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THERMAL HYDRODEALKYLATION OF NAPHTHALENE PRECURSORS

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The present invention relates to producing naphthalene by the dealkylation of heavy alkylaromatic hydrocarbons, particularly alkylnaphthalenes. It is especially concerned with a process for substantially eliminating the formation of carbon while obtaining good yields of naphthalene from charging stocks of types that are generally regarded as undesirable for the purpose.

Much has been written on dealkylation of alkyl benzenes and alkylnaphthalenes in the presence of hydrogen by catalytic and thermal reactions for the production of the more valuable benzene and naphthalene respectively. Although the noncatalytic thermal reaction requires a higher temperature than catalytic dealkylation, the thermal treatment possesses numerous important advantages, particularly in the case of naphthalene production. Naphthalene yields about 5 to 8 volume percent greater and apparently due to higher conversions of tetralins, indanes and indenes have been obtained by the thermal method in one series of comparative tests. Less cracking of aromatic rings to by-products is another superior characteristic observed in the thermal process. Also, lower yields of dry gas have been obtained with this treatment. Higher reaction rates are obtainable; and apparently, this may be accomplished with a consumption of less hydrogen at any given conversion level than is possible in the catalytic method. Moreover, even with a desirable alkylnaphthalene feed stock boiling below 500° F. and containing not more than very small quantities of nonaromatic hydrocarbons, a high coke lay down of the order of 5 to 8% by weight has been encountered in the catalytic process.

It is well understood in the prior art that carbon formation or coking is a serious problem in the dealkylation of alkylnaphthalenes by noncatalytic thermal methods. In U.S. Patent 2,674,635, the production of coke in amounts of the order of 3% of the liquid feed is mentioned in a number of examples; and it is indicated that the coke deposited on the inert ceramic pellets in the reactor is removed later by passing air over these pellets in another vessel in this particular system. Another solution of the problem of coking produced by high boiling feeds is suggested in U.S. Patent 2,768,219 wherein a fraction rich in aromatic hydrocarbons is subjected to an additional distillation step prior to dealkylation in order to increase the dealkylation on stream period from about 7 to about 24 hours before the coke deposits build up sufficiently in the dealkylation reactor to produce a substantial pressure drop therethrough. Here a portion of the alkylnaphthalene content is necessarily separated along with the heavier aromatics for less valuable utilization than naphthalene production. Such methods of reducing the formation of coke or of disposing of coke formed in the reaction require additional processing steps and more complex equipment; consequently, they increase the cost of production.

At the present time, it is believed that there is only one commercial unit in the United States producing naphthalene by the thermal hydrodealkylation of a hydrocarbon stream from a petroleum refinery. That particular stream is understood to be a rather carefully refined one in which the nonaromatic hydrocarbon content has been reduced to a value well below 10% and care taken that the end boiling point of the feed stock does not exceed 525° F. at the most.

An object of the invention is to provide an improved method for the production of naphthalene.

Another object of the invention is to provide an improved method for the production of naphthalene from feed stocks usually considered unsuitable for the purpose.

A further object of the invention is to provide for the prolonged production of naphthalene without formation of coke or carbon from hydrocarbon mixtures rich in naphthalene precursors but also containing substantial amounts of undesirable, normally liquid, nonaromatic hydrocarbons and having end points substantially in excess of 525° F.

Other objects and advantages of the invention will be apparent to those skilled in the art upon consideration of the detailed disclosure that follows. Unless otherwise indicated herein all temperatures are expressed in degrees Fahrenheit, partial and gage pressures in pounds per square inch (p.s.i. and p.s.i.g. respectively), proportions in parts by weight and boiling ranges at normal atmospheric pressure by the A.S.T.M. procedure.

The difficult feed stocks which have heretofore been considered unsuitable for the production of naphthalene by thermal dealkylation are hydrocarbon charging stocks having high end boiling points at atmospheric pressure which also contain substantial amounts of nonaromatic hydrocarbons. Petroleum fractions rich in alkylaromatic hydrocarbons and having distillation ranges extending above 525° display a strong tendency to form carbon under the high temperature conditions required for thermal dealkylation of such materials to naphthalene in the presence of hydrogen.

