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(54) Title: SYSTEMS AND METHODS FOR CRACKING HYDROCARBON STREAMS SUCH AS CRUDE OILS UTILIZING CATALYSTS WHICH INCLUDE ZEOLITE MIXTURES

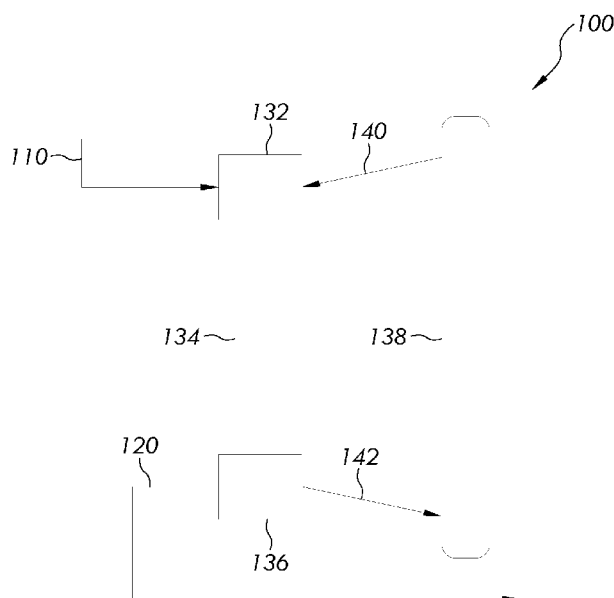


FIG. 1

(57) Abstract: A hydrocarbon feed stream may be cracked by a method including contacting the hydrocarbon feed stream with a cracking catalyst in a reactor unit. The hydrocarbon feed stream has an API gravity of at least 40 degrees. The cracking catalyst may include one or more binder materials, one or more matrix materials, *BEA framework type zeolite, FAU framework type zeolite, and MFI framework type zeolite.



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SYSTEMS AND METHODS FOR CRACKING HYDROCARBON STREAMS SUCH AS CRUDE OILS UTILIZING CATALYSTS WHICH INCLUDE ZEOLITE MIXTURES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application Serial 62/462,689, filed February 23, 2017, which is incorporated by reference herein in its entirety.

BACKGROUND

Field

[0002] The present disclosure relates to the cracking of hydrocarbons, and more particularly to systems and method for the cracking of hydrocarbon streams by zeolite-containing catalyst systems.

Technical Background

[0003] Light olefins such as ethylene, propylene, and butene are basic intermediates for a large portion of the petrochemical industry. They are mainly obtained through the thermal cracking (sometimes referred to as “steam pyrolysis” or “steam cracking”) of petroleum gases and distillates such as naphtha, kerosene, or even gas oil. However, as demands rise for these basic intermediate compounds, other production sources must be considered beyond traditional thermal cracking processes utilizing petroleum gases and distillates as feedstocks.

[0004] These intermediate compounds may also be produced through refinery fluidized catalytic cracking (FCC) processes, where heavy feedstocks such as gas oils or residues are converted. For example, an important source for propylene production is refinery propylene from the cracking of distillate feedstocks such as gas oils or residues. However, these feedstocks are usually limited and result from several costly and energy intensive processing steps within a refinery.

BRIEF SUMMARY

[0005] Accordingly, in view of the ever growing demand of these intermediary petrochemical products such as butene, there is a need for processes and catalyst systems to produce these intermediate compounds from other types of feedstock materials, such as relatively light crude oil supplies like gas condensate. For example, there is a need for catalysts and processes for converting gas condensate crude feedstock. According to one embodiment, the present disclosure is related to processes and cracking catalysts for producing these intermediate compounds such as light olefins, sometimes referred to in this disclosure as “system products,” by the direct conversion of feedstock crude oils such as gas condensate. For example, production of light olefins from light hydrocarbon feedstocks, such as gas condensate, may be beneficial as compared with the conversion of other feedstocks in producing these intermediate compounds because the light hydrocarbon feedstocks may be more widely available, may involve less processing costs to convert to light olefins, or both. However, new cracking catalysts are needed to selectively convert light hydrocarbon feedstocks to products with relatively high yields of light olefins such as butene.

[0006] According to one or more embodiments, a hydrocarbon feed stream may be cracked by a method comprising contacting the hydrocarbon feed stream with a cracking catalyst in a reactor unit. The hydrocarbon feed stream has an API gravity of at least 40 degrees. The cracking catalyst may include one or more binder materials in an amount of from 5 weight percent (wt.%) to 30 wt.% of the total cracking catalyst, one or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst, *BEA framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst, FAU framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst, and MFI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

[0007] According to another embodiment, a hydrocarbon feed stream may be cracked by a method comprising contacting the hydrocarbon feed stream with a cracking catalyst in a reactor unit. The hydrocarbon feed stream has an API gravity of at least 40 degrees. The cracking catalyst may comprise pseudoboehmite in an amount of from 5 wt.% to 30 wt.% of

the total cracking catalyst, kaolin in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst, zeolite Beta in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst, zeolite Y in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst, and ZSM-5 in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

[0008] According to yet another embodiment, a system for cracking a hydrocarbon feed stream may comprise a reactor, a hydrocarbon feed stream entering the reactor, where the hydrocarbon feed stream has an API gravity of at least 40 degrees, a product stream exiting the reactor, and a cracking catalyst positioned at least in the reactor, where the cracking catalyst comprises. The cracking catalyst may include one or more binder materials in an amount of from 5 weight percent (wt.%) to 30 wt.% of the total cracking catalyst, one or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst, *BEA framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst, FAU framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst, and MFI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

[0009] Additional features and advantages of the technology described in this disclosure will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the technology as described in this disclosure, including the detailed description which follows, the claims, as well as the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

[0011] FIG. 1 depicts a generalized schematic diagram of an embodiment of a fluid catalytic cracking reactor unit, according to one or more embodiments described in this disclosure; and

[0012] FIG. 2 depicts boiling point data for an example gas condensate feedstock, according to one or more embodiments described in this disclosure.

[0013] For the purpose of describing the simplified schematic illustrations and descriptions of FIG. 1, the numerous valves, temperature sensors, electronic controllers and the like that may be employed and well known to those of ordinary skill in the art of certain chemical processing operations are not included. Further, accompanying components that are often included in conventional chemical processing operations, such as refineries, such as, for example, air supplies, catalyst hoppers, and flue gas handling are not depicted. It should be understood that these components are within the spirit and scope of the present embodiments disclosed. However, operational components, such as those described in the present disclosure, may be added to the embodiments described in this disclosure.

[0014] It should further be noted that arrows in the drawings refer to process streams. However, the arrows may equivalently refer to transfer lines which may serve to transfer process streams between two or more system components. Additionally, arrows that connect to system components define inlets or outlets in each given system component. The arrow direction corresponds generally with the major direction of movement of the materials of the stream contained within the physical transfer line signified by the arrow. Furthermore, arrows which do not connect two or more system components signify a product stream which exits the depicted system or a system inlet stream which enters the depicted system. Product streams may be further processed in accompanying chemical processing systems or may be commercialized as end products. System inlet streams may be streams transferred from accompanying chemical processing systems or may be non-processed feedstock streams.

[0015] Additionally, arrows in the drawings may schematically depict process steps of transporting a stream from one system component to another system component. For example, an arrow from one system component pointing to another system component may represent “passing” a system component effluent to another system component, which may include the contents of a process stream “exiting” or being “removed” from one system component and “introducing” the contents of that product stream to another system component.

[0016] Reference will now be made in greater detail to various embodiments, some embodiments of which are illustrated in the accompanying drawings. Whenever possible, the same reference numerals will be used throughout the drawings to refer to the same or similar parts.

