

[54] **CATALYTIC HYDROCRACKING
PROCESS FOR DISTILLATION
RESIDUES**

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[56]

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[57]

ABSTRACT

A feed stock composed of one or more members of the group consisting of polyalkylbenzenes, indenenes, naphthalenes, diphenyls, acenaphthenes, phenanthrenes and aromatic polymeric materials is subjected to hydrocracking by the use of a catalyst which may be a mixture of oxide of molybdenum and cobalt, molybdenum and nickel, or molybdenum, cobalt and nickel, and a carrier, such as alumina.

20 Claims, No Drawings

CATALYTIC HYDROCRACKING PROCESS FOR DISTILLATION RESIDUES

This application is a continuation-in-part of U.S. Pat. application Ser. No. 17,901, filed March 9, 1970, now U.S. Pat. No. 3,639,495, which in turn is a continuation-in-part of application Ser. No. 706,806, filed Feb. 20, 1968, now U.S. Pat. No. 3,505,209.

This invention relates generally to the catalytic hydrocracking of heavy aromatic residues, particularly those which result from the production of alkylbenzene compounds, such as ethylbenzene, methylethylbenzene, and diethylbenzene and alkenylbenzene compounds, such as styrene, divinylbenzene and ethylvinylbenzene. More particularly, this invention relates to the catalytic hydrocracking of heavy aromatic compounds such as those found in the distillation residues from the alkylation of benzene and alkylbenzene, such as toluene and ethylbenzene, with ethylene to produce alkylbenzenes, such as ethylbenzene, methylethylbenzene, and diethylbenzene and of distillation residues from the dehydrogenation of these compounds to produce alkenylbenzene compounds such as styrene, divinylbenzene and ethylvinylbenzene. The process of this invention converts a substantial amount of these residues, which have very low if any economic value, to valuable aromatic compounds.

In a widely used method for the production of vinylbenzenes, benzene and alkylbenzenes, such as toluene and ethylbenzene, are alkylated with ethylene by the use of Friedel-Crafts type catalysts or other alkylation catalysts, such as alumina. The product from the alkylation reaction is removed by distillation at reduced pressure until all mono-, di- and tri- and some tetrasubstituted benzene compounds have been removed. In the production of ethylbenzene, the distillation is stopped when the temperature is about 400°F. at a pressure of about 25 mm. of mercury. The residue from the distillation comprises a mixture of polymethyl and polyethylbenzenes, as well as aromatic compounds, such as indenes, naphthalenes, diphenyls, acenaphthenes, and phenanthrenes. This distillation residue is generally only suitable for use as fuel oil.

The product from the alkylation step is catalytically dehydrogenated to provide vinylbenzenes, such as styrene, vinyltoluene, ethylvinylbenzene, and divinylbenzene. The crude product from the dehydrogenation step is sensitive to polymerization and a polymerization inhibitor such as elementary sulfur or a non sulfur-containing polymerization inhibitor or mixture of inhibitors may, if desired, be added to the stream coming from the dehydrogenation reactor, although, it is not always necessary or desirable to add polymerization inhibitors to this product. The product from the dehydrogenation reaction is removed by distillation. The distillation is continued until all of the mono- and disubstituted and some trisubstituted benzene compounds have been removed. In the production of styrene, the distillation is stopped when the bottom temperature is about 230°F. at a pressure of about 30 mm. of mercury. The amount of residue from the vinylbenzene distillation varies from about 2 percent to about 5 percent of the styrene produced. The residue is a highly viscous tarry material and is a complex mixture of monomeric compounds and aromatic polymeric compounds. The monomeric compounds are present in both unsaturated and saturated forms. The monomeric

substances include small amounts of polyalkylbenzenes, such as polymethyl and polyethylbenzenes, diphenyl and substituted diphenyls, and fused ring compounds such as indanes, indenes, naphthalenes, acenaphthenes, and phenanthrenes. The polymeric compounds include polystyrene, polyethylvinylbenzene, polydivinylbenzene and mixtures of these and other aromatic polymeric compounds. This distillation residue is usually discarded or burned. The product from the alkylation step is catalytically dehydrogenated to provide vinylbenzenes, such as styrene, vinyltoluene, ethylvinylbenzene, and divinylbenzene.

