

PARAFFIN HYDRO-NORMALIZATION TO IMPROVE THE CARBON FOOTPRINT OF STEAM CRACKING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/518,372, filed on 09 August 2023, the disclosure of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Process for hydro-normalizing the long (C_{12}^{+}) n-paraffins in a heavy feedstock. This thereby tailors a suitable feed stream for naphtha steam crackers.

BACKGROUND

[0003] Steam crackers can be distinguished based on feed type. Most contemporary gas crackers are designed to pyrolyze mostly ethane. More typically, gas crackers can handle feedstocks including liquefied petroleum gas (LPG). Liquid crackers tend to focus on naphtha. Mixed feed stream crackers have the flexibility to crack both gas and liquid feeds. Mixed feed steam crackers were commercialized with the ability to pyrolyze feedstocks efficiently with an end boiling point as high as 700°F viz. by including a Heavy Oil Processing System or HOPS. However, most commercial liquid steam crackers are referred to as “naphtha crackers” because they are limited to feedstocks in the naphtha boiling range (90-380°F). Such naphtha crackers are particularly prevalent in geographies where ethane is in short supply.

[0004] Previously, both UOP and ExxonMobil have tried n-paraffin pressure swing adsorption processes (e.g., Molex™, IsoSiv™, Maxene™, and Ensorb™) to concentrate the n- paraffins from oils to enable subsequent octane upgrading through isomerization or to enhance the ethylene yield in subsequent steam cracking. The added operational and energy costs of a concentration process, however, are quite high because the desorption of n-paraffins requires excess energy when n-paraffins become much longer than n-heptane and because thermodynamics disfavors isomerization of iso-paraffins into n-paraffins -it favors the reaction into the opposite direction.

[0005] Revamping a steam cracker to enable higher boiling feed components is expensive. Thus, lowering the feed boiling point to a level that existing steam crackers

can handle without degrading the feedstock by forming isomers becomes the most practical objective. This is difficult when dealing with a heavy feed having long n-paraffins, e.g., C_{12}^+ in length.

[0006] For over a century, hydrocracking and catalytic cracking have been used to reduce the boiling point and to increase the H/C ratio of crude oils and coal-derived liquids in refineries. Inherently, these catalytic processes also increased the iso-paraffin content of the lighter fractions. This was desirable when the intended use of the cracking products was combustion in an internal combustion engine. However, crude oil is now increasingly used for chemical manufacture, and high iso-paraffin content has become an undesirable side effect of acid-catalyzed (hydro)cracking.

[0007] Nobel Laureate George Olah established that acid catalysts do not crack n-paraffins directly into n-paraffins. Instead acids first catalyze the conversion of n-paraffins into iso-paraffins, and only then do they crack the iso-paraffins. Consequently, a product slate with a high iso-paraffin content is generally considered the signature of acid-catalyzed cracking. By contrast, a product slate with a high n-paraffin content is the signature of thermal or metal-catalyzed cracking (see Schmidt et al, ACS Catalysis vol. 13, 2023 pp 6710-6720).

[0008] There is an urgent need in the industry to diversify the crude oil value chain and turn crude oil into a superior steam cracking feedstock. Iso-paraffins are a less desirable steam cracker feed stream in that they generate desirable olefins, but at the cost of significant quantities of undesirable pyrolysis oil and at the cost of a lower ethylene-to-propylene ratio. Particular difficult problems arise when the feed needing end boiling point reduction comprises a large percentage of long, C_{12}^+ n-paraffins, in terms of finding an appropriate catalyst that can be efficient and stable. The industry would welcome a straight-forward stable and efficient catalytic process for hydroconverting long normal paraffins into lighter normal paraffins in high yields so that feedstocks containing long C_{12}^+ n-paraffins can be readily tailored as a feed stream for an existing naphtha steam cracker.