DETAILED DESCRIPTION

[0017] Described in this disclosure are various embodiments of systems and methods for processing hydrocarbon feed streams, such as light crude oils, into petrochemical products such as streams that include one or more of ethylene, propylene, and butene. Generally, the processing of the hydrocarbon feed stream may include cracking of the hydrocarbon feed stream by contacting the hydrocarbon feed stream with a cracking catalyst. According to one or more embodiments, the hydrocarbon feed stream may comprise a relatively light crude oil, such as gas condensate. According to one or more embodiments, the cracking catalyst may include a zeolite mixture comprising a *BEA framework type zeolite (such as, but not limited to, zeolite Beta), an FAU framework type zeolite (such as, but not limited to, zeolite Y), and an MFI framework type zeolite (such as, but not limited to, ZSM-5). It should be understood that *BEA, MFI, and FAU refer to zeolite framework types as identified by their respective three letter codes established by the International Union of Pure and Applied Chemistry (IUPAC). In addition to the zeolite mixture, the cracking catalyst may comprise other materials, such as, without limitation, one or more alumina-containing materials, one or more binder materials, or both. The cracking catalyst converts the hydrocarbon feed stream into a product stream that may include, without limitation, dry gases (that is, one or more of hydrogen gas, methane, and ethane), liquefied petroleum gases (that is, one or more of propane and butane), light olefins (that is, one or more of ethylene, propylene, and butene), gasoline (that is, hydrocarbons having 4 to 12 carbons per molecule, including alkanes, cycloalkanes, and olefins), and coke. It should be understood that not all hydrocarbons of the feed stream are cracked by the cracking catalyst and, generally, mostly heavier components of the feed are cracked.

[0018] According to some embodiments described in the present disclosure, the hydrocarbon feed stream which is converted to the product stream by contact with the cracking catalyst may include, consist essentially of, or entirely consist of a relatively light crude oil. For example, the hydrocarbon feed stream may have a relatively great American Petroleum Institute (API) gravity. For example, the API gravity of the hydrocarbon feed stream may be at least 30 degrees, at least 40 degrees, or even at least 50 degrees. For example, in one embodiment, the hydrocarbon feed stream comprises or consists of gas condensate having an API gravity of from 50 degrees to 55 degrees. As described in the present disclosure, “crude oil” refers to fuels which have been minimally processed or not processed following extraction from their respective sources. For example, gas condensate is considered a crude oil even though it may undergo minimal processing to separate vapor fractions from liquid fractions in the formation of the gas condensate. Additionally, crude oils may include hydrocarbon feedstocks which have been minimally processed such as by the partial or full removal of unwanted contaminants such as one or more of sulfur, heavy metals, nitrogen, or aromatics, such as by hydroprocessing. Additionally, it should be understood that while some embodiments presently described are related to the cracking of crude oil feedstocks, other embodiments may be directed to the cracking of fractions of crude oil feedstocks or partially refined hydrocarbon feedstocks.

[0019] Without being bound by theory, it is believed that the combination of zeolites in the zeolite mixture (that is, the combination of *BEA framework type zeolite, FAU framework type zeolite, and MFI framework type zeolite, for example, a zeolite mixture including zeolite Beta, zeolite Y, and ZSM-5) promotes conversion of the hydrocarbon feed stream to a product stream having an enhanced yield of light olefins. For example, the utilization of zeolite Beta in combination with zeolite Y and ZSM-5 may promote the formation of light olefins from a hydrocarbon feedstock that is relatively light, such as gas condensate. Without being bound by theory, it is believed that in order to increase the light olefin yield, gasoline octane number, or both, it may be advantageous to use a catalyst composition containing a large pore zeolite, such as an FAU framework type zeolite or *BEA framework type zeolite as the primary cracking component in addition to a medium pore zeolite such as MFI framework type zeolite. For example, zeolite Y may be utilized for the

production of gasoline, while ZSM-5 may be utilized to increase the yield of propylene and the octane number. Zeolite Beta may be utilized to produce olefins and the octane number of gasoline. By having these zeolites in one catalyst formulation, a petrochemical FCC (fluid catalytic cracking) catalyst system that results in a significant increase in light olefin yield and gasoline octane from relatively light feedstock fuels may be obtained.

[0020] As used in this disclosure, a “cracking catalyst” refers to any substance which increases the rate of a cracking chemical reaction. As used in this disclosure, “cracking” generally refers to a chemical reaction where a molecule having carbon to carbon bonds is broken into more than one molecule by the breaking of one or more of the carbon to carbon bonds, or is converted from a compound which includes a cyclic moiety, such as an aromatic, to a compound which does not include a cyclic moiety or contains fewer cyclic moieties than prior to cracking. However, while cracking catalysts promote cracking of a reactant, the cracking catalyst is not limited to cracking functionality, and may, in some embodiments, be operable to promote other reactions.

[0021] In one or more embodiments, the catalyst composition may comprise an FAU framework type zeolite, such as zeolite Y. As used herein, “zeolite Y” refers to zeolite having a FAU framework type according to the IUPAC zeolite nomenclature and consisting of silica and alumina, where the molar ratio of silica to alumina is at least 3. For example, the molar ratio of silica to alumina in the zeolite Y may be at least 5, at least 12, or even at least 30, such as from 5 to 30, from 12 to 30, or from about 15 to about 30. The unit cell size of the zeolite Y may be from about 24 Angstrom to about 25 Angstrom, such as 24.56 Angstrom.

[0022] According to one or more embodiments, the cracking catalyst may comprise an amount of FAU framework type zeolite (such as zeolite Y) in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst. For example, according to embodiments, the cracking catalyst may comprise FAU framework type zeolite in an amount of from 5 wt.% to 40 wt.% of the total cracking catalyst, from 5 wt.% to 35 wt.% of the total cracking catalyst, from 5 wt.% to 30 wt.% of the total cracking catalyst, from 5 wt.% to 25 wt.% of the total cracking catalyst, from 5 wt.% to 20 wt.% of the total cracking catalyst, from 5 wt.% to 15 wt.% of the total cracking catalyst, from 5 wt.% to 10 wt.% of the total cracking catalyst,

from 10 wt.% to 45 wt.% of the total cracking catalyst, from 15 wt.% to 45 wt.% of the total cracking catalyst, from 20 wt.% to 45 wt.% of the total cracking catalyst, from 25 wt.% to 45 wt.% of the total cracking catalyst, from 30 wt.% to 45 wt.% of the total cracking catalyst, from 35 wt.% to 45 wt.% of the total cracking catalyst, or from 40 wt.% to 45 wt.% of the total cracking catalyst. According to additional embodiments, the cracking catalyst may comprise FAU framework type zeolite in an amount of from 10 wt.% to 20 wt.% of the total cracking catalyst, from 15 wt.% to 30 wt.% of the total cracking catalyst, or from 10 wt.% to 40 wt.% of the total cracking catalyst. In one or more embodiments, all or a portion of the FAU framework type zeolite may be zeolite Y.

[0023] In one or more embodiments, the cracking catalyst may comprise a *BEA framework type zeolite, such as zeolite Beta. As used in this disclosure, “zeolite Beta” refers to zeolite having a *BEA framework type according to the IUPAC zeolite nomenclature and consisting of silica and alumina. The molar ratio of silica to alumina in the zeolite Beta may be at least 10, at least 25, or even at least 100. For example, the molar ratio of silica to alumina in the zeolite Beta may be from 5 to 500, such as from 25 to 300. The zeolite Beta may be in the form of H-Beta, the acidic form of zeolite Beta usually derived from NH_4 -Beta via calcination. In one or more embodiments, the zeolite Beta may be stabilized by direct reaction with phosphoric acid (H_3PO_4) or by impregnation with ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$.

[0024] According to one or more embodiments, the *BEA framework type zeolite may comprise one or more phosphorous-containing compounds, such as a phosphorous oxide, such as phosphorous pentoxide (“ P_2O_5 ”). For example, the *BEA framework type zeolite may include one or more phosphorous-containing compounds in an amount of from 1 wt.% to 20 wt.% of the total amount of the *BEA framework type zeolite, such as from 5 wt.% to 10 wt.% of the total amount of *BEA framework type zeolite. According to additional embodiments, the amount of phosphorous-containing compounds relative to the total amount of *BEA framework type zeolite may be from 1 wt.% to 18 wt.%, from 1 wt.% to 16 wt.%, from 1 wt.% to 14 wt.%, from 1 wt.% to 12 wt.%, from 1 wt.% to 10 wt.%, from 1 wt.% to 8 wt.%, from 1 wt.% to 6 wt.%, from 1 wt.% to 4 wt.%, from 1 wt.% to 2 wt.%, from 2 wt.% to 20 wt.%, from 4 wt.% to 20 wt.%, from 6 wt.% to 20 wt.%, from 8

wt.% to 20 wt.%, from 10 wt.% to 20 wt.%, from 12 wt.% to 20 wt.%, from 14 wt.% to 20 wt.%, from 16 wt.% to 20 wt.%, or from 18 wt.% to 20 wt.%.