The presence of more than 10%, and especially of more than 15%, of nonaromatic hydrocarbons in such feed stocks aggravates the problem inasmuch as naphthenes, paraffins and olefins within the normally liquid range tend to crack and form compounds of lower molecular weight in the hydrodealkylation reaction in contrast with the relatively stable lower hydrocarbons, such as methane and ethylene. Such cracked fragments are hydrogenated under the prevailing conditions in reactions which are highly exothermic and thus tend to produce excessive temperatures in the hydrodealkylation reactor, or at least in some localities therein, and these temperatures are conducive to both rapid coke formation and the undesired cracking of aromatic rings.

For all practical purposes, coke formation must be eliminated in a thermal hydrodealkylation system employing a simple reactor containing no moving bed of solids for the collection of carbon deposits, because once coke formation commences in such a system, the deposition continues at increasing rates until the equipment is plugged with such deposits. The cleaning of such deposits is not only laborious, but also, requires lengthy shutdowns while the equipment is slowly cooled down for the coke removal operation and then slowly reheated after cleaning.

The present invention is a process for the production of naphthalene which comprises reacting a charge comprising between about 8,400 and 21,000 standard cubic feet of hydrogen per barrel of a normally liquid hydrocarbon feed stock containing at least one naphthalene precursor at a pressure between about 250 and 800 p.s.i.g. and at reaction temperatures maintained constant within about 20° of a predetermined temperature but not below about 1,200° and not above about 1,400° F. More particularly, the invention is concerned with the thermal hydrodealkylation of charge stocks having end boiling points substantially above 525° and significant contents of alkyl naphthalenes as well as nonaromatic hydrocarbon contents exceeding about 10% by weight and especially those with more than 15% of the nonaromatic hydrocarbons. Other aspects of the novel process involve more specific reaction conditions which provide superior results.

This process now enables one to thermally dealkylate the aforesaid feed stocks which were previously considered unsuitable for the purpose in a simple reaction system without the formation of carbon and without additional processing steps. This is accomplished by the aforesaid combination of carefully selected reaction conditions which are controlled within the specified ranges including particularly the improved control of temperatures throughout the reaction zone and the unusually high hydrogen charging rate.

In addition to maintaining the reaction temperatures substantially constant within the stated narrow range which approximates isothermal conditions, the maximum temperature of the reaction mixture should not be allowed to exceed about 1400° F. since excessive cracking of the naphthalene rings and consequent deterioration of yields occurs above this point. Also, the predetermined average reaction temperature should be selected with a view to maintaining the minimum temperature of the materials within the reaction space above about 1,200° F. because lower temperatures produce unacceptably low reaction rates for commercial purposes in a reactor of practical size and efficient conversion of the alkylnaphthalenes into naphthalene. It is preferable to control the reaction temperatures so that the minimum temperature in the reactor is at least about 1,250° F. It should be understood, however, that this does not mean that the material charged must always be preheated to at least about 1,200 or 1,300° F., for it is possible to rapidly elevate the temperature of the gaseous charge 100° or even more—up to within a few degrees of the preselected reaction temperature in only a small fraction of the residence time within the reactor. This last step up to reaction temperature is substantially instantaneous in the case of an internal circulation reactor where the elapsed time must be measured in hundredths of a second.

In raising the temperature of the charge to the selected reaction temperature level, especially if that level is near the upper part of the 1200–1400° range, it will be appreciated that there will usually be a time interval in which the charge is above the dealkylation reaction threshold (probably about 1100° with typical feeds and conditions described herein) but more than 20° below the predetermined average reaction temperature, but by suitable selection and operating control of the preheater and reactor it is possible to keep that time interval so brief that it exerts no significant detrimental effect on the present process. In other words, having the reactants rising in temperature from the reaction threshold to the bottom of the selected band (+ and −20°) of reaction temperatures for a relatively short time amounting to say about 25% or less of the residence time within said reaction temperature band does not destroy the substantially isothermal nature of the instant process. Expressed another way, the reacting materials should be maintained within plus and minus 20° of the average temperature in the reactor for at least about 80 percent of the time these materials are at temperatures higher than the threshold temperature, and the usually short interval during which the reaction products are being cooled or quenched to a point below the threshold temperature may be ignored here. With a properly designed preheater, this rising temperature interval may amount to less than 10% of the reactor residence time.

