

PCT PATENT APPLICATION

**PROCESS FOR THE PRODUCTION OF XYLENES AND LIGHT OLEFINS FROM
HEAVY AROMATICS**

Field of the Invention

[0001] This invention relates to the use of heavy reformate for the production of xylenes. More specifically, this invention relates to the use of heavy reformate for production of xylenes through transalkylation, and also relates to the use of by-product light gases as feedstock for the production of ethylene, propylene and butadiene.

Background of the Invention

[0002] Heavy reformate, which typically includes greater than about 90% by weight C9+ aromatics, was blended into gasoline stream. With current regulations on the aromatics content and high end boiling point of gasoline, however, it is no longer possible to blend heavy reformate into gasoline. Considering the market growth rate of demand on *para*-xylene, the conversion of heavy aromatics to *para*-xylene by transalkylation is considered to be one economically viable way to utilize the heavy reformate.

[0003] The restrictions on the aromatics content in gasoline are compelling the petroleum refiners to find alternative routes for utilization of excess heavy reformate obtained from catalytic reforming of naphtha. Heavy reformate streams are typically include a high concentration of C9+ aromatics, typically consisting of at least 90% by weight C9 aromatics. Thus, because of the strict restrictions on the content of aromatics in gasoline, additional uses for aromatics, such as are found in a heavy reformate stream, must be found.

SUMMARY OF THE INVENTION

[0004] Generally, a method for the transalkylation of a heavy reformate to produce a xylenes-rich stream is provided.

[0005] A method for the transalkylation of a heavy reformate includes the steps of: providing a heavy reformate comprising at least about 90% by weight C9+ aromatics and hydrogen gas to a transalkylation reactor, the transalkylation reactor being charged with a transalkylation catalyst to selectively convert the C9+ aromatics to a xylene-rich product stream, the transalkylation catalyst including at least two solid-acid zeolites selected from the group consisting of mordenite, beta zeolite, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, MFI topology zeolite, NES topology zeolite, EU-1, MAPO-36, SAPO-5, SAPO-11, SAPO-34, and SAPO-41, and at least three metal selected from the Group 4 Lanthanoids, Group 6 and Group 10 of the Periodic Table of the Elements; separating the xylene-rich product stream into a light gas recycle stream, a C9+ heavy aromatic recycle stream and a mixed aromatics product stream; separating the mixed aromatics product stream into a benzene stream, a toluene stream and a xylenes stream; and separating light alkanes from the light gas recycle stream and supplying the light alkanes to a steam cracker, wherein the light alkanes are converted to mixed olefins.

[0006] In certain embodiments, the method also includes separating hydrogen gas from the light gas recycle stream and recycling the hydrogen gas to the transalkylation reactor. In certain embodiments, the transalkylation reaction zone is maintained at a temperature in a range of from about 200 °C to about 540 °C. In certain embodiments, the transalkylation reaction zone is maintained at a pressure in a range of from about 1 MPa to about 5 MPa. In certain embodiments, the ratio of hydrogen to heavy reformate is in a range of from about 0.1:1 to about 10:1. In certain embodiments, the steam cracker includes a reaction zone that is maintained at a temperature in a range of from about 600 °C to about 850 °C. In certain embodiments, the residence time of the light alkanes in the steam cracker reaction zone is less than about 0.1 seconds. In certain embodiments, the two solid acid zeolite components of the catalyst have different physical and chemical characteristics. In certain embodiments, the transalkylation catalyst includes a first solid acid zeolite that is present in an amount in a range of from about 10 % to about 90 % by weight of the total catalyst weight. In certain embodiments, the transalkylation catalyst includes a second solid acid zeolite that is present in an amount in a range of from about 10 % to about 90 % by weight of the total catalyst weight. In certain embodiments, the transalkylation catalyst further includes a binder

selected from inorganic oxides. In certain embodiments, the metal components are present in an amount in a range of from about 0.01 % to about 5 % by weight of the total catalyst weight.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] These and other features, aspects, and advantages of the present invention are better understood with regard to the following Detailed Description of the Preferred Embodiments, appended Claims, and accompanying Figures, where:

[0008] Figure 1 shows desired transalkylation reactions;

[0009] Figure 2 shows undesired transalkylation side reactions; and

[0010] Figure 3 is a schematic of an embodiment of a transalkylation apparatus.

DETAILED DESCRIPTION OF THE INVENTION

[0011] Although the following detailed description contains many specific details for purposes of illustration, it is understood that one of ordinary skill in the art will appreciate that many examples, variations and alterations to the following details are within the scope and spirit of the invention. Accordingly, the exemplary embodiments of the invention described herein and provided in the appended figures are set forth without any loss of generality, and without imposing limitations, on the claimed invention.

[0012] As previously noted, heavy reformat streams typically have high concentrations of C9+ aromatics. Due to strict restrictions on the amount of aromatics that can be included in gasoline, portions of these streams cannot be used directly as gasoline additives. One economically viable option for making use of the aromatics found in heavy reformat streams is to convert the C9+ aromatics present in the stream into xylenes by transalkylation.

[0013] Transalkylation allows for the integration of certain refining processes and results in the production of economically valuable petrochemicals. The extra C9+ aromatics that result from the refining process that are typically rejected and removed from the gasoline blending pool because of environmental regulations and maximum boiling point restriction, can be used as a feedstock for production of valuable petrochemicals and light olefins including *para*-xylene, ethylene, propylene and the butenes.