In the process of this invention the feed stock which may comprise the residues from the distillations of the alkylation and the dehydration products or one or more of the individual compounds present in these residues, such as polystyrene, or polydivinylbenzene is passed into a reactor, preferably at an elevated temperature, such as from about 300°F. to about 600°F., and it is mixed with hydrogen as it enters the reactor. The amount of hydrogen mixed with the feed stock is at least an amount which is sufficient to saturate any unsaturated hydrocarbon compounds which result from cracking the feed stock components, and preferably from about 22.6 to about 40 standard cubic feet of hydrogen per pound of feed stock. If the amount of hydrogen is below about 22.6 standard cubic feet per pound of feed stock, the unsaturated compounds formed are not fully hydrogenated and if the amount of hydrogen is above about 40 standard cubic feet per pound of feed stock, some hydrogen is not utilized. The mixture of feed stock and hydrogen is passed through a bed of catalyst which is maintained at a temperature of from about 800°F. to about 1,300°F., preferably from about 1,000°F. to about 1,200°F. If the temperature of the catalyst bed is below about 800°F., the reaction rate is undesirably low and if the temperature of the catalyst bed is above about 1,300°F., an excessive amount of carbon is formed as a result of the cracking of the hydrocarbon components of the feed stock, which decreases the catalyst activity and lowers the yield of desirable aromatic products. The pressure within the reactor is maintained within the range of from about 150 to about 700 psig., preferably from about 200 to about 400 psig. If the pressure is below about 150 psig., the hydrocracking reactions do not go the desired completion because the partial pressure of hydrogen is too low. If the pressure is greater than about 700 psig., there is excessive cracking of the hydrocarbon components of the feed stock, which results in carbon formation and a shortened life of the catalyst. The feed stock is passed through the catalyst bed at a rate of from about 0.3 to about 3.5 pounds of feed stock per pound of catalyst per hour. If the rate is below about 0.3 pound of feed stock per pound of catalyst per hour, the process is inefficient and uneconomical. If the rate is greater than about 5 pounds of feed stock per pound of catalyst per hour, the hydrocracking reactions are incomplete and this results in a low conversion and a low yield of the desired saturated aromatic compounds.

The end product of the hydrocracking reactions is a low viscosity liquid which may be degassed and fractionally distilled. By distilling the degassed stream to a temperature of up to 165°C., at atmospheric pressure, a distillate is obtained which contains utilizable materi-

als, such as benzene, toluene, ethylbenzene, xylenes, methylethylbenzenes, and diethylbenzene. The distillate may be recycled to the alkylation reaction or further fractionated to provide substantially pure components. The residue from the distillation is composed largely of polyalkylbenzenes and saturated polymeric materials and may be used as fuel oil, or recycled and combined with the hydrocracking feed stock.

In general, hydrocracking catalysts suitable for use in the practice of this invention are oxides of metals, such as cobalt, nickel, and molybdenum, which are supported on a material such as alumina. The preferred catalysts contain a combination of cobalt and molybdenum oxides, a combination of nickel and molybdenum oxides, and a combination of cobalt and molybdenum oxides promoted by nickel oxides.

More particularly the catalysts which may be used in the process of this invention are cobalt-molybdenum oxides, nickel oxide promoted cobalt-molybdenum oxide, or nickel-molybdenum oxides on a support material, preferably alumina, and are prepared in general by adding controlled amount of strong acid to a mixture of the metallic compounds and a carrier, such as alumina. Sufficient water is added to reduce the mixture to a somewhat fluid consistency suitable for extrusion and the batch is passed through a suitable die, preferably of stainless steel, to form shaped extrudates. The extruded material is then dried and/or calcinated at high temperature to drive off the water and convert the metallic compounds to oxides supported on the carrier.

