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(54) **Title:** ALIPHATIC CRACKING AND DEALKYLATION WITH HYDROGEN DILUENT

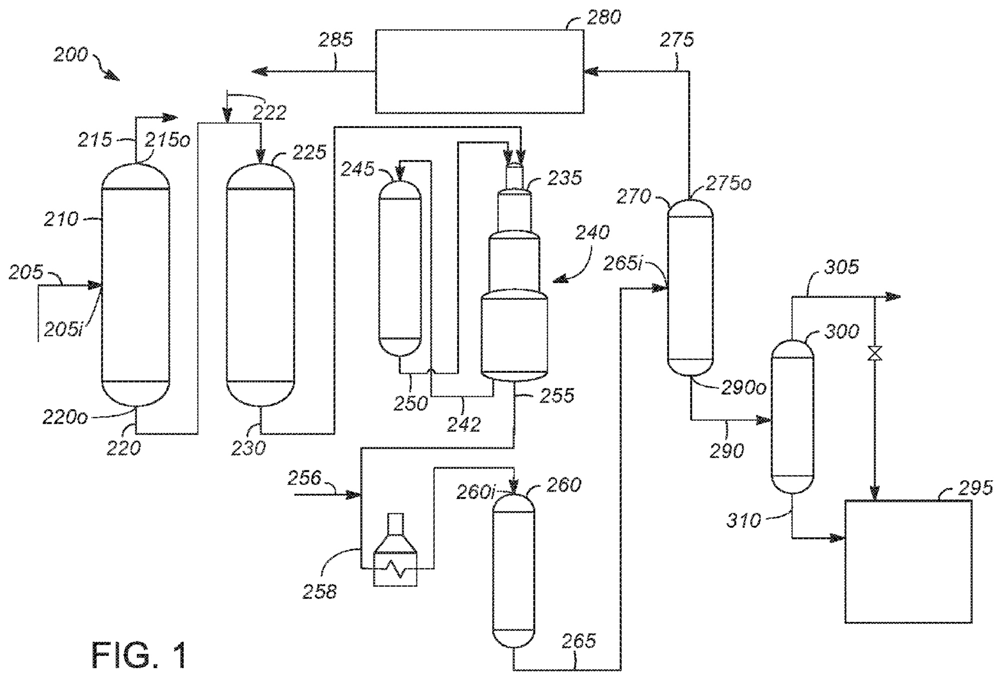

FIG. 1

(57) **Abstract:** A naphtha cracking feed stream is taken, heated and passed to a cracking reactor. Hydrogen is added to the cracking reactor to mitigate catalyst deactivation. The aliphatic compounds are selectively cracked and at least a portion of the alkyl groups on the aromatic compounds are selectively dealkylated in the presence of a cracking catalyst to produce a cracked effluent stream comprising aromatic compounds and cracked olefins.

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ALIPHATIC CRACKING AND DEALKYLATION WITH HYDROGEN DILUENT

STATEMENT OF PRIORITY

[0001] This application claims priority to U.S. Application No. 62/439337 which was filed December 27, 2016, the contents of which are hereby incorporated by reference in its entirety.

BACKGROUND

[0002] Aromatics, particularly benzene, toluene, ethylbenzene, and the xylenes (ortho, meta, and para isomers), which are commonly referred to as "BTEX" or more simply "BTX," are extremely useful chemicals in the petrochemical industry. They represent the building blocks for materials such as polystyrene, styrene-butadiene rubber, polyethylene terephthalate, polyester, phthalic anhydride, solvents, polyurethane, benzoic acid, and numerous other components. Conventionally, BTX is obtained for the petrochemical industry by separation and processing of fossil-fuel petroleum fractions, for example, in catalytic reforming or cracking refinery process units, followed by BTX recovery units.

[0003] Typically, integrated refining-petrochemical complexes separate a crude feedstock into a "straight run" or desired fraction of naphtha, such as C_6-C_{10} naphtha, *i.e.*, naphtha containing hydrocarbons having six to ten carbon atoms, and a heavier fraction containing longer chain hydrocarbons such as heavy oils and residues. The naphtha stream typically undergoes reforming to produce a reformate stream with an increased aromatic content. The reformate stream is processed in an aromatics complex to produce selected aromatic products, such as benzene and para-xylene.

[0004] Some of the naphtha, typically 5-20 wt% of the C_{5+} reformer feed stream remains as aliphatic C_{5+} hydrocarbon in the reformate after the reforming reaction. The reformate is separated from the C_{4-} components in a flash separator and a debutanizer column, and then split in a reformate splitter column between the C_{8-} fraction having the majority of the aliphatics and the C_{8+} fraction having a higher concentration of aromatics than the C_{8-} fraction. The aliphatics are in the C_{8-} fraction which are separated in an extractive unit, which commonly uses Sulfolane solvent, as a raffinate from the aromatic benzene and toluene. The benzene is further fractionated as a pure petrochemical product. The raffinate is then normally blended into gasoline or sent to a thermal cracking unit to produce ethylene, propylene, and heavier components.

[0005] The reformate splitter column and the extractive unit, which may include three columns, are expensive to build and to operate. In addition, the utilization of the raffinate stream from the extractive distillation unit rich in aliphatics or light boiling naphtha streams with T95 boiling point of less than 82°C is often difficult for gasoline blending as it has relatively low octane number and high vapor pressure or for thermal steam cracking to convert to ethylene and propylene because it requires a large investment in a downstream cracking unit.

[0006] Therefore, there is a need for processes for converting naphtha into aromatics which reduce capacity of expensive distillation columns and improve the value of the raffinate stream and other light naphthas at lower capital cost.

SUMMARY

[0007] One aspect of the subject matter is a process for making olefins. Another aspect of the subject matter is a process for dealkylating alkylaromatics olefins. In an embodiment, the process comprises taking a cracking feed stream boiling in the naphtha range comprising aromatic compounds and aliphatic compounds, wherein at least a portion of the aromatic compounds contain alkyl groups and passing the cracking feed stream at a temperature of at least 500°C to the cracking reactor comprising a cracking catalyst including a zeolite with a pore size greater than 5 Angstroms. The aliphatic compounds are selectively cracked and the alkyl groups on the aromatic compounds are selectively dealkylated in the presence of the cracking catalyst in the cracking reactor under cracking conditions to cracked olefins and aromatic compounds in a cracked effluent stream. We have found that providing adding at least 60 mol% hydrogen to the cracking reactor stably preserves the cracking catalyst against deactivation. We have also found that providing at least 50 mol% hydrogen to the cracking reactor with a hydrogen partial pressure under 345 kPa (50 psia) maintains a higher ratio of olefins to paraffins.

BRIEF DESCRIPTION OF THE DRAWING

[0008] FIG. 1 is an illustration of an embodiment of a process for converting naphtha into aromatics according to the present invention.

[0009] FIG. 2 is another embodiment of a process for converting naphtha into aromatics according to the present invention.

[0010] FIG. 3 is a plot of iC_5 conversion versus time on stream.

[0011] FIG. 4 is a plot of C_{5+} aliphatics conversion versus time on stream.

[0012] FIG. 5 is a plot of iC_5 conversion versus time on stream.

[0013] FIG. 6 is a plot of iC_5 conversion versus time on stream.