[0014] Steam cracking is one petrochemical process by which saturated hydrocarbons can be broken down into smaller, often unsaturated, hydrocarbons. It is the most common industrial method for producing light alkenes (that is, olefins), including ethene and propene.

[0015] The feedstock to the transalkylation process can include heavy reformat. The composition of a useful heavy reformat is provided in Table 1.

Major Compound	Composition (wt.%)
Iso-propyl benzene	1.7
n-propyl benzene	4.3
1-methyl-2-ethyl benzene	6.5
1-methyl-3-ethyl benzene	18.5
1-methyl-4-ethyl benzene	9.1
1,2,3-tri-methyl benzene	6.6
1,2,4-tri-methyl benzene	39.0
1,3,5-tri-methyl benzene	10.0
Total C9 aromatics	95.9
n-butyl benzene	0.5
1,4-diethyl benzene	0.8
1,3-diethyl benzene	0.4
1,3-dimethyl,5-ethyl benzene	0.8
1,4-dimethyl,2-ethyl benzene	0.4
Other C10 compounds	1.2
Total C10 aromatics	4.1

Table 1. A useful heavy reformat composition.

[0016] In certain embodiments, an integrated process is provided where a heavy reformat feedstock can be utilized as the hydrocarbon feed to a transalkylation process to produce xylenes and byproduct light gases. The byproduct light gases can include light paraffins that can be fed into a steam cracker for the production of light olefins. During the transalkylation of the heavy reformat feedstock, as shown in Figure 1, the most desirable reactions lead to the production of mixed xylenes, benzene and methyl aromatics. Undesirable side reactions

are shown in Figure 2. During the transalkylation reaction, approximately 10-20 % by weight of the light gases that are present, which generally include C1-C5 paraffins, are produced. A typical composition of the light gases produced by the transalkylation of a heavy reformat is listed in Table 2.

Compound	Concentration (wt.%)	Normalized concentration (wt.%)
Methane	0.2206	1.44
Ethane	10.4601	68.41
Propane	3.7252	24.36
Isobutane	0.5212	3.41
N-butane	0.308	2.01
Isopentane	0.0558	0.37

Table 2. Composition of light gases produced in the catalytic transalkylation of heavy reformat at reaction temperature of 400 °C.

[0017] In certain embodiments, provided is a method for using heavy reformat for the production of xylenes through transalkylation, and the subsequent use of by-product light gases as the feedstock to a steam cracker for the production light olefin, such as ethylene, propylene and butadiene. In this regard, in certain other embodiments is provided is an integrated apparatus for transalkylation processes and steam cracking processes. Paraffin gases resulting from the transalkylation process can then be used as a feedstock for steam cracker.

[0018] A schematic for an embodiment of an integrated process for the transalkylation of heavy reformat and the subsequent steam cracking of light gases is provided in Figure 3. A heavy reformat feed and hydrogen gas is provided via line 102 to transalkylation reactor 104. Transalkylation reactor 104 can include the transalkylation catalyst as described in a transalkylation reaction zone. The transalkylation effluent product stream from transalkylation reactor 104 can be supplied via line 106 to splitter 108, which separates the product stream into a light gas recycle stream 110, a C9+ heavy aromatic recycle stream 116, a mixed aromatics product stream, that can then be separated into a benzene stream 118, a toluene stream 120 and a xylene stream 122. Light gas recycle stream 110 can include hydrogen, as well as light alkanes, and can be supplied via line 114 to the reaction zone of

ethane steam cracker 124, which produces light olefins, including ethylene, propylene and butadiene, which are collected via lines 126, 128 and 130, respectively. Alternatively, the light recycle stream can be diverted to other uses, such as to benzene and toluene recovery, or alternatively can be recycled partially to the transalkylation zone. Optionally, a portion of the light olefin stream can be recycled with hydrogen from splitter 108 via line 112 to the transalkylation reactor 104. Similarly, C9+ heavy aromatic recycle stream 116 can be partially or wholly recycled to transalkylation reactor 104, where it can be combined with feedstock and hydrogen gas supplied via line 102. Alternatively, C9+ heavy aromatic recycle stream can be removed from the process for disposal or other processing.

[0019] “Mixed xylenes” refers a class of C8 aromatics used for the production of *para*- and *ortho*-xylene, and in certain applications as solvents. These compounds have many different uses and can be used as feedstock for the preparation of certain industrial scale chemical reactions.

[0020] For example, *para*-xylene can be used as a principal feedstock for the preparation of polyester, which continues to enjoy a high growth rate from large base demand; *ortho*-xylene can be used as feedstock for the preparation of phthalic anhydride, which is used in high-volume and has mature markets; and *meta*-xylene can be used for the preparation of various products, including plasticizers, dyes and wood preservatives, although typically in lesser but growing volumes as compared with *ortho*- and *para*-xylene. Ethylbenzene is another compound that can be present in xylene mixtures, and is occasionally recovered for use in the production of styrene. Ethylbenzene, however, is generally considered to be a less desirable component of C8 aromatics, and for this reason is not always separated and recovered.

[0021] In general, the production of xylenes can be increased in a variety of known ways. For example, xylene production can be increased through: (i) xylenes isomerization, (ii) toluene dis-proportionation, and (iii) transalkylation of toluene and C9+ aromatics. Comparing the economics of the various different processes for increasing xylenes production depends upon a variety of factors, including the current market situation, separation costs, C9+ aromatics availability, and environmental concerns. Transalkylation of toluene is a maximum xylene production mode and disproportionation is a maximum benzene production mode. The flexibility of the reaction mode that is selected enables a transalkylation unit to be operated in accordance with market dynamics and feedstock availability.

