

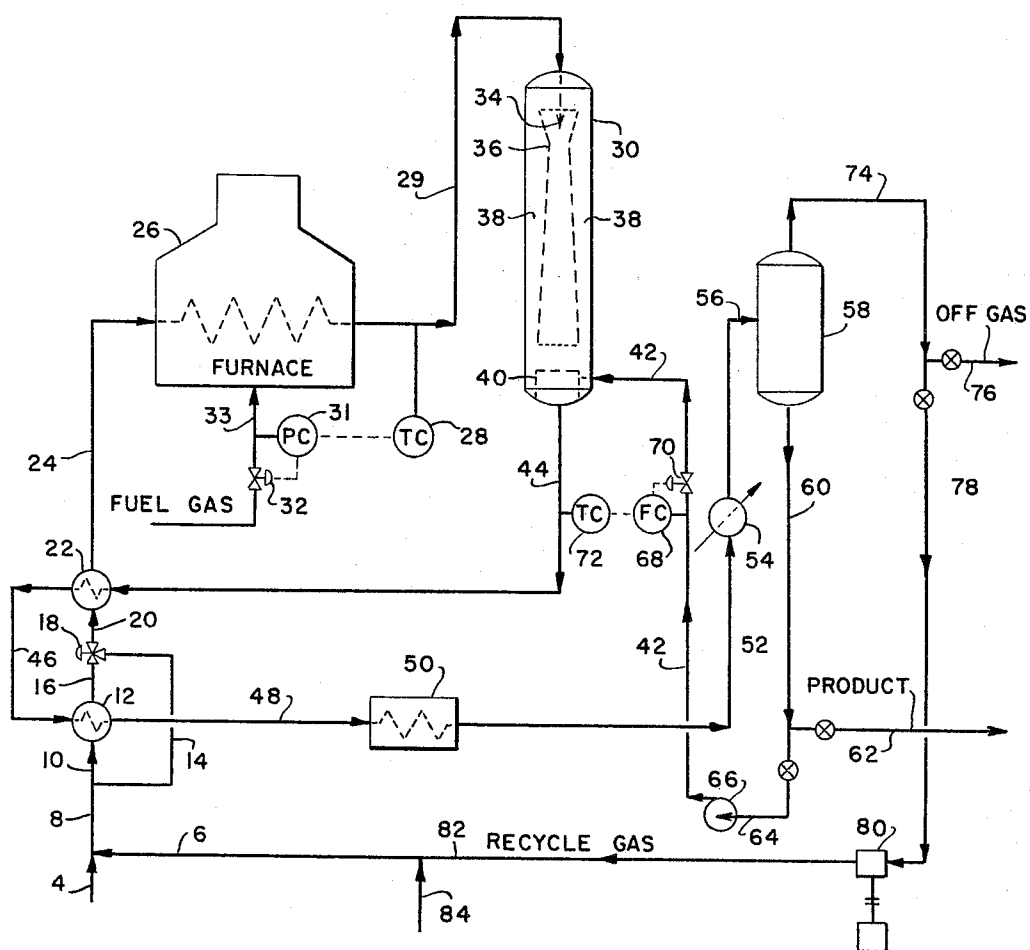
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J. D. HAMMOND ET AL

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HYDROCARBON DEALKYLATION PROCESS

Filed June 27, 1963



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HYDROCARBON DEALKYLATION PROCESS

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17 Claims. (Cl. 260—672)

The present invention relates to the dealkylation of feed stocks containing alkylaromatic hydrocarbons, especially the thermal dealkylation of such hydrocarbons in the presence of hydrogen. It is particularly concerned with the production of benzene by thermal hydrodealkylation of alkylbenzenes.

Alkylaromatic hydrocarbons have been subjected to hydrodealkylation in the presence of catalysts and also in non-catalytic thermal reactions. In one series of comparative tests, the thermal method has been found to have a number of significant advantages over the catalytic treatment. Among these benefits are producing higher yields of benzene or naphthalene, less cracking of aromatic rings and lower dry gas yields; consuming less hydrogen at any given conversion level, reacting at faster rates and showing less proclivity to lay down coke in the apparatus.