DETAILED DESCRIPTION

[0014] The present subject matter may involve cracking aliphatics and dealkylating alkylaromatics in a naphtha stream. A stream boiling in the naphtha range may be taken as a cracking feed stream. The naphtha stream may be reformer effluent stream. The reformer effluent stream may be taken directly to the cracking reactor without separating the reformer effluent stream into various components or a portion of the reformer effluent stream may be taken from the reformer effluent stream and fed to the cracking reactor as a cracking feed stream. The aliphatics remaining in the cracking feed stream are converted directly to at least one of ethylene, propylene, and butylene at conversion rates of 30% or more. Aliphatics are also covered to light paraffins. Furthermore, there is a concurrent increase in hydrogen and significant dealkylation of the ethyl and longer substituents on the aromatic rings. The dealkylated substituents are also converted to olefins. Under some conditions, new aromatic rings can be produced.

[0015] The process produces at least one of ethylene, propylene, and butylene from the naphtha stream. By converting aliphatics in a naphtha stream that is a reformer effluent stream, the flow rate of aliphatics in the reformate to an aromatic extractive distillation section and thermal naphtha cracker if present is reduced. The process also converts a large amount of the benzene co-boiler material, which may reduce the load on an aromatics extraction section for benzene purification. In addition, the increase in the production of aromatics will lead to higher production of combined benzene and para-xylene from the aromatics complex for a given amount of naphtha feed. Furthermore, the dealkylation of ethyl and longer aromatic substituents on the aromatic compounds from the reformer will add to the yield of light olefins and decrease the size of equipment and utilities in the aromatics complex by reducing the amount of ethylbenzene circulating in the para-xylene separation, xylene isomerization loop and reducing the amount of dealkylation required in the transalkylation reactor.

[0016] We have surprisingly found that dilution of the cracking feed with hydrogen diluent preserves a cracking catalyst against deactivation particularly when the catalyst is deficient in hydrogenation metals. The dilution enables the catalyst to crack the naphtha to olefins at high yields for extended duration on stream. By utilizing a steamed silicalite or other low acidity zeolite with a high ratio of silica to alumina as catalyst at relatively low pressure, aliphatics including saturates can crack at elevated temperature without significant deactivation or hydride transfer reactions which would cause rapid coke deposition and co-generation of heavy aromatics and paraffins rather than desired olefins.

[0017] If the process is used for reformate cracking, hydrogen is readily available, so the cracking process may be close-coupled to the reformer allowing the reformer effluent to cascade into the cracking reactor.

[0018] While this process is particularly well suited for reformate cracking where hydrogen is readily available, other configurations such as cracking naphtha, Sulfolane raffinate, FCC cracked naphtha, pentanes or other feeds containing aliphatics and combinations thereof are envisioned.

[0019] A cracking feed stream boiling in the naphtha range may be taken for the subject process. In some embodiments, the naphtha stream may have a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 140°C to 215°C. In another embodiment, the naphtha stream may be split into a light naphtha stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C, and a heavy naphtha stream having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C. In this embodiment, the heavy naphtha stream may be taken as the cracking feed stream. As used herein, the term "T5" or "T95" means the temperature at which 5 mass percent or 95 mass percent, as the case may be, respectively, of the sample boils using ASTM D-6352.

[0020] A naphtha feed stream may be reformed to produce aromatics, such as BTX and aliphatic compounds, such as C_5, C_6 and C_7 branched and normal paraffins and cyclic paraffins. The term "C_x" or "A_x" are to be understood to refer to aliphatic and aromatic molecules, respectively, having the number of carbon atoms represented by the subscript "x". Similarly, the term "C_x-" or "A_x-" refers to aliphatic and aromatic molecules, respectively, that contain less than or equal to x and preferably x and less carbon atoms. The term "C_{x+}" or "A_{x+}" refers to aliphatic and aromatic molecules, respectively, with more than or equal to x and preferably x and more carbon atoms. C_2-C_4 alkyl aromatics are defined such that an alkyl aromatic that contains an alkyl chain with x carbon atoms and an additional or additional chain or chains with other numbers of carbon atoms. For example, 2-ethyltoluene is a C_2-C_4 alkyl aromatic.

[0021] A cracking feed stream may be taken from the reforming effluent stream and is heated and passed to a cracking reactor. In some embodiments, a feed stream to the reforming unit can be produced by introducing a naphtha stream to a naphtha splitter column. The naphtha stream may be split into at least two streams. In some embodiments, the naphtha stream is split into a light naphtha stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C, and a heavy naphtha stream having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C. The heavy naphtha stream may be sent to a naphtha hydrotreating reactor to produce a hydrotreated naphtha stream. The hydrotreated naphtha stream could then be introduced into the reforming unit. In some embodiments, the light naphtha stream from the naphtha splitter column can be sent to the cracking reactor, and the hydrocarbons in the overhead stream can be selectively cracked to produce additional olefins. However, if this is done, the naphtha hydrotreating reactor should precede the naphtha splitter to remove sulfur and nitrogen compounds which can be detrimental to the cracking catalyst at high concentrations.

[0022] In some embodiments, an additional stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C can be sent to the cracking reactor. Suitable sources for the additional stream can be light naphtha from hydrotreated straight run naphtha, light naphtha from straight run naphtha, aromatics extraction raffinate, hydrocracked light naphtha, hydrotreated fluidized catalytic cracker light, heavy or full range naphtha perhaps from gas oil, or combinations thereof.

[0023] In some embodiments, the cracked olefins, comprising at least one of ethylene, propylene, and butylene, from the cracking reactor are recovered. In some embodiments, an aromatic lean fraction is sent to a downstream cracking zone to produce additional olefins, comprising at least one of ethylene, propylene, and/or butylene, which are then recovered along with the cracked olefins produced in the cracking reactor. The recovered cracked olefins and additional olefins can be fractionated to obtain ethylene and propylene streams greater than 90 wt% pure, or greater than 95 wt% pure, or greater than 99 wt-% pure, or greater than 99.5 wt-% pure.

[0024] FIG. 1 shows one embodiment of a process 200 for converting a reformed heavy naphtha stream into aromatics. The naphtha feed stream 205 is sent to a naphtha splitter column 210. The term "column" means a distillation column or columns for separating one or more components of different volatilities. Unless otherwise indicated, each column includes a condenser on an overhead of the column to condense and reflux a portion of an overhead stream back to the top of the column and a reboiler at a bottom of the column to vaporize and send a portion of a bottoms stream back to the bottom of the column. Feeds to the columns may be preheated. Unless otherwise indicated, overhead lines and bottoms lines refer to the net lines from the column downstream of any reflux or reboil to the column. Stripping columns may omit a reboiler at a bottom of the column and instead provide heating requirements and separation impetus from a fluidized inert vaporous media such as steam. The naphtha splitter column 210 has an inlet 205i, an overhead outlet 215o and a lower outlet 220o in a lower half of the column which may be a bottoms outlet. The naphtha feed stream 205 is separated into a light naphtha stream in a naphtha splitter overhead line 215 having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C and a heavy naphtha stream in a naphtha splitter bottoms line 220 having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C.

[0025] The heavy naphtha stream in the naphtha splitter bottoms line 220 is sent to a naphtha hydrotreating reactor 225. The naphtha hydrotreating reactor 225 may be used to prepare the heavy naphtha stream 220 for downstream reforming with sensitive noble metal catalyst systems. In an exemplary process, the heavy naphtha stream in the naphtha splitter bottoms line 220 is mixed with hydrogen from line 222, heated to a reaction temperature and is brought into the naphtha hydrotreating reactor 225 and contacted with a hydrotreating catalyst. The naphtha hydrotreating reactor 225 may be in downstream communication with the lower outlet 220o of the naphtha splitter column 220. The term "downstream communication" means that at least a portion of material flowing to the subject in downstream communication may operatively flow from the object with which it communicates. Exemplary hydrotreating catalysts include metals from CAS Group VIB, VIIB, VIII, and combinations thereof. The naphtha hydrotreating reactor 225 may have multiple distinct stages with different catalytic zones. For example, the first stage can be operated at low temperature (*e.g.*, 40°C to 250°C) for mainly diolefin saturation, and the second stage can be operated at higher temperature (*e.g.*, up to 400°C) for olefin saturation, hydrodesulfurization, and hydrodenitrogenation. For a single stage, exemplary reaction temperatures are from 250°C to 400°C. The main catalytic reactions in naphtha hydrotreating zone 225 convert the contaminants detrimental to noble metal catalyst systems, such as sulfur, nitrogen, and oxygenates, via hydrogenolysis reactions to hydrogen sulfide, ammonia, and water, so that they can be removed from the naphtha stream as gas. Metals in the bottoms stream may be removed by adsorption onto the hydrotreating catalyst. As a result, olefins and/or diolefins are also saturated.