SUMMARY

[0009] Provided is a stable and efficient process for preparing ethylene in improved yields when starting with an industrial feedstock, in one embodiment a first stage hydrocracker effluent in the vacuum gas oil boiling range. Such industrial feedstocks generally comprise at least 5 wt. % C_7^+ , or in one embodiment, C_{12}^+ n-paraffins, in

another embodiment, at least 10 wt. % C_7^+ , or in one embodiment, C_{12}^+ n-paraffins, and in another embodiment at least 20 wt. % C_7^+ , or in one embodiment, C_{12}^+ n-paraffins. The process first involves a hydroprocessing reaction. In one embodiment, the reaction is run in the presence of an LTA zeolite, which zeolite has an acid site concentration in the range of from 2.6 to 3.0 mol/l, and in one embodiment an acid site concentration of about 2.7 mol/l or greater. This acid site concentration has been found important. A chosen boiling range of n-paraffins is then collected from the hydroprocessing reactor. The range generally comprises C_2 - C_6 n-paraffins. After conversion of the longer n-paraffins, the isoparaffins or naphthenics can then be separately subjected to destructive cracking to further increase their hydrogen content and -thereby- their suitability for steam cracking, if desired. Concentrating the n-paraffins in the C_2 - C_6 carbon range and depleting the steam cracker feed from n-paraffins with a higher carbon number dramatically improves ethylene yields.

[0010] Among other factors the present process is stable and efficient in providing a feed that pyrolyzes into more ethylene. It has been surprisingly found that the LTA zeolite used, with an acid site concentration around 2.7 mol/l, can reduce long n-paraffins in the vacuum gas oil boiling range in high yield to the n-paraffins in the ethane to naphtha boiling range of C_2 - C_6 n-paraffins. Based on 3 months of operation without activity loss after line-out, current models indicate that a catalyst based on LTA-type zeolite would exhibit the typical run length of 2-4 years for base metal catalyst formulations and of 10-15 years for noble metal catalyst formulations at typical feeds and conditions. The catalyst sustainably hydrocracks extremely long n-paraffins, such as C_{23}^+ in length. The stability of the hydrocracking process on the LTA-type zeolite catalyst is surprising because it is well-established that a (de)hydrogenation function needs to activate n-paraffins into n-olefins, and that these n-olefins need to enter ~11 nm wide LTA-type cages before isomerizing into iso-olefins (see J.E. Schmidt et al, ACS Catalysis vol. 13, 2023 pp 6710-6720). These iso-olefins are trapped inside the LTA-type cages, for they are too large to egress through the ~5 nm wide LTA-type windows (see P.B. Weisz, V.J. Frilette, J.Phys.Chem. vol.64, 1960, p382). Well-established mechanisms explain how iso-olefins crack into mixtures of iso-paraffins, iso-olefins, n-paraffins and n-olefins (J. Weitkamp, P.A. Jacobs, J.A. Martens, Appl.Catal. vol.8, 1983, pp.123-141). An iso-paraffin would require activation into an iso-olefin to enable isomerization into an n-olefin and escape from the LTA-type cage. Without a noble metal function iso-paraffins would accumulate inside the LTA-type cages, blocking access to the zeolite and

deactivating the catalyst. Surprisingly, this deactivation was not observed, so that the catalyst sustainably converted longer n-paraffins into desirable linear paraffins in the C₂-C₆ carbon number range. By providing such a suitable feedstock for a steam cracker, the preparation of ethylene and other lower olefins as chemical building blocks can be efficiently realized in good yield while using a steam cracker.

BRIEF DESCRIPTION OF THE FIGURES OF THE DRAWING

[0011] FIG. 1 graphically depicts the paraffin composition of a vacuum gas oil feed used as quantified through GCxGC.

[0012] FIG. 2 graphically depicts the wt-% i- and n-paraffins as a function of carbon number achieved from hydro-normalizing the vacuum gas oil (with the paraffin composition described in FIG. 1) at 81% n-C₁₂⁺ conversion in accordance with the present process.

[0013] FIG. 3 graphically depicts the change in product paraffin composition as a function of conversion of the n- C₁₂⁺ paraffins in the vacuum gas oil feed.

[0014] FIG. 4 graphically depicts the wt-% i- and n-paraffins as a function of carbon number achieved from hydro-normalizing the vacuum gas oil (with the paraffin composition described in FIG. 1) at 60% n-C₁₂⁺ conversion in accordance with the present process. A steam cracker pyrolyzed this product.