A great deal has been written on the thermal hydrodealkylation of alkylaromatic hydrocarbons but little or no recognition has been given to the related problem of "metal dusting" which often occurs in such reactions. This is a form of corrosion so rapid and destructive as to be termed "catastrophic corrosion." Apparently a carburization of the metal or alloy takes place that causes grains of metal or a metal carbide to drop out of the walls of processing equipment, as analyses have indicated both types of substances along with carbon to be present in the dust found in the bottom of a thermal hydrodealkylation reactor. However, the phenomenon is not yet fully understood.

This corrosive action is so fast that it has been observed to penetrate 18-8 stainless steel tubing within a matter of four or five days at temperatures of the order of 1320° F. in another hydrocarbon conversion process. Even some higher chromium-nickel alloy steels are seriously corroded in a short time. The common practice of constructing pipes and vessels with walls of extra thickness to provide corrosion allowances does not appear to be a feasible countermeasure against such rapid attack.

Metal dusting occurs particularly when a metal surface is exposed to a mixture of hydrogen and a lower hydrocarbon, such as methane, etc., at temperatures of the order of about 1275 or 1300° F. and higher. It is also possible that this destructive reaction occurs at lower temperatures over a long period of time. An increase in the proportion of lower hydrocarbon relative to hydrogen has been observed to increase the degree of corrosive attack. The problem is particularly acute with the dealkylation of a straight or unblended alkylaromatic hydrocarbon stock such as nitration grade toluene in the presence of a hydrogen-methane mixture.

An object of the invention is to provide an improved process for the thermal hydrodealkylation of alkylaromatic hydrocarbons.

Another object of the invention is to provide an improved thermal hydrodealkylation process for the conversion of alkylaromatic hydrocarbons wherein little or no metal dusting occurs throughout the system.

A further object of the invention is to provide for the thermal dealkylation in the presence of hydrogen of an alkyl benzene in which substantially no corrosion is encountered in the processing apparatus.

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Further objects and advantages of the invention will be apparent to those skilled in the art upon consideration of the detailed disclosure hereinafter.

The present invention is concerned with a combination of processing conditions in a dealkylation process comprising indirectly preheating hydrogen and a normally liquid alkylaromatic hydrocarbon feed stock in a ratio of at least 4000 standard cubic feet of hydrogen per barrel of said feedstock under conditions wherein the maximum temperature of heat transfer surfaces in the preheating zone in contact with said charge is maintained at not more than about 65° F. (preferably not more than about 50°) above the temperature of the proximate portion of said charged, introducing said preheated charge at a temperature between about 1100 and 1175° F. into a dealkylation zone, and dealkylating said preheated charge at average reaction temperatures between about 1200 and 1275° F. for a period sufficient to effect the conversion of at least 65% by volume of the alkylaromatic content of said feed, based on disappearance of alkylaromatic compounds.

Another important aspect of the invention relates to producing substantial internal circulation in the dealkylation zone to quickly boost the temperature of a charge through a substantial range to a temperature high enough to induce an effective dealkylation reaction rate and also to prevent excessive reaction temperature. This may be accomplished by injecting the charge into a reactor as a high velocity jet at a nozzle velocity between about 100 and 850 feet per second.

Narrower aspects of the invention relate to quenching the reaction products with a vaporizable liquid, a comparatively long reaction time between about 30 and 120 seconds, introducing normally gaseous hydrocarbons with the charge, charging relatively low proportions of hydrogen to permit a relatively low degree of preheat and a large temperature increase upon a mixture with the hot circulating reaction mixture. In the case of toluene, the hydrogen charge is desirably between about 3.5 and 6 mols of hydrogen per mol of toluene. The charge gas also desirably contains between about 0.2 and 1.2 mols of normally gaseous hydrocarbons per mol of hydrogen. The volumetric ratio of recirculating reaction mixture to fresh charge may be between about 2:1 and 15:1, respectively, and preferably is between about 4:1 and 10:1.