[0026] The reforming reactor 235 may be in downstream communication with naphtha hydrotreating reactor 225. The resulting hydrotreated stream 230 contains paraffins, naphthenes and aromatics, and low levels of olefins and is fed to a reforming unit 240 for conversion of paraffins and naphthenes into aromatics. An exemplary reforming unit 240 is a catalytic reforming reactor 235 with a continuous catalyst regeneration (CCR) unit 245. The reforming reactor 235 may be operated at a temperature of from 450°C to 560°C. A spent catalyst stream 242 from the bottom of the reforming reactor 235 may be sent to a top of a catalyst regenerator 245. A regenerated catalyst stream 250 from a bottom of the catalyst regenerator 245 may be sent to the top of the reforming reactor 235. Alternatively, the catalyst can be regenerated in situ by taking one of multiple reactors off-line for regeneration in cyclical fashion or in semi-regenerative mode where all reactors are taken offline for regeneration at one time.

[0027] Compounds in the hydrotreated stream 230 are reformed in the reforming reactor 235 over reforming catalyst to produce a reformer effluent stream in a reformate line 255. Specifically, naphthenes are dehydrogenated to form aromatics, normal paraffins are isomerized to form isoparaffins, and paraffins are dehydrocyclized, *i.e.*, dehydrogenated and aromatized, to form aromatics.

[0028] A cracking feed stream may be taken from the reformer effluent stream in reformate line 255 with or without separating the reformer effluent stream 255 into different streams with different compositions. Accordingly, some or all of the reformer effluent stream in reformate line 255 may be taken by aliquot or separation by volatility or solubility as the cracking feed stream to a cracking reactor 260. The cracking feed stream may comprise the reformer effluent stream passing directly to the cracking reactor 260. By passing directly to the cracking reactor, we mean that the reformer effluent stream's composition is not changed by separation into component streams (*e.g.*, the reformer effluent stream is not fractionated). However, the composition can be changed by adding one or more streams to the reformer effluent stream and still be considered as passing directly to the cracking reactor. In an alternative embodiment, a portion of the reformer effluent stream may be taken as the cracking feed stream and passed to the cracking reactor. The cracking feed stream may be taken by separation, flashing, distillation, extraction or by aliquot appropriation of the reformer effluent stream.

[0029] The cracking reactor 260 may be in downstream communication with the reforming reactor 235. The cracking reactor 260 may be in direct, downstream communication with the reforming reactor 235. The term "direct communication" means that flow from the upstream component enters the downstream component without passing through a fractionation or conversion unit to undergo a compositional change due to physical fractionation or chemical conversion.

[0030] In FIG. 1, all of the reformer effluent stream is taken as the cracking feed stream to the cracking reactor 260 in a cracking feed line 258. In FIG. 1, the cracking reactor 260 is in direct, downstream communication with the reforming reactor 235. The cracking feed stream enters the cracking reactor 260 through the inlet 260i.

[0031] An additional stream in line 256 which may have a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C may supplement the cracking feed stream in cracking feed line 258 and be sent to the cracking reactor 260 therewith. Consequently, the light naphtha stream in line 215 that would not benefit from reforming may bypass the reforming unit 240 and be fed to the cracking reactor 260 as the cracking feed stream.

[0032] In an embodiment, any naphtha stream boiling in the naphtha boiling range may be taken as cracking feed stream to the cracking reactor 260. The cracking feed stream may comprise C_4 to C_{11} hydrocarbons having at least 10 wt% paraffins and at least 15 wt% alkylaromatics. The cracking feed stream may have an aromatic content of at least 30 wt%, with at least 50 wt% preferred. The feed stream may have 5 to 40 wt% and typically 10 to 25 wt% alkyl aromatics with C_2 to C_4 alkyl groups. Moreover, the cracking feed stream may have a concentration of aromatic alkyl groups in the C_1-C_4 range of 10 to 30 wt% and preferably 15 to 25 wt%. At least 10 wt%, preferably at least 15 wt% of the aromatic alkyl groups in the feed stream may comprise C_2-C_4 alkyl groups. The cracking feed stream may have 5 to 40 wt%, preferably 10 to 30 wt% aliphatics in the C_5 to C_9 range. The cracking feed stream need not comprise olefins.

[0033] The cracking feed stream in the cracking feed line 258 may be heated to at least 500°C if it is not already at reactor temperature and passed to the cracking reactor 260. The cracking feed stream in the cracking feed line 258 may be cracked over an acidic cracking catalyst to produce cracked olefins comprising at least one of ethylene, propylene, and butylene, methane, ethane, propane, butane and dealkylated aromatics. Typically, substantial yields of ethylene, propylene and butylene are produced in the cracking reactor. Substantial yields means at least 5 wt%, suitably at least 10 wt% and preferably at least 20 wt% of ethylene, propylene and butylene combined. "Yield" in this case is defined as the weight of the product component in the cracked effluent stream, divided by the combined weight of aliphatics and the alkyl-aromatic side chains in the feed. Accordingly, the aromatic rings are not counted as feed in the yield calculation.

[0034] Examples of suitable cracking reactors include, but are not limited to, fixed bed reactors, moving bed reactors, fluidized bed reactors, and ebullated bed reactors. For example, the reactors could be a series of multiple reactors with interstage heating. In a moving bed reactor, the cracking catalyst is contacted with the cracking feed stream while slowly moving from a top of the cracking reactor 260 to a bottom of the cracking reactor where it is taken to a catalyst regenerator for regeneration and returned to the top of the cracking reactor. The cracking reactor may comprise an interstage heater to maintain reactor temperature. The acid catalyst may be continuously regenerated, for example in a continuous catalyst regenerator. A swing bed reactor may also be used for a cracking reactor that uses a fixed bed of catalyst.

[0035] The cracking catalyst may include a zeolite that has one of the MFI, TON, MTT, FER, EUO or FAU framework. The preferred zeolite has an MFI type framework. The catalyst does not include a hydrogenating metal function. For example, the catalyst may have 0 to 0.1 wt-% transition metals in IUPAC Groups 5 to 12 on the Periodic Table on the catalyst, with zero being preferred. The absence of such hydrogenating transition metals assures that olefins will not be hydrogenated in the cracking reactor to preserve olefins, particularly when substantial hydrogen is present. Catalysts may be of many formulations including pure zeolites, or formed catalysts such as extruded, oil dropped, or spray dried catalysts. Suitable catalysts may also contain silica, aluminum, phosphate, alumina, zirconia, titania or other binders which do not have a hydrogenation function. A suitable cracking catalyst includes, but is not limited, a ZSM-5 zeolite. For example, a silicalite can be used.

