

SHORTENING N-PARAFFINS TO INCREASE STEAM CRACKER ETHYLENE YIELD

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 63/518,376, filed on 09 August 2023, the disclosure of which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Process for preparing ethylene using steam cracker feed with improved yields. The feed to the steam cracker comprises C₂-C₆ n-paraffins prepared in a hydroconversion process.

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. They can be equipped with a Heavy Oil Processing System (HOPS) to extend the boiling range beyond naphtha and into the vacuum gasoil (VGO) boiling range with an end boiling range as high as 1050 °F. 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 1050°F. However, most commercial liquid steam crackers are referred to as “naphtha crackers” because they are limited to feedstocks in the naphtha boiling range (32-193°C). 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 conversion into ethylene through steam cracking. The added 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.

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

handle without forming isomers becomes the most practical objective. However, 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.

[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 to produce ethylene. 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. The industry would welcome a straight-forward stable and efficient catalytic process for hydroconverting normal paraffins into lighter normal paraffins, and in particular ethylene, in high yields.

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. % n-paraffins, in one embodiment, at least 10 wt. % n-paraffins, and in another embodiment at least 20 wt. % n-paraffins. The feedstock can comprise the long n-paraffins in a vacuum gas oil ($350^{\circ}\text{F}+$ boiling range).

[0010] The process first involves a hydroprocessing reaction. The reaction is run in the presence of an LTA zeolite, comprising 10-1000 nm crystals, 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 C₂-C₆ n-paraffins. The collected C₂-C₆ n-paraffins can then be passed to steam cracker with good results including improved ethylene production.

[0011] 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 a catalyst based on the LTA zeolite used, with an acid site concentration around 2.7 mol/l, can reduce long n-paraffins in high yield to the n-paraffins in the ethane to naphtha boiling range of C₂-C₆ n-paraffins, and can do so continuously for months on end without losing its catalytic activity. The reaction is stable and does not exhibit any issues with feeds having extremely long n-paraffins, such as C₂₃⁺ in length. By providing such a suitable feedstock for steam cracker on a consistent and long term basis, the preparation of ethylene and other lower olefins as chemical building blocks can be efficiently realized in good yield.

BRIEF DESCRIPTION OF THE FIGURES OF THE DRAWING

[0012] FIG. 1 graphically depicts the n- and iso-paraffin composition as a function of carbon number of a hydrotreated vacuum gasoil feed used as quantified by GC x GC.

[0013] FIG. 2 graphically depicts the n- and iso-paraffin composition as a function of carbon number after hydroconversion of the n-paraffins in feed into mostly C₂ - n-C₆ n-paraffins as quantified by GC x GC in accordance with the present process.

DETAILED DESCRIPTION

[0014] Definitions:

[0015] 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 more aromatics and pyrolysis fuel oils.

[0016] An ethane cracker is generally limited to feeding ethane and some LPG, as it cracks the ethane to make ethylene. Such ethane crackers are well known in the industry. Most commercial liquid and gas steam crackers in current operation include ethane and naphtha crackers.

[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 processes and feedstocks that make incrementally more ethylene have large financial benefits.

[0018] 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.

[0019] 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.

[0020] 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 $d_{long} \geq 0.50$ nm, but only normal-paraffins can pass through apertures with $d_{long} < 0.50$ nm provided $d_{short} > 0.30$ nm.

[0021] 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 $d_{void}/d_{app} \geq 1.4$ nm/nm. An LTA zeolite exhibits a topology with a defined combination of apertures and voids.

[0022] The first step of the present process involves the hydro-normalization of the eventual feedstock to the 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 a particular 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 is comprised of 10-1000 nm crystals and 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.

[0023] 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.

[0024] 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.

[0025] 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.

[0026] 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.

[0027] 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 $n\text{-C}_{12}^+$ 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 a year. This is counter intuitive, yet this is what has been discovered.

[0028] 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. %.

[0029] 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.

[0030] 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. 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.

[0031] 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.

[0032] 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.

[0033] The product enriched in lower normal paraffins (particularly C₂-C₆ linear paraffins) recovered from the hydroconversion can then be passed to a steam cracker. Using the present LTA zeolite-based catalyst which combines a higher acid site concentration with a smaller (< 100 nm) crystal size concentrates the C₂-C₆ linear paraffin fraction in the hydroprocessing products at the expense of the fraction of longer (C₇⁺) n-alkanes. The process enriches the product stream by at least 2 wt. %, more preferably at least 3 wt. %, and in one embodiment at least 4 wt. % C₂-C₆ n-paraffins. The C₂-C₆ product stream can be split into streams comprising C₂-C₃ and C₄-C₆ n paraffins, or the C₂-C₆ n-paraffins can be used as a single stream.