[0022] The transalkylation of heavy aromatics into xylenes as previously described is one method for complying with the current stringent gasoline specifications, thereby responding to a future decline in gasoline demand and complying with growing market demands of xylenes and benzene. Where heavy aromatics were previously used as additives, now the transalkylation of heavy aromatics allows for certain synergies between the refining and petrochemical operations to be realized. The economics of the transalkylation of heavy aromatics depends on the price differential between gasoline and xylene, and can in certain instances be further influenced by site specific constraints. Although higher in investment compared to classical xylenes production, transalkylation can be successful in an environment with low reformat availability.

[0023] Typical aromatic production processes yield xylene mixtures having a ratio approaching thermodynamic equilibrium (i.e., about 24:53:23 for *para*-, *meta*-, and *ortho*-xylene isomers, respectively), while the current market demand for each of these xylene isomers is in the ratio of about 80:2:18. Efforts have been made to adjust the composition of the xylene mixture beyond the thermodynamic value. These efforts have included certain innovations both in catalyst development and process design.

[0024] Typically, production of mixed xylenes can be achieved via catalytic naphtha reforming, particularly when used in recovery of and purification into *ortho*- or *para*-xylene. Alternatively, mixed xylenes can also be recovered from pyrolysis gasoline (an aromatic-rich by-product of an ethylene cracker process), but the ethylbenzene content of the resultant stream is generally prohibitively high, limiting use in the solvent market.

[0025] In certain embodiments, it is desirable to increase the yield of xylenes and to de-emphasize benzene production. It is understood that demand for xylene derivatives is growing at a greater rate than demand for benzene derivatives. In certain processes, refinery modifications can be effected to reduce the benzene content of gasoline in industrialized countries, which will in turn increase the supply of benzene available to meet demand. A higher yield of xylenes at the expense of benzene is a favorable objective and the result of certain processes as described. In certain embodiments, processes to transalkylate C9+ aromatics along with benzene or toluene have been commercialized, resulting in high xylene yields.

[0026] In certain embodiments, mixed xylenes can be obtained from the disproportionation of toluene or the transalkylation of C9 aromatics. The various production

routes (and the considerations) can include: distillation of mixed xylenes (C8 aromatics feed at blend value); extraction of xylenes (with C8 aromatics at gasoline blending value, and extraction costs distributed on a prorated yield basis across benzene, toluene and xylenes (BTX)); conventional toluene disproportionation (with toluene at its extraction cost and market value as pertinent); selective toluene disproportionation producing benzene and xylenes in similar proportions, while permitting the selective production of *para*-xylene (with toluene at its extraction cost and market value as pertinent); combined toluene disproportionation and C9 transalkylation (with toluene at its chemical value and market value and the C9 aromatics at its gasoline blend value as pertinent; and transalkylation alone (which treats feeds comprising heavy reformat C9+ and produces principally xylenes and, in lower amounts, benzene and liquefied petroleum gases).

[0027] The complexity of xylene production can vary substantially depending upon the process employed. There can be, by design and unit synergy, much flexibility with which to vary the product slate regardless of the distribution of aromatics from the reforming unit. These processes can include processes to alkylate, dealkylate, isomerize, disproportionate and transalkylate aromatics, such that the production of the desired aromatic can be increased from the distribution produced in the reforming unit. In certain embodiments, xylenes production can be selectively converted to any of the desired *para*-, *meta*- or *ortho*-xylene isomers by separating the desired component and reestablishing the equilibrium distribution of the remaining xylenes.

[0028] There are many known transalkylation processes for xylenes production available in the world chemical market. The primary function of all these processes is to increase the production of *para*-xylene from an aromatics complex by converting surplus low-value heavy aromatic streams to additional xylenes via rearrangement of the alkyl groups attached to the benzene ring. The selection of which process or technology to employ depends on many considerations, and generally the choice is the technology that offers the highest overall yield of *para*-xylene from fresh feedstock. Table 3 provides a list of the various advantages and disadvantages associated with certain major transalkylation processes, as well as the various properties of different transalkylation technologies.

Technology	Advantages	Disadvantages
Toluene Disproportionation	No metals on catalyst, high quality benzene byproduct, and low hydrogen consumption	No utilization of heavy aromatics, low xylenes yield, high benzene yield, shorter catalyst cycle length
Selective Toluene Disproportionation	High <i>para</i> -xylene yield, no metals on catalyst, and low hydrogen consumption	No utilization of heavy aromatics, low xylenes yield, high benzene yield, shorter catalyst cycle length
Transalkylation of Toluene and C ₉ Aromatics	Highest xylenes yield, low benzene yield, no metals on catalyst, high – quality benzene byproduct, low hydrogen consumption	Low utilization of C ₁₀ , C ₁₁ , shorter catalyst cycle length
Transalkylation of Toluene and C ₉ /C ₁₀	High xylenes yield, low benzene yield, longer catalyst cycle length, higher utilization of C ₁₀ , C ₁₁	Catalyst requires metals, benzene requires extraction
Transalkylation of C ₉ /C ₁₀	High xylenes yield, low benzene yield, longer catalyst cycle length, higher utilization of C ₁₀ , C ₁₁	No utilization of toluene, catalyst contains metals, benzene requires extraction, high hydrogen consumption
Transalkylation of Benzene and C ₉ /C ₁₀	Utilization of ethyl groups, utilization of surplus benzene, higher <i>para</i> -xylene yield	Shorter catalyst cycle length

Table 3. Properties of different transalkylation technologies.