[0036] The cracking catalyst should have an acidic functionality in order to crack aliphatic molecules and dealkylate alkylaromatics. In some embodiments, the cracking catalyst may have a molar ratio of silica to alumina in the zeolite of 200 to 1200, suitably 300 to 1100, typically no more than 700, and preferably between 300 and 500. The cracking catalyst particles should include a zeolite having a maximum pore diameter of greater than 5 Angstroms. For example, the maximum pore diameter should be at least 5.1 Angstroms and preferably at least 5.3 Angstroms. Moreover, it is preferred that the zeolite have a minimum pore diameter of at least 5.1 Angstroms. A maximum pore diameter of more than 8 Angstroms would not be desirable. Preferably, the pore index should be at least 28 Angstroms^2. More than 90 wt% and preferably at least 95 wt% of the catalyst particles in the reactor should include a zeolite with the foregoing pore diameter specifications to promote dealkylation of alkyl groups from aromatic rings. The catalyst particles may include 30 to 80 wt% zeolite with the remaining support and binder being non-zeolitic and/or low-acidic. Low acidic binder has no more than 0.2, preferably no more than 0.15 millimoles of acid sites per gram as determined by gas-phase ammonia titration.

[0037] The cracking feed temperature should at least be 500°C when passed to the reactor. The temperature in the cracking reactor may be in the range of 500°C to 700°C, or 525°C to 650°C and preferably 5350 to 590°C. Temperature in the reactor refers to the weight average bed temperature which is the average of the bed temperature taken at the inlet and the outlet of the catalyst bed and evenly spaced intervals between an inlet and an outlet of the bed. The pressure can be of 0 kPa (gauge) (0 psig) to 750 kPa (g) (109 psig), or 100 kPa (g) (15 psig) to 400 kPa (g) (58 psig). The molar ratio of hydrogen to C_{5+} hydrocarbon at the inlet 260i to the cracking reactor may be at least 0.5:1, or at least 1:1, preferably at least 2:1 and no more than 6:1, and most preferably no more than 5:1. The hydrogen may be provided from the reformate stream 255. The reaction conditions include a weight hourly space velocity (WHSV) in the range of 0.75 to 6.0 hr^{-1}, suitably no more than 4 hr^{-1}, preferably no more than 3.75 hr^{-1} and preferably no more than 3.0 hr^{-1}. The term "WHSV is defined as the mass flow rate of liquid feed divided by the mass of the catalyst. The liquid hourly space velocity (LHSV) in the cracking reactor may be between 0.1 to 4.0 hr^{-1} and preferably 0.5 to 2 or 2.5 hr^{-1}. The term "LHSV" is defined herein as the volumetric flow rate of feed divided by the volume of the catalyst bed. The relationship between LHSV and WHSV depends on the feed density and the catalyst apparent bulk density.

[0038] In some embodiments, at least a portion of the ethyl and larger alkyl groups on the aromatic compounds are dealkylated in the cracking reactor to produce additional olefins, comprising at least one and typically substantial yields of ethylene, propylene, and butylene, and a dealkylated aromatic compound. Demethylation of aromatic rings are undesirable.

[0039] We have found that A_6-A_{10} are generated in the cracking reactor in many cases in addition to aromatic products resulting from dealkylation of alkyl aromatics. These conditions will be such that at least 50 to 80 wt-% of aliphatics will be converted and at least 50 to 80 wt-% of the C_2-C_4 alkyl aromatics will be dealkylated to the corresponding light olefin and aromatics. Aromatic C_1-C_4 alkyl groups are dealkylated to olefins and aromatics at over 10% by weight, but aromatic C_2-C_4 alkyl groups are dealkylated at over 50% by weight, and typically at over 60% by weight. Aromatic C_1 alkyl groups are converted at less than 10% by weight, typically at less than 6% by weight and preferably less than 3% by weight. Altogether, C_{5+} aliphatics and aromatic alkyls groups are converted at over 40%. Preferably, C_{5+} aliphatic conversion is 50 to 80% by weight. At higher conversion olefin selectivity decreases.

[0040] The aliphatic compounds in the cracking feed stream are selectively cracked to produce cracked olefins, including at least one and typically substantial yields of ethylene, propylene, and butylene. Due to the lack or low concentration of hydrogenating, transition metal on the catalyst, the olefin to paraffin weight ratio of C_1-C_4 hydrocarbons in the cracking effluent stream may be at least 0.1 and typically at least 0.25 and suitably at least 0.7, preferably at least 1, and in some exemplary embodiments at least 1.8. The cracking effluent stream from the cracking reactor contains dealkylated aromatics that were alkylaromatics from the reformer effluent stream or cracking feed stream and olefins dealkylated from aromatics and cracked from paraffins in the cracking reactor, as well as paraffins and hydrogen. Alkyl groups may also be transferred from one aromatic molecule to another, effecting transalkylation.

[0041] Surprisingly, we found hydrogen in the reactor helps to stabilize the catalyst against deactivation by coke formation even without a hydrogenation metal present. This effect is not observed when using other gases as diluent, like nitrogen or steam. We observed stable aliphatic conversion of over 90 wt% for extended periods with little catalyst deactivation with hydrogen concentration of at least 60 mol% in the cracking reactor.

Hydrogen concentration of at least 70 mol% would be suitable and at least 80 mol% would be preferable. Hydrogen concentration should not exceed 90 mol% in the cracking reactor. The mole ratio of hydrogen to hydrocarbon should be at least 2, suitably at least 3 and preferably at least 4. The mole ratio of hydrogen to hydrocarbon should not exceed 6.

[0042] We have observed at lower pressure, more olefins, fewer paraffins and fewer aromatics are produced. At high pressures of 253 kPa (absolute) (65 psia) to 448 kPa (115 psia), olefin yield is lower and yields of propane, ethane, methane and aromatics is higher. We observed that higher pressures provided longer effective residence time which led to more extensive reaction of olefins to aromatics. We also observed high light paraffin yield at higher pressures indicating that some hydrogenation may occur at high hydrogen partial pressure. Consequently, hydrogen partial pressure greater than 345 kPa (absolute) (50 psia) should be avoided. Despite the presence of hydrogen, olefins do not substantially hydrogenate back to form paraffins in the hydrogen partial pressure range of no more than 345 kPa (absolute) (50 psia) enabling a light olefin-to-paraffin ratio of at least 0.7. With hydrogen mol% of at least 50, a hydrogen partial pressure range of no more than 345 kPa (absolute) (50 psia) enables achievement of a light olefin-to-paraffin ratio of at least 0.6 With hydrogen mol% of at least 60, a hydrogen partial pressure range of no more than 345 kPa (absolute) (50 psia) enables achievement of a light olefin-to-paraffin ratio of at least 1.0. A hydrogen partial pressure range of no more than 241 kPa (absolute) (35 psia) enables achievement of a light olefin-to-paraffin ratio of at least 1.8, provided that the residence time is less than 6 seconds to prevent conversion of olefins to aromatics.

[0043] Hydrogen partial pressure should be maintained above 62 kPa (absolute) (9 psia). Low conversion and fast deactivation are observed in the presence of steam, but high conversion and no deactivation are observed in the presence of hydrogen.

[0044] Stated differently, hydrogen may be used as a co-feed diluent with a mole ratio of hydrogen to hydrocarbon of at least 2 and a hydrogen partial pressure between 138 kPa (absolute) (20 psia) and 345 kPa (absolute) (50 psia) with a total pressure of at least 207 kPa (absolute) (30 psia) or with a hydrogen partial pressure of at least 62 kPa (absolute) (9 psia) with total pressure between 69 kPa (absolute) (10 psia) and 207 kPa (absolute) (30 psia).