The instant process is designed to avoid the problems occasioned by metal dusting in thermal hydrodealkylation under conventional conditions. Especial attention is given to the matter of avoiding temperatures in the metal dusting range, that is temperatures at which the metal dusting or carburization reaction proceeds at a significant rate, while maintaining satisfactory dealkylation rates in equipment of reasonable size. The lower temperatures, an important feature of the present invention, not only eliminates or at least minimizes the metal dusting problem but also enable one to use construction materials with thinner walls or lower alloys or both in view of the well-known fact that all metallic construction materials lose a great deal of their normal strength at high temperatures. This emphasizes the need for running such reactions at the lowest possible temperatures since considerable pressures are desirable in thermal hydrodealkylation reactions.

Mention is made herein of a certain temperature differential being held within a range of 65° F., and preferably within 50°, in the preheating furnace. This refers to the difference in temperature between (1) the maximum temperature at any point on a heat transfer surface in contact with the charge (usually the inner surface of an externally fired tube or coil) of all of the heat transfer elements in the furnace and (2) the proximate portion of the charge—that is the part of the charge

which is in the same location, region or zone as the point on the internal surface where the aforesaid maximum temperature is attained. Generally, this point is located near the charge outlet of the preheating furnace. It should be noted that the stated temperature differential applies only in the region of the maximum tube temperature because greater temperature differentials are permissible at other locations, as for instance, near the charge inlet of the heater. It has no application to any preliminary heat exchangers, etc. for the charge, which are located upstream of the preheating furnace, as their highest surface temperatures are below the surface temperatures to which the charge is exposed in the preheating furnace.

The dealkylation reaction may be carried out in several different kinds of reactors. The preferred type provides rapid internal recirculation of the reaction mixture with thorough mixing of the charge therewith in the manner described and claimed in the concurrently filed application, Ser. No. 291,100 of John W. Payne et al. entitled "Hydrodealkylation of Alkylaromatic Hydrocarbons." Good control of the relatively low reaction temperatures and rapid heating of the charge entering the reactor above its low degree of preheat are among the significant features of the invention, and internal recirculation is a good means for obtaining them. A suitable internal recycle reactor is illustrated in the accompanying drawing.

Another suitable reactor is the single pass flow reversal type described in detail and claimed in the concurrently filed application, Ser. No. 291,077 of Vernon O. Bowles entitled "Apparatus and Method for High Temperature Reactions." This reactor comprises two concentric tubes with the inner tube open at the bottom to provide an annular zone communicating with the inner cylindrical zone at the bottom only. The charge is heated in the upper portion of the annular space by a combination of external firing and indirect heat exchange with the reaction products, then it is reacted principally in the lower annular zone and lower part of the central passage. The lower annular zone is desirably in indirect heat exchange with a second and separate external heat exchange medium. Finally the reaction products in the upper central passage transfer a sizable amount of their heat content to the incoming charge in the surrounding annular zone.

While the above two reactors will generally facilitate better control of the highly exothermic hydrodealkylation reactions, a "plug" flow reactor (i.e., a single pass straight flow reactor) may be used if some provision for removing sufficient heat to avoid excessively high reaction temperatures. In order to keep such a reactor within a reasonable size it will also probably be necessary to heat the first section of the reactor sufficiently to bring incoming charge quickly to a commercially feasible reaction rate.

With any of the reactors mentioned, the level of the reaction temperatures may be raised or lowered by increasing or decreasing the charge inlet temperature by suitable operation of the preheat furnace. Usually the inlet temperature is at least 70° F. below the average reaction temperature.

The combination of the present invention also includes careful control of the hydrogen charge. The use of a relatively low quantity of excess hydrogen and accompanying and inert diluents therewith permits the exothermic heat of reaction to more quickly heat the entire charge to the selected reaction temperature; however, the inlet ratio of hydrogen to alkylaromatic hydrocarbons should not be allowed to drop to the point where the deposition of carbon in the reactor occurs. The hydrogen rate may be maintained in most instances between about 4,000 and 8,000 standard cubic feet per barrel of liquid hydrocarbon feed referring to 42 gallon barrels and cubic feet measured at 60° F. and 29.92 inches of mercury pressure (hereinafter abbreviated as s.c.f./b.). For toluene or monomethylnaphthalene undiluted with