[0029] In certain embodiments, a solution is provided for the production of valuable xylenes from inexpensive heavy reformat feedstock. A typical composition of a heavy reformat feedstock contemplated for use herein is summarized in Table 1. The light gases, which are by products from transalkylation process and which include mainly light paraffins, can be further processed in a steam cracker to produce ethylene, propylene and butadiene. In certain embodiments, the catalyst utilized in the transalkylation process can be any of the catalysts described in U.S. Published Patent Application No. 2010/0029467. The

transalkylation reaction temperature of the process can be in a range from about 200 °C to about 540 °C, the reaction pressure can be in a range from about 1 MPa to about 5 MPa, and liquid hourly space velocity (LHSV) can be in a range from about 1 to about 5 per hour. The ratio of hydrogen to heavy reformat ratio can be in a range from about 1 to about 4.

[0030] As shown in Figure 3, liquid products from the transalkylation includes benzene, toluene and xylenes. Hydrogen gas and C9+ hydrocarbons can be separately recycled back into the transalkylation reactor. The light gas, such as may be collected from the top of the splitter, will be recovered and supplied into a steam cracker under typical steam cracker reaction conditions to produce ethylene, propylene and butadiene. As is known in the art, steam cracking is a process by which saturated hydrocarbons can be broken down into smaller, often unsaturated, hydrocarbons. Steam cracking is a principal industrial method for producing light alkenes (or olefins), including ethene (or ethylene) and propene (or propylene).

[0031] Generally, during steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG or ethane is diluted with steam and then heated in a furnace. The reaction temperature is typically very high, greater than about 600 °C and typically about 850 °C, but the reaction residence time is very short, typically less than 0.1 seconds and more frequently less than about 0.01 seconds, resulting in gas velocities reaching speeds beyond the speed of sound, in an effort to improve the yield of desired products. After the cracking temperature has been reached, the gas is quickly quenched in a transfer line heat exchanger to stop the reaction.

[0032] The products produced by the steam cracking reaction will depend upon the specific composition of the feedstock, the hydrocarbon to steam ratio, the cracking temperature and furnace residence time.

[0033] In certain embodiments, based upon the transalkylation reaction conditions, the light hydrocarbon feedstock (which can include ethane, LPGs or light naphtha) can produce a product stream that is rich in the lighter alkenes, such as ethylene, propylene and butadiene.

[0034] Tables 4 and 5 provide recent trends for gasoline specification trends in North America and Europe. As shown in each of the tables, the amount of aromatic content has steadily declined. This makes it necessary to find other uses for the heavy reformat produced catalytic reformers in refineries. The reduced RVP (Reid vapor pressure) also dictates for decreased reformat concentrations in gasolines.

Fuel (Gasoline)	Prior to 1994	1995-2000	Beyond 2000
Lead	Phase out	0.0 %	0.0 %
Benzene (vol%)	--	1 %	0.8 %
Aromatics (vol%) max	--	25 %	22 %
Olefin (vol%) max	--	--	4 %
Oxygen (vol%) min (oxygenates)	--	2	2
RVP psi	Lower RVP	7.8/8.1 psi max	7 psi max

Table 4. Trend in gasoline specification in North America.

Fuel (Gasoline)	1994	1995	2000	2005	2010
Sulfur (ppm max)	1000	500	150	50/10	<10
Benzene (vol%)	5%	--	1%	1%	<1%
Aromatics (vol%) max	--	--	42%	35%	<35%
Olefin (vol%) max	--	--	18%	18%	<10%
Oxygen (wt%) min (oxygenates)	--	2.7%	2.7%	2.7%	--

Table 5. Trend in gasoline specification in Europe.

[0035] In an embodiment of the system, the transalkylation reactor includes a novel multimetal zeolites-based catalyst developed for converting a heavy reformat feedstock into benzene, toluene and xylenes (hereinafter, "BTX"), and in particular the commercially-valuable xylenes. Additionally, the multimetal zeolite-based catalyst produces petrochemical feedstocks, particularly C2 and C3 hydrocarbons, as a byproduct of the transalkylation reaction.

[0036] In certain embodiments, the multimetal catalyst can be formed by mixing at least two zeolites selected from the group consisting of mordenite, beta zeolite, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, MFI topology zeolite, NES topology zeolite, EU-1, MAPO-36,

SAPO-5, SAPO-11, SAPO-34 and SAPO-41, and the addition of at least three metal components selected from the Group 4 Lanthanoids and Group 10 of the Periodic Table of the Elements. The two zeolites should have different physical and chemical characteristics, for example, pore size and acidity. One exemplary catalyst includes zeolites such as zeolite beta and ZSM-5, and metals such as cerium, nickel and platinum.