[0034] The second step is a steam cracking step.

[0035] The ethane steam cracking process is known in the art. An ethane cracking process cracks the ethane into ethylene. Ethylene is the desired product, although other lower olefins are useful. But it is ethylene which is most desired. The present hydroconversion process using the present LTA zeolite provides an excellent feedstock for an ethane steam cracker because it increases the ethylene yield at the cost of propylene and aromatics yields. The present hydroconversion process increases the ethylene plus butadiene yield at least 4 wt. %, and in one embodiment, at least 8 wt. %, while the steam cracker is run at high severity. The present hydroconversion process also

results in an increase of ethylene plus butadiene by at least 3 wt. %, and in one embodiment, at least 6 wt. %, while the steam cracker is run at low severity.

[0036] Ethane crackers are typically designed to only crack C₂ and C₃ n-paraffins. Thus, if the C₂-C₆ product stream is split, only the C₂-C₃ portion can be fed to an ethane cracker. However, if the heater in the ethane cracker is revamped with appropriate piping, which is known, all of the C₂-C₆ can be cracked in the ethane cracker.

[0037] In an ethane steam cracking process, 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.

[0038] 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 hydroconversion process using the present LTA zeolite based catalyst prepares a feedstock that can improve the ethylene yield in a steam cracker. The C₂-C₆ light naphtha range prepared by the first step hydroconversion allows for high yields of lower alkenes such as ethylene. The impact of increased ethylene production by the present process is dramatic. The dollar value in the larger yield of desirable products (olefins and BTX) and the lower feed rate and the lower associated energy consumption is massive.

[0039] The following examples are provided in order to further illustrate the present process. However, the examples are not meant to be limiting.

Example 1

[0040] Example of LTA zeolite based noble metal catalyst.

[0041] A catalyst was made by extruding 50 wt. % LTA-type zeolite with 50- wt-% alumina (Pural TH80 from Sasol). The resulting extrudates were 1/20th inch in diameter and in an asymmetric quadrilobed shape were loaded with 0.5 wt. % Pd. The LTA zeolite used had an acid site concentration of about 2.7 mol/l.

Example 2

[0042] 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 dedicates more furnace to pyrolyze the feedstock with a higher C₂-C₆ n-paraffins and a lower n-C₇⁺ paraffin content to monetize these hydro-normalized products as higher ethylene yield and lower by-product (particularly methane and pyrolysis oil) yields.

[0043] 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 and optimum 10-1000 nm wide crystals. 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).

[0044] See FIG. 1 which shows a feed exclusively containing n-C₁₂⁺ n-paraffins with negligible n-C₁₂⁻ n-paraffins. The products at 81% n-C₁₂⁺ conversion are nearly exclusively C₂-C₆ n-paraffins. See FIG. 2.

[0045] 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-C₂₃ (716°F boiling point). Longer n-paraffins (n-triacontane or n-C₃₀, 840°F boiling point and longer) are still successfully processed. In addition to a remarkable selectivity for hydrocracking selectively n-C₁₂ and longer n-alkanes, the catalyst also makes minimal iso-paraffins.

Example 3

[0046] Example of steam cracker feed properties.

[0047] A hydrotreated vacuum gasoil is hydroprocessed into an improved steam cracker feed as described in Table 1 below at 1550 psia H₂, 1.6 LHSV, 5100 scf/b H₂. A steam cracker feed produced at 60% n-C₁₂⁺ conversion in the present hydro-normalization step is characterized in Table 1 as follows:

TABLE 1

	Feed	Hydroprocessed
API (°)	35.4	not measured
S (pp,-wt)	5.3	<0.3
N (ppm-wt)	<0.3	<0.3
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%	392/478	95/445
0.5/5%	519/606	495/598
10/30%	666/	660/
50%	719/799	716/796
70/90%	842/955	840/956
95/99.5%	392/478	95/445

[0048] Switching from an as-is feed where the n-paraffins reside in the 350 F⁺ boiling range to a feed where some 60% of the n-paraffins have been transferred to the front end of the boiling range (-128° F to 156° F) as quantified the by n-C₁₂⁺ conversion (FIG. 1), increases the yield in valuable C₂ olefins, hydrogen gas, lowers the yield of lower-value byproducts such as pyrolysis gasoline (PGO) and pyrolysis fuel oil (PFO), residues and coke, prolongs operating cycles, lower operating severity (Table 2), and lower utilities, CO₂ production and CAPEX per kiloton/annum (kta) of olefins produced. (See Table 2

below). This amounts to a dramatic increase in carbon, energy and capital efficiency in the steam cracking process (FIG. 2).