[0025] According to one or more embodiments, the cracking catalyst may comprise an amount of *BEA framework type zeolite (such as zeolite Beta) in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst. For example, according to embodiments, the cracking catalyst may comprise *BEA framework type zeolite in an amount of from 5 wt.% to 40 wt.% of the total cracking catalyst, from 5 wt.% to 35 wt.% of the total cracking catalyst, from 5 wt.% to 30 wt.% of the total cracking catalyst, from 5 wt.% to 25 wt.% of the total cracking catalyst, from 5 wt.% to 20 wt.% of the total cracking catalyst, from 5 wt.% to 15 wt.% of the total cracking catalyst, from 5 wt.% to 10 wt.% of the total cracking catalyst, from 10 wt.% to 45 wt.% of the total cracking catalyst, from 15 wt.% to 45 wt.% of the total cracking catalyst, from 20 wt.% to 45 wt.% of the total cracking catalyst, from 25 wt.% to 45 wt.% of the total cracking catalyst, from 30 wt.% to 45 wt.% of the total cracking catalyst, from 35 wt.% to 45 wt.% of the total cracking catalyst, or from 40 wt.% to 45 wt.% of the total cracking catalyst. According to additional embodiments, the cracking catalyst may comprise *BEA framework type zeolite in an amount of from 5 wt.% to 35 wt.% of the total cracking catalyst, from 15 wt.% to 35 wt.% of the total cracking catalyst, from 20 wt.% to 35 wt.% of the total cracking catalyst, or from 25 wt.% to 40 wt.% of the total cracking catalyst.

[0026] In one or more embodiments, the catalyst composition may comprise MFI framework type zeolite, such as ZSM-5. As used in this disclosure, “ZSM-5” refers to zeolites having an MFI framework type according to the IUPAC zeolite nomenclature and consisting of silica and alumina. ZSM-5 refers to “Zeolite Socony Mobil-5” and is a pentasil family zeolite that can be represented by the chemical formula $\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$, where $0 < n < 27$. According to one or more embodiments, the molar ratio of silica to alumina in the ZSM-5 may be at least 5. For example, the molar ratio of silica to alumina in the zeolite Y may be at least 10, at least 12, or even at least 30, such as from 5 to 30, from 12 to 30, or from 5 to 80. Examples of suitable ZSM-5 include those commercially available from Zeolyst International, such as CBV2314, CBV3024E, CBV5524G, and CBV28014.

[0027] According to one or more embodiments, the MFI framework type zeolite may comprise one or more phosphorous-containing compounds, such as a phosphorous oxide, such as phosphorous pentoxide (“P₂O₅”). For example, the MFI framework type zeolite may include one or more phosphorous-containing compounds in an amount of from 1 wt.% to 20 wt.% of the total amount of MFI framework type zeolite, such as from 5 wt.% to 10 wt.% of the total amount of MFI framework type zeolite. According to additional embodiments, the amount of phosphorous containing compounds relative to the total amount of MFI framework type zeolite may be from 1 wt.% to 18 wt.%, from 1 wt.% to 16 wt.%, from 1 wt.% to 14 wt.%, from 1 wt.% to 12 wt.%, from 1 wt.% to 10 wt.%, from 1 wt.% to 8 wt.%, from 1 wt.% to 6 wt.%, from 1 wt.% to 4 wt.%, from 1 wt.% to 2 wt.%, from 2 wt.% to 20 wt.%, from 4 wt.% to 20 wt.%, from 6 wt.% to 20 wt.%, from 8 wt.% to 20 wt.%, from 10 wt.% to 20 wt.%, from 12 wt.% to 20 wt.%, from 14 wt.% to 20 wt.%, from 16 wt.% to 20 wt.%, or from 18 wt.% to 20 wt.%.

[0028] According to one or more embodiments, the cracking catalyst may comprise MFI framework type zeolite, such as ZSM-5, in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst. For example, according to embodiments, the cracking catalyst may comprise MFI framework type zeolite in an amount of from 5 wt.% to 40 wt.% of the total cracking catalyst, from 5 wt.% to 35 wt.% of the total cracking catalyst, from 5 wt.% to 30 wt.% of the total cracking catalyst, from 5 wt.% to 25 wt.% of the total cracking catalyst, from 5 wt.% to 20 wt.% of the total cracking catalyst, from 5 wt.% to 15 wt.% of the total cracking catalyst, from 5 wt.% to 10 wt.% of the total cracking catalyst, from 10 wt.% to 45 wt.% of the total cracking catalyst, from 15 wt.% to 45 wt.% of the total cracking catalyst, from 20 wt.% to 45 wt.% of the total cracking catalyst, from 25 wt.% to 45 wt.% of the total cracking catalyst, from 30 wt.% to 45 wt.% of the total cracking catalyst, from 35 wt.% to 45 wt.% of the total cracking catalyst, or from 40 wt.% to 45 wt.% of the total cracking catalyst. According to additional embodiments, the cracking catalyst may comprise MFI framework type zeolite in an amount of from 10 wt.% to 30 wt.% of the total cracking catalyst, from 10 wt.% to 20 wt.% of the total cracking catalyst, from 5 wt.% to 10 wt.% of the total cracking catalyst, or from 10 wt.% to 25 wt.% of the total cracking catalyst.

[0029] According to one or more embodiments, one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite may be substantially free of transition metals (that is, comprises less than 1 wt.% of transition metal). For example, one or more of the ZSM-5, zeolite Beta, and zeolite Y may consist of less than or equal to 1 wt.%, 0.5 wt.%, 0.3 wt.%, 0.1 wt.%, 0.01, or even 0.001 wt.% of transition metals. As described in this disclosure, transition metals include scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, rutherfordium, dubnium, seaborgium, bohrium, hassium, meitnerium, darmstadtium, roentgenium, and copernicium.

[0030] In one or more embodiments, the catalyst composition may comprise one or more binder materials, such as alumina-containing compounds or silica-containing compounds (including compounds containing alumina and silica). As used in this disclosure, “binder materials” refer to materials which may serve to “glue” or otherwise hold zeolite and the matrix together in the microsphere. It may improve the attrition resistance of the catalyst particle. The binder acts as For example, the binder material may comprise alumina (such as amorphous alumina), silica-alumina (such as amorphous silica-alumina), or silica (such as amorphous silica). According to one or more embodiments, the binder material may comprise pseudoboehmite. As used in this disclosure, “pseudoboehmite” refers to an aluminum-containing compound with the chemical composition $\text{AlO}(\text{OH})$ consisting of crystalline boehmite. Suitable pseudoboehmite includes CATAPAL® aluminas, commercially available from Sasol Limited of Johannesburg, South Africa. Boehmite refers to aluminum oxide hydroxide as well, but pseudoboehmite generally has a greater amount of water than boehmite. The binder material, such as pseudoboehmite, may be peptized with an acid, such as a mono-protic acid, such as nitric acid (“ HNO_3 ”) or hydrochloric acid (“ HCl ”).

[0031] According to one or more embodiments, the cracking catalyst may comprise the one or more binder materials in an amount of from 5 wt.% to 30 wt.% of the total cracking catalyst. For example, according to embodiments, the cracking catalyst may comprise binder material in an amount of from 5 wt.% to 25 wt.% of the total cracking

catalyst, from 5 wt.% to 20 wt.% of the total cracking catalyst, from 5 wt.% to 15 wt.% of the total cracking catalyst, from 5 wt.% to 10 wt.% of the total cracking catalyst, from 10 wt.% to 30 wt.% of the total cracking catalyst, from 15 wt.% to 30 wt.% of the total cracking catalyst, 20 wt.% to 30 wt.% of the total cracking catalyst, or from 25 wt.% to 30 wt.% of the total cracking catalyst. According to additional embodiments, cracking catalyst may comprise the binder materials in an amount of from 10 wt.% to 20 wt.% of the total cracking catalyst, such as from 12 wt.% to 18 wt.% of the total cracking catalyst, or from 14 wt.% to 16 wt.% of the total cracking catalyst. It should be understood that, in one or more embodiments, the cracking catalyst may include any single disclosed binder material in an amount of the disclosed wt.% ranges. In additional embodiments, the cracking catalyst may include any two or more binder materials in combination in an amount of the disclosed wt.% ranges.