[0037] The transalkylation reaction can be conducted in one or more reactors with a fixed bed, moving bed or radial flow reactor. The reaction temperature can be in a range of from about 200 °C to about 540 °C, alternatively in a range of from about 200 °C to about 400 °C, alternatively in a range of from about 350 °C to about 540 °C, alternatively in a range of from about 200 °C to about 300 °C, alternatively in a range of from about 300 °C to about 400 °C, alternatively in a range of from about 400 °C to about 500 °C, or alternatively in a range of from about 450 °C to about 540 °C. The reaction pressure can be in a range of from about 1 MPa to about 5 MPa, alternatively in a range of from about 1 MPa to about 3 MPa, alternatively in a range of from about 3 MPa to about 5 MPa, alternatively in a range of from about 1 MPa to about 2 MPa, alternatively in a range of from about 2 MPa to about 3 MPa, alternatively in a range of from about 3 MPa to about 4 MPa, alternatively in a range of from about 4 MPa to about 5 MPa. The liquid hourly space velocity can be in a range of from about 1 per hour (hr^{-1}) to about 5 hr^{-1} , alternatively in a range of from about 1 hr^{-1} to about 3 hr^{-1} , alternatively in a range of from about 3 hr^{-1} to about 5 hr^{-1} , alternatively in a range of from about 1 hr^{-1} to about 2 hr^{-1} , alternatively in a range of from about 2 hr^{-1} to about 3 hr^{-1} , alternatively in a range of from about 3 hr^{-1} to about 4 hr^{-1} , alternatively in a range of from about 4 hr^{-1} to about 5 hr^{-1} .

[0038] The heavy aromatics feed stream to the conversion process can be a heavy reformat, generally including alkylaromatic hydrocarbons in the carbon number range of C9 to C11+ that may include, for example, such hydrocarbons as propylbenzenes, ethylmethylbenzenes, tetramethylbenzenes, ethyldimethylbenzenes, diethylbenzenes, methylpropylbenzenes and mixtures thereof.

[0039] The heavy aromatics feed stream, characterized mainly by C9+ aromatics, results in effective transalkylation of light aromatics such as benzene and toluene with the heavier C9+ aromatics, yielding additional C8 aromatics that are preferably xylenes. The heavy aromatics stream preferably comprises at least about 95% by weight C9 aromatics. In certain embodiments, the heavy aromatic feed stream can be derived from the same or different known refinery and petrochemical processes. In certain embodiments, the heavy aromatics

feed stream can include, at least in part, feedstream that is recycled from the separation of the product stream and light gases from transalkylation.

[0040] Transalkylation of the feed stream can occur in the vapor phase and in the presence of hydrogen. The hydrogen is typically supplied with the feed stream, and with any optionally recycled hydrocarbons, in an amount from about 0.1 moles hydrogen per mole of alkylaromatics up to about ten moles per mole of alkylaromatics (that is, a hydrogen:alkylaromatic ratio in a range of from about 0.1:1 to about 10:1). In certain embodiments, the hydrogen:alkylaromatic ratio can be in a range of from about 0.1:1 to about 2:1; alternatively in a range of from about 2:1 to about 5:1, alternatively in a range of from about 5:1 to about 10:1. The ratio of hydrogen to alkylaromatics may also be referred to as the hydrogen-to-hydrocarbon ratio.

[0041] In certain embodiments, the heavy aromatic feed to the transalkylation reaction zone can be heated. For example, in certain embodiments, the feedstock can be heated first by indirect heat exchange against the effluent of the reaction zone, and then heated to reaction temperature. The feedstock can then be passed through a reaction zone, which may include one or more individual reactors. In certain embodiments, the reactor includes a single reaction vessel having a fixed cylindrical bed of catalyst. In alternate embodiments, a moving catalyst bed or radial flow reactor, or combination of one or more of the above reactors, can be employed. Passage of the combined hydrogen and heavy aromatic feed feed through the reaction zone results in the production of an effluent stream comprising unconverted feed and the desired product hydrocarbons.

[0042] The transalkylation reaction uses the transalkylation catalyst as described in at least one zone. The process can also include the use of additional catalysts. The heavier aromatic compounds present in the feedstock readily undergo conversion into lighter aromatics. The conditions employed in the transalkylation zone normally include a temperature in a range of from about 200 °C to about 540 °C, and moderately elevated pressures, broadly in a range of from about 1 MPa to about 5 MPa.

[0043] The transalkylation catalyst utilized herein is based upon solid-acid materials combined with a metal component. Generally, the catalyst can include two solid-acid zeolite materials. The first solid-acid zeolite can include all forms and types of mordenite, beta zeolite, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, MFI topology zeolite, NES topology zeolite, EU-1, MAPO-36, SAPO-5, SAPO-11, SAPO-34 and SAPO-41, and silica-alumina or

ion-exchanged versions of such solid acids. The first zeolite can be present in an amount in a range of from about 10 % to about 90 % by weight of the total catalyst amount in its final dried and calcined form.

[0044] The second zeolite incorporated in the catalyst recipe is different from the first zeolite in both physical and chemical characteristics, generally having a higher acidity, and is a zeolite that is also selected from the group including mordenite, beta zeolite, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, MFI topology zeolite, NES topology zeolite, EU-1, MAPO-36, SAPO-5, SAPO-11, SAPO-34 and SAPO-41. The second zeolite can be present in an amount in a range of from about 10 % to about 90% by weight of the total catalyst amount in its final dried and calcined form.

[0045] The catalyst can optionally include a refractory binder or matrix is to facilitate fabrication of the catalyst, provide strength to the catalyst and reduce fabrication costs. The binder should be uniform in composition and relatively refractory to the conditions used in the process. Suitable binders can include inorganic oxides, such as one or more of alumina, magnesia, zirconia, chromia, titania, boria, phosphate, zinc oxide and silica. In certain embodiments, alumina can be used as the binder. Typically, the two zeolite materials are mixed with the alumina binder in dry powdered form to yield a homogeneous mixture, thus ensuring that a homogeneous composition of the extrudates formed therefrom.