More particularly, the preferred method of catalyst manufacture comprises mixing alumina hydrate and molybdenum oxide with an aqueous solution of a cobalt salt or with a nickel salt or with a mixture of cobalt and nickel salts, which are convertible to cobalt oxide and nickel oxide upon calcination. In the preferred mixing procedure, the molybdenum oxide, cobalt and nickel compounds are dispersed uniformly throughout the alumina and a damp solid mixture is formed. Then a strong mineral acid, such as nitric acid, hydrochloric acid, or sulfuric acid, is added in a controlled amount to convert the damp solid into an extrudable paste. When the acid is nitric acid, the amount of acid selected should be at least 2.5 percent by weight of commercial concentrated (63 percent) acid, based on the total weight of the finished product, 5 to about 10 percent being the preferred range. The amount of concentrated acid can exceed 10 percent by weight, as the excess is removed during calcination, but for reasons of economy such an excess is usually undesirable. With other mineral acids, mole equivalent quantities of acid are selected. Sufficient water is added to the mixture, simultaneously and/or subsequently, to form an extrudable paste and the catalyst mixture is passed through a die or other apparatus to form extrusions. The amount of water used in preparing the extrudable paste is determined with regard to the consistency of the mixture after the acid has been added. A certain amount of water is added with the acid and the additional water which may be required to produce an extrudable mass is determined by simple experimentation to achieve a paste of the proper consistency. The extrusions are calcined at a temperature such that the moisture is evaporated, the salts of cobalt and nickel are decomposed, the alumina is partially dehydrated,

and the extrusions are converted into hard catalyst pellets which have great physical strength and will withstand repeated regeneration without appreciable deterioration.

Certain variations from the above-described preferred procedure may be employed if desired. For example, if the compounds utilized are compatible with the acid used, the acid addition may be made simultaneously with the cobalt and nickel compounds. Moreover, it is not necessary that the acid be highly concentrated at the time of addition, and if desired, all or some of the water added to adjust the composition to an extrudable paste may be mixed with the acid prior to addition of the acid to the mixture.

The carrier or support material used in forming the extruded catalyst according to this invention is alumina, preferably a hydrated alumina, such as that containing approximately equal proportions of beta- $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and alpha- $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which upon calcination at a temperature within the range of from 700°F. to 900°F. is converted largely to gamma- Al_2O_3 . Other hydrated aluminas, such as alpha- $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, as well as calcined or otherwise dehydrated alumina can be used in producing the catalyst. During the calcination of the extruded alumina catalyst, high temperatures should be avoided or "dead burned" alumina may result. The preferred calcining temperature is in the range of 600°F. to 1,000°F., although higher temperatures not exceeding the sublimation temperature (approximately 2,300°F.) of molybdenum trioxide may be used.