A hydrogen-rich gas is charged along with the normally liquid hydrocarbons in hydrodealkylation reactions. For a difficult feed stock, the normally gaseous portion of the charge should be introduced in such quantities as to provide between about 8,400 and 21,000 standard cubic feet (measured at 60° F. and normal atmospheric pressure) of hydrogen per barrel (42 gallons) of the normally liquid hydrocarbons (hereinafter abbreviated as s.c.f./b.) at the reactor inlet. It is to be noted that these rates refer to the hydrogen content of the inlet gas and not to the total gas admitted to the reactor. With charge stocks of the nature disclosed herein, these hydrogen rates correspond to a range of about 12 to 30 moles of hydrogen admitted per mol of normally liquid hydrocarbons in the charge. A lower hydrogen feed rate than the stated range under the overall conditions described herein may be expected to result in coke deposition, whereas a quantity substantially greater than the range will increase the compressor power costs and reduce the productive capacity of the system without any corresponding benefits. These proportions of hydrogen in the charge are unusually high and considerably lower amounts, as for instance, 4,000 to 8,000 s.c.f./b., are typical for the conversion of monoalkylnaphthalene stocks with low contents of nonaromatic hydrocarbons.

The normally gaseous part of the charge (inlet gas) should contain between about 20 and 85% of hydrogen by volume, and preferably at least about 40%. When the hydrogen content is below 20%, the level of the conversion of naphthalene precursors becomes unacceptably low from a commercial standpoint while the cost of compressing and circulating the gas tends to become excessive. However, pure hydrogen is not desired for the purpose even if this is economically feasible because coking problems are encountered when the hydrogen concentration in the inlet gas exceeds about 85%. The diluents making up the balance of this gas are commonly normally gaseous hydrocarbons containing 1 to 3 carbon atoms per molecule, and methane is usually the predominant component. Gaseous mixtures of this nature, that are rich in hydrogen, are available at low cost in a great many petroleum refineries as the by-product gases of catalytic reformers, etc. It is believed that diluents and excess hydrogen in the gaseous mixture charged alleviate coking by providing a heat reservoir of inert material which reduces the temperature rise and prevents the occurrence of local "hot spots" in this highly exothermic reaction. Also, lower hydrocarbons appear to repress coking.

The total pressure within the reactor is also important, and it is desirably maintained between about 250 and 800 p.s.i.g. A lower pressure will not insure the desired high conversion of naphthalene precursors. The degree of conversion is a function of total pressure, and a substantial amount of ring cracking apparently occurs at higher pressures. The pressure range from about 400 to 700 p.s.i.g. is particularly recommended.

The partial pressure of hydrogen in the charge at the time of admission to the reactor, that is inlet partial pressure, is also significant. It should be kept within the limits between about 130 and 785 p.s.i., and preferably between about 250 and 550 p.s.i.

High conversions are obtainable according to the process of this invention within reasonable reactor residence times of between about 2 and 80 seconds, about 10 to 70 seconds being preferred usually. In general, such conversions amount to at least about 50 mol percent of naphthalene based on the total mols of alkylnaphthalenes charged. By employing reaction conditions within the preferred ranges, yields of 70% and more on this basis can be procured. Occasional conversions above 100% result from the formation of substantial amounts of naphthalene from compounds such as the tetralins, indanes or indenes. These figures are applicable to operations involving no recycle of liquid products and even higher yields may be produced by recycling unconverted naphthalene precursors in the product stream back to the reactor after separation of the products.

In view of the high reaction temperatures involved and the necessity for maintaining them substantially constant within a narrow band, it is necessary to not only vaporize the liquid hydrocarbon feed stock, but also, to preheat the entire charge strongly. Accordingly, the temperature of the charge at the inlet of the reactor should be within the broad range of about 1,000 to 1,350° F.; and it is usually preferable to keep this temperature between about

1,100 and 1,300° F. Temperature levels in the lower parts of these ranges are particularly suitable for reactors of the internal recirculation type in which the fresh charge and hot reaction products are thoroughly mixed, whereas the degree of preheat is desirably brought up at least fairly close to the selected reaction temperature in the case of a reactor designed for straight through or "plug" flow. In any event, it will be appreciated that the incoming reaction mixture entering at a temperature below the threshold of the reaction will receive at least some heat from the walls of the reactor and from the reactants which are already reacting. The average reaction temperature may be readily increased or decreased by correspondingly raising or lowering the charge inlet temperature.