DETAILED DESCRIPTION

[0015] Definitions:

[0016] Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. It is the principal industrial method for producing the lighter alkenes (or commonly olefins), including ethylene and propylene. Steam cracker units are facilities in which feedstocks such as ethane, propane, butane, liquefied petroleum gas (LPG), and naphtha are thermally cracked or pyrolyzed in the presence of steam by a short residence time in a furnace at high temperature to produce lighter hydrocarbons. After the cracking temperature has been reached, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil. The feed composition, the hydrocarbon-to-steam ratio, the cracking temperature and furnace residence time determine the product composition. Light hydrocarbon feeds such as ethane, LPGs, or light naphtha yield mostly lighter alkenes, including ethylene, propylene, and butadiene. Heavier

hydrocarbon (full range and heavy naphtha or even heavier oil fractions) feeds yield some of these same products, but also aromatic pyrolysis oils.

[0017] Olefins such as ethylene, propylene and butylene are the raw materials of polyolefins. Polyolefins are one of the key building blocks of the global economy. Illustrating its critical roll to economic growth, steam cracking capacity tends to grow slightly ahead of global gross domestic product (GDP). Ethylene capacity in 2021 was 150,000 kiloton/annum (kta) and is growing at 6000-8000 kta of ethylene, produced in ever larger facilities. A current state-of-the-art cracker can produce 2000 kta of ethylene. At such large volumes feedstocks that make incrementally more ethylene have large financial benefits.

[0018] A “naphtha” cracker is generally limited to feedstocks in the naphtha boiling range of 32-193°C (C₄-C₁₀). An ethane cracker is generally limited to feeding ethane and some LPG. Most commercial liquid and gas steam crackers in current operation are naphtha and ethane crackers.

[0019] Hydroconversion and hydroconverting: A catalytic process which operates at pressures greater than atmospheric in the presence of hydrogen and which converts normal paraffins into lighter normal paraffins with a minimum of isomerization and without excessive formation of methane and ethane. This can also be referred to as hydro-normalization. Hydrotreating and hydrocracking are distinctly different catalytic processes but which also operate at pressures greater than atmospheric in the presence of hydrogen. Hydrocracking converts normal paraffins into lighter products comprising significant amounts of iso-paraffins. Hydrotreating does not convert significant quantities of the feedstock to lighter products but does remove impurities such as sulfur- and nitrogen-containing compounds. Also in comparative contrast, thermal cracking converts normal paraffins into lighter products with a minimum of branching, but this process does not use a catalyst, typically operates at much higher temperatures, forms more methane, and makes a mixture of olefins and normal paraffins.

[0020] A LTA (Linde Type A) zeolite is a zeolite that has voids greater than 0.50 in diameter, and apertures characterized by a longest diameter of less than 0.5 nm and a shortest diameter of more than 0.30 nm. Such LTA zeolites are described in the Atlas of Zeolite Structure Types, Fourth Revised Edition 1996.

[0021] An “aperture” in a zeolite is the narrowest passage through which an absorbing or desorbing molecule needs to pass to get into the zeolite’s interior. The diameter of the aperture, d_{app} (nm), is defined as the average of the shortest, d_{short} (nm), and the longest,

d_{long} (nm) axis provided in the IZA (International Zeolite Association) Zeolite Atlas (<http://www.iza-structure.org/databases/>). Both normal- and iso-paraffins with a methyl group can pass through apertures with a $d_{\text{long}} \geq 0.50$ nm, but only normal-paraffins can pass through apertures with $d_{\text{long}} < 0.50$ nm provided $d_{\text{short}} > 0.30$ nm.

[0022] Apertures provide access to “voids”, the wider parts in the zeolite topology. The diameter of the void, d_{void} (nm), is characterized by the maximum diameter of a sphere that one can inflate inside such a void as per the IZA Zeolite Atlas (<http://www.iza-structure.org/databases/>). This characterizes, e.g., a fairly spherical LTA void (or cage) as one with a diameter of 1.1 nm, and an elongated AFX-type void as one with a spherical diameter of 0.78 nm. Voids are defined as cages if $d_{\text{void}}/d_{\text{app}} \geq 1.4$ nm/nm. An LTA zeolite exhibits a topology with a defined combination of apertures and voids.