[0046] The multimetal zeolites based catalyst also includes at least three metal components, selected from the Group 4 Lanthanoids, and the Group 6 and 10 metals. In certain embodiments, two of the preferred metal components are selected from Group 10, such as nickel and platinum metals, although palladium may be used in lieu of, or in addition to, platinum. In certain embodiments, a Group 6 metal, such as molybdenum, chromium or tungsten, can be included in the catalyst. The third metal component can be selected from the Group 4 Lanthanoids, such as cerium. In certain embodiments, the metal components can be included within the final catalytic composite as an oxide, sulfide or halide, in chemical combination with one or more of the other ingredients of the composite. In certain embodiments, the Group 4 Lanthanoid can be included in elemental form. The metal component can be present in the final catalyst composite in an amount that is catalytically effective, for example between about 0.01 % and about 5% by weight of the final catalyst as calculated on an elemental basis. The metal component can be incorporated into the catalyst in by any suitable manner, such as co-precipitation or co-gelation with the carrier material, ion exchange or impregnation.

Examples

[0047] In the examples as provided, the exemplary heavy reformat used for testing had a composition as provided in Table 6.

Major Hydrocarbons	Amount (wt%)
Isopropyl benzene	1.8
n-Propyl-benzene	4.4
1-Methyl, 3-ethyl benzene	18.5
1-Methyl, 4-ethyl benzene	9.1
1,3,5-tri-methyl benzene	10.1
1-Methyl,2-ethyl benzene	6.5
1,2,4-trimethyl benzene	39.1
1,2,3-trimethyl benzene	6.6
Total C9 Components	96.1
Total C10 Components	3.9
Total Components	100

Table 6. Composition of a typical heavy reformat.

[0048] For exemplary purposes, a zeolites-mixed-zeolite multimetal catalyst according to the present invention, designated as Catalyst of the Example 1, was prepared and tested. The catalyst of the Example 1 has a zeolite-mixed-zeolite support, and includes three metal components loaded on the zeolite and alumina binder in a predefined fashion, and then mixed and bind together into extrudates.

Example 1: Preparation of the Catalyst.

[0049] Beta zeolite (ammonium form, HSZ-940NHA, obtained from Tosoh Chemical Corporation, Japan), having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 37, BET surface area of 570 squared meters per gram (m^2/g), a mean particle size 6 microns and a nominal content of Na_2O 0.05 % by weight was used in the catalyst preparation. The Beta zeolite was stirred with nickel nitrate hexahydrate aqueous solution to ion-exchange nickel, and the solid that was obtained was dried and impregnated with platinum chloride aqueous solution to produce Ni-Beta-Pt

according to the following procedure: Nickel nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was dissolved in distilled water to produce 200 milliliters (mL) of 10 % by weight solution. Thirty g of uncalcined Beta zeolite was added to this solution and stirred continuously for 1 hour, then filtered, and finally washed two times to remove the nitrate ions. The resulting solid was dried at room temperature for 2 hours, and then oven dried at 120 °C for 3 hours. The Ni-Beta was then impregnated with 0.1 % by weight platinum solution. In this method based on the wettability test, 0.038 g of platinum chloride, $\text{Pt}(\text{Cl})_2$, was dissolved in 36.1 g of distilled water. To dissolve the platinum chloride completely, 2.5 mL of ammonium hydroxide solution was added to the mixture with stirring. The Ni-Beta was then impregnated by incipient wetness method using this solution. The resultant solid was dried at room temperature for 2 hours and then oven dried at 120 °C for 3 hours. Then 4 g of alumina binder (Cataloid AP-3, obtained from CCIC, Japan) in dry powder form was dispersed in a 16 mL aqueous solution containing 0.62 g cerium nitrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and stirred continuously for 30 minutes to prepare a homogenously dispersed alumina. To this mixture, 4 g of uncalcined and untreated ZSM-5 (CT-435, obtained from CATAL, UK) having silica to alumina molar ratio of 27 was added in powder form to the slurry. Subsequently 12 g of Ni-Beta-Pt was added and mixed thoroughly to produce a thick paste which was then converted into 1.0 millimeters (mm) extrudates. The ratio of Beta to ZSM-5 to AP3 was 3:1:1. The extrudates were dried at room temperature overnight, then dried in air-circulated oven at 120 °C, and then calcined in a furnace at 500 °C for 3 hours. The catalyst developed can be symbolized as follows: $[(\text{Ni-Beta-Pt})+\text{ZSM5}+(\text{Ce-AP3})]$.

Example 2: Testing of Catalyst of Example 1.

[0050] The catalyst of the Example 1 was tested for transalkylation reaction in a bench top reaction system using heavy reformat to test the effectiveness of the catalyst for C9 conversion and products selectivity. The testing method consisted of loading a vertical reactor with 2.0 mL of the catalyst extrudates in the middle of reactor together with the inert alumina balls in the lower and upper parts of the reactor. The total volume of the reactor was 5 mL. The catalyst was activated and reduced under a flow of pure hydrogen at 50 mL/minute gas and was maintained at a temperature of 400 °C for 2 hours. Then, the reactor temperature was reduced to 340 °C and 20 bar pressure and the heavy reformat was supplied at a rate of 4.8 mL/h. The composition of heavy reformat is provided in Table 6. The reaction was run 3 hours at this temperature before collecting the sample. The reaction product was then directly injected into an on-line gas chromatograph equipped with flame

ionization detector. The hydrocarbon separation was carried out on 50 meter long and 0.15 mm diameter column under temperature programmed conditions. The temperature was increased to 360 °C and the reaction was continued for 2 hours before analyzing the gas and liquid products. The reaction was also run at reaction temperatures of 380 °C and 400 °C. In this manner, the reaction product were analyzed at 340 °C, 360 °C, 380 °C and 400 °C reaction temperatures. The components were separated according to their boiling points. The components were identified using a calibration that was accomplished using a standard hydrocarbon mixture sample having the components of known composition. The composition of the gaseous product was analyzed off-line by a Shimadzu gas chromatograph model 14B, equipped with a flame ionization detector and thermal conductivity detector. The gaseous hydrocarbons and hydrogen were separated on alumina PLOT, 50 meter capillary column. Various feed conversion levels were obtained at different temperatures and the results show low and high severity conversion of C9 components. Total C9 conversion (by wt%) was calculated using the following equations. An analogous expression was also used for calculating conversion of individual C9 compounds.