Naphthalene precursors include alkyl-substituted and unsubstituted tetralins, indanes and indenes as well as the preferred monoalkyl and polyalkylated naphthalenes, such as mono methyl and diethylnaphthalene. Accordingly, the feed stock may contain one or more of such substances as 1-, 2-, 4- or 5-monomethylindane, 1,1- or 1,2-dimethylindane, 1,2,3-trimethylindane in the hydrocarbon mixture as well as various monomethylnaphthalenes, tetralin, naphthalene, etc. Such substances as toluene, xylenes, benzene, methylethylbenzene, etc. may also be present but will not contribute to the yield of naphthalene. From a technical standpoint, charging stocks for the instant process may have a content of naphthalene precursors as low as about 20% by weight; but from a commercial point of view, it is desirable that this content should exceed about 30%. The proportion of normally liquid nonaromatic hydrocarbons, including paraffins, olefins and naphthalenes, may be as high as about 35% of the feedstock; but it may be uneconomic in some instances to charge a material containing more than about 25 or 30% of them.

The process of the present invention may be carried out in commercial equipment known in the art which is accordingly not illustrated here. Conventional single or multistage compressors and pipe furnaces may be used to compress, vaporize and preheat the components of the charge which is then introduced into a suitable reactor. There hydrogen and the naphthalene precursors react to form naphthalene along with methane and other lower paraffins. The hot effluent from the reactor may be quenched if desired by the introduction of a suitable liquid quenching medium, such as condensed products of the instant process. The reaction products are then cooled to a suitable temperature and subjected to fractional distillation into a normally gaseous fraction consisting of hydrogen along with C_{1-3} hydrocarbons as well as liquid hydrocarbon fractions including a naphthalene product cut and one of more heavier aromatic fractions.

It is particularly desirable that the dry gas fraction should be recycled to the reactor for maximum economy in the use of hydrogen. A make up gas which is usually richer in hydrogen than the recycle gas is also charged to the reactor to replace the hydrogen consumed in the process. Recycling of part or all of the aromatics heavier than naphthalene is also contemplated as an optional feature of this process. In this case, it may be desirable in some instances to avoid the highest boiling material by fractionating and recycling only the fraction boiling below about 625° F. to avoid the buildup of polymer forming material in the system.

A number of different designs of reactors may be employed in obtaining the necessary approximately isothermal conditions in this highly exothermic process. The preferred type is of the internal recirculation variety wherein the gaseous charge is injected at relatively high velocity into the confined reaction space through a small nozzle aligned with a continuous passage or channel inside the reactor so that the kinetic energy of the entering high velocity gas stream causes the entire reaction mixture to recirculate through the reactor and produce such mixing at the fresh charge with reaction products that the charge is heated substantially instantaneously to reaction temperature. Reactors of this type and reactions therein are described in detail in the concurrently filed application Ser. No. 291,100 of John W. Payne et al., entitled "Hydrodealkylation of Alkylaromatic Hydrocarbons."

Examples 1 to 4 inclusive in Table II hereinafter are performed in a small internal recirculation reactor which is a cylinder closed at both ends with internal dimensions of 3 inches diameter and a length of 6 feet with a concentrically mounted stainless steel inner tube therein of 2 inch internal diameter and a wall thickness of 1/16 inch. This inner tube is 5 feet 8 inches long and spaced equally from each end of the reactor shell. The reaction mixture therein is set in rapid motion by means of a high velocity jet of the preheated gaseous charge issuing from a 0.080 inch diameter nozzle in a tube extending through the center of one end wall of the cylindrical reactor while the effluent products are eventually removed through a small pipe connected to the other end of the reactor. The kinetic energy of the high velocity jet of charge at a velocity of about 100 to 850 feet per second sets the entire reaction mixture circulating through the center of the inner tube and back through the annular space between the inner tube and reactor walls for a number of circuits with surprisingly thorough mixing and uniformity of reaction temperatures throughout the reaction chamber. The volumetric ratio of recirculating reaction mixture to freshly injected charge is about 2:1 to 15:1 depending chiefly on the nozzle velocity. Thus on the average, a molecule of a reaction mixture makes 2 to 15 circuits or passes through the reactor before leaving. The charge inlet temperature is measured outside the reactor.

The isothermal type combination preheater reactor employed in Examples 5 to 10 inclusive in Table II is constructed of a 0.875 inch internal diameter stainless steel tube over 30 inches long surrounded by three massive 3-inch outside diameter stainless steel heat transfer blocks in several sections and surrounded by electrical heating coils. The vessel is divided longitudinally into two zones, namely a preheat zone about 10 inches long followed by a reaction zone comprising two sections about 13.5 inches and 7 inches in length respectively. Each of the 3 sections is provided with individual heating elements as well as skin thermocouples in the exterior of the actual reactor tube and thermocouples in the center of the walls of the various heat transfer blocks in order to control the heating of the reactor to maintain a close approach to isothermal conditions within the reaction space.