[0032] In one or more embodiments, the catalyst composition may comprise one or more matrix materials. As use in this disclosure, “matrix materials” may refer to a clay material such as kaolin. Without being bound by theory, it is believed that the matrix materials of an the catalyst serves both physical and catalytic functions. Physical functions include providing particle integrity and attrition resistance, acting as a heat transfer medium, and providing a porous structure to allow diffusion of hydrocarbons into and out of the catalyst microspheres. The matrix can also affect catalyst selectivity, product quality and resistance to poisons. The matrix materials may tend to exert its strongest influence on overall catalytic properties for those reactions which directly involve relatively large molecules.

[0033] In one or more embodiments, the matrix material comprises kaolin. As used in this disclosure, “kaolin” refers to a clay material that has a relatively large amount (such as at least about 50 wt.%, at least 60 wt.%, at least 70 wt.%, at least 80 wt.%, at least 90 wt.%, or even at least 95 wt.%) of kaolinite, which can be represented by the chemical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Kaolin is sometimes referred to as “china clay.” In additional embodiments, the matrix material may comprise other clay materials.

[0034] According to one or more embodiments, the cracking catalyst comprises or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst.

For example, according to embodiments, the cracking catalyst may comprise the matrix material in an amount of from 30 wt.% to 55 wt.% of the total cracking catalyst, from 30 wt.% to 50 wt.% of the total cracking catalyst, from 30 wt.% to 45 wt.% of the total cracking catalyst, from 30 wt.% to 40 wt.% of the total cracking catalyst, from 30 wt.% to 35 wt.% of the total cracking catalyst, from 35 wt.% to 60 wt.% of the total cracking catalyst, from 40 wt.% to 60 wt.% of the total cracking catalyst, from 45 wt.% to 60 wt.% of the total cracking catalyst, from 50 wt.% to 60 wt.% of the total cracking catalyst, or from 55 wt.% to 60 wt.% of the total cracking catalyst. According to additional embodiments, the cracking catalyst may comprise the matrix material in an amount of from 35 wt.% to 55 wt.% of the total cracking catalyst, such as from 40 wt.% to 50 wt.% of the total cracking catalyst, or from 43 wt.% to 47 wt.% of the total cracking catalyst. It should be understood that, in one or more embodiments, the cracking catalyst may include any single disclosed matrix material in an amount of the disclosed wt.% ranges. In additional embodiments, the cracking catalyst may include any two or more matrix materials in combination in an amount of the disclosed wt.% ranges.

[0035] As described in this disclosure, the cracking catalyst may be in the form of shaped microparticles, such as microspheres. As described, “microparticles” refer to particles having of size of from 0.1 microns and 100 microns. The size of a microparticle refers to the maximum length of a particle from one side to another, measured along the longest distance of the microparticle. For example, a spherically shaped microparticle has a size equal to its diameter, or a rectangular prism shaped microparticle has a maximum length equal to the hypotenuse stretching from opposite corners.

[0036] According to embodiments, the zeolites of the zeolite mixture (for example, ZSM-5, zeolite Beta, and zeolite Y) may all be included in each microparticle. However, in other embodiments, microparticles may be mixed, where the microparticles contain only a portion of the zeolite mixture. For example, a mixture of three microparticle types may be included in the cracking catalyst, where one type of microparticle includes only ZSM-5, one type of microparticle includes only zeolite Beta, and one microparticle type includes only zeolite Y.

[0037] The cracking catalyst may be formed by a variety of processes. According to one embodiment, the matrix material may be mixed with a fluid such as water to form a slurry, and the zeolites may be separately mixed with a fluid such as water to form a slurry. The matrix material slurry and the zeolite slurry may be combined under stirring. Separately, another slurry may be formed by combining the binder material with a fluid such as water. The binder slurry may then be combined with the slurry containing the zeolites and matrix material to form an all-ingredients slurry. The all-ingredients slurry may be dried, for example by spraying, and then calcinated, to produce the microparticles of the cracking catalyst.

[0038] The cracking catalyst may be deactivated by contact with steam prior to use in a reactor to convert hydrocarbons. The purpose of steam treatment is to accelerate the hydrothermal aging which occurs in an operational FCC regenerator to obtain an equilibrium catalyst. Steam treatment may lead to the removal of aluminum from the framework leading to a decrease in the number of sites where framework hydrolysis can occur under hydrothermal and thermal conditions. This removal of aluminum results in an increased thermal and hydrothermal stability in dealuminated zeolites. The unit cell size may decrease as a result of dealumination since the smaller SiO_4 tetrahedron replaces the larger AlO_4^- tetrahedron. The acidity of zeolites may also be affected by dealumination through the removal of framework aluminum and the formation of extra-framework aluminum species. Dealumination may affect the acidity of the zeolite by decreasing the total acidity and increasing the acid strength of the zeolite. The total acidity may decrease because of the removal of framework aluminum, which act as Bronsted acid sites. The acid strength of the zeolite may be increased because of the removal of paired acid sites or the removal of the second coordinate next nearest neighbor aluminum. The increase in the acid strength may be caused by the charge density on the proton of the OH group being highest when there is no framework aluminum in the second coordination sphere.

[0039] According to one or more embodiments, the hydrocarbon feed stream may be contacted by the cracking catalyst in a reactor unit. As used in this disclosure, a “reactor unit” refers to a vessel or series of vessels in which one or more chemical reactions may occur between one or more reactants in the presence of one or more catalysts. For example, a

reactor may include a tank or tubular reactor configured to operate as a batch reactor, a continuous stirred-tank reactor (CSTR), or a plug flow reactor. Example reactors include packed bed reactors such as fixed bed reactors, and fluidized bed reactors.

[0040] As depicted in FIG. 1, according to one or more embodiments, the reactor unit used to convert the hydrocarbon feed stream may be a fluidized bed reactor. As used in this disclosure, a “fluid catalytic cracking reactor” refers to a reactor unit that can be operable to contact a fluidized reactant with a solid material (usually in particulate form), such as a cracking catalyst. As described in this disclosure, a fluidized bed reactor which cracks a reactant stream with a fluidized solid cracking catalyst may be referred to as a fluid catalytic cracking reactor unit.

[0041] FIG. 1 schematically depicts a fluid catalytic cracking reactor unit 100 which converts a hydrocarbon feed stream 110 into a product stream 120. The embodiment of FIG. 1 includes cracking catalyst regeneration functionality.

[0042] Still referring to FIG. 1, the hydrocarbon feed stream 110 may be passed to a fluid catalytic cracking reactor unit 100. The fluid catalytic cracking reactor unit 100 may include a cracking catalyst/feed mixing zone 132, a reaction zone 134, a separation zone 136, and a cracking catalyst regeneration zone 138. The hydrocarbon feed stream 110 may be introduced to the cracking catalyst/feed mixing zone 132 where it is mixed with regenerated cracking catalyst from regenerated catalyst stream 140 passed from the cracking catalyst regeneration zone 138. The hydrocarbon feed stream 110 is reacted by contact with the regenerated cracking catalyst in the reaction zone 134, which cracks the contents of the hydrocarbon feed stream 110. Following the cracking reaction in the reaction zone 134, the contents of the reaction zone 134 are passed to the separation zone 136 where the cracked product of the reaction zone 134 is separated from spent catalyst, which is passed in a spent catalyst stream 142 to the cracking catalyst regeneration zone 138 where it is regenerated by, for example, removing coke from the spent cracking catalyst. The product stream 120 is passed from the fluid catalytic cracking reactor unit, where it may be further processed, for example by separation into multiple streams.