[0051] Tables 7 and 8 demonstrate that the Catalyst of the Example 1 shows relatively high C2-C4 petrochemical feedstock production at low severity reaction temperatures of 340 °C and 360 °C, as well as at high severity reaction temperatures of 380 °C and 400 °C.

[0052] The C6-C8 compositional data shown in Tables 9 and 10 demonstrates that the Catalyst of the Example 1 shows high production amount of mixed xylenes, at low severity reaction temperatures of 340 °C and 360 °C, as well as at high severity reaction temperatures of 380 °C and 400 °C. The data shows that the catalyst is quite active and gave high xylenes yields at low temperatures. The data also shows low benzene and toluene production, indicating low selectivity for C6 and C7 components. Ethylbenzene production was negligible at both low and high severity reaction conditions.

[0053] Tables 11 and 12 provide the C9-C10 product composition data at low reaction temperature of 340 °C and 360 °C as well as at high reaction temperature of 380 °C and 400 °C.

[0054] Tables 13 and 14 show relatively high conversion of individual C9 hydrocarbons at low severity reaction temperatures of 340 °C and 360 °C, as well as at high severity reaction temperature of 380 °C and 400 °C. The data also shows that C9 hydrocarbons conversion was quite high even at low severity. Conversion of methyl-ethyl benzenes (MEBs) was

higher as compared to trimethyl benzene (TMBs) conversion, thus showing xylenes production selectivity.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	340°C	360°C
C2	4.88	6.41
C3	4.63	6.08
C4	3.02	3.96

Table 7. C2-C4 Composition (vol.%) of the reaction products obtained using the catalyst of the Example 1 at low severity reaction temperatures of 340 °C and 360 °C, LHSV of 2.4 h⁻¹, and 20 bar hydrogen pressure.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	380°C	400°C
C2	7.98	11.52
C3	3.25	4.03
C4	1.22	0.45

Table 8. C2-C4 Composition (vol.%) of the reaction products obtained using the catalyst of the Example 1 at high severity reaction temperature of 380 °C and 400 °C, hydrogen pressure of 20 bar, and LHSV of 2.4 h⁻¹.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	340°C	360°C
LHSV	2.4	2.4
Benzene	0.87	1.19
Toluene	10.49	13.10
Ethylbenzene	0.75	0.31
<i>p</i> -xylene	6.69	7.38
<i>m</i> -xylene	14.88	16.44

<i>o</i> -xylene	5.96	6.63
Total Xylenes	27.53	30.45

Table 9. C6-C8 Composition (wt%) of the reaction products obtained using the catalyst of the Example 1 at low severity reaction temperature of 340°C and 360°C, hydrogen pressure of 20 bar, and LHSV of 2.4 h⁻¹.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	380°C	400°C
Benzene	1.86	1.32
Toluene	15.26	13.57
Ethylbenzene	0.17	0.00
<i>p</i> -xylene	7.65	7.74
<i>m</i> -xylene	16.90	17.06
<i>o</i> -xylene	6.94	7.17
Total Xylenes	31.49	31.97

Table 10. C6-C8 Composition (wt%) of the reaction products obtained using the catalyst of the Example 1 at high severity reaction temperature of 380°C and 400°C, hydrogen pressure of 20 bar, and LHSV of 2.4 h⁻¹.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	340°C	360°C
1-methyl-4-ethyl benzene	0.60	0.43
1-methyl-3-ethyl benzene	1.77	1.18
1,3,5-trimethyl benzene	6.08	6.44
1-methyl-2-ethyl benzene	0.43	0.34
1,2,4-trimethyl benzene	13.49	15.02
1,4-diethyl benzene	1.03	0.58
1,2,3-trimethyl benzene	1.66	2.01

1,2- diethyl benzene	0.83	0.39
1,2,4,5-tetramethyl benzene	1.91	1.52
1,2,3,5-tetramethyl benzene	2.42	1.93
1,2,3,4-tetramethyl benzene	0.54	0.54

Table 11. C9-C10 Composition (wt%) of the reaction products obtained using the catalyst of the Example 1 at low severity reaction temperature of 340°C and 360°C, hydrogen pressure of 20 bar, and LHSV of 2.4 h⁻¹.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	380°C	400°C
1-methyl-4-ethyl benzene	0.00	0.00
1-methyl-3-ethyl benzene	0.36	0.20
1,3,5-trimethyl benzene	6.20	6.15
1-methyl-2-ethyl benzene	0.00	0.00
1,2,4-trimethyl benzene	14.02	14.12
1,4-diethyl benzene	0.22	0.00
1,2,3-trimethyl benzene	1.81	1.87
1,2- diethyl benzene	0.18	0.00
1,2,4,5-tetramethyl benzene	1.41	1.42
1,2,3,5-tetramethyl benzene	1.77	1.77
1,2,3,4-tetramethyl benzene	0.42	0.42