When the catalyst is a cobalt-molybdenum or nickel-molybdenum oxide mixture, the atomic ratio of cobalt to molybdenum and nickel to molybdenum may vary from 1 to 5 to 1 to 1. When the catalyst is a nickel oxide promoted cobalt-molybdenum oxide mixture, the atomic ratio of the combined nickel and cobalt to the molybdenum may vary from 1 to 5 to 1 to 1. The relative quantities may be controlled by adjusting the amounts of molybdenum oxide and nickel and cobalt salts used in the initial steps of the catalyst manufacture. The cobalt salt and nickel salt may be any cobalt or nickel salt which is soluble in water and convertible to the oxide upon calcination, such as cobalt or nickel chlorides, cobalt or nickel nitrates, and cobalt or nickel sulfates. The pH of the solution must be less than about 7 or the cobalt and nickel salts may precipitate early. The amounts of catalytically active materials in the finished catalyst should usually be as small as possible consistent with the required activity to accomplish the desired reaction. Generally speaking, the amount of cobalt and molybdenum in the cobalt-molybdenum catalyst will fall within the range of: Cobalt as CoO —1 to 5 percent by weight, Molybdenum as MoO_3 —2 to 20 percent by weight. The amounts of nickel and molybdenum in the nickel-molybdenum catalyst will fall within the range of: Nickel as NiO —1 to 5 percent by weight, Molybdenum as MoO_3 —2 to 20 percent by weight. The amounts of nickel and molybdenum in the nickel-molybdenum catalyst will fall within the range of: Nickel as NiO —1 to 5 percent by weight, Molybdenum as MoO_3 —2 to 20 percent by weight. The amounts of nickel, cobalt, and molybdenum in a nickel oxide promoted cobalt-molybdenum oxide mixture will fall within the range of: Cobalt as CoO plus Nickel as NiO —1 to 5 percent by weight, Molybdenum as

MoO₃—2 to 20 percent by weight. The remainder of the catalyst is carrier.

Methods for preparing four different catalysts suitable for use in the process of this invention are given below. However, these methods are presented only by way of illustration of catalysts which may be used in the successful carrying out of the hydrocracking process of the appended claims.

CATALYST NO. 1

A mixture of 100 lbs. of hydrated alumina (27 percent water) and 9 lbs. of molybdenum trioxide is dry mulled for approximately 20 minutes. The hydrated alumina comprises approximately equal proportions of beta-Al₂O₃·3H₂O and alpha-Al₂O₃·H₂O. Then 26.5 lbs. of an aqueous solution of cobalt nitrate (sp. gr. 1.196) containing 1.8 lbs. of CoO is added and the mixture is wet mulled for approximately 10 minutes. The cobalt nitrate solution is prepared by dissolving cobalt metal in dilute nitric acid and controlling the excess of acid so that not more than 2 percent free acid is present. Next, 2.5 lbs. of nitric acid (63 percent) diluted with water are added and wet mulling is continued. Additional water (approximately 4.5 gal.) is added to give a paste of proper consistency for extrusion. The catalyst past is then extruded through a 3/16 inch stainless steel die and the extrusions are calcined for 1 hour at 400°F., 1 hour at 650°F., and 6 hours at 950°F. The catalyst thus formed shows an analysis of 2.5% CoO and 12.0% MoO₃. It has a side crush strength of 29 lbs. dead weight load (DWL), and abrasion loss of only 5.05 percent and a bulk density of 45.4 lbs per cubic foot.

CATALYST NO. 2

A mixture of 22 lbs. of hydrated alumina (27 percent water) and 2 lbs. of molybdenum trioxide is dry mulled for approximately 20 minutes. The hydrated alumina comprises approximately equal proportions of beta-Al₂O₃·3H₂O and alpha-Al₂O₃·H₂O. Then 91.5 ml. of an aqueous solution of cobalt nitrate (sp. gr. 1.530) and 9.65 ml. of an aqueous solution of nickel nitrate (sp. gr. 1.546) are added and the mixture is wet mulled for approximately 10 minutes. The cobalt nitrate solution is prepared by dissolving cobalt metal in dilute nitric acid and controlling the excess of acid so that not more than 2 percent free acid is present. Next, 340 ml. of 63 percent nitric acid are added and wet mulling is continued. Additional water (approximately 910 ml.) is added to give a paste of proper consistency for extrusion. The catalyst paste is then extruded through a 3/16 inch stainless steel die and the extrusions are calcined for hour at 400°F., 1 hour at 650°F., and 6 hours at 950°F. The catalyst thus formed shows an analysis of 2.33% CoO, 2.81% NiO, and 9.25% MoO₃.