other hydrocarbons, the preferred range is between about 3.5 and 6 mols of hydrogen per mol of toluene, which is equivalent to between about 4,500 and 7,500 s.c.f./b. of toluene. Polyalkylated benzenes or naphthalenes combine with more hydrogen in the dealkylation reaction than the monoalkylaromatic compounds. Accordingly, a greater hydrogen charge is desirable when these compounds are present in quantity and the same is true of normally liquid nonaromatic hydrocarbons which tend to crack under hydrodealkylation conditions and then consume relatively large amounts of hydrogen in hydrogenating the cracked fragments. For the dealkylation of high boiling alkyl naphthalene feedstocks with a substantial content of normally liquid nonaromatic hydrocarbons that crack readily under hydrodealkylation conditions, a hydrogen charge rate between about 8,400 and 21,000 s.c.f./b. is preferred; see the concurrently filed application Ser. No. 290,942 of Edward J. Moll, Jr. entitled "Thermal Hydrodealkylation of Naphthalene Precursors."

The least expensive source of hydrogen usually available in petrochemical plants are the off gases of catalytic naphtha reforming operations and these always contain substantial amounts of lower hydrocarbons along with the hydrogen. Within limits, this is desirable since it has been found that such gases tend to provide a somewhat higher dealkylation conversion than undiluted hydrogen. Moreover, methane inhibits coke formation under the reaction conditions herein. Thus, it is desirable to have some normally gaseous hydrocarbons in the charge; but such inert materials and excess hydrogen function as a heat sink or reservoir in the reactor thereby requiring a higher degree of preheating of the charge, so excessive quantities of these inert diluents are best avoided here. It is recommended that the gaseous charge contain between about 0.2 and 1.2 mols of such hydrocarbons per mol of hydrogen.

The total pressure in the reactor may be maintained between about 250 and 800 pounds per square inch gage pressure (hereinafter abbreviated as p.s.i.g.). It appears that ring cracking occurs to an undesirable extent at pressures lower and higher than that range, and coking problems are encountered at pressures less than about 250 p.s.i.g. It is further recommended that the inlet hydrogen partial pressure be maintained between about 200 and 600 p.s.i.

Quenching the products of the exothermic reaction to temperatures below about 1000° F. is an optional but often desirable feature of the invention as it alleviates the otherwise severe operating conditions to which the piping and other equipment downstream of the reactor are otherwise exposed. When quenching is used, it is desirable to perform this cooling with a vaporizable liquid in close proximity to the reaction space, for example, in a small compartment within the shell of the reactor separate from the reaction space and located near the outlet.

For a better understanding of the nature and objects of the present invention, reference should be had to the accompanying drawing which is a flow sheet or schematic diagram with many details omitted which are well known to those skilled in the art. In addition, the tubular example hereinafter sets forth the flow rates and composition of all of the significant streams of materials in the system identified by the same reference numerals as in the drawing.

Nitration grade toluene is introduced at a constant rate in conduit 4 as the material to be dealkylated. A circulating gas comprising recycled, normally gaseous products of the reaction and also hydrogen-rich make-up gas are added from line 6 to the toluene. The two streams are commingled in pipe 8 at a temperature of 120° F. and a pressure of 660 ps.i.g.

The mixture of liquid gases is now heated by the interchange of heat with the reaction effluent in two steps. The charge is divided between line 10 leading to the heat

exchanger 12 in which all liquid components in that charge stream are vaporized and the by-pass line 14. A portion of the charge leaves the exchanger 12 at a temperature of 540° F. in line 16 which leads to the 3-way valve 18. This valve may be adjusted manually to by-pass enough of the charge to line 14 around the first heat exchanger 12 in order to maintain a temperature between 375 and 480° F. in the inlet line 20 to second heat exchanger 22. It is considered most desirable to have the charge in line 20 at a temperature approaching the lowest temperature at which the entire charge is safely maintained in the vapor state under the prevailing pressure of 645 p.s.i.g., that is about 375° F. With the charge completely vaporized, there is no danger of slugs of liquid creating excessive thermal shock by sudden chilling of the heat transfer surfaces in the second exchanger. The heated effluent from exchanger 22 at a temperature of 830-910° F. depending on the cleanliness of the tubes therein and a pressure of 625 p.s.i.g. now passes through the line 24 to the preheating furnace 26 wherein the temperature is further boosted to 1125° F. while the maximum temperature of the internal surface of the externally fired heating tubes near the charge outlet is maintained at 1175° F. or somewhat lower by regulating the burners in that part of the furnace.