[0043] It should be understood that fluid catalytic cracking reactor unit 100 of FIG. 1 is a simplified schematic of one particular embodiment of a fluid catalytic cracking reactor unit, and other configurations of fluid catalytic cracking reactor units may be suitable for the presently disclosed hydrocarbon cracking methods. For example, in some embodiments, the catalyst may not be recycled, and in such embodiments, the components of FIG. 1 related to the regeneration of the cracking catalyst would not be present.

[0044] As referred to in this disclosure, the hydrocarbon feed stream is a fluid stream (either gaseous or liquid) which has a relatively great API gravity, such as at least 30 degrees, and often greater than 50 degrees. In some embodiments, the hydrocarbon feed stream 110 may have an API gravity of at least about 30 degrees, at least 35 degrees, at least 40 degrees, at least 45 degrees, at least 50 degrees, at least 55 degrees, or even at least 60 degrees.

[0045] The hydrocarbon feed stream 110 may be a crude oil feedstock, or may be processed in some way prior to being cracked. For example a relatively heavy oil may be separated into two or more components to form the hydrocarbon feed stream 110. In some embodiments, the hydrocarbon feed stream 110 may be processed to remove components such as one or more of metals, sulfur, or nitrogen prior to being treated with the cracking catalysts presently described. According to various embodiments, at least 50 wt.%, 60 wt.%, 70 wt.%, 80 wt.%, 90 wt.%, 95 wt.%, or even 99 wt.% of the hydrocarbon feed stream is crude oil such as gas condensate.

[0046] According to one or more embodiments, the hydrocarbon feed stream 110 which is cracked consists of gas condensate, such as gas condensate available from the Khuff geological formation. Khuff gas condensate properties, an example feedstock fuel for the cracking process of the present disclosure, is shown in Table 1. Additionally, FIG. 2 shows the boiling point profile for Khuff gas condensate. In FIG. 2, “IBP” refers to the initial boiling point and “FBP” refers to the final boiling point. FIG. 2 depicts weight percentages of oil boiled as a function of increasing temperature.

Table 1 - Example of Khuff Gas Condensate

Property	Units	Value
American Petroleum Institute (API) gravity	degrees	52.8
Density	grams per cubic centimeter (g/cm ³)	0.7695
Sulfur Content	weight percent (wt.%)	0.03
Nickel	parts per billion by weight (ppbw)	Less than 20
Vanadium	ppbw	Less than 20
Iron	ppbw	Less than 20
Copper	ppbw	Less than 20
Sodium Chloride (NaCl) Content	ppbw	50
Conradson Carbon	wt.%	0.03
Basic nitrogen	Parts per million (ppm)	Less than 10

[0047] According to one or more embodiments, the hydrocarbon feed stream 110 may have a boiling point profile as described by the 5 wt.% boiling temperature, the 25 wt.% boiling temperature, the 50 wt.% boiling temperature, the 75 wt.% boiling temperature, and the 95 wt.% boiling temperature. These respective boiling temperatures correspond to the temperature at which a given weight percentage of the hydrocarbon feed stream boils. In some embodiments, the hydrocarbon feed stream 100 may have one or more of a 5 wt.% boiling temperature of less than 150°C, a 25 wt.% boiling temperature of less than 225°C, a 50 wt.% boiling temperature of less than 300°C, a 75 wt.% boiling temperature of less than 400°C, and a 95 wt.% boiling temperature of less than 600°C. According to one or more embodiments, the hydrocarbon feed stream 100 may have one or more of a 5 wt.% boiling temperature of from 0°C to 100°C, a 25 wt.% boiling temperature of from 75°C to 175°C, a 50 wt.% boiling temperature of from 150°C to 250°C, a 75 wt.% boiling temperature of from 250°C to 350°C, and a 95 wt.% boiling temperature of from 450°C to 550°C.

[0048] According to one or more embodiments, the reaction fluid catalytic cracking reaction may be a high severity fluid catalytic cracking reaction. As used in this disclosure,

“high severity” fluid catalytic cracking refers to cracking under reaction temperatures of at least about 500 degrees Celsius (“°C”). According to one or more embodiments, the reaction zone 134 of the fluid catalytic cracking reactor unit 100 may operate at a temperature of from 500°C to 700°C, such as from about 600°C to about 700°C, or from about 625°C to about 675°C.

[0049] According to embodiments, the catalyst to oil weight ratio may be from 7 to 10, such as from 7.5 to 9.5 or from 7.75 to 8.25. In one or more embodiments, the residence time of the mixture in the reaction zone 127 may be from 0.2 to 2 seconds.

[0050] According to one or more embodiments, the contacting of the hydrocarbon feed stream 125 with the cracking catalyst produces a product stream 120 that may comprise at least 20 wt.% of light olefins selected from ethylene, propylene, and butene. For example, in embodiments, the product stream 120 may comprise at least 22 wt.% of light olefins, at least 25 wt.% of light olefins, at least 30 wt.% of light olefins, or even at least at least 40 wt.% of light olefins. In additional embodiments, the product stream 120 may comprise at least 3 wt.% of ethylene, at least 5 wt.% of ethylene, at least 7 wt.% of ethylene, or even at least 8 wt.% of ethylene, at least 13 wt.% of propylene, at least 15 wt.% of propylene, at least 19 wt.% of propylene, or even at least 21 wt.% of propylene, at least 8 wt.% of butene, at least 10 wt.% of butene, at least 14 wt.% of butene, or even at least 18 wt.% of butene.

Examples

[0051] The various embodiments of methods and systems for cracking hydrocarbon feed streams will be further clarified by the following examples. The examples are illustrative in nature, and should not be understood to limit the subject matter of the present disclosure.

Example 1 – Cracking Catalyst Preparation

[0052] A number of cracking catalysts were prepared with varying amounts of ZSM-5, zeolite Y, and zeolite Beta. Additionally, comparative catalysts were prepared under the same procedures. The catalyst compositions prepared are show in Tables 2. Additionally,

comparative catalyst compositions were prepared and are shown in Table 3. It is noted that Sample 2 was prepared from microspheres of Comparative Sample A (25 wt.%), Comparative Sample B (15 wt.%), and Comparative Sample C (60 wt.%). The ZSM-5 zeolite used was CBV 2314 zeolite commercially available from Zeolyst International, which has a silica to alumina ratio of 23. The zeolite Beta used was CP814E zeolite commercially available from Zeolyst International, which has a silica to alumina ratio of 25. The zeolite Y used was SP13-0159 zeolite commercially available from W.R. Grace and Company, which had a silica to alumina ratio of 6.

Table 2

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
wt.% Kaolin	45	45	35	35	35
wt.% Alumina	15	15	15	15	15
wt.% ZSM-5	10	10	10	10	10
wt.% zeolite Beta	10	6	30	20	10
wt.% zeolite Y	20	24	10	20	30

Table 3

	Comparative Sample A	Comparative Sample B	Comparative Sample C	Comparative Sample D
wt.% Kaolin	45	45	45	45
wt.% Alumina	15	15	15	15
wt.% ZSM-5	0	0	40	10
wt.% zeolite Beta	0	40	0	30
wt.% zeolite Y	40	0	0	0

[0053] To prepare the catalysts, first, ZSM-5, zeolite Y, and zeolite Beta were impregnated with phosphorus. The targeted phosphorus content was 3.5 wt.% P₂O₅ of the total cracking catalyst weight.

[0054] The catalysts were prepared by blending kaolin clay powder with de-ionized water. In a separate step, the zeolite mixture (dry basis) was made into a slurry with de-ionized water. While stirring the zeolite slurry, an appropriate amount of ortho-phosphoric acid (concentration 85 wt %) was gradually added to achieve 3.5 wt.% of total zeolite weight. Stirring was continued for another 15 minutes. The zeolite-phosphoric acid slurry was then added to the kaolin slurry and stirred for 5 minutes.

[0055] Separately, a slurry of Catapal alumina was prepared by mixing Catapal alumina (dry basis) with distilled water, which was peptized by adding an appropriate amount of concentrated nitric acid (concentration of 70 wt.%) and stirring for thirty minutes. The resulting peptized Catapal slurry was added to the zeolite-kaolin slurry and blended for 10 minutes, producing a slurry with high viscosity where the individual particles remain suspended.