CATALYST NO. 3

A cobalt-nickel-molybdenum alumina extruded catalyst is prepared from the following materials:

NiO (as nickel nitrate solution)	37.5
CoO (as cobalt nitrate solution)	50.0
MoO ₃	300
Alumina hydrate	2850
Nitric acid	62.5

The alumina and molybdenum trioxide are dry mulled together for 10 minutes. The cobalt nitrate and nickel nitrate solutions are added followed by addition of the nitric acid (equivalent to 2.5 percent by weight of the finished product) and wet mulling is continued for a period of 2 hours. Then the consistency of the paste is adjusted by the addition of water to form an extrudable product which is extruded through a 3/16 inch die. The extruded material is calcined for 1 hour at 450°F., 1 hour at 650°F., and 6 hours at 950°F. On analysis, the catalyst is found to contain 1.9% CoO, 1.5% NiO, and 11.2% MoO₃.

CATALYST NO. 4

A nickel-molybdenum-alumina extruded catalyst is prepared from the following materials:

	Parts
NiO (as nickel nitrate solution)	87.5
MoO ₃	300
Alumina hydrate	2850
Nitric acid (63%)	62.5

The alumina and molybdenum trioxide are dry mulled together for 10 minutes. The nickel nitrate solution is added followed by the nitric acid (equivalent to 2.5 percent by weight of the finished product) and wet mulling is continued for a period of two hours. Then the consistency of the paste is adjusted by the addition of water to form an extrudable product which is extruded through 3/16 inch die. The extruded material is calcined for 1 hour at 450°F., 1 hour at 650°F., and 6 hours at 950°F. On analysis, the catalyst is found to contain 3.4% NiO, and 11.2% MoO₃.

The following examples, which illustrate the hydrocracking process of this invention, are given for the purpose of illustrating the invention but are not to be construed as limiting it in scope. It will be readily appreciated by those skilled in the art that numerous modifications in conditions, concentrations, relative quantities of materials, and the like, may be made without departing from the invention.

EXAMPLE 1

A feed stock which comprises the residue from the distillation up to a temperature of 400°F. at 25 mm. of mercury of crude ethylbenzene from the catalytic alkylation of benzene with ethylene, is heated to 300°F. and pumped into the top of a reactor containing a bed of Catalyst No. 2. Hydrogen is also introduced at the top of the reactor and mixed with the feed stock. The mixture of the feed stock and hydrogen is passed through the catalyst at a rate such that 0.35 pound of feed stock per hour per pound of catalyst and 23.0 standard cubic feet of hydrogen per pound of feed stock pass through the reactor. The average catalyst temperature is 800°F. and any heat required to keep the catalyst up to temperature, which is not provided by the heat of reaction, is supplied by electrical heating elements about the catalyst case. The total pressure within the reactor is 150 psig. The reaction product is removed from the reactor at such a rate that the pressure within the reactor is maintained at the above level.

The product represents 70 percent by weight of the hydrocarbon content of the feed stock.

The product is degassed and fractionally distilled up to 165°C. at 760 mm of Hg. The amount of distillate is 75 percent by weight of the product.

EXAMPLE 2

The procedure of Example 1 is repeated except that the rate of feed is 0.4 pound of feed stock per hour per pound of catalyst, the amount of hydrogen is to 26.0 standard cubic feet per pound of feed stock, the average catalyst temperature is 960°F., and the total pressure within the reactor is 250 psig.

The product represents 74 percent of the hydrocarbon content of the feed stock.

EXAMPLE 3

The procedure of Example 1 is repeated except that the rate of feed is 0.8 pound of feed stock per hour per pound of catalyst. The amount of hydrogen is 30.0 standard cubic feet per pound of feed stock, the average catalyst temperature is 1,000°F., and the total pressure within the reactor is 300 psig.

The product represents 79 percent of the hydrocarbon content of the feed stock.

EXAMPLE 4

The procedure of Example 1 is repeated except that the rate of feed is 2.0 pounds of feed stock per hour per pound of catalyst, the amount of hydrogen is 30.0 standard cubic feet per pound of feed stock, the average catalyst temperature is 1,100°F., and the total pressure within the reactor is 300 psig.