The charge is introduced at room temperature into the preheat zone of the apparatus wherein a closely fitting solid member with an external helical thread is mounted inside the stainless steel tube to direct the charge at high velocity along a narrow helical path contiguous with the wall of the preheat chamber. A thermocouple at the junction of the preheat and reaction zones is employed in determining the charge inlet temperatures. After being preheated to the proper inlet temperature in a brief interval, the charge is admitted to the unobstructed reaction space in which it proceeds downward at a much lower linear velocity in straight or plug flow until it reaches the bottom of the tube. Of the open space in the combination apparatus, 10% of the volume is located in the helical preheat zone and 90% in the cylindrical reaction zone. Consequently, the residence time in the preheat zone amounts to only about 11% of the reactor residence time and the charge is above the reaction threshold temperature for only a minor portion of the time in the preheat zone.

Three different charge stocks are provided for the examples which follow. Although all are derived from the same fraction of California crudes with aromatics concentrated therein by sulfur dioxide extraction and have

the same boiling range in the raw state, there are some differences in composition as is apparent from the analyses listed in Table I for two feedstocks in the raw state. The third charging stock is a portion of Stock A which has been desulfurized in a conventional catalytic hydrodesulfurization treatment. It is designated Stock AD.

TABLE I

Composition—Weight percent, 423–638° F., charge stocks

Stock	A	B
Alkyl Benzenes	18.7	20.0
Naphthalene	0.3	
Monomethylnaphthalenes	4.2	(*)
Other Alkylnaphthalenes	30.1	38.2
Tetralins, Indanes and Indenes	11.3	8.7
Other Aromatics	16.2	12.6
Nonaromatics	19.2	20.7

*Included in other alkyl naphthalenes.

For a better understanding of the nature and objects of this invention, reference should be had to the following table of examples of continuous runs, lasting longer than 21 days in some instances, which illustrate thermal hydrodealkylation without the deposition of any carbon whatsoever according to the present invention of feedstocks of a type normally considered unsuitable for the dealkylation. The internal circulation reactor and the plug flow isothermal one employed in the various examples as well as the various charge stocks are described hereinbefore. Probe thermocouples are used for measuring the various temperatures set forth in Table II and the reactor effluents are quickly cooled and then fractionated and analyzed.

The normally gaseous portion of the charge (inlet gas) is obtained by recycling a part of the gaseous reaction products and mixing it with a make-up gas in the form of undiluted commercial grade hydrogen. The make-up hydrogen is introduced in a quantity equal to the hydrogen consumed in dealkylation plus the hydrogen withdrawn in the unrecycled portion of the gaseous reaction products.

In contrast to the above results, it is estimated that in dealkylating a feedstock of the same type under conventional conditions in a conventional (adiabatic) reactor with a hydrogen charging rate of 5000 s.c.f./b. and inlet temperature of 1150° F., the temperature in the reactor would reach a maximum of more than 1400° F. and deposits of coke laid down in the equipment would be so heavy as to require shutting down for cleaning after operating only a few hours.

While the process of the present invention has been illustrated by a number of examples which set forth the method of carrying out this invention in specific detail, it will be understood by those skilled in the art that the invention is not limited to these details except as they may be included in the appended claims or required to distinguish this invention over the prior art.

I claim:

1. A process for the production of naphthalene which comprises reacting a charge comprising between about 8,400 and 21,000 standard cubic feet of hydrogen per barrel of a normally liquid hydrocarbon feed stock containing a naphthalene precursor at a pressure between about 250 and 800 p.s.i.g. and at reaction temperatures maintained constant within about 20° F. of a predetermined temperature but not below about 1200° F. and not above about 1,400° F.

2. A process for the production of naphthalene which comprises reacting a charge comprising between about 8,400 and 21,000 standard cubic feet of hydrogen per barrel of a normally liquid hydrocarbon feed stock containing a naphthalene precursor at a pressure between about 250 and 800 p.s.i.g. and at reaction temperatures maintained constant within about 20° F. of a predetermined temperature but not below about 1,200° F. and not above about 1,400° F. for a sufficient length of time between about 2 and 80 seconds to effect a substantial conversion to naphthalene of the naphthalene precursor content of said charge.

