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PRODUCTION OF AROMATICS-RICH GASOLINE WITH LOW BENZENE CONTENT

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(56) Prior Art Documents
US 3114696
US 3770614
US 4834866

(57) Claim

1. A process for upgrading a hydrocarbon feedstream comprising C_6 hydrocarbons to produce high octane gasoline, comprising the steps of:

a) separating the feedstream into a first fraction rich in n-hexane and a second fraction rich in other hexane isomers;

b) reforming said first fraction to produce a reformate containing benzene and C_7+ hydrocarbons;

c) separating said reformate into a C_7- hydrocarbon stream containing benzene and paraffins and a C_7+ hydrocarbon stream;

d) contacting said C_7- hydrocarbon stream and an alkylating agent with a zeolite catalyst to produce high octane gasoline containing C_7+ aromatic hydrocarbons.

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Complete Specification for the invention entitled:

PRODUCTION OF AROMATICS-RICH GASOLINE WITH LOW BENZENE CONTENT

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The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

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PRODUCTION OF AROMATICS-RICH GASOLINE WITH LOW BENZENE CONTENT

This invention relates to a process for upgrading naphtha to produce aromatics-rich gasoline with a low benzene content.

In recent years, a major technical challenge presented to the petroleum refining industry has been the development of alternate processes for manufacturing high octane gasoline in view of the regulated requirement to eliminate lead additives as octane enhancers as well as the development of more efficient, higher compression ratio gasoline engines requiring higher octane fuel. To meet these requirements the industry has developed non-lead octane boosters and has reformulated high octane gasoline to incorporate an increased fraction of aromatics. While these and other approaches will fully meet the technical requirements of regulations requiring elimination of gasoline lead additives and allow the industry to meet the burgeoning market demand for high octane gasoline, the economic impact on the cost of gasoline is significant. Accordingly, workers in the field have intensified their effort to discover new processes to manufacture the gasoline products required by the market place.

Gasolines manufactured to contain a higher concentration of aromatics such as benzene, toluene and xylenes can adequately meet the octane requirements of the marketplace for a high octane fuel. Aromatics, particularly benzene, are commonly produced in refinery processes such as catalytic reforming which have been a part of the conventional refinery complex for many years. However, their substitution for the environmentally unsuitable lead octane enhancers is

complicated by environmental problems of their own. Environmental and health related studies have raised serious questions regarding the human health effects of benzene. The findings suggest that exposure to high levels of benzene should be avoided with the result that benzene concentration in gasoline to enhance octane number is limited and controlled to a relatively low value. Alkylated aromatics, such as toluene and xylenes do not suffer under the same health effects liabilites as benzene and can be readily used for their octane enhancing properties.

When hydrocarbons boiling in the gasoline boiling range are reformed in the presence of a hydrogenation-dehydrogenation catalyst, a number of reactions take place which include dehydrogenation of naphthenes to form aromatics, dehydrocyclization of paraffins to form aromatics, isomerization reactions and hydrocracking reactions. It is well known that reforming conditions can be varied to favor the production of certain products. However, when the reforming conditions are severe coke formation in the catalyst occurs with consequent deactivation of the catalyst. Clearly, the composition of the charge to the reformer will influence the reforming conditions selected and the composition of the reformate produced. For instance, it is known that the production of benzene in the reforming process is favored when the charge contains a significant portion of benzene precursors such as hexanes. Typically, both n-hexane and isohexane are converted in the reformer, although only n-hexane has an unacceptably low octane number for consideration as part of the gasoline pool.

The treatment of a reformate with crystalline aluminosilcate zeolites is known in the art and has included both physical treatments such as selective adsorption, as well as chemical treatments such as selective conversion thereof. In U.S. Patent 3,770,614

a process combination is described for upgrading naptha boiling range hydrocarbons by a combination of catalytic reforming and selective conversion of paraffinic components to enhance yield of aromatic hydrocarbons by contact with crystalline aluminosilicate catalyst having particular conversion characteristics. In U.S. Patent 3,649,520 a process is described for the production of lead free gasoline by an integrated process of reforming, aromatics recovery and isomerization including C_6 hydrocarbons upgrading to higher octane product for blending.

It is an object of the present invention to provide a process for the manufacture of high octane gasoline containing a reduced amount of benzene.

According to the invention, there is provided a process for upgrading a hydrocarbon feedstream containing C_6 hydrocarbons to produce high octane gasoline, the process comprising the steps of:

a) separating the feedstream into a first fraction rich in n-hexane and a second fraction rich in other hexane isomers;

b) reforming said first fraction to produce a reformate containing benzene and gasoline boiling range hydrocarbons;

c) separating said reformate into a C_6- hydrocarbon stream containing benzene and paraffins and a C_7+ hydrocarbon stream;

d) contacting said C_6- hydrocarbon stream and an alkylating agent with a zeolite catalyst to alkylate benzene therein to produce high octane gasoline containing C_7+ aromatic hydrocarbons.