The product represents 79 percent of the hydrocarbon content of the feed stock.

EXAMPLE 5

The procedure of Example 1 is repeated except that the rate of feed is 3.5 pounds of feed stock per hour per pound of catalyst, the amount of hydrogen is 35.0 standard cubic feet per pound of feed stock, the average catalyst temperature is 1,125°F., and the total pressure within the reactor is 450 psig.

The product represents 82 percent of the hydrocarbon content of the feed stock.

EXAMPLE 6

The procedure of Example 1 is repeated except that the rate is 4.5 pounds of feed stock per hour per pound of catalyst, the amount of hydrogen is 38.0 standard cubic feet per pound of feed stock, the average catalyst temperature is 1,250°F., and the total pressure within the reactor is 650 psig.

The product represents 86 percent of the hydrocarbon content of the feed stock.

The compositions of the distillates of Example 1 through 6 are given in Table 1.

TABLE 1

	1	2	3	4	5	6
Distillate	75.3%	78.4%	80%	80.5%	82.6%	86.2%
Residue	24.7%	21.6%	20%	19.5%	17.4%	13.8%
	Composition of Distillate in %					
Benzene	5	8	8	7.5	8	6
Toluene	10	12	12.5	11.5	12	11
Ethylbenzene	30	39	38.5	37	39	32
Intermediates	10	10	11	11.5	11	13

Diethylbenzene	15	18	17	16	15.5	13
Polyalkylated-benzenes	30	13	13	16.5	14.5	25

EXAMPLE 7

The procedure of Example 1 is repeated except that Catalyst No. 1 is used, the rate of feed is 1.3 pounds of feed stock per hour per pound of catalyst, 30.0 standard cubic feet of hydrogen per pound of feed stock pass through the reactor, the average catalyst temperature is 1,100°F., and the total pressure within the reactor is 300 psig.

The product represents 76 percent of the hydrocarbon content of feed stock.

EXAMPLE 8

The procedure of Example 1 is repeated except that Catalyst No. 1 is used, the average catalyst temperature is 1,100°F., the rate of feed is 1.7 pounds of feed stock per hour per pound of catalyst, 32.0 standard cubic feet of hydrogen per pound of feed stock pass through the reactor, and the total pressure within the reactor is 300 psig.

The product represents 78 percent of the hydrocarbon content of the feed stock.

EXAMPLE 9

The procedure of Example 1 is repeated except that Catalyst No. 3 is used, the rate of feed is one pound of feed stock per hour per pound of catalyst, 40.0 standard cubic feet of hydrogen per pound of feed stock pass through the reactor, the average catalyst temperature is 1,200°F., and the total pressure in the reactor is 150 psig.

The product represents 69 percent of the hydrocarbon content of the feed stock.

EXAMPLE 10

The procedure of Example 1 is repeated except that Catalyst No. 3 is used. The rate of feed is one pound of feed stock per pound of catalyst per hour, 40.0 standard cubic feet of hydrogen per pound of feed stock pass through the reactor, the average catalyst temperature is 1,200°F., and the total pressure in the reactor is 300 psig.

The product represents 72 percent of the hydrocarbon content of the feed stock.

EXAMPLE 11

The procedure of Example 1 is repeated except that Catalyst No. 4 is used. The rate of feed is 0.5 pound of feed stock per pound of catalyst per hour, 30.0 standard cubic feet of hydrocarbon per pound of feed stock pass through the reactor, the average catalyst temperature is 1,150°F., and the total pressure in the reactor is 150 psig.

The product represents 63 percent of the hydrocarbon content of the feed stock.

EXAMPLE 12

The procedure of Example 1 is repeated except that Catalyst No. 4 is used, the rate of feed is 1.5 pounds of feed stock per pound of catalyst per hour, 30.0 standard cubic feet of hydrocarbon per pound of feed stock pass through the reactor, the average catalyst tempera-

ture is 1,150°F., and the total pressure in the reactor is 300 psig.