[0056] The resulting slurry was made up of 30 wt.% solids was spray dried to produce particles of 20-100 microns. The dried particles were then calcined at 500°C for 3 hours.

Example 2 – Catalytic Testing

[0057] Catalytic cracking of Khuff Gas Condensate (composition shown in Table 1) was carried out in a fixed-bed microactivity testing unit (“MAT”) unit, manufactured by Sakuragi Rikagaku of Japan, according to ASTM D-3907 and D-5154 testing protocols. For each MAT run, a full mass balance was obtained and was found to be around 100%. All MAT runs were performed at a cracking temperature of 650°C and a time-on-stream of 30 seconds. All samples were steamed at 750°C for 3 hours prior to experimentation.

[0058] Data related to the catalytic activity of the catalyst formulations of Tables 2 and 3 are provided in Tables 4 and 5, respectively. For the purpose of assessing the catalyst performance on conversion of light fractions (that is, those with hydrocarbons of 5 or less carbon molecules), is defined as the total weight percent of gas products and coke for the cracking of Arab Extra Light Crude fractions. “CONV. (wt.%)” in Tables 4 and 5 is the total dry gas, LPG and coke formed.

Table 4

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
catalyst to oil ratio by weight	8	8	8.02	9.23	8.34
CONV. (wt%)	60	59	62.33	62.61	64.95
Yields					
ethylene	5	7	7.99	7.65	7.46
propylene	13	19	15.39	11.98	12.17
butene	6	11	7.84	5.37	5.65
Groups (wt.%)					
H ₂ -C ₂ (dry gas)	15	15	20.91	25.46	25.43
C ₃ -C ₄ (LPG)	40	41	40.54	36.15	38.6
C ₂ =-C ₄ = (light olefins)	25	36	31.22	25	25.28
Gasoline	34	28	28.3	26.06	26.8
Coke	5.1	3.9	0.88	1.01	0.91

Table 5

	Comparative Sample A	Comparative Sample B	Comparative Sample C	Comparative Sample D
catalyst to oil ratio by weight	8	8	8.33	8
CONV.(wt%)	68	59	52.93	46
Yields				
ethylene	5	7	9.54	4
propylene	9	17	15.78	16
butene	4	9	8.49	11
Groups (wt%)				
H ₂ -C ₂ (dry gas)	21	16	20.45	8
C ₃ -C ₄ (LPG)	36	41	31.61	30
C ₂ =-C ₄ = (light olefins)	18	33	33.81	27
Gasoline	28	33	34.48	45

Coke	11.3	2.4	0.87	0.8
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[0059] The results show the effect of zeolite Beta on conversion and the yield of light olefins. Conversion and light olefin yield increase with the amount of zeolite Beta in the formulation. The results also show the synergetic effect of having zeolite Y, zeolite Beta and ZSM-5 in the formulation as improved light olefin yield is realized than when just only either ZSM-5 or zeolite Y are in the formulation. Therefore it may be advantageous to supplement the conventional FCC catalyst with zeolite beta in order to increase the light olefin yield and gasoline octane. Having a catalyst formulation containing a large pore zeolite, such as zeolite Y or zeolite Beta, as the primary cracking component and a medium pore zeolite such as ZSM-5 provides a more active catalyst with better light olefin yield.

[0060] It is noted that one or more of the following claims utilize the term “where” as a transitional phrase. For the purposes of defining the present technology, it is noted that this term is introduced in the claims as an open-ended transitional phrase that is used to introduce a recitation of a series of characteristics of the structure and should be interpreted in like manner as the more commonly used open-ended preamble term “comprising.”

[0061] It should be understood that any two quantitative values assigned to a property may constitute a range of that property, and all combinations of ranges formed from all stated quantitative values of a given property are contemplated in this disclosure.

[0062] Having described the subject matter of the present disclosure in detail and by reference to specific embodiments, it is noted that the various details described in this disclosure should not be taken to imply that these details relate to elements that are essential components of the various embodiments described in this disclosure, even in cases where a particular element is illustrated in each of the drawings that accompany the present description. Rather, the claims appended hereto should be taken as the sole representation of the breadth of the present disclosure and the corresponding scope of the various embodiments described in this disclosure. Further, it will be apparent that modifications and variations are possible without departing from the scope of the appended claims.

[0063] According to a first aspect of the present disclosure, a method for cracking a hydrocarbon feed stream may comprise contacting the hydrocarbon feed stream with a cracking catalyst in a reactor unit, where the hydrocarbon feed stream has an API gravity of at least 40 degrees, and where the cracking catalyst comprises: one or more binder materials in an amount of from 5 wt.% to 30 wt.% of the total cracking catalyst; one or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst; *BEA framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; FAI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; and MFI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

[0064] A second aspect of the present disclosure may include the first aspect, where the hydrocarbon feed stream has an API gravity of from 45 degrees to 60 degrees.

[0065] A third aspect of the present disclosure may includes the first or second aspects, where at least 95 wt.% of the hydrocarbon feed stream is crude oil.

[0066] A fourth aspect of the present disclosure may include any of the first through third aspects, where the reactor unit is a fluidized bed reactor.

[0067] A fifth aspect of the present disclosure may include any of the first through fourth aspects, where the amount of the FAU framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

[0068] A sixth aspect of the present disclosure may include any of the first through fifth aspects, where the amount of the MFI framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

[0069] A seventh aspect of the present disclosure may include any of the first through sixth aspects, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise phosphorous pentoxide.

[0070] An eighth aspect of the present disclosure may include the seventh aspect, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise from 1 wt.% to 20 wt.% of phosphorous pentoxide.

[0071] A ninth aspect of the present disclosure may include any of the first through eighth aspects, where at least one of the one or more binder materials is pseudoboehmite.

[0072] A tenth aspect of the present disclosure may include any of the first through ninth aspects, where the cracking catalyst comprises from 5 wt.% to 30 wt.% of pseudoboehmite.

[0073] An eleventh aspect of the present disclosure may include any of the first through tenth aspects, where the amount of the one or more binder materials is from 10 wt.% to 20 wt.% of the total cracking catalyst.

[0074] A twelfth aspect of the present disclosure may include any of the first through eleventh aspects, where one or more of the binders is kaolin.

[0075] A thirteenth aspect of the present disclosure may include any of the first through twelfth aspects, where cracking catalyst comprises the one or more binder materials in an amount of from 30 wt.% to 50 wt.% of the total cracking catalyst.

[0076] A fourteenth aspect of the present disclosure may include any of the first through thirteenth aspects, where the catalyst to oil weight ratio is from 7 to 10.

[0077] A fifteenth aspect of the present disclosure may include any of the first through fourteenth aspects, where the MFI framework type zeolite comprises ZSM-5.

[0078] A sixteenth aspect of the present disclosure may include any of the first through the fifteenth aspects, where the FAU framework type zeolite comprise zeolite Y.

[0079] A seventeenth aspect of the present disclosure may include any of the first through the sixteenth aspects, where the *BEA framework type zeolite comprises zeolite Beta.

[0080] An eighteenth aspect of the present disclosure may include any of the first through the seventeenth aspects, where the contacting of the hydrocarbon feed stream with the

cracking catalyst produces a product stream comprising at least 20 wt.% of light olefins selected from ethylene, propylene, and butene.

[0081] According to a nineteenth aspect of the present disclosure, a method for cracking a hydrocarbon feed stream may comprise contacting the hydrocarbon feed stream with a cracking catalyst in a reactor unit, where the hydrocarbon feed stream has an API gravity of at least 40 degrees, and where the cracking catalyst comprises: pseudoboehmite in an amount of from 5 wt.% to 30 wt.% of the total cracking catalyst; kaolin in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst; zeolite Beta in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; zeolite Y in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; and ZSM-5 in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

[0082] A twentieth aspect of the present disclosure may include the nineteenth aspect, where the hydrocarbon feed stream is a crude oil feedstock.

[0083] A twenty-first aspect of the present disclosure may include the nineteenth or twentieth aspects, where the hydrocarbon feed stream is gas condensate.

[0084] A twenty-second aspect of the present disclosure may include any of the nineteenth through the twenty-first aspects, where the reactor unit is a fluidized bed reactor.