[0045] A cracked effluent stream from the cracking reactor 260 in a cracked effluent line 265 may be cooled and separated into an aromatic rich stream and an aromatic lean stream by fractionation. By aromatic rich stream, we mean a stream containing at least 90 wt% aromatic compounds, or at least 95 wt%, or at least 97 wt%, or at least 99 wt%. By aromatic lean stream, we mean a stream containing less than 30 wt% aromatic compounds, or less than 20 wt%, or less than 10 wt%. The cracked reformer effluent stream in a cracked effluent line 265 comprising the aromatics and the olefins may be sent to an aromatics fractionation column 270, for example a depentanizer or debutanizer column, from which an aromatics lean stream comprising C_4- or a C_5- stream in an aromatics overhead line 275 is removed. The aromatics fractionation column may be a vapor-liquid separator. As used herein, the term “separator” means a vessel which has an inlet and at least an overhead vapor outlet and a bottoms liquid outlet and may also have an aqueous stream outlet from a boot. A flash drum is a type of separator which may be in downstream communication with a separator that may be operated at higher pressure.

[0046] The aromatics fractionation column 270 has an inlet 265i, an overhead outlet 275o, and a lower outlet 290o in the bottom half of the column which may be a bottoms outlet. The inlet 265i of the aromatics fractionation column 270 may be in downstream communication with the cracking reactor 260.

[0047] The aromatic rich stream can be recovered from the lower outlet 290o in aromatics bottoms line 290 and used to produce benzene and/or para-xylene. In some embodiments, the aromatic rich stream can be passed directly to an aromatics complex 295 without subjecting the aromatic rich stream to a distillation column or other separation process. In other embodiments, the aromatic rich stream is fractionated in a reformate splitter column 300 into at least a reformate splitter overhead stream comprising C_6- or C_7- hydrocarbons in a reformate splitter overhead line 305 that may be forwarded to a gasoline pool perhaps after isomerization and a reformate splitter bottoms stream comprising C_{7+} or C_{8+} hydrocarbons in a reformate splitter bottoms line 310 that may be forwarded to the aromatics complex 295. In some embodiments, both the reformate splitter overhead stream and the reformate splitter bottoms stream may be delivered to the aromatics complex 295. In an aspect, at least 50 wt%, or at least 60 wt%, or at least 70 wt%, or at least 75 wt%, or at least 80 wt%, or at least 85 wt%, or at least 90 wt%, or at least 95 wt% of the aromatics rich stream in the aromatics bottoms line 290 may be sent to the aromatics complex 295.

[0048] A downstream cracking reactor 280 may be in downstream communication with the overhead outlet 275o of the aromatics fractionation column 270. Hydrogen and light gases may be removed from the aromatics lean stream in the aromatics overhead line 275 upstream of the downstream cracking reactor 280. The overhead stream in the overhead line 275 may be sent to a downstream cracking reactor 280, with or without removing the produced olefins before the downstream cracking reactor, such as a steam cracker where it is cracked to produce additional olefins comprising at least one and typically substantial amounts of ethylene, propylene, and/or butylene. A downstream cracked stream 285 comprises the cracked olefins from the cracking reactor 260 and the additional olefins produced in the downstream cracking reactor 280, and heavier components. The aromatics complex 295 may be in downstream communication with the lower outlet 290o of the fractionation column 270.

[0049] FIG. 2 is similar to FIG. 1, except that the naphtha feed stream in naphtha feed line 205 is mixed with hydrogen from hydrogen line 222 and sent to the naphtha hydrotreating reactor 225 before a hydrotreated naphtha stream in a hydrotreater effluent line 230 is fed from the naphtha hydrotreating reactor 225 to the naphtha splitter column 210 through an inlet 205i. The hydrotreated naphtha stream in a hydrotreater effluent line 230 is sent to the naphtha splitter column 210 in which it is separated into a hydrotreated light naphtha stream in a naphtha splitter overhead line 215 from an outlet 215o having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C and a hydrotreated heavy naphtha stream in a naphtha splitter bottoms line 220 from a lower outlet 220o having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C. The hydrotreated bottoms stream 220 may be sent to the reformer 235.

[0050] The hydrotreated light naphtha stream in the naphtha splitter overhead line 215 may be split between a recovered portion stream in line 216 that may be further processed or used as product and an advance portion stream in an advance line 218. The advance portion stream may be advanced in advance line 218 to be mixed with a reformer effluent stream in a reformate line 255. The inlet 205i of the naphtha splitter column 210 may be in downstream communication with the naphtha hydrotreating reactor 225. Moreover, in FIG. 2 a light naphtha stream in the advance line 218 is mixed with the reformer effluent stream in the reformate line 255 to provide the cracking feed stream in the cracking feed line 258. Consequently, at least a portion of the overhead stream in the overhead line 215 may be passed to the cracking reactor 260 in which hydrocarbons from the overhead stream are selectively cracked and dealkylated. With these exceptions, everything else in FIG. 2 is the same as described for FIG. 1.

[0051] As will be understood by those of skill in the art, the figures do not show all of the equipment involved in these processes. There may be heat exchanger, coolers, flash drums, other component separators such as membranes or adsorbent, compressors, or pumps and the like between the various pieces of equipment that are shown.

[0052] While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

EXAMPLES

[0053] The catalyst used in Examples 1-8 was an extruded catalyst prepared from 70 wt% silicalite zeolite with a ratio of silica to alumina of 460 and 30 wt% silica binder. The extruded catalyst was dealuminated, calcined and depleted of alkali metal. The finished catalyst had a BET surface area of 313 m^2/g and micropore volume of 0.14 cc/g as determined by nitrogen adsorption. The finished catalyst including binder had 30 wppm sodium, 0.17 wt% aluminum, 46.8 wt% silicon analyzed by inductively coupled plasma-atomic emission spectroscopy.

EXAMPLE 1

[0054] The silicalite catalyst was ground and sized to 40 x 60 mesh. Two grams of the catalyst was loaded in a 9 mm quartz reactor. The reactor was operated at atmospheric pressure and at 600°C. Pure isopentane (iC_5) was fed at 0.029 mL/min and vaporized at 190°C into a vortex mixer where the vapor was mixed with a gas mixture containing 67 mol% nitrogen and 33 mol% hydrogen flowing at 15 standard cc/min. The resulting weight space velocity was 0.54 hr^{-1} and the space time was 3.1 seconds. Space time was calculated as the volume of the catalyst bed over the gas volumetric flow rate. Hydrocarbon partial pressure was 27 kPa (4 psig). The product mixture was analyzed as vapor by gas chromatography. In this example, the vapor feed mixture contained 27 mol% isopentane, 24 mol% hydrogen and 49 mol% nitrogen.

Initial isopentane conversion was 96.5% on average for the first 3 hours and decreased throughout the run at a rate of 0.19% conversion per hour as shown by the squares in FIG. 3. Product selectivities for hours 1 through 5 are shown in Table 1.

EXAMPLE 2

[0055] The silicalite catalyst was ground and sized to 40 x 60 mesh. Two grams of the 70% zeolite catalyst was loaded in a 9 mm quartz reactor. The reactor was operated at atmospheric pressure and at 600°C. Pure isopentane was fed at 0.029 mL/min and vaporized at 190°C into a vortex mixer where the vapor was mixed with a gas mixture containing 100 mol% hydrogen flowing at 15 standard cc/min. The resulting weight space velocity was 0.54 hr^{-1} and the space time was 3.1 seconds. The hydrocarbon partial pressure was 76 kPa (11 psig). The product mixture was analyzed as vapor by gas chromatography. In this example, the vapor feed mixture contained 27 mol% isopentane and 73 mol% hydrogen. Initial isopentane conversion was 98.8% on average for the first 3 hours and decreased throughout the run at a rate of 0.05% conversion per hour as shown by the diamonds in FIG. 3. The increased presence of hydrogen diminished deactivation of the catalyst. Product selectivities for hours 1 through 5 are shown in Table 1.