The product represents 65 percent of the hydrocarbon content of the feed stock.

The compositions of the distillates of Examples 7 through 12 are given in Table 2.

TABLE 2

	7	8	9	10	11	12
Distillate	78.8%	80.2%	74.5%	77.5%	80%	81.5%
Residue	21.2%	19.8%	25.5%	22.5%	20%	18.5%
	Composition of Distillate in %					
Benzene	6	5.5	6.5	7.5	8.5	9.0
Toluene	9	8.5	10.5	11.0	7.5	8.5
Ethylbenzene	41	44	31	34	26	29.5
Intermediates	9.5	8.5	10.0	10.5	14	14.5
Diethylbenzene	15.5	14.5	16	15	12	12.5
Polyalkylated-benzenes	19	19	26	22	32	26

The intermediates contain xylenes and methyl-ethyl-benzenes which boil over a narrow range. The polyalkylated benzenes have at least three alkyl groups. Both of these fractions may be recycled to the reactor.

EXAMPLE 13

The procedure of Example 1 is repeated, except that the feed stock is comprised substantially of polystyrene. The product contains a major amount of volatile aromatic hydrocarbon compounds, such as benzene and ethylbenzene, and a minor amount of higher molecular weight residue.

The above Example demonstrates the operation of the invention when the feed stock is comprised substantially of polystyrene. Polystyrene having any desired molecular weight range may be treated in accordance with the invention. For instance, liquid polystyrene, that is, polystyrene having a molecular weight range up to about 20,000 or more, or solid polystyrene that is polystyrene having a molecular weight range from about 20,000 up to a million or more may be treated according to the process of the invention.

The above descriptions and particularly the examples are set forth by way of illustration only. Various changes and modifications in the novel process described herein, such as will be apparent to those skilled in the art, may be made without departing from the spirit and scope of the invention herein disclosed.

What is claimed is:

1. A process for the recovery of valuable aromatic hydrocarbons by hydrocracking a feed stock containing at least one member selected from the group consisting of polyalkylbenzenes, diphenyls, fused ring aromatic compounds and vinyl aromatic polymeric compounds, which comprises passing a mixture of the feed stock and hydrogen through a bed of hydrocracking catalyst, the amount of hydrogen being sufficient to saturate any unsaturated hydrocarbon which results from cracking the feed stock components, the rate of flow of the feed stock through the catalyst bed being maintained at about 0.3 to about 3.5 pounds per pound of the catalyst per hour, the temperature of the catalyst bed being maintained within the range of about 800°F.

to about 1300°F., and the pressure of the feed stock and hydrogen being maintained within the range of about 150 to about 700 psig.

2. A process according to claim 1 in which the feed stock is passed through the catalyst bed at a rate of from about 0.35 to about 1.5 pounds of feed stock per pound of catalyst per hour, the amount of hydrogen is from about 22.6 to about 40 standard cubic feet of hydrogen per pound of feed stock, the catalyst is at a temperature within the range of from about 1,000°F. to about 1200°F. and the pressure is within the range from about 200 to about 400 psig.

3. A process according to claim 1 in which the catalyst comprises oxides of cobalt, nickel, and molybdenum on an alumina carrier and the atomic ratio of cobalt plus nickel to molybdenum is in the range of 1 to 5 to 1 to 1.

4. A process according to claim 1 in which the catalyst comprises oxides of cobalt and molybdenum on an alumina carrier and the atomic ratio of cobalt to molybdenum is within the range of 1 to 5 to 1 to 1.

5. A process according to claim 1 in which the catalyst comprises oxides of nickel and molybdenum on an alumina carrier and the atomic ratio of nickel to molybdenum is within the range of 1 to 5 to 1 to 1.