This furnace plays an important part in the present invention as the heat fluxes therein are carefully controlled. In the conventional preheating furnaces used for heating hydrocarbon streams to high temperatures of the order involved here, it is common to have temperature differentials between the maximum metal temperature of an internal tube surface and the proximate portion of the charge in the range of 80 to 110° F. or more. However, by employing a heater designed for low heat flux rates or low ratios of maximum to average flux densities or both, it is possible to hold said temperature differential down to a 50° F. spread. Such furnaces attain these results by various design factors, especially those involving the number, size and arrangement of both heating tubes and burners.

One heater suitable for the purpose is a multicellular box type vertical tube heater which incorporates two independent firing zones to facilitate the control of any desired heat distribution. The cold end zone may have a double row of tubes arranged on a staggered pitch, but a single row of tubes spaced at least two nominal diameters apart is recommended for the hot end zone. Firing from the hearth on both sides of the double and the single rows of tubes from burners arranged close to and directionally angled towards the walls creates in effect a completely radiant vertical heating plane. The article "An Improved Pyrolysis Furnace" by K. R. Wagner and S. A. Lee in "The Petroleum Times" (England) issue of December 14, 1962, on pages 740-741 further describes furnaces suitable for the present process.

The degree of preheating employed with the charge is controlled by the temperature controller 28 which senses the temperature close to the preheat furnace outlet of the stream passing through a short transfer line 29 on its way to the reactor 30 and automatically adjusts or resets the pressure controller 31 which regulates the automatic valve 32 to decrease or increase the supply of fuel gas flowing through pipe 33 to the furnace. When the charge reaches about 1100° F., an exothermic reaction commences therein, therefore a temperature rise of few degrees occurs while the charge is in transit between the furnace and the reactor.

The charge containing hydrogen in a low ratio of 4 mols per mol of toluene feed is injected at a temperature of 1130° F. and pressure of 605 p.s.i.g. through the nozzle 34 into a venturi tube or cylindrical partition 36 longitudinally aligned with the central axis of the cylindrical reactor. The pressure in the reactor is 575 p.s.i.g. and the 30 p.s.i. pressure drop through the nozzle produces a high velocity jet which maintains the contents of the reactor in relatively rapid recirculating flow down the reactor

venturi tube 36 and up through the annular space 38 between the venturi and the insulated wall of the reactor. The jet issues from nozzle 34 at a velocity of 500 feet per second and the velocity of the entire mixture in the throat of the venturi is 58 feet per second. The circulation induced by the kinetic energy of the injected stream is sufficient to produce the circulation of about 7.5 parts by volume of reaction mixture per part of fresh charge injected. The average residence time in the reaction zone is 68 seconds, so it is apparent that most of the gaseous material makes numerous circuits of the continuous reaction channel.

The resulting thorough mixing in combination with the relatively small quantity of excess hydrogen and normally gaseous hydrocarbons that play no direct part in the present reaction enable the relatively low temperature charge to be boosted almost instantaneously about 100° F. in temperature to a reaction temperature of 1230° F. This is due to the large quantity of sensible heat available in the large mass of recirculating reaction mixture in this highly exothermic reaction. The high circulation rate also keeps the temperature throughout the reactor remarkably constant, within a range of plus and minus 10° F. of the average reaction temperature. Thus the entire reaction space is at substantially the same temperature. By restricting the diluents, that is excess hydrogen and other normally gaseous components, in the charge to a relatively small amount; the exothermic heat of reaction raises the charge through a considerably higher temperature spread than usual, and this effect is intensified by the high internal circulation rate within the reaction zone in which large quantities of hot reaction products of high heat content are almost immediately mixed with the charge at the point of entry into the reactor. The overall effect is a large and easily controlled rise in the temperature of the incoming charge immediately upon its introduction. This, of course, means that the degree of preheating can be held lower to minimize any possibility of metal dusting occurring in the furnace tubes and transfer line as well to minimize the loss in strength of construction materials at high temperatures.