TABLE 1

Selectivity (wt%)	Example 1	Example 2
Methane	9.3	11.4
Ethane	3.5	4.4
Ethylene	24.8	24.6
Propane	3.7	4.2
Propylene	26.9	24.6
Butanes	3.6	3.6
Butylenes	10.0	8.5
C_5's	2.1	1.1
C_6-C_7 aliphatics	0.0	0.7
Benzene	5.7	6.4
Toluene	7.2	7.2
Xylenes	2.5	2.5
Ethylbenzene	0.5	0.5
Other	0.2	0.2

EXAMPLES 3-6

[0056] Examples 3-6 were run using the same silicalite catalyst as examples 1 and 2, but without grinding and sieving. The unground catalyst has apparent bulk density of 0.667 g/cm^3. Sixty cubic centimeters (40.0 g) of the catalyst were loaded in a fixed bed reactor in three separate catalyst plugs of 15, 15 and 30 cubic centimeters separated by quartz wool and spherical alpha alumina filler. A reformate feed with the composition shown in Table 2 and specific gravity of 0.829 g/cm^3 was vaporized and mixed with hydrogen. Liquid and vapor products were separated at the reactor outlet which was maintained at 172 kPa (g) (25 psig). The gas and liquid products were analyzed separately by gas chromatography.

TABLE 2
Reformate Feed

Component	Wt%
C_1 Paraffin	0.000
C_2 Paraffins	0.000
C_3 Paraffins	0.080
C_4 Paraffins	0.780
C_5 Paraffins	2.350
C_6 Paraffins	8.170
C_7 Paraffins	3.670
C_8 Paraffins	0.940
C_5 Naphthenes	0.040
C_6 Naphthenes	0.170
C_7 Naphthenes	0.180
C_8 Naphthenes	0.100
C_{5+} Aliphatics	17.7
C_{9+} Paraffins, Naphthenes and Olefins	0.210
Ethylene	--
Propylene	--
C_4 Olefins	0.000
C_5 Olefins	0.000
C_6 Olefins	--
C_7 Olefins	1.230
C_8 Olefins	--
Benzene	2.790
Toluene	19.340
Xylene	27.040

Ethylbenzene	3.760
Trimethylbenzene	12.510
Methyl-Ethyl-Benzene	7.960
Propyl-Benzene	1.810
Tetra-Methyl Benzene	1.420
Di-Methyl-Ethyl Benzene	2.100
Methyl-Propyl-Benzene	0.880
Di-Ethyl-Benzene	0.240
Butyl-Benzene	0.110
C_{11+} Aromatics	1.450
Aromatic Alkyls[a]	23.2
Aromatic C_2-C_4 Alkyls[a]	4.3

aAromatic alkyls counted the weight of aromatic alkyl substituents assuming molecular weights of 56.11 g/mol for butyl, 42.08 g/mol for propyl, 28.05 g/mol for ethyl and 16.04 g/mol for methyl substituents.

EXAMPLE 3

[0057] In this example, the liquid feed rate was 60 cc/hr (49.74 g/hr), and the mole ratio of hydrogen to feed was 1:1, corresponding to a hydrogen mol% of 50 and a hydrogen partial pressure of 138 kPa (20 psia) with a total pressure of 276 kPa (40 psia). The space time in the catalyst bed was 8.4 seconds and the WHSV was 1.24 hr^{-1}. Feed to the reactor was cut in at 425°C and the temperature was ramped to 600°C, reaching reaction temperature at 5 hours on stream. As shown by the solid circles in FIG. 4, aliphatic conversion reached 91 wt% at 11 hours on stream and remained constant until 40 hours on stream, corresponding to 35 bed volumes of liquid feed at reaction temperature, after which conversion began to drop. Between 41 hours on stream and the end of the run at 76 hours on stream, aliphatic conversion dropped to 75 wt% constituting an average deactivation rate of 0.36 wt% conversion lost per hour.

EXAMPLE 4

[0058] In this example, the liquid feed rate was 30 cc/hr (24.9 g/hr), and the mole ratio of hydrogen to feed was 4.5:1, corresponding to a hydrogen mol% of 82 and a hydrogen partial pressure of 228 kPa (33 psia) with a total pressure of 276 kPa (40 psia). The space time in the catalyst bed was 6.1 seconds and the WHSV was 0.62 hr^{-1}. Feed to the reactor was cut in at 425°C and the temperature was ramped to 600°C, reaching reaction temperature at 5 hours on stream. As shown by the hollow squares in FIG. 4, aliphatic conversion reached 91 wt% at 31 hours on stream and remained constant until the run was stopped at 173 hours on stream, corresponding to 84 bed volumes of liquid feed at reaction temperature. From 31 to 173 hours on stream the average deactivation rate was 0.009% conversion lost per hour.

EXAMPLE 5

[0059] Experiments were run under conditions, feed and experimental set-up similar to Example 3 at various pressures to obtain product yields in the first 10-20 hours of a reaction at various total pressures. For all runs, the reaction temperature was 600°C, the mole ratio of hydrogen to hydrocarbon feed was 1:1 corresponding to a hydrogen mol% of 50 and the WHSV was 1.24 hr^{-1}. Conditions and results for the four runs are given in Table 3.

[0060] Conversion was determined by the difference in component in the product and the feed in weight percent and dividing the difference by the component in the feed in wt%. Specifically, conversion of aliphatics was determined by summing aliphatics in the feed and summing the aliphatics in the gas and liquid products in weight percent and dividing the difference by aliphatics in the feed in weight percent. Aromatic alkyl group conversion was calculated by determining the amount of each aromatic component in mol/100 g, and then converted to weight percent by multiplying each aromatic component by the molar mass of the aromatic alkyl group (or groups). Aromatic alkyl groups are counted assuming molecular weights of 56.11 g/mol for butyl, 42.08 g/mol for propyl, 28.05 g/mol for ethyl and 16.04 for methyl. For determining C_1-C_4 aromatic alkyl group conversion the conversions of aromatic methyl, ethyl, propyl and butyl groups were summed. C_{5+} aliphatic and aromatic alkyls conversion was determined by the difference in C_{5+} aliphatic and C_1-C_4 aromatic alkyls in the product and the feed in weight percent and dividing the difference by the C_{5+} aliphatic and aromatic alkyls in the feed in weight percent.

[0061] Yields were calculated by dividing the difference of a particular product component in the product less the particular product in the feed in wt% by the amount of C_{5+} aliphatics and aromatic side chains in the feed in wt%. Aromatic side chains were counted assuming molecular weights as given above. Aromatic side chains are the same as aromatic alkyl groups. The C_{4-} olefin/paraffin ratio was determined by: calculating selectivities for each C_{4-} olefin and paraffin by dividing yield in wt% for that component by C_{5+} aliphatic and aromatic alkyls conversion, adding the selectivities for C_{4-} olefins and for C_{4-}paraffins and taking their ratio of the sums.

[0062] Aromatic ring balance was the ratio of the difference of the C_6-C_{10} aromatics in the effluent and the C_6-C_{10} aromatics in the feed in mol/100 g to the C_6-C_{10} aromatics in the feed in mol/100 g. In these calculations, hydrogen gas diluent was not considered in the component weight and mol percentages.