The present invention provides an integrated reforming/alkylation process which can improve the economics of meeting the benzene specification of tne gasoline pool, preferably reducing the pool benzene content below five percent. This is achieved in a combination of steps which includes using an alkylating

agent, such as a lower alkanol, e.g., methanol, a light olefin, e.g., propylene, or a light olefin containing fuel gas, to alkylate benzene over a zeolite catalyst. In a preferred embodiment of the invention ~~another step,~~ the process utilizes a fractionator upstream of the reformer section to separate high octane iso-hexane components from the reformer feed. Separation of iso-hexane components results in a reduced benzene yield in the reformer by limiting reforming of C_6 aliphatic hydrocarbons only to those of low octane number, e.g., n-hexane. The low benzene yield also advantageously affects the alkylation process by lowering the alkylation process exotherm and reducing the consumption of alkylating agent such as methanol or light olefins. Preferably, the iso-hexane components separated from the reformer feed are blended into the gasoline pool.

The reformer section of the integrated process of the invention is preferably operated in conventional manner using a platinum-containing reforming catalyst at a pressure up to 3200 kPa (450 psig) and a temperature of 450-540°C.

The alkylation section employs a fixed bed zeolite catalyst and operates at a pressure of 200-5600 kPa (30-800psi) and a temperature of 200-500°C. The zeolite employed in the alkylation section preferably has a Constraint Index (as defined in U.S. Patent No. 4016218) less than 12, and preferably 2-12. Suitable zeolites include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, zeolite beta and zeolite Y, with ZSM-5 being particularly preferred. ZSM-5 is more particularly described in U.S. Reissue Patent No. 28,341 (of original Patent No. 3,702,886). ZSM-11 is more particularly described in U.S. Patent No. 3,709,979. Zeolite ZSM-12 is described in U.S.Patent No.3,832,449. ZSM-23 is more particularly described in U.S. Patent No. 4,076,842. ZSM-35 is more particularly described in U.S. Patent No. 4,016,245. Zeolite Beta is described in

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U.S. Reissue Patent No. 28,341 (of original U.S. Patent No. 3,308,069). Zeolite Y is described in U.S. Patent No. 3,130,007.

The zeolite(s) selected for use herein will generally possess an alpha value of at least 1, preferably at least 10 and more preferably at least 100. "Alpha value", or "alpha number", is a measure of zeolite acidic functionality and is more fully described together with details of its measurement in U.S. Patent No. 4,016,218, J. Catalysis, 6, pp. 278-287 (1966) and J. Catalysis, 61, pp. 390-396 (1980).

Reactivation of the fixed bed zeolite alkylation catalyst can be accomplished by utilizing a hydrogen purge stream which is typically available from the reformer unit. Advantageously, in the integrated process of the present invention, the regeneration or reactivation of spent zeolite catalyst may be incorporated with the reforming catalyst regeneration capabilities in such a way as to utilize the ancillary equipment of reformer catalyst regeneration, such as compressors and heat exchangers, to provide and treat the regenerating gas required for zeolite spent catalyst regeneration.

The invention will now be more particularly described with reference to the accompanying drawing which is a schematic illustration of a process of upgrading a naphtha feedstream according to one example of the invention.

Referring to the drawing, in the process shown a C_6 hydrocarbon feedstream 110 is passed to fractionator 120 for separation into a higher boiling n-hexane stream 130 and a lower boiling iso-hexane stream 140. The n-hexane stream is passed to a catalytic reformer 150 to produce a reformate stream 155, which is passed to a fractionator 160 for separation of a C_7+ or C_8+ stream 165, a C_6 or $C6$-C_7 stream 170, and a C_5-C_6 overhead stream 161. The

C_6 or C_6-C_7 stream containing benzene, or benzene and toluene, and paraffins is passed to alkylation reactor 175 containing ZSM-5 catalyst. Alkylating agents comprising preferably methanol or light olefins are passed to the alkylation reactor via conduit 180. The alkylation reactor effluent 185 containing unconverted benzene, toluene and C_8-C_{11} aromatics is sent to the recovery section. Typically, 30-60% of benzene is converted per pass. Part of the reactants, preferably olefins, may be used as reactor internal quench. Optionally, the reformate may be passed via line 191 to debutanizer 190 for separation of C_6 or C_6-C_7 stream 192.

In the drawing, there is also shown catalyst regeneration sections 105 and 106. Section 105 comprises the regeneration section for the reforming unit while section 106 comprises the regeneration section for the zeolite alkylation process. These sections include fixed bed reactors which are taken off line for catalyst regeneration or are subject to regeneration when the entire process is down. In the example shown the facilities of the reformer regenerator section 105, i.e., compressors, pumps, heat exchangers, instrumentation, etc., can be used in the regeneration of zeolite alkylation catalyst in section 106. Regeneration of fixed bed zeolite can be carried out by passing regeneration gas 107 from regenerator section 105 to zeolite section 106 and recycling 108 to the reformer regenerator section 105. Reactivation of the zeolite alkylation catalyst can be effected using the reformer hydrogen product stream.