The interior of the reactor 30 is lined with a refractory insulation both to conserve heat and also to keep the hot reactants out of contact with the metal shell of the reactor. This insulation not only permits a reactor shell with a thinner metal wall to be used but also obviates the need for a high heat resistant stainless steel. Thus, the reactor may be constructed of a low alloy steel containing small percentages of chromium and molybdenum except for the exposed metal of nozzle 34, venturi 36 and the quench box 40 wherein the reaction effluent is quenched with a vaporizable liquid, namely a portion of condensed products of this reaction admitted via conduit 42. The quenching operation reduces the effluent from a temperature of 1230° to 975° F.

The resulting quenched but still gaseous products mixed with the vaporized quench fluid leave through line 44 which carries them to the heat exchanger 22 wherein they are cooled to a temperature of 630° F. and then transferred via pipe 46 to the low temperature heat exchanger 12 in which their temperature is further reduced to 410° F. Conduit 48 carries this stream to an air cooler 50 where the stream is brought down to a temperature of 200° F. prior to being transported in pipe 52 to the water-cooled cooler 54 in which the temperature is lowered to 100° F. The crude reaction products are delivered via line 56 to the high pressure separator 58 at a temperature of 100° F. and pressure of 525 p.s.i.g.

The liquid phase condensed by the cooling separates in the separator and is drawn off under the regulation of a liquid level controller (not shown) in the bottom line 60. This bottoms stream is divided between the two valved conduits 62 and 64. The former carries the product liquid which is made up predominantly of benzene and toluene in a 3:1 approximate molar ratio to a stabilizing

tower (not shown) wherein the small weight of dissolved normally gaseous hydrocarbons is boiled off. The resulting stabilized liquid may then be employed as a mixed solvent or separated by fractional distillation into benzene and toluene as is more likely.

A major portion, that is more than half, of the bottoms in line 60 may be recycled at substantially ambient temperatures through conduit 64, pump 66 and pipe 42 to the quench box 40 in the bottom of the reactor 32. The flow of quench liquid is desirably governed by the flow controller 68 with an associated automatic valve 70 in line 42 under the regulation of the temperature controller 72 which has a temperature sensing element projecting into the reactor bottoms line 44.

The gaseous phase leaves separator 58 in pipe 74 and is also split between the valved lines 76 and 78. Line 76 takes off the by-product gas for use as a fuel gas or as a source of hydrogen. For the latter purpose, it may be desirable to purify the by-product and also perhaps to increase the hydrogen content by the removal of a substantial amount of the hydrocarbon gases therein.

A far larger proportion of the separator gas is recycled to the process through line 78, compressor 80 and pipe 82 and 6. In conduit 6, it is joined by a makeup hydrogen-rich gas of about 90% purity introduced from supply line 84 at a pressure of 660 p.s.i.g. The quantity of make-up gas must be sufficient to replace not only the hydrogen amounting to 940 s.c.f./b. of liquid feed, which is consumed in the process but also 800 s.c.f./b. of hydrogen in the fuel gas which is being taken off continually as a by-product in line 76. In speaking of hydrogen herein, reference is being made to the actual hydrogen content of the gaseous mixtures and not to the total mixed gas. The hydrogen-rich streams generally available at low cost in a refinery typically contains from 45 to 90% hydrogen by volume and it is seldom if ever commercially feasible to use pure hydrogen.

high boiling aromatic hydrocarbons or gas oils, may be employed for quenching; but the products of the instant reaction are generally preferred for this operation and moreover are readily available.