TABLE 3

Run	1	2	3	4	5
Pressure, kPa (psia)	793 (115)	448 (65)	276 (40)	172 (25)	276 (40)
Hydrogen partial pressure, kPa (psia)	396 (57)	223 (32)	137 (20)	86 (12)	137 (20)
Residence Time (sec)	24.1	13.6	8.4	5.2	16.7
Conversion					
C_{5+} Aliphatics	98.2	89.4	89.5	77.1	82.1
Aromatic Methyl	8.2	2.3	2.1	0.0	5.1
Aromatic Ethyl	65.5	46.6	64.3	46.2	63.3
Aromatic Propyl	82.2	82.1	84.6	81.1	86.3
Aromatic Butyl	96.1	90.2	93.2	86.9	93.8
C_1-C_4 Aromatic Alkyls	20	12	15	10	17
C_2-C_4 Aromatic Alkyls	69	54	69	54	68
C_{5+} Aliphatic and C_1-C_4 Aromatic Alkyls	53.6	45.5	47.0	39.1	45.2
Yields					
Methane	13.2	7.8	6.0	3.7	7.8
Ethane	11.1	6.5	4.7	2.8	8.0
Ethylene	2.8	5.6	8.5	8.6	7.5
Propane	9.2	6.1	5.2	2.8	5.7
Propylene	2.4	5.9	8.5	10.7	8.6
Butanes	-0.1	0.7	1.0	0.6	0.8
Butylenes	0.8	2.3	3.1	4.1	3.3
C_6-C_{10} rings	8.1	7.0	6.7	3.4	0.7
C_{11}+	6.6	3.8	3.0	2.2	3.4
C_1-C_4 olefin	6.0	13.8	20.2	23.4	19.3
C_1-C_4 paraffin	33.3	21.0	16.9	9.9	22.4
Ratios and Ring Balance					
C_{4-} olefin/paraffin ratio	0.18	0.65	1.19	2.37	0.87

C_6-C_{10} aromatic ring balance	105.6	104.9	104.7	102.3	100.5

EXAMPLE 6

[0063] Experiments were run under conditions and experimental set-up similar to Example 4 at various pressures to obtain product yields in the first 10-20 hours of a reaction at various total pressures. For all runs, the reaction temperature was 575°C, the mole ratio of hydrogen to hydrocarbon feed was 4.5:1 corresponding to a hydrogen mol% of 82. The lower temperature than in Example 5 was designed to increase olefin selectivity at the expense of producing less aromatics. Conditions for the four runs are given in Table 3. Calculations were made as in Example 5.

TABLE 4

Run	6	7	8	9
Pressure, kPa (psia)	793 (115)	345 (50)	276 (40)	276 (40)
Hydrogen partial pressure, kPa (psia)	647 (94)	280 (41)	224 (33)	224 (33)
WHSV (hr^{-1})	1.24	0.62	0.62	1.24
Residence Time (sec)	9.0	7.8	6.3	3.1
Conversion				
C_{5+} Aliphatics	87.3	85.1	84.8	74.4
Aromatic Methyl	8.2	2.3	2.1	0.0
Aromatic Ethyl	65.5	46.6	64.3	46.2
Aromatic Propyl	82.2	82.1	84.6	81.1
Aromatic Butyl	96.1	90.2	93.2	86.9
C_1-C_4 Aromatic Alkyls [a]	16	17	17	14
C_2-C_4 Aromatic Alkyls [a]	66	69	70	64
C_{5+} Aliphatics and C_1-C_4 Aromatic Alkyls	46.7	46.4	46.4	40.0
Yields				
Methane	7.3	6.1	5.5	3.3
Ethane	7.7	4.8	4.2	2.5
Ethylene	5.6	9.7	11.0	10.2
Propane	9.9	6.1	5.5	3.3

Propylene	6.0	10.5	12.0	12.5
Butanes	6.0	4.4	3.8	3.5
Butylenes	2.4	3.9	4.1	4.5
C_6-C_{10} rings	1.9	0.3	-0.4	-0.1
C_{11}+	0.9	1.2	1.1	0.2
C_1-C_4 olefin	14.0	24.0	27.0	27.3
C_1-C_4 paraffin	30.9	21.3	19.1	12.7
Ratios and Ring Balance				
C_{4-} olefin/paraffin ratio	0.45	1.13	1.42	2.14
C_6-C_{10} aromatic ring balance	105.6	104.9	104.7	102.3

[0064] As shown in Tables 3 and 4, at lower pressure and thus lower hydrogen partial pressure produced more olefins, fewer paraffins and fewer aromatics. At high pressures of 253 kPa (absolute) (65 psia) to 448 kPa (115 psia), olefin yield is lower and yields of propane, ethane, methane and aromatics are higher.

[0065] A portion of this effect is due to longer effective residence time at higher pressure leading to more extensive reaction of olefins to aromatics. However, the high light paraffin yield indicates that some hydrogenation may occur at high hydrogen partial pressure, so hydrogen partial pressure greater than 345 kPa (absolute) (50 psia) should be avoided. Despite the presence of hydrogen, olefins do not substantially hydrogenate back to form paraffins in the hydrogen partial pressure range of no more than 345 kPa (absolute) (50 psia) enabling a light olefin-to-paraffin ratio of at least 0.6. With hydrogen mol% of at least 60, hydrogen partial pressure range of no more than 345 kPa (absolute) (50 psia) enables a light olefin-to-paraffin ratio of at least 1.0.

[0066] Aromatic C_6-C_{10} ring balance of over 100% indicates that aromatics are being generated in the cracking reactor. C_{5+} aliphatics were converted at over 70%. Aromatic C_1-C_4 alkyl groups were dealkylated to olefins and aromatics at over 10%, but aromatic C_2-C_4 alkyl groups were dealkylated at over 50%, and over 60% in some examples. Altogether, C_{5+} aliphatics and aromatic alkyls were converted to produce light olefins at over 40%.

EXAMPLE 7

[0067] The silicalite catalyst was ground and sized to 40 x 60 mesh. Two grams of the catalyst was loaded in a 9 mm quartz reactor. The catalyst was pretreated in nitrogen for 2 hours at 550°C. The reactor was operated at atmospheric pressure. Pure isopentane was fed to the reactor in vapor phase along with steam and/or hydrogen. The conditions of each run and composition of each mixture is shown in Table 5. Nitrogen diluent provided the balance to the reactor. The results of isopentane conversion as a function of time are shown in Figure 5. Symbols in FIG. 5 are provided in Table 5.

TABLE 5

Run	Sample load, g	Temp., °C	Hydrocarbon, mol%	Water, mol%	Hydrogen, mol%	Nitrogen, mol%	Hydrocarbon WHSV, Hr^{-1}	Res time, s	Symbol in FIG. 5
A	1.25	650	19.8	49.5	--	30.7	1.55	0.74	◊
B	0.7	650	11.0	49.4	--	39.6	1.55	0.41	-
C	0.7	650	19.8	49.5	--	30.7	2.77	0.41	●
D	1.25	650	11.0	49.4	--	39.6	0.87	0.74	□
E	1.25	600	19.8	49.5	--	30.7	1.55	0.78	*
F	1.25	650	21.2	26.2	--	52.6	1.55	0.78	x
G	1.25	650	11.0	--	89.0	0.0	0.96	0.73	+
H	1.25	650	27.0	--	73.0	0.0	0.86	1.8	◆
I	1.25	650	11.0	--	29.7	59.3	0.86	0.73	○

Low conversion and fast deactivation is observed in the presence of steam, but high conversion and no deactivation are observed in the presence of hydrogen.

EXAMPLE 8

[0068] The silicalite catalyst was ground sized to 40 x 60 mesh. Two grams of the catalyst was loaded in a 9 mm quartz reactor. The reactor was operated at atmospheric pressure and at 600°C. Pure isopentane was fed at 0.0145 mL/min to the reactor after being combined with a gas feed. In two separate runs the gas contained 100 mol% hydrogen or 100 mol% nitrogen, respectively, flowing at 7.5 standard cc/min, such that the molar flow rate of the gas was 2.7 times the molar flow rate of the isopentane. The product mixture was analyzed as vapor by gas chromatography. Isopentane conversion as a function of time on stream is shown in FIG. 6 for the two runs.