[0023] The first step of the present process involves the hydro-normalization of the eventual feedstock to the naphtha steam cracker by hydroconverting normal paraffins into lighter normal paraffins with minimal formation of iso-paraffins. The process comprises hydroconverting a hydrocarbon feedstock comprising normal paraffins under hydroconversion conditions, in the presence of an LTA zeolite catalyst. The zeolite has voids greater than 0.50 in diameter, accessible through apertures characterized by a longest diameter of less than 0.50 nm and a shortest diameter of more than 0.30 nm. Most important, the present LTA zeolite exhibits an acid site concentration in the range of 2.6 to 3.0 mol/l, and most preferably about 2.7 mol/l. The present zeolite can be bound with alumina and extruded into a pellet or extrudate. The extrudate is loaded with 0.1 to 0.5 wt. % Pd, although any pellet or bound zeolite can be loaded with any hydrogenation function metal.

[0024] It is the zeolite-containing base into which the metal is loaded that is critical to the present processes. For it has been found that the present catalyst comprising a LTA zeolite in accordance herewith can provide the high conversion and minimal formation of iso-paraffins. It has been found that the key features of the catalyst zeolite include access to a pore system through apertures of a size less than 0.45 nm, and with the pore system containing voids greater than 0.50 nm in diameter. In another embodiment, the zeolite has voids greater than 0.50 nm in diameter, which are accessible through apertures characterized by a longest diameter of less than 0.5 nm and a shortest diameter of more than 0.30 nm. The LTA zeolite has such a zeolite framework. The present LTA zeolite must also exhibit an acid site concentration of from 2.6 to 3.0 mol/l, in one embodiment

from 2.6 to 2.8 mol/l, and preferably about 2.7 mol/l. This is an LTA zeolite with a higher alumina concentration than normal.

[0025] Linde Type A, framework code LTA, is one of the most used zeolites in separations, adsorption, and ion exchange. This structure contains large spherical cages (diameter ~ 11.4 Å) that are connected in three dimensions by small 8-membered ring (8MR) apertures with a diameter of 4.1 Å. LTA is normally synthesized in hydroxide media in the presence of sodium with Si/Al ~ 1 mol/mol. By changing the cation, the limiting diameter of the 8MR apertures can be tuned, creating the highly used series of adsorbents 3A (potassium form, 2.9 Å diameter), 4A (sodium form, 3.8 Å diameter) and 5A (calcium form, 4.4 Å diameter) that are used to selectively remove species such as water, NH_3 , SO_2 , CO_2 , H_2S , C_2H_4 , C_2H_6 , C_3H_6 and other n-paraffins from gases and liquids. Detergents deploy zeolite 4A because it softens water by replacing calcium and magnesium ions in “hard” water with sodium ions. While LTA zeolites are used in vast quantities for the aforementioned applications, the industry has considered the low framework Si/Al ratio and subsequent poor hydrothermal stability limits as limiting factors to succeeding under more demanding process conditions that are commonly found in catalytic applications. Yet surprisingly, the present process is found to be stable and efficient using an LTA zeolite with the requisite acid site concentration of from 2.6 to 3.0 mol/l.

[0026] The stability of the present LTA zeolites with 0.4 nm wide constrictions in hydroconverting n-alkanes longer than n-hexane (n-C_6) is stunning. The discovered stability of the present LTA zeolites with 0.4 nm wide constrictions that hydrocrack n-C_{12}^+ and longer n-alkanes out of feed stocks in the vacuum gasoil boiling range for at least three months is not intuitive. It is not intuitive because n-C_{12}^+ and longer n-alkanes inherently hydrocrack into branched alkanes. This would imply that the primary branched alkene and alkane products would have further isomerized into n-alkenes so as to egress through 0.4 nm wide constrictors. Particularly for i-butanes (that are allegedly primary cracking products) it is not clear what mechanism would be involved to let them egress.