[0085] A twenty-third aspect of the present disclosure may include any of the nineteenth through twenty-second aspects, where one or more of the ZSM-5, zeolite Beta, and zeolite Y comprise phosphorous pentoxide.

[0086] According to a twenty-fourth aspect of the present disclosure, a system for cracking a hydrocarbon feed stream may comprise a reactor; a hydrocarbon feed stream entering the reactor, where the hydrocarbon feed stream has an API gravity of at least 40 degrees; a product stream exiting the reactor; and a cracking catalyst positioned at least in the reactor, where the cracking catalyst comprises: one or more binder materials in an amount of from 5 wt.% to 30 wt.% of the total cracking catalyst; one or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst; *BEA framework type zeolite in an

mount of from 5 wt.% to 45 wt.% of the total cracking catalyst; FAU framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; FAU framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; and MFI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

[0087] A twenty-fifth aspect of the present disclosure may include the twenty-fourth aspect, where the hydrocarbon feed stream has an API gravity of from 45 degrees to 60 degrees.

[0088] A twenty-sixth aspect of the present disclosure may include the twenty-fourth aspect or the twenty-fifth aspect, where at least 95 wt.% of the hydrocarbon feed stream is crude oil.

[0089] A twenty-seventh aspect of the present disclosure may include any of the twenty-fourth through twenty-sixth aspects, where the reactor unit is a fluidized bed reactor.

[0090] A twenty-eighth aspect of the present disclosure may include any of the twenty-fourth through twenty-seventh aspects, where the amount of the FAU framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

[0091] A twenty-ninth aspect of the present disclosure may include any of the twenty-fourth through twenty-eighth aspects, where the amount of the MFI framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

[0092] A thirtieth aspect of the present disclosure may include any of the twenty-fourth through twenty-ninth aspects, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise phosphorous pentoxide.

[0093] A thirty-first aspect of the present disclosure may include any of the twenty-fourth through thirtieth aspects, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise from 1 wt.% to 20 wt.% of phosphorous pentoxide.

[0094] A thirty-second aspect of the present disclosure may include any of the twenty-fourth through thirty-first aspects, where at least one of the one or more binder materials is pseudoboehmite.

[0095] A thirty-third aspect of the present disclosure may include any of the twenty-fourth through thirty-second aspects, where the cracking catalyst comprises from 5 wt.% to 30 wt.% of pseudoboehmite.

[0096] A thirty-fourth aspect of the present disclosure may include any of the twenty-fourth through thirty-third aspects, where the amount of the one or more binder materials is from 10 wt.% to 20 wt.% of the total cracking catalyst.

[0097] A thirty-fifth aspect of the present disclosure may include any of the twenty-fourth through thirty-fourth aspects, where one or more of the binders is kaolin.

[0098] A thirty-sixth aspect of the present disclosure may include any of the twenty-fourth through thirty-fifth aspects, where cracking catalyst comprises the one or more binder materials in an amount of from 30 wt.% to 50 wt.% of the total cracking catalyst.

[0099] A thirty-seventh aspect of the present disclosure may include any of the twenty-fourth through thirty-sixth aspects, where the catalyst to oil weight ratio is from 7 to 10.

[00100] A thirty-eighth aspect of the present disclosure may include any of the twenty-fourth through thirty-seventh aspects, where the MFI framework type zeolite comprises ZSM-5.

[00101] A thirty-ninth aspect of the present disclosure may include any of the twenty-fourth through thirty-eighth aspects, where the FAU framework type zeolite comprise zeolite Y.

[00102] A fortieth aspect of the present disclosure may include any of the twenty-fourth through thirty-ninth aspects, where the *BEA framework type zeolite comprises zeolite Beta.

CLAIMS

1. A method for cracking a hydrocarbon feed stream, the method comprising:

contacting the hydrocarbon feed stream with a cracking catalyst in a reactor unit, where the hydrocarbon feed stream has an API gravity of at least 40 degrees, and where the cracking catalyst comprises:

one or more binder materials in an amount of from 5 wt.% to 30 wt.% of the total cracking catalyst;

one or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst;

*BEA framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst;

FAU framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; and

MFI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

2. The method of claim 1, where the hydrocarbon feed stream has an API gravity of from 45 degrees to 60 degrees.

3. The method of claims 1 or 2, where the amount of the FAU framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

4. The method of any of claims 1-3, where the amount of the MFI framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.
5. The method of any of claims 1-4, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise phosphorous pentoxide.
6. The method of any of claims 1-5, where at least one of the one or more binder materials is pseudoboehmite.
7. The method of any of claims 1-6, where the amount of the one or more binder materials is from 10 wt.% to 20 wt.% of the total cracking catalyst.
8. The method of any of claims 1-7, where one or more of the matrix materials is kaolin.
9. The method of any of claims 1-8, where cracking catalyst comprises the one or more matrix materials in an amount of from 30 wt.% to 50 wt.% of the total cracking catalyst.
10. The method of any of claims 1-9, where the catalyst to oil weight ratio is from 7 to 10.
11. The method of any of claims 1-10, where the MFI framework type zeolite comprises ZSM-5

12. The method of any of claims 1-11, where the FAU framework type zeolite comprise zeolite Y.

13. The method of any of claims 1-12, where the *BEA framework type zeolite comprises zeolite Beta.

14. The method of any of claims 1-13, where the contacting of the hydrocarbon feed stream with the cracking catalyst produces a product stream comprising at least 20 wt.% of light olefins selected from ethylene, propylene, and butene.

15. The method of any of claims 1-14, where the hydrocarbon feed stream is gas condensate.

16. A system for cracking a hydrocarbon feed stream, the system comprising:

a reactor;

a hydrocarbon feed stream entering the reactor, where the hydrocarbon feed stream has an API gravity of at least 40 degrees;

a product stream exiting the reactor; and

a cracking catalyst positioned at least in the reactor, where the cracking catalyst comprises:

one or more binder materials in an amount of from 5 wt.% to 30 wt.% of the total cracking catalyst;

one or more matrix materials in an amount of from 30 wt.% to 60 wt.% of the total cracking catalyst;

*BEA framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst;

FAU framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst; and

MFI framework type zeolite in an amount of from 5 wt.% to 45 wt.% of the total cracking catalyst.

17. The system of claim 16, where the hydrocarbon feed stream has an API gravity of from 45 degrees to 60 degrees.

18. The system of claims 16 or 17, where the reactor unit is a fluidized bed reactor.

19. The system of any of claims 16-18, where the amount of the FAU framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

20. The system of any of claims 16-19, where the amount of the MFI framework type zeolite is from 10 wt.% to 20 wt.% of the total cracking catalyst.

21. The system of any of claims 16-20, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise phosphorous pentoxide.

22. The system of any of claims 16-21, where one or more of the MFI framework type zeolite, *BEA framework type zeolite, and FAU framework type zeolite comprise from 1 wt.% to 20 wt.% of phosphorous pentoxide.