3. A process for the thermal hydrodealkylation of alkylnaphthalenes which comprises introducing into a confined reaction zone a charge in the gaseous phase comprising between about 8,400 and 21,000 standard cubic feet of hydrogen per barrel of a normally liquid hydrocarbon feed stock of high end boiling point and containing at least one alkylnaphthalene wherein the hydrogen content of the normally gaseous portion of said charge is

TABLE II

Example	1	2	3	4	5	6	7	8	9	10
Charge Stock	AD	AD	A	A	B	B	AD	AD	AD	AD
Type of Flow	Recirc.	Recirc.	Recirc.	Recirc.	Plug	Plug	Plug	Plug	Plug	Plug
Average Reaction Temp., ° F	1,300	1,329	1,331	1,351	1,326	1,323	1,323	1,334	1,331	1,350
Charge Inlet Temp., ° F	1,135	1,175	1,150	1,185	1,360	1,333	1,337	1,339	1,333	1,354
Minimum Reaction Temp., ° F	1,292	1,319	1,326	1,348	1,325	1,309	1,320	1,328	1,327	1,344
Maximum Reaction Temp., ° F	1,310	1,339	1,338	1,358	1,359	1,347	1,340	1,351	1,338	1,356
Total Reaction Pressure, p.s.i.g.	600	600	600	600	600	600	600	600	600	600
H_2 Partial Pressure, p.s.i.	404	406	377	381	419	425	436	328	142	155
Residence Time, sec.[1]	20	20	20	20	18	19	20	20	20	20
H_2:NLHC Charge, Mol Ratio [2]	21.6	24.2	26.1	25.8	15.2	18.3	18	18.9	14.1	14.6
H_2:NLHC Charge, s.c.f./b.[2]	15,246	17,061	18,300	18,076	11,005	13,247	12,360	12,914	9,652	10,106
H_2 in Inlet Gas, Vol. Percent	67.8	66.9	62.9	63.4	71.5	71.8	73.8	55.0	23.4	25.9
H_2 Consumed, s.c.f./b. NLHC Charge [2]	2,719	3,220	3,089	3,087	2,971	2,839	3,090	2,980	2,420	3,020
Products, Wt. Percent of NLHC Charge: [2]										
Coke	0	0	0	0	0	0	0	0	0	0
C_{1-3} Hydrocarbons	46.5	50.4	44.7	45.8	44.0	44.3	49.0	48.8	42.8	47.2
C_{4-5} Hydrocarbons	0.2	0.6		0.2	1.6		1.1	0.3	0.7	3.0
C_6-400° F. Fraction	16.7	15.8	7.9	8.3	9.7	*11.6	13.5	14.5	10.2	9.6
400° F. plus Fraction	41.1	39.2	52.3	50.6	49.6	*45.8	41.4	41.3	50.3	45.2
Naphthalene	19.4	25.8	24.5	25.1	25.1	*22.8	26.9	19.1	13.2	14.4
Monomethylnapthalenes	7.5	14.4	10.0	7.1	9.7	*10.0	6.1	8.0	10.5	8.8
Other Alkylnaphthalenes	4.4		5.0	4.1	2.1	*1.6	0.6	1.4	3.3	2.1
Other Aromatics	9.8		12.8	14.3	12.7	*11.4	7.8	12.8	23.2	19.9
Conversion to Naphthalene, Mol. Percent [3]	74.0	98.0	93.5	96.0	86.0		102.0	73.0	50.2	54.8

[1] Uncorrected for volume changes during reaction.
[2] NLHC charge denotes the content of normally liquid hydrocarbons in the charge at the inlet of the reactor.
[3] Includes small amount of naphthalene present in stocks A and AD.
*Denotes value in volume percent of charge.

From the above group of examples, it is apparent that excellent yields of naphthalene are obtained from undesirable feedstocks under the controlled conditions of the present invention without encountering any coking difficulties in prolonged operations.

between about 20 and 85 percent by volume, reacting said charge at a total pressure between about 250 and 800 p.s.i.g. and an inlet hydrogen partial pressure between about 130 and 785 p.s.i. at reaction temperatures maintained constant within about 20° F. of a predetermined temperature but not below about 1,200° F. nor above about 1,400° F. for a sufficient residence time between about 2 and 80 seconds to effect a conversion to naphthalene of at least about 50 percent based on the mols of alkylnaphthalenes in said charge without substantial deposition of carbon.