[0027] The discovered hydroprocessing stability of LTA zeolites with an acid concentration as high as 2.7 mol/l is truly a surprise. Previously, it has been shown that the stability is inversely proportional to acid concentration, and the longheld belief in the industry is that stable operation requires an acid concentration of at most 1.8 mol/l. At acid concentrations higher than 1.8 mol/l, catalysts are supposed to coke up or crumble.

[0028] The stable operation of the present LTA zeolite with an acid concentration as high as 2.7 mol/l (well above the historically suggested 1.8 mol/l threshold) in the hydro-normalization of n-alkanes as long as n-C₁₂⁺ remains a bit of a mystery and surprise. The present LTA zeolite having the requisite acid site concentration can continue in operation for at least 3 months and even longer, e.g., 6 months to two years or even 5 years or longer. This is counter intuitive, yet this is what has been discovered.

[0029] The catalyst based on the present LTA zeolite can typically contain a catalytically active hydrogenation metal. The presence of a catalytically active hydrogenation metal leads to product improvement, especially IV and stability. Typical catalytically active hydrogenation metals include chromium, molybdenum, nickel, vanadium, cobalt, tungsten, zinc, platinum, and palladium. The metals platinum and palladium are especially preferred, with platinum most especially preferred. If platinum and/or palladium is used, the total amount of active hydrogenation metal is typically in the range of 0.1 wt. % to 5 wt. % of the total catalyst, usually from 0.1 wt. % to 2 wt. %.

[0030] The zeolite can be loaded with a hydrogenation function metal or a mixture of such metals either as is or bound with a suitable binder, such as silica, alumina or titania. Such hydrogenating metals are known in the art and have been discussed generally earlier. The preferred metal is typically either a noble metal, such as Pd, Pt, and Au, or a base metal, such as Ni, Mo and W. A mixture of the metals and their sulfides can be used. The loading of the zeolite with the metals can be accomplished by techniques known in the art, such as impregnation or ion exchange. The hydrogenation function metal is loaded on such a selected zeolite to create the catalyst. The created catalyst can then be used in the hydroconversion process.

[0031] The feedstock for the first step of the process is a hydrocarbon feedstock which comprises at least 5 wt. % normal paraffins. Greater benefit is achieved when the hydrocarbon feedstock comprises at least 20 wt. %, even better when at least 50 wt. % normal paraffins, and in particular at least 80 wt. % normal paraffins. The normal paraffins in the feedstocks of the present process comprise large amounts of C₇⁺ normal paraffins, or in one embodiment, C₁₂⁺ n-paraffins. The amount of C₁₂⁺ n-paraffins based on the total weight of the hydrocarbon feedstock is generally at least 5 wt. %, but more likely at least 10 wt. %, or in one embodiment at least 20 wt. %. Such feedstocks can be obtained from a wide variety of sources. Typical heavy feedstocks can include hydrotreated or hydrocracked gas oils, biogenic animal fats, vegetable oils, or greases (FOG). Other hydrocarbon feedstocks suitable for use in the present process scheme may

be selected, for example, from gas oils, vacuum gas oils, oils derived from waste plastics, sorted municipal waste, end-of-life tires or biomass through pyrolysis or through hydrothermal liquefaction; residuum fractions from an atmospheric pressure distillation process; solvent-deasphalted petroleum residua; shale oils, and cycle oils. Biogenic oils and so-called circular oils (i.e., oils made from waste materials). Vacuum gas oils is a preferred feedstock for the first step of the present process.

[0032] In an embodiment, the feedstock's aromatics and organic nitrogen, sulfur, oxygen, halogen and silicon content is reduced. This can be achieved by hydrotreating the feedstock prior to the hydroconversion. Contacting the feedstock with a hydrotreating catalyst may serve to effectively hydrogenate aromatics in the feedstock and to remove N-, S-, O-, Cl-, Br-, F-, Si- containing compounds from the feed.