~~XXXXXXXX~~ The claims defining the invention are as follows:

1. A process for upgrading a hydrocarbon feedstream comprising C_6 hydrocarbons to produce high octane gasoline, comprising the steps of:

a) separating the feedstream into a first fraction rich in n-hexane and a second fraction rich in other hexane isomers;

b) reforming said first fraction to produce a reformate containing benzene and C_7+ hydrocarbons;

c) separating said reformate into a C_7- hydrocarbon stream containing benzene and paraffins and a C_7+ hydrocarbon stream;

d) contacting said C_7- hydrocarbon stream and an alkylating agent with a zeolite catalyst to produce high octane gasoline containing C_7+ aromatic hydrocarbons.

2. The process of claim 1 wherein said separation step (a) is effected by fractionation.

3. The process of claim 1 or claim 2 wherein said separation step (c) is effected by fractionation.

4. The process of any preceding claim wherein said alkylating agent is a light olefin, a lower alkanol or fuel gas containing a light olefin.

5. The process of claim 4 wherein said light olefin comprises propylene.

6. The process of claim 4 wherein said lower alkanol comprises methanol.

7. The process of any preceding claim wherein said zeolite comprises ZSM-5.

8. The process of any preceding claim wherein the second fraction is blended with the high octane gasoline produced in step (d).

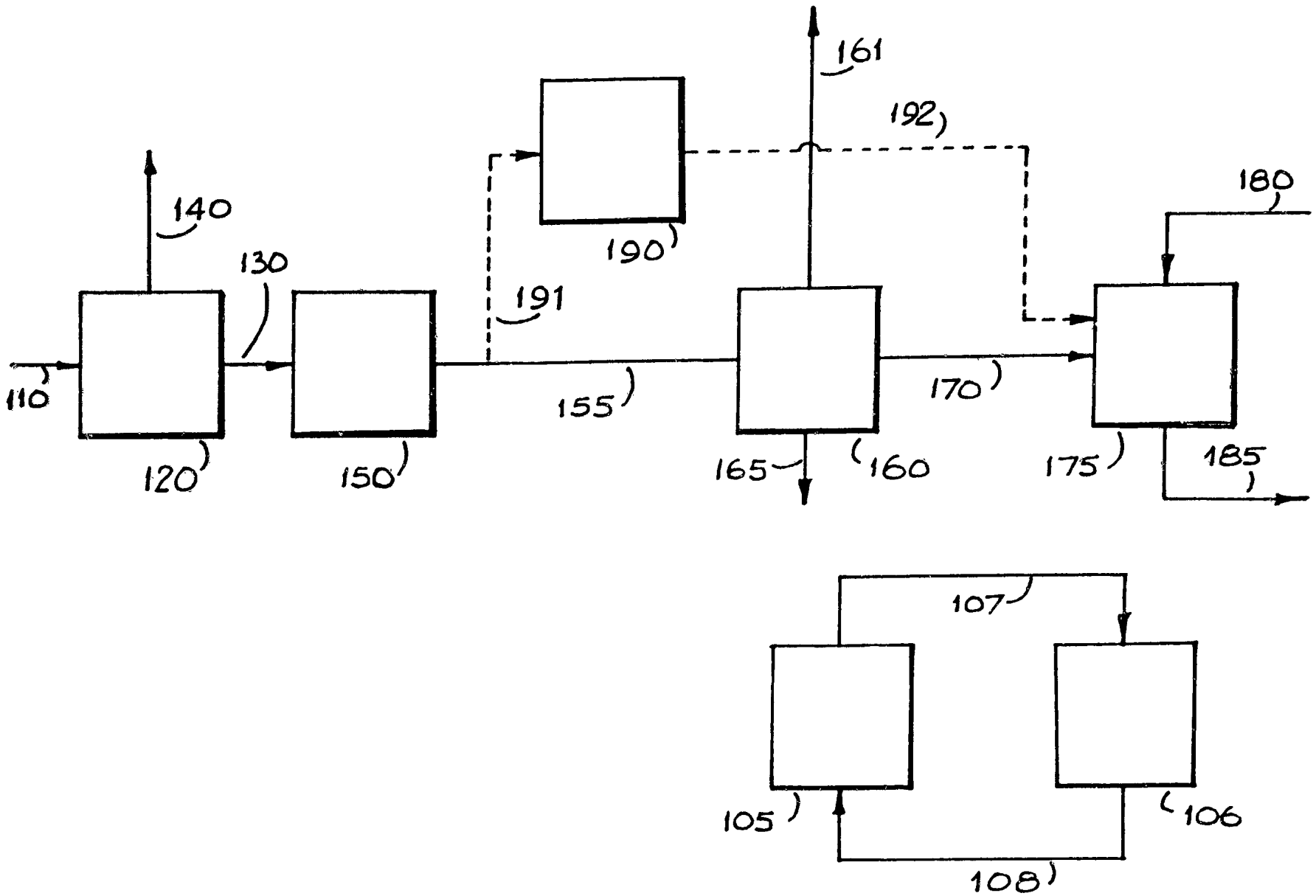
9. The process according to claim 1 substantially as hereinbefore described with reference to the drawing.

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