If desired, the quenching step may be omitted entirely and all of the separator liquid in line 60 diverted into the product line 62. This procedure would subject the reactor effluent line 44 to some risk of metal dusting and expose the second heat exchanger 22 to considerably higher temperatures, but it would conserve the heat lost in quenching. The dealkylation temperature selected and the metal dusting tendencies of the reaction mixture are largely determinative as to whether or not a quench liquid should be employed.

While the instant process has been illustrated in full details for a better understanding of the principles of this invention, it will be apparent to those skilled in the art that the invention is of broader scope and may be practiced in numerous embodiments with many variations. Accordingly, the present invention is not to be regarded as restricted to the specific details disclosed herein except as they may be included in the appended claims.

We claim:

1. A process for the dealkylation of an alkylaromatic hydrocarbon which comprises indirectly preheating a charge comprising hydrogen and a normally liquid alkylaromatic hydrocarbon feed stock in a ratio of at least 4000 s.c.f. of hydrogen per barrel of said feed stock in a preheating zone wherein the maximum temperature of heat transfer surfaces in contact with said charge is maintained at not more than about 65° F. above the temperature of the proximate portion of the charge, introducing said preheated charge at a temperature between about 1100 and 1175° F. into a dealkylation zone and dealkylating said preheated charge therein at temperatures above about 1200 and not exceeding about 1275° F. for a period of time sufficient to effect the conversion of at least 65% of

EXAMPLE

Pound mols per hour

Pipe No.-----	4	29	-----	44	60	64	74	76	78	84	6	62
Stream-----	Toluene Feed	Reactor Charge	Reaction Products	Quenched Reactor Effluent	Sepa-rator Liquid	Quench Liquid	Sepa-rator Vapor	Off Gas	Cycle Gas	Fresh Gas	Total Charge Gas	Liquid Prod.
Hydrogen-----		976.0	794.0	795.0	2.2	1.0	792.8	154.6	638.2	337.8	976.0	1.2
Methane-----		940.6	1,132.6	1,141.9	20.0	9.3	1,121.9	218.9	903.0	37.6	940.6	10.7
C ² Hydrocarbons-----		15.5	21.0	22.5	3.3	1.5	19.2	3.7	15.5	-----	15.5	1.8
C ³ Hydrocarbons-----		0.8	1.2	1.4	0.4	0.2	1.0	0.2	0.8	-----	0.8	0.2
Benzene-----	1.8	18.8	192.6	341.0	319.9	148.4	21.1	4.1	17.0	-----	17.0	171.5
Toluene-----	241.3	243.5	62.5	114.2	111.5	51.7	2.7	0.5	2.2	-----	2.2	59.8
Other Aromatics-----	0.9	0.9	2.3	4.4	4.4	2.1	-----	-----	-----	-----	-----	2.3
Total-----	244.0	2,196.1	2,206.2	2,420.4	461.7	214.2	1,958.7	382.0	1,576.7	375.4	1,952.1	247.5

The above example represents a material balance in which 1764 barrels per day of nitration grade toluene is dealkylated with a total hydrogen charge of 5040 s.c.f./b. to achieve a conversion of 75% by volume based on toluene disappearance during a residence time of 68 seconds. The volume of charge entering the reactor amounts to 1128 cubic feet per minute under the conditions in the reactor, and this is injected through a suitably sized nozzle at the aforesaid nozzle velocity of 500 feet per second to set up an internal recirculation rate of about 7.5 parts per volume of reaction mixture per part of freshly injected charge. Neither metal dusting nor the deposition of any appreciable amount of coke are observed in the operation.

Alternatively, an extraneous quenching fluid may be employed in the quench box. This material should be vaporizable but substantially inert to the reaction products under the reaction conditions and it preferably should be readily separable from the reaction products by distillation; thus other streams boiling above 275° F. such as

the alkylaromatic hydrocarbon content of said feed stock.

2. A process according to claim 1 in which said reaction time is between about 30 and 120 seconds.

3. A process according to claim 1 in which said charge contains normally gaseous hydrocarbons.

4. A process according to claim 1 in which said charge contains between about 0.2 and 1.2 mols of normally gaseous hydrocarbons per mol of hydrogen.

5. A process according to claim 1 for the dealkylation of toluene in which from 3.5 to 6 mols of hydrogen is charged per mol of toluene.