6. A process according to claim 1 in which the catalyst comprises oxides of cobalt, nickel, and molybdenum on an alumina carrier in which the amount of cobalt as CoO plus the nickel as NiO is within the range of from about 1 to 5 percent by weight, the amount of molybdenum as MoO₃ is within the range of from about 2 to 50 percent by weight, and the remainder is alumina.

7. A process according to claim 1 in which the catalyst comprises oxides of cobalt and molybdenum on an alumina carrier in which the amount of cobalt as CoO is within the range of from about 1 to 5 percent by weight, the molybdenum as MoO₃ is within the range of from about 2-50 percent by weight, and the remainder is alumina.

8. A process according to claim 1 wherein the catalyst comprises oxides of nickel and molybdenum on an alumina carrier in which the nickel as NiO is present in an amount within the range of from about 1 to 5 percent by weight, the molybdenum as MoO₃ is present in an amount of from about 2 to 20 percent by weight and the remainder is alumina.

9. A process according to claim 1 wherein the feed stock is comprised substantially of aromatic polymeric compounds.

10. A process according to claim 9 in which the catalyst comprises oxides of cobalt, nickel, and molybdenum on an alumina carrier and the atomic ratio of cobalt plus nickel to molybdenum is in the range of 1 to 5 to 1 to 1.

11. A process according to claim 9 in which the catalyst comprises oxides of cobalt and molybdenum on an alumina carrier and the atomic ratio of cobalt to molybdenum is within the range of 1 to 5 to 1 to 1.

12. A process according to claim 9 in which the catalyst comprises oxides of nickel and molybdenum on an alumina carrier and the atomic ratio of nickel to molybdenum is within the range of 1 to 5 to 1 to 1.

13. A process according to claim 9 wherein the feed stock consists substantially of at least one member of

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the group consisting of polystyrene, polydivinylbenzene, polyethylvinylbenzene and mixtures of these.

14. A process according to claim 13 in which the catalyst comprises oxides of cobalt, nickel, and molybdenum on an alumina carrier and the atomic ratio of cobalt plus nickel to molybdenum is in the range of 1 to 5 to 1 to 1.

15. A process according to claim 13 in which the catalyst comprises oxides of cobalt and molybdenum on an alumina carrier and the atomic ratio of cobalt to molybdenum is within the range of 1 to 5 to 1 to 1.

16. A process according to claim 13 in which the catalyst comprises oxides of nickel and molybdenum on an alumina carrier and the atomic ratio of nickel to molybdenum is within the range of 1 to 5 to 1 to 1.

17. A process for the recovery of valuable aromatic hydrocarbons from polystyrene comprising passing a mixture of polystyrene and hydrogen through a bed of hydrocracking catalyst comprised of at least one oxide selected from a group consisting of cobalt, nickel and molybdenum on an alumina carrier, the amount of hydrogen being sufficient to saturate any unsaturated

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hydrocarbons which result from cracking the polystyrene, the rate of flow of the polystyrene through the catalyst bed being maintained at about 0.3 to about 3.5 lbs. per pound of the catalyst per hour, the temperature of the catalyst bed being maintained within the range of about 800°F. to about 1,300°F., and the pressure of the polystyrene and hydrogen being maintained within the range of about 150 to about 700 psig.

18. A process according to claim 17 in which the catalyst comprises oxides of cobalt, nickel, and molybdenum on an alumina carrier and the atomic ratio of cobalt plus nickel to molybdenum is in the range of 1 to 5 to 1 to 1.

19. A process according to claim 17 in which the catalyst comprises oxides of cobalt and molybdenum on an alumina carrier and the atomic ratio of cobalt to molybdenum is within the range of 1 to 5 to 1 to 1.

20. A process according to claim 17 in which the catalyst comprises oxides of nickel and molybdenum on an alumina carrier and the atomic ratio of nickel to molybdenum is within the range of 1 to 5 to 1 to 1.

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