[0033] The conditions under which the first step of the present processes, i.e., the hydro-normalization reaction or hydroconversion reaction, is carried out will generally include a temperature within a range from about 390° F to about 800° F (199° C to 427° C). In an embodiment, the temperature is in the range from about 550° F to about 700° F (288° C to 371° C). In a further embodiment, the temperature may be in the range from about 590° F to about 675° F (310° C to 357° C). The pressure may be in the range from about 50 to about 5000 psig, and typically in the range from about 100 to about 2000 psig.

[0034] The normal paraffin-rich product recovered from the hydroconversion can then be passed to a steam cracker. Using the present LTA zeolite-based catalyst with the higher acid site concentration provides a C₂-C₆ product in improved yields, which product can be collected from the hydroconversion process. The second step is a steam cracking step in a steam cracker. The steam cracking process is known in the art. Steam cracking a hydrocarbon feedstock produces olefin streams containing olefins such as ethylene, propylene, and butenes as well as aromatics. The present hydroconversion process provides an excellent feedstock for a steam cracker because it increases the ethylene yield at the cost of propylene and aromatics yields.

[0035] In steam cracking, a gaseous or liquid hydrocarbon feed like ethane, LPG, light or full-range naphtha is diluted with steam and heated in a furnace in the absence of oxygen. Typically, the reaction temperature is between 800 and 900°C and the residence time is on the order of milliseconds. The pyrolyzing gases flow at close to the speed of sound. After pyrolysis, the gas is quickly quenched to stop the reaction in a transfer line heat exchanger or inside a quenching header using quench oil.

[0036] The products produced in the reaction depend on the composition of the feed and on the conditions, such as the hydrocarbon-to-steam ratio, the cracking temperature and furnace residence time. Light hydrocarbon feeds (ethane, LPG, light naphtha) yield lighter alkenes, including ethylene, propylene, and butadiene. Heavier hydrocarbon feeds (full range and heavy naphtha, hydrogenated gas oils) also yield these lighter products as well as aromatic pyrolysis oils suitable for aromatics extraction and for use in the production of needle coke or synthetic graphite. The present process is directed to preparing lower alkenes, and in particular ethylene and at minimizing pyrolysis oil make. The C₂-C₆ light naphtha range prepared by the first step hydroconversion allows for high yields of lower alkenes such as ethylene.

[0037] The following examples are provided in order to further illustrate the present process. However, the examples are not meant to be limiting.

Example 1

[0038] Example of LTA zeolite based noble metal catalyst.

[0039] A catalyst was made by extruding 50 wt. % LTA zeolite with 50- wt-% alumina (Pural TH80 from Sasol). The KAQ-type extrudates were loaded with 0.5 wt. % Pd. The LTA zeolite used had an acid site concentration of about 2.7 mol/l.

Example 2

[0040] A process to selectively hydro-normalize the long n-paraffins in a feedstock into particularly C₂-C₆ n-paraffins has been discovered. The process thereby provides a tailored feedstock for a naphtha steam cracker, which selectively pyrolyzes the C₂-C₆ n-paraffins to monetize these hydro-normalized products.

[0041] Hydro-normalization is accomplished through hydroprocessing an industrial feedstock (e.g., a 1st stage hydrocracker effluent in the vacuum gasoil boiling range at 1550 psia H₂, 1.6 LHSV, 5100 scf/b H₂,) on a hydroprocessing catalyst as described in Example 1, comprising a LTA zeolite with an optimum acid site concentration around 2.7 mol/l. Key features of the hydro-normalization process are that the catalyst selectively converts longer normal paraffins in the feed into C₂-C₆ n-paraffins. Since the feed in the example has an initial boiling point of 390 F, the shortest n-paraffin in feed is n-dodecane (or n-C₁₂ with a 421 F boiling point, whereas n-undecane or n-C₁₁ exhibits a 385 F boiling point).

[0042] See FIG. 1 which shows a feed exclusively containing $n\text{-C}_{12}^{\text{plus}}$ with negligible $n\text{-C}_{12}^{\text{minus}}$. The products at 81% $n\text{-C}_{12}^{\text{plus}}$ conversion are nearly exclusively $\text{C}_2\text{-C}_5$ n -paraffins. See FIG. 2.