Table 12. C9-C10 Composition (wt%) of the reaction products obtained using the catalyst of the Example 1 at high severity reaction temperature of 380°C and 400°C, hydrogen pressure of 20 bar, and LHSV of 2.4 h⁻¹.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	340°C	360°C
LHSV	2.4	2.4

123TMB Conversion	74.85	69.55
124TMB Conversion	65.50	62.07
135TMB Conversion	39.80	36.24
Total TMBs Conversion	61.95	57.94
1M2EB Conversion	93.38	94.77
1M3EB Conversion	90.43	93.62
1M4EB Conversion	93.41	95.27
Total MEBs Conversion	91.79	94.28

Table 13. Conversion (wt%) of C9 hydrocarbons at low severity reaction temperature of 340°C and 360°C, at LHSV of 2.4 h⁻¹, using the Catalyst of Example 1.

	Catalyst of Example 1	Catalyst of Example 1
Temperature	380°C	400°C
123TMB Conversion	72.58	71.67
124TMB Conversion	64.60	64.34
135TMB Conversion	38.61	39.11
Total TMBs Conversion	60.52	60.32
1M2EB Conversion	100.00	100.00
1M3EB Conversion	98.05	98.92
1M4EB Conversion	100.00	100.00
Total MEBs Conversion	98.94	99.41

Table 14: Conversion (wt%) of individual C9 hydrocarbons at high severity reaction temperature of 380°C and 400°C LHSV of 2.4 h⁻¹, using the Catalyst of Example 1.

[0055] The methods and compositions as provided solve several problems that are frequently encountered.

[0056] Although the present invention has been described in detail, it should be understood that various changes, substitutions, and alterations can be made hereupon without departing from the principle and scope of the invention. Accordingly, the scope of the

present invention should be determined by the following claims and their appropriate legal equivalents.

[0057] The singular forms "a", "an" and "the" include plural referents, unless the context clearly dictates otherwise.

[0058] Optional or optionally means that the subsequently described event or circumstances may or may not occur. The description includes instances where the event or circumstance occurs and instances where it does not occur.

[0059] Ranges may be expressed herein as from about one particular value, and/or to about another particular value. When such a range is expressed, it is to be understood that another embodiment is from the one particular value and/or to the other particular value, along with all combinations within the range.

[0060] Throughout this application, where patents or publications are referenced, the disclosures of these references in their entireties are intended to be incorporated by reference into this application, in order to more fully describe the state of the art to which the invention pertains, except when these references contradict the statements made herein.

[0061] As used herein and in the appended claims, the words "comprise," "has," and "include" and all grammatical variations thereof are each intended to have an open, non-limiting meaning that does not exclude additional elements or steps.

[0062] As used herein, terms such as "first" and "second" are arbitrarily assigned and are merely intended to differentiate between two or more components of an apparatus. It is to be understood that the words "first" and "second" serve no other purpose and are not part of the name or description of the component, nor do they necessarily define a relative location or position of the component. Furthermore, it is to be understood that the mere use of the term "first" and "second" does not require that there be any "third" component, although that possibility is contemplated under the scope of the present invention.

CLAIMS

1. A method for the transalkylation of a heavy reformat to produce a xylenes stream and mixed olefins, the method comprising the steps of:

providing a heavy reformat comprising at least 90% by weight C9+ aromatics and hydrogen gas to a transalkylation reactor, the transalkylation reactor being charged with a transalkylation catalyst to selectively convert the C9+ aromatics to a xylene-rich product stream, the transalkylation catalyst comprising

zeolites comprising beta zeolite and ZSM-5, and

a metal component comprising cerium, nickel, and platinum;

separating the product stream into a light gas recycle stream, a C9+ heavy aromatic recycle stream and a mixed aromatics product stream;

separating the mixed aromatics product stream into a benzene stream, a toluene stream and the xylenes stream; and

separating light alkanes from the light gas recycle stream and supplying the light alkanes to a steam cracker, where the light alkanes are converted to mixed olefins.

2. The method of claim 1 further comprising the step of separating hydrogen gas from the light gas recycle stream and recycling the hydrogen gas to the transalkylation reactor.

3. The method of claim 1 or claim 2 where the transalkylation reaction zone is maintained at a temperature in a range of from 200 °C to 540 °C.

4. The method of any one of claims 1 to 3 where the transalkylation reaction zone is maintained at a pressure in a range of from 1 MPa to 5 MPa.

5. The method of any one of claims 1 to 4 wherein the ratio of hydrogen to heavy reformat is in a range of from 0.1:1 to 10:1.

6. The method of any one of claims 1 to 5 wherein the steam cracker includes a reaction zone that is maintained at a temperature in a range of from 600 °C to 850 °C.

7. The method of any one of claims 1 to 6 wherein the residence time of the light alkanes in the steam cracker reaction zone is less than 0.1 seconds.
8. The method of any one of claims 1 to 7 wherein the beta zeolite is present in an amount in a range of from 10 % to 90% by weight of the total catalyst weight.
9. The method of any one of claims 1 to 8 where the ZSM-5 is present in an amount in a range of from 10 % to 90% by weight of the total catalyst weight.
10. The method of any one of claims 1 to 9 where the transalkylation catalyst further includes a binder selected from inorganic oxides.
11. The method of any one of claims 1 to 10 where the metal component is present in an amount in a range of from 0.01 % to 5% by weight of the total catalyst weight.