TABLE 2

		High Severity			Low Severity	
		Orig. Feed	Hydr. Feed		Orig. Feed	Hydr. Feed
Feed, kta		5800	5800		7000	7000
hydrogen		43	45		39	39
methane		666	699		610	620
ethylene		1790	1885		1783	1846
propylene		825	790		1109	1132
butadiene		326	336		390	401
butenes		204	185		428	439
butane		7	8		11	11
C5-400F PGO		1099	1095		1376	1409
400F+ PFO		841	762		1255	1104
Selectivity,w/w		31	33		25	26
C₂H₄		45	46		41	43
C₂H₄+C₃H₆		51	52		47	48
C₂H₄+C₃H₆+C₄H₈		12	13		7	7
BTX		31	33		25	26

According to the above yield structure (Table 2), a state-of-the-art steam cracker that feeds 5800 kta of the feeds described in Table 1 produces about 1800 kta ethylene. The hydroprocessed feed produces 95 kta more ethylene at the cost of mostly (80 kta) low-value PFO (Figure 2). At the current ethylene prices of 1000-1100 \$/ton this increase in ethylene make amounts to a ~100 MMS\$/annum increase in steam cracker value creation. [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 increasing the steam cracker ethylene yield at the cost of the pyrolysis fuel oil yield by hydrocracking long n-paraffins in a vacuum gas oil (350° F⁺ boiling range) into lighter C₂-C₆ n-paraffins (-128° F to 156° F boiling range), comprising:
 - a) subjecting a hydrocarbon feedstock comprising at least 5 wt. % normal paraffins to a hydroconversion reaction under hydroconversion conditions in the presence of an LTA zeolite-based catalyst comprising of 10-1000 nm crystals with an acid site concentration in the range of from 2.6 to 3.0 mol/l; and
 - b) forwarding a product stream enriched in C₂-C₆ n-paraffins and depleted in longer n-paraffins by the prior hydroconversion reaction to a steam cracker for pyrolysis into ethylene.
2. The process of claim 1, wherein the fraction in the -128° F to 400° F boiling range from the hydroprocessed product stream passes on to a naphtha cracker.
3. The process of claim 1, wherein the fraction in the -128° F to 156° F boiling range from the hydroprocessed product stream passes to a gas cracker.
4. The process of claim 1, wherein the hydroconversion process enriches the hydroprocessed product stream by at least 2 wt-%, more preferably by at least 3 wt-% and most preferably by at least 4 wt-% in C₂-C₆ n-paraffins
5. The process of claim 1, wherein the hydroconversion process converts at least 10 %, more preferably by at least 20 % and most preferably by at least 40 % of the n-paraffins in feed into mostly C₂-C₆ n-paraffins.
6. The process of claim 1, wherein the hydroconversion increases the ethylene plus butadiene yield by at least 4 wt-%, more preferably by at least 8 wt-% while the steam cracker is run at high severity.

7. The process of claim 1, wherein hydroconversion increases the ethylene plus butadiene yield by at least 3 wt-%, more preferably by at least 6 wt-% while the steam cracker is run at low severity.
8. The process of claim 1, wherein hydroconversion decreases the undesirable pyrolysis fuel oil ("PFO") yield by at least 5 wt-%, more preferably by at least 10 wt-% while the steam cracker is run at high severity.
9. The process of claim 1, wherein hydroconversion decreases the undesirable pyrolysis fuel oil ("PFO") yield by at least 6 wt-%, more preferably by at least 12 wt-% while the steam cracker is run at low severity.
10. The process of claim 1, wherein hydroconversion increases the ethylene yield by at least 4 wt-%.
11. The process of claim 1, wherein wherein hydroconversion increases the valuable chemicals (viz. ethylene, propylene, butadiene and pyrolysis gasoline ("PGO")) by at least 4 wt-%, more preferably by at least 10 wt-%.
12. The process of claim 1, wherein the bound LTA zeolite loaded with a hydrogenation function 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.
13. The process of claim 12, wherein the wherein the per-pass conversion of the normal paraffins in the feedstock in a hydroconversion recycle operation is between 10 and 99%.
14. The process of claim 12, wherein the feedstock comprises at least 10 wt. % C₇⁺ normal paraffins.
15. The process of claim 1, wherein the feedstock is a vacuum gas oil based feedstock.

16. The process of claim 1, wherein the product stream from hydroprocessing passes on to a mixed-feed steam cracker.

17. The process of claim 1, wherein a hydroconversion process increases the mass of iso-paraffins in the feed by more than 5 wt-% but less than 50 wt-%.