[0043] Contrary to the expectations of the art, the present LTA zeolites have been surprisingly found to not exhibit a dramatic preference for processing n -paraffins up to the length that could easily fit inside a single LTA cage, which would limit the length of readily hydrocracked n -paraffins to that of n -tricosane or $n\text{-C}_{23}$ (716°F boiling point). Longer n -paraffins (n -triacontane or $n\text{-C}_{30}$, 840°F boiling point and longer) are still successfully processed. In addition to a remarkable selectivity for hydrocracking selectively $n\text{-C}_{12}$ and longer n -alkanes, the catalyst also makes some minimal i -paraffins.

[0044] For the specific feed used, i -paraffin production picks up above 50% $n\text{-C}_{12}^{\text{plus}}$ conversion. See FIG. 3. The increase in i -paraffin fraction (and a concomitant decrease in the n -paraffin fraction) signals a likely increase in the total paraffin yield through dealkylation and ring opening.

Example 3

[0045] Example of steam cracker feed properties.

[0046] A hydrotreated vacuum gasoil is hydroprocessed into an improved steam cracker feed as described in Table 1 below at 1550 psia H_2 , 1.6 LHSV, 5100 scf/b H_2 . A steam cracker feed produced at 60% $n\text{-C}_{12}^+$ conversion in the present hydro-normalization step is characterized in Table 1 as follows:

TABLE 1

	Feed	Hydroprocessed
API (°)	35.4	not measured
S (ppm-wt)	5.3	<0.3
N (ppm-wt)	<0.3	<0.3
wt-% paraffins (GCxGC)	45	52
wt-% $n\text{-C}_{12}^+$	18	0
wt-% $\text{C}_2\text{-}n\text{-C}_6$	0	12
Composition	Wt%	Wt%
Methane	0.00	0.03

Ethane	0.00	0.04
Propane	0.00	1
i-Butane	0.00	0.2
n-Butane	0.00	1.29
C4-	0.00	2.56
C5-180°F	0.00	2.2
180-350°F	0.00	0.59
350-500°F	7.2	9.58
500°F+	92.8	86.13
C5+	100.0	98.5
WLP Dist. By Wt%		
0.5/5%	392/478	95/445
10/30%	519/606	495/598
50%	666/	660/
70/90%	719/799	716/796
95/99.5%	842/955	840/956

[0047] The distribution between n- and iso-paraffins as determined by GC x GC is as shown in FIG. 4.

[0048] When switching from a feed without hydro-normalization to one with hydro-normalization, a dramatically lower feed rate (ton/hr) is needed to reach the same desirable ethylene (C_2H_4) yield. At this feed rate, the hydronormalized feed exhibits a shift toward desirable olefins (C_2H_4 , C_3H_6 , C_4H_8) and aromatics (benzene, toluene, xylenes or BTX) at the cost of heavier products (particularly pyrolysis fuel oil or PFO) (see Table 2 below). This amounts to a dramatic increase in carbon and energy efficiency of the steam cracking process.

TABLE 2

	Original Feed		Hydroprocessed	
	High Sev	Low Sev	High Sev	Low Sev
Feed, T/h	324.1	392.7	307.7	379.1

H2		2.4	2.2		2.4	2.1
CH4		37.2	34.2		37.1	33.6
C2H4		100	100		100	100
C3H6		46.1	62.2		41.9	61.3
C4H6		18.2	21.9		17.8	21.7
C4H8		11.4	24		9.8	23.8
C4H10		0.4	0.6		0.4	0.6
C5-400F PGO		61.4	77.2		58.1	76.3
400F+ PFO		47	70.4		40.4	59.8
Selectivity,w/w						
C2H4		30.86	25.46		32.5	26.38
C2H4+C3H6		45.07	41.3		46.12	42.53
C2H4+C3H6+C4H8		50.69	46.87		51.9	48.27
BTX		12.08	7.44		12.6	7.45

[0049] As used in this disclosure the word “comprises” or “comprising” is intended as an open-ended transition meaning the inclusion of the named elements, but not necessarily excluding other unnamed elements. The phrase “consists essentially of” or “consisting essentially of” is intended to mean the exclusion of other elements of any essential significance to the composition. The phrase “consisting of” or “consists of” is intended as a transition meaning the exclusion of all but the recited elements except for only minor traces of impurities.