4. A process for the thermal hydrodealkylation of alkylnaphthalenes which comprises feeding a charge in the gaseous phase comprising a normally gaseous mixture with a hydrogen content between about 20 and 85 percent by volume and a normally liquid alkylnaphthalene charge stock having an end boiling point substantially above 525° F. and a nonaromatic hydrocarbon content exceeding about 10 percent by weight into a confined dealkylation zone at rates adjusted to introduce between about 8,400 and 21,000 standard cubic feet of hydrogen per barrel of said stock, reacting said charge under a total pressure between about 250 and 800 p.s.i.g. and an inlet hydrogen partial pressure between about 130 and 785 p.s.i. at reaction temperatures maintained constant within about 20° F. of a predetermined temperature but not below about 1,200° nor above about 1,400° F. for a sufficient residence time between about 2 and 80 seconds to effect a conversion to naphthalene of at least about 50 percent based on the mols of alkylnaphthalenes in said charge without substantial deposition of carbon.

5. A process for the thermal hydrodealkylation of alkylnaphthalenes which comprises feeding into a confined dealkylation zone a charge in the gaseous phase comprising a normally gaseous mixture with a hydrogen content between about 20 and 85 percent by volume and a normally liquid hydrocarbon feed stock having an end boiling point substantially above 525° F. and containing at least one alkylnaphthalene and a nonaromatic hydrocarbon content exceeding about 10 percent by weight, adjusting the feed rates to said zone to introduce between about 8,400 and 21,000 standard cubic feet of hydrogen per barrel of said stock, reacting said charge under a total pressure between about 250 and 800 p.s.i.g. and an inlet hydrogen partial pressure between about 130 and 785 p.s.i. at reaction temperatures maintained constant within about 20° F. of a predetermined temperature but not below about 1,200° nor above about 1,400° F. for a sufficient residence time between about 2 and 80 seconds to effect a conversion to naphthalene of at least about 50 percent based on the mols of alkylnaphthalenes in said charge without substantial deposition of carbon.

6. A process according to claim 4 in which material boiling at a higher temperature than naphthalene is separated from the products of said reaction and said material is recycled to said reaction as a portion of said charge.

7. A process for the thermal hydrodealkylation of alkylnaphthalenes which comprises feeding a charge in the gaseous phase comprising a normally gaseous mixture with a hydrogen content between about 45 and 85 percent by volume and a normally liquid alkylnaphthalene charge stock having an end boiling point substantially above 525° F. and a nonaromatic hydrocarbon content exceeding about 15 percent by weight into a confined dealkylation zone at rates adjusted to introduce between about 10,500 and 17,500 standard cubic feet of hydrogen per barrel of said stock, reacting said charge under a total pressure between about 400 and 700 p.s.i.g. and an inlet hydrogen partial pressure between about 250 and 550 p.s.i. at reaction temperatures maintained constant within 20° F. of a predetermined temperature but not below about 1,250° nor above about 1,400° F. for a sufficient residence time between about 10 and 70 seconds to effect a conversion to naphthalene of at least about 70 percent based on the number of mols of alkylnaphthalenes in said charge without substantial deposition of carbon.

8. A process according to claim 7 in which material boiling at a higher temperature than naphthalene is separated from the products of said reaction and at least a portion of said material is recycled to said reaction as a portion of said charge.

9. A process for the thermal hydrodealkylation of alkylnaphthalenes which comprises feeding into a confined dealkylation zone a charge in the gaseous phase comprising a normally gaseous mixture with a hydrogen content between about 40 and 85 percent by volume and a normally liquid hydrocarbon feed stock having an end boiling point substantially above 525° F. and containing at least one alkylnaphthalene and a nonaromatic hydrocarbon content exceeding about 15 percent by weight, adjusting the feed rates to said zone to introduce between about 10,500 and 17,500 standard cubic feet of hydrogen per barrel of said stock, reacting said charge under a total pressure between about 400 and 700 p.s.i.g. and an inlet hydrogen partial pressure between about 250 and 550 p.s.i. at reaction temperatures maintained constant within 20° F. of a predetermined temperature but not below about 1,250° nor above about 1,400° F. for a sufficient residence time between about 10 and 70 seconds to effect a conversion to naphthalene of at least about 70 percent based on the number of mols of alkylnaphthalenes in said charge without substantial deposition of carbon.

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