23. The system of any of claims 16-22, where the catalyst to oil weight ratio is from 7 to 10.

24. The system of any of claims 16-23, where the MFI framework type zeolite comprises ZSM-5

25. The system of any of claims 16-24, where the FAU framework type zeolite comprise zeolite Y.

26. The system of any of claims 16-25, where the *BEA framework type zeolite comprises zeolite Beta.

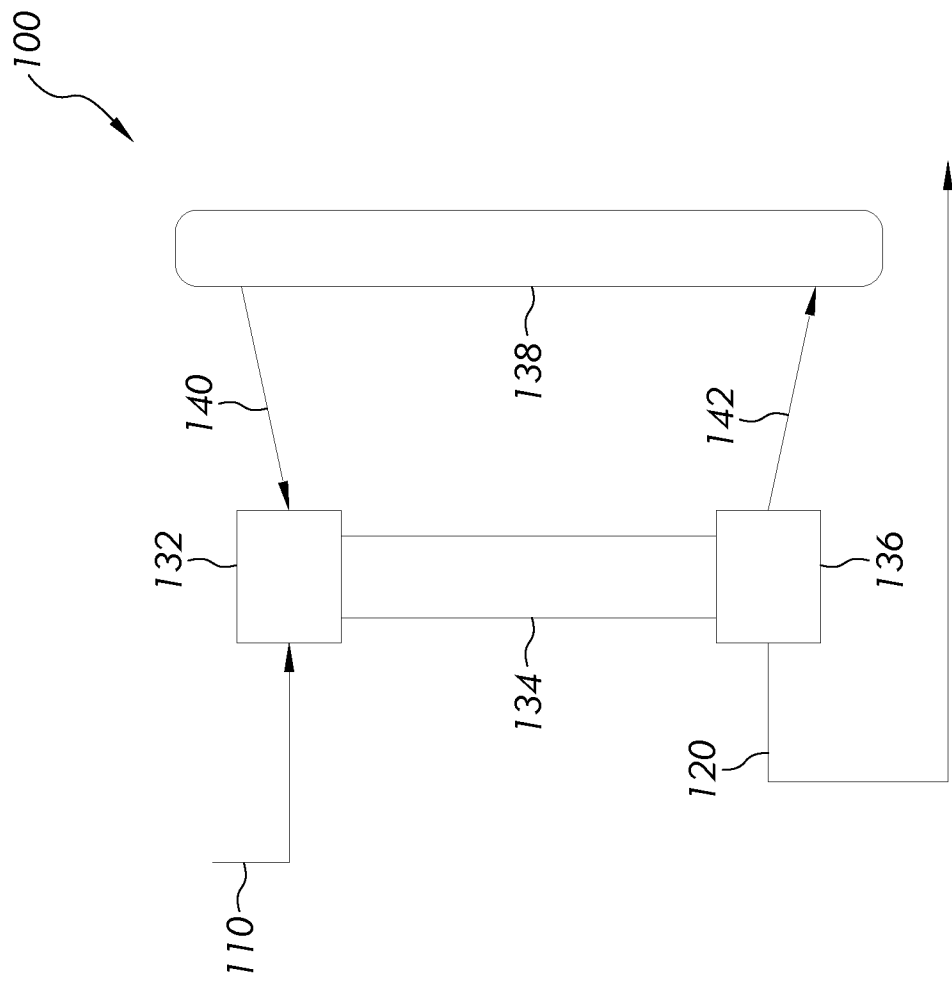


FIG. 1

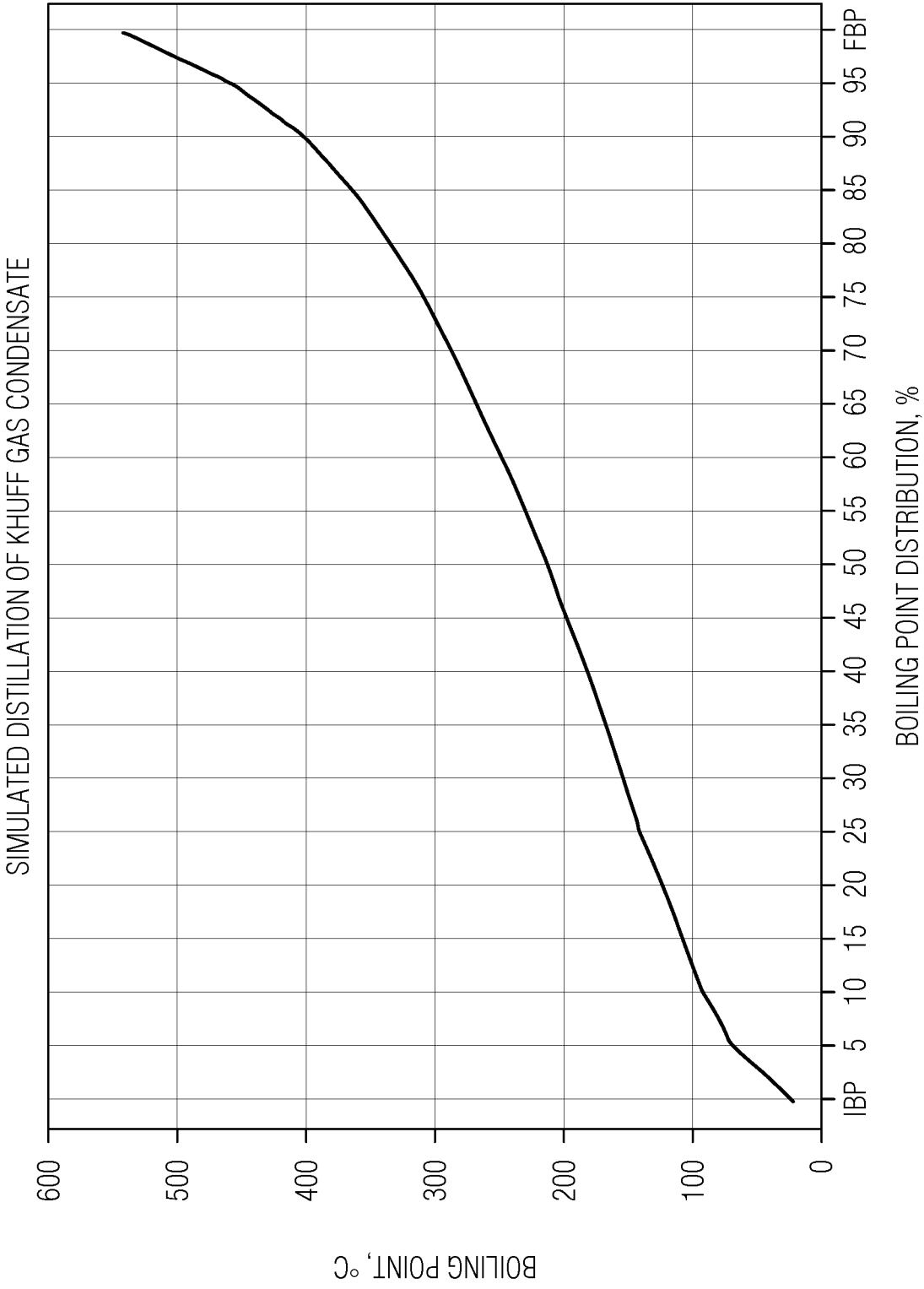


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2018/018482

A. CLASSIFICATION OF SUBJECT MATTER INV. C10G11/05 C10G11/18 B01J29/08 B01J29/40 B01J29/80 B01J29/70 ADD. According to International Patent Classification (IPC) or to both national classification and IPC														
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C10G B01J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data														
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 2009/325786 A1 (LIU YUJIAN [CN] ET AL) 31 December 2009 (2009-12-31) claims 1-12 paragraphs [0032], [0043], [0044], [0139] table 2 examples 15, 16 -----</td> <td>1-26</td> </tr> <tr> <td>A</td> <td>CN 1 103 105 A (PETROCHEMICAL INDUSTRY SCIENCE [CN]) 31 May 1995 (1995-05-31) claims 1-6 -----</td> <td>1-15</td> </tr> <tr> <td>A</td> <td>US 2013/066131 A1 (HARRIS DAVID H [US]) 14 March 2013 (2013-03-14) claims 1-20 -----</td> <td>1-15</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2009/325786 A1 (LIU YUJIAN [CN] ET AL) 31 December 2009 (2009-12-31) claims 1-12 paragraphs [0032], [0043], [0044], [0139] table 2 examples 15, 16 -----	1-26	A	CN 1 103 105 A (PETROCHEMICAL INDUSTRY SCIENCE [CN]) 31 May 1995 (1995-05-31) claims 1-6 -----	1-15	A	US 2013/066131 A1 (HARRIS DAVID H [US]) 14 March 2013 (2013-03-14) claims 1-20 -----	1-15
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X	US 2009/325786 A1 (LIU YUJIAN [CN] ET AL) 31 December 2009 (2009-12-31) claims 1-12 paragraphs [0032], [0043], [0044], [0139] table 2 examples 15, 16 -----	1-26												
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A	US 2013/066131 A1 (HARRIS DAVID H [US]) 14 March 2013 (2013-03-14) claims 1-20 -----	1-15												
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.														
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Date of the actual completion of the international search 25 April 2018		Date of mailing of the international search report 07/05/2018												
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Pardo Torre, J												

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Information on patent family members

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