6. A process according to claim 1 in which said charge contains between about 4000 and 7500 standard cubic feet of hydrogen per barrel of said feed stock.

7. A process according to claim 1 in which said preheating operation takes place immediately prior to introducing said preheated charge into said dealkylation zone.

8. A process according to claim 1 in which the products of said reaction are quenched to a temperature below

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about 1000° F. in close proximity to said dealkylation zone by admixture with a vaporizable liquid.

9. A process according to claim 8 in which said quench liquid contains normally liquid hydrocarbons.

10. A process according to claim 8 in which said quench liquid contains condensed normally liquid products of said reaction.

11. A continuous dealkylation process which comprises indirectly preheating an alkylaromatic hydrocarbon and hydrogen in a furnace so constructed and arranged that the maximum temperature of heat transfer surfaces in contact with said charge is maintained within about 65° F. above the temperature of the proximate portion of said charge, introducing said preheated charge with a content of at least about 4000 s.c.f. of hydrogen per barrel of normally liquid hydrocarbon feed stock at a temperature between about 1100 and 1175° F. into a dealkylation zone wherein a reaction mixture is recirculating through a continuous substantially unobstructed channel whereby said reaction mixture is continually mixing with fresh preheated charge, and reacting said charge in said channel at temperatures above about 1200 and not exceeding about 1275° F. for a period of time sufficient to effect the conversion of at least about 65% of said alkylaromatic hydrocarbon.

12. A process according to claim 11 in which the volumetric ratios of recirculating reaction mixture to charge are between about 2:1 and 15:1.

13. A continuous process for the dealkylation of a normally liquid hydrocarbon feed stock rich in alkylaromatic hydrocarbons which comprises indirectly preheating a charge comprising hydrogen and said feed stock in proportions of at least about 4000 s.c.f. of hydrogen per barrel of said feed stock under conditions wherein the maximum temperature of heat transfer surfaces in the preheating zone in contact with said charge is maintained at a temperature within about 65° of the temperature attained by the proximate portion of the charge, injecting said preheated charge at a temperature between about 1100 and 1175° F. as a high velocity jet into a dealkylation zone wherein the reaction mixture is circulating through a continuous confined path substantially free of obstructions whereby said reaction mixture is continuously mixing with

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said injected charge, reacting said charge in said path at temperatures above about 1200 and not exceeding about 1275° F. for a period of time sufficient to effect the conversion of at least about 65% of the alkylaromatic hydrocarbon content of said feed stock and continuously withdrawing a stream of said reaction mixture as the product of the process.

14. A process according to claim 13 in which said charge is injected into said dealkylation zone at a nozzle velocity between about 100 and 850 feet per second.

15. A process according to claim 13 in which said charge contains normally gaseous hydrocarbons, hydrogen and toluene in proportions between about 0.2 and 1.2 mols of normally gaseous hydrocarbons per mol of hydrogen and between 3.5 and 6.0 mols of hydrogen per mol of toluene, said charge is injected into said dealkylation zone at a nozzle velocity between about 100 and 850 feet per second thereby recirculating between about 2 and 15 volumes of said reaction mixture per volume of said injected charge, and maintaining said reaction mixture at a pressure between 250 and 800 p.s.i.g. for an average residence time between about 30 and 120 seconds.

16. A process according to claim 1 in which said preheated charge is injected into a confined dealkylation zone as a high velocity jet of gaseous material at a sufficient initial velocity to produce rapid and thorough mixing of the material in said dealkylation zone.

17. A process according to claim 1 in which said preheated charge is injected in gaseous form into a confined dealkylation zone at a nozzle velocity of at least 100 feet per second.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,288,876

November 29, 1966

James D. Hammond et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the heading to the printed specification, line 5, for "Mobile Corporation" read -- Mobil Oil Corporation --; column lines 23 and 24, for "dalkylation" read -- dealkylation --; column 4, line 73, for "liquid gases" read -- liquid and gases --.

Signed and sealed this 19th day of September 1967.

(SEAL)

Attest:

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Commissioner of Patents