[0050] As those skilled in the art will appreciate, numerous modifications and variations of the present invention are possible considering these teachings, and all such are contemplated hereby. For example, in addition to the embodiments described herein, the present invention contemplates and claims those inventions resulting from the combination of features of the invention cited herein and those of the cited prior art references which complement the features of the present invention. Similarly, it will be appreciated that any described material, feature, or article may be used in combination with any other material, feature, or article, and such combinations are considered within the scope of this invention.

[0051] All of the publications cited in this disclosure are incorporated by reference herein in their entireties for all purposes.

What is claimed is:

1. A process for pyrolyzing a feedstock comprising C₂-C₆ n-paraffins in a steam cracker, comprising:
 - a) subjecting a hydrocarbon feedstock comprising at least 5 wt. % C₇⁺ normal paraffins to a hydroconversion reaction under hydroconversion conditions in the presence of a catalyst that converts n-C₇⁺ paraffins into linear paraffins in the C₂-C₆ range; and
 - b) collecting a stream with an increased C₂-C₆ n-paraffin concentration at the expense of the n-C₇⁺ concentration from the hydroconversion reaction and pyrolyzing same in a steam cracker into lower olefins.
2. The process of claim 1, wherein the catalyst is based on LTA-type zeolite loaded with mixed metal sulfides, and wherein the process can run for at least 3 months without changing the catalyst or regenerating the LTA-type zeolite-based catalyst.
3. The process of claim 1, wherein the catalyst is based on LTA-type zeolite loaded with mixed metal sulfides, and wherein the process can run for at six months without changing the catalyst or regenerating the LTA-type zeolite-based catalyst.
4. The process of claim 1, wherein the catalyst is based on LTA-type zeolite loaded with mixed metal sulfides, and wherein the process can run for at least two years without changing the catalyst or regenerating the LTA-type zeolite-based catalyst.
5. The process of claim 1, wherein the catalyst is based on LTA-type zeolite loaded with one or more noble metals, and wherein the process can run for at least five years without changing the catalyst or regenerating said based catalyst.
6. The process of claim 1, wherein C₂-C₆ linear paraffin concentration increases the ethylene yield on a feed basis preferably by 3%, more preferably by 4% and most preferably by 5%.
7. The process of claim 1, wherein the acid site concentration of the LTA-type zeolite is about 2.6 to 3.0 mol/l.

8. The process of claim 1, wherein the acid site concentration of the LTA-type zeolite is about 2.7 mol/l.
9. The process of claim 1, wherein the hydrocarbon feedstock comprises at least 5 wt. % to C₇⁺ normal paraffins.
10. The process of claim 1, wherein the LTA zeolite is shaped with a binder into a pellet, and the catalyst pellets are loaded with a hydrogenation function metal.
11. The process of claim 10, wherein the hydrogenation function metal comprises a noble metal.
12. The process of claim 11, wherein the metal comprises Pd, Pt, Re, Ru, Sn, Au or a mixture thereof.
13. The process of claim 10, wherein the hydrogenation function metal component comprises Ni, Co, Mo, W, their sulfides, or a mixture thereof.
14. The process of claim 10, wherein the loaded LTA zeolite is used in a hydroconversion reaction of hydroconverting normal paraffins to a normal paraffin-rich lighter product with the feedstock comprising at least 5 wt. % C₇⁺ normal paraffins.
15. The process of claim 14, wherein the feedstock comprises at least 10 wt. % C₇⁺ normal paraffins.
16. The process of claim 1, wherein the feedstock is a vacuum gas oil based feedstock.
17. The process of claim 1, wherein the feedstock is subjected to a hydrotreatment prior to the hydroconversion reaction.

18. The process of claim 1, wherein the per-pass conversion of the normal paraffins in the feedstock is between 25 and 99%.