst, yield and selectivity. The configuration is also invented to install bulk catalyst in the column by installing Johnson Screens in the column, so the catalyst and holddown grid with Johnson screen to secure the catalyst at the top of the bed. This allows easy revamp of the existing reactive distillation applications, but are cumbersome to install catalyst and the cost is higher than the catalyst from the vendor. The art of by passing the vapor with chimney trays or external pipes is being used as these reaction are taking place in liquid phase (vapor does not contribute to the reaction). Multiple beds can be used.
- F) Either sidedraw from the debutanizer can be used to take IPA with C₄ stream, or the IPA together with iso-octene can be sent to another column or existing alcohol recovery column. The existing alcohol recovery column or the Iso-octene column, can be used for the separation of IPA, and is recycled whereas Iso-octene sent to OSBL after cooling or can be sent to Iso-octane unit without cooling as required. The C₄ sidedraw are still taken from the debutanizer column for dilution for the 1st reactor and also feed to the side reactor.
- G) This invention also covers the dimerization of iso-amylene to produce Di-isoamylene. RHT process provides selectively, similar to Iso-octene process.
- H) Normal precautions are taken for removing the poison from the Feed by either water wash or adsorbent media.
2. The method of claim 1,
- A) Where as in the art of this invention uses dual catalyst system. The first bed at the top, in the 1st reactor is a trifunctional catalyst (sulfonated Resin catalyst doped in Palladium e.g. Amberlyst CH10 or Levatit K 2624) or Palladium or Nickel catalyst so as to selectively hydrogenate the diolefins and stabilize the olefins, which enhances the catalyst life. This is done at very high space velocity so as to keep the catalyst cost low. The selective hydrogenation neither in the iso-octene unit or upstream is exclusively being claimed by RHT Iso-octene process and one of the major claims for this application.
- B) Hydrogen is expected to be close to stoichiometric for diolefin selective hydrogenation in the reactor, as the intention is to see that all the hydrogen is consumed and no olefins are saturated.
- C) The process claims the highest yield, low n-butylene loss to codimers, high selectivity and enhanced catalyst life due to dual catalyst bed and also using a better selectivator (IPA) and low isobutylene concentration due to dilution by recycle.
3. The process is designed to hydrogenate the Iso-octene to Iso-octane:
- A) The method of claim 3, the invention uses the art so as to have milder conditions and using two stage approach for hydrogenation of olefins to paraffins, by using, Nickel Catalyst (or Nickel/Molybdenum, Nickel/Tungsten, Palladium, Palladium/Platinum) in the 1st Reactor with excess hydrogen than stoichiometric. Reactor effluent is flashed, the liquid after the flash from first reactor, is recycled to first reactor as heat sink (after cooling to remove the heat of reaction) and part of this liquid is forward feed to the Finishing Reactor which could have either Palladium Catalyst (Palladium/Platinum or Nickel catalyst similar to in the 1st reactor). The invention claims 99% hydrogenation of olefins to paraffins.
- B) The method of claim 3, Where 1st Reactor operates at inlet pressure of 250 psig to 450 psig (preferably closer to 250 psig) and temperature of 200 to 350 F (preferably 260 F), and recycle liquid is provided after the flash as shown in FIG. 6, as a heat sink so as to have temperature rise in the reactor of 50 to 150 F (preferably 100 F). Part of the flashed liquid after 70 to 90% hydrogenation in the 1st Reactor, is sent to the finishing reactor to complete the olefin hydrogenation to Paraffin to 99%.
- C) The method of claim 3, where WHSV in the 1st Reactor is kept in the range 1 to 4 (closer to 2) based on fresh Feed basis, Finishing Reactor WHSV is 2 to 4 (closer to 2). The FIG. 6 shows the detail of this configuration.
- D) The method of claim 3, where the hydrogen is 1.2 to 2.0 times (closer to 1.4 times) the stoichiometric required for olefin saturation to Paraffin. The Reactor is designed to operate in single phase or two-phase operation, which ever is most cost effective.

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