[0069] When nitrogen gas was used, isopentane conversion deactivated at 1.38% per day after 4 hours on stream as shown by the solid circles. When hydrogen gas was used, isopentane conversion deactivated at 0.78% per day after 4 hours on stream as shown by the squares in FIG. 6.

EXAMPLE 9

[0070] A zeolite-water suspension was prepared by addition of 9,978 g of silicalite, weighed on a volatile-free basis, to 9956 g water while stirring. The zeolite had a molar ratio of silica to alumina of 420 and was calcined, steamed and acid-washed. The resulting mixture was then circulated through a bead mill for 10 minutes. Three solutions were prepared: 13,861 g of a solution of aluminum chlorohydrate was weighed out comprising 11.08 wt-% aluminum and 12.64 wt-% chlorine. A solution was prepared containing 44.5 wt-% of hexamethylenetetramine (HMT) in water and a third containing 85.7 wt-% H_3PO_4 acid. All solutions were then cooled to 3 to 10°C. The silicalite-water suspension and the aluminum chlorohydrate solution were combined by pumping together at 98.2 and 60.9 g/min respectively. The HMT and H_3PO_4 solutions were combined with the silicalite/water/aluminum chlorohydrate suspension at rates of 34.8 and 30.8 g/min respectively. The mixture was then pumped through a vibrating tube or cylinder with perforations at the outlet end to form droplets which are directed into a vertical column containing paraffin oil heated to 90 to 100°C. As the droplets fall though the oil column, spherical gel particles form and were collected at the outlet. The spheres were then drained of oil, transferred into a vertical washing column and washed for 1 hour at 69 to 72°C in a continuous flow of water containing 0.005 to 0.5 wt-% NH_3, then washed with water at 49 cm^3/min for 30 min at 67 to 71 °C. The washed spheres were drained, dried at 79 to 121°C and oven-calcined in air at 345 to 625°C for 135 minutes. The preparation yielded the final spherical catalyst. The catalyst had a silicalite to binder ratio of 60/40 by weight and apparent bulk density of 0.547 g/cm^3.

EXAMPLE 10

[0071] Sixty cubic centimeters (32.8 g) of a catalyst prepared in Example 9 were loaded in a fixed bed reactor in a furnace in three separate catalyst plugs of 15, 15 and 30 cubic centimeters separated by quartz wool and alpha alumina filler. The reactor was configured such that the reformate feed with the composition shown in Table 6 and specific gravity of 0.82 g/cm^3 was vaporized and mixed with hydrogen in a reactor pre-heat zone. Liquid and vapor products were separated at the reactor outlet which was maintained at 172 kPa (gauge) (25 psig). The reactor was heated to 424°C, measured at 2 inches above catalyst bed inlet, under hydrogen, and liquid feed flow was initiated at a flow rate to achieve a WHSV of 3 hr^{-1} and a mole ratio of hydrogen to hydrocarbons of 4.5:1. Then temperature was increased to 496°C for 10 hours. Finally, temperature was increased to 579°C, liquid feed rate was decreased to achieve a WHSV of 0.9 hr^{-1} and hydrogen flow rate was decreased to achieve mole ratio of hydrogen to hydrocarbons of 3:1 thus comprising a hydrogen concentration of 75 mol%. Flows continued for an additional 40 hours. The gas and liquid products were analyzed separately by gas chromatography. Effluent composition is shown in Table 6.

TABLE 6
Reformate Feed

Component	Feed, wt%	Product, wt%
C_1 Paraffin	0.000	1.362
C_2 Paraffins	0.000	2.198
C_3 Paraffins	0.001	2.341
C_4 Paraffins	0.002	1.041
C_5 Paraffins	1.829	0.998
C_6 Paraffins	11.377	3.267
C_7 Paraffins	9.992	1.961
C_8 Paraffins	2.742	0.485
C_5 Naphthenes	0.022	0.000
C_6 Naphthenes	0.316	0.065
C_7 Naphthenes	0.431	0.295
C_8 Naphthenes	0.305	0.107
C_{5+} Aliphatics	28.1	8.6

C_{9+} Paraffins, Naphthenes and Olefins	0.309	0.749
Ethylene	--	4.189
Propylene	0.001	6.303
C_4 Olefins	0.002	2.691
C_5 Olefins	0.056	0.486
C_6 Olefins	0.335	0.144
C_7 Olefins	0.205	0.006
C_8 Olefins	0.141	0.044
Benzene	6.643	9.802
Toluene	18.806	23.812
Xylene	20.940	20.870
Ethylbenzene	3.117	0.712
Trimethylbenzene	8.941	8.703
Methyl-Ethyl-Benzene	6.191	1.829
Propyl-Benzene	1.577	0.219
Tetra-Methyl Benzene	1.810	1.491
Di-Methyl-Ethyl Benzene	0.212	9.802
Methyl-Propyl-Benzene	1.198	23.812
Di-Ethyl-Benzene	0.841	20.870
Butyl-Benzene	0.149	0.712
C_{11+} Aromatics	1.508	8.703
Aromatic Alkyls[a]	18.7	16.2
Aromatic C_2-C_4 Alkyls[a]	3.6	1.1

[0072] Yields and conversions are shown in Table 7. Yields, ratios, conversions, and balances were calculated as explained for Example 5.

TABLE 7

Conversion	
C_{5+} Aliphatics	69.3
Aromatic Methyl	0

Aromatic Ethyl	65.3
Aromatic Propyl	83.6
Aromatic Butyl	91.9
C_1-C_4 Aromatic Alkyls	13
C_2-C_4 Aromatic Alkyls	70
C_{5+} Aliphatic and C_1-C_{4-} Aromatic Alkyls	47.0
Yields	
Methane	2.9
Ethane	4.7
Ethylene	9.0
Propane	5.0
Propylene	13.5
Butanes	2.2
Butylenes	5.7
C_6-C_{10} rings	2.0
C_{11}+	1.9
C_1-C_4 olefin	28.2
C_1-C_4 paraffin	14.8
Ratios and Ring Balance	
C_{4-} olefin/paraffin ratio	1.9
C_6-C_{10} aromatic ring balance	101.8

[0073] Results indicate C_{5+} aliphatics cracked and C_{4-} alkyl aromatics were dealkylated at significant conversion levels to substantial yields of light olefins ethylene, propylene and butylene. Conversion to light olefins is more significant than conversion to light paraffins. Additionally, the C_6-C_{10} aromatic ring balance of over 100% indicates that aromatics are being generated in addition to aromatics resulting from dealkylation.

SPECIFIC EMBODIMENTS

[0074] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0075] A first embodiment of the invention is a process for making aromatics comprising taking a cracking feed stream boiling in the naphtha range comprising aromatic compounds and aliphatic compounds, wherein at least a portion of the aromatic compounds contain alkyl groups; passing the cracking feed stream at a temperature of at least 500°C to a cracking reactor comprising a cracking catalyst including a zeolite with a maximum pore diameter of greater than 5 Angstroms; adding at least 60 mol% hydrogen to the cracking reactor to preserve the cracking catalyst against deactivation; selectively cracking the aliphatic compounds and selectively dealkylating the alkyl groups on the aromatic compounds in the presence of the cracking catalyst in the cracking reactor under cracking conditions to cracked olefins and aromatic compounds in a cracked effluent stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising reforming a naphtha stream in a reforming unit under reforming conditions to produce a reformer effluent stream and taking the cracking feed stream from the reformer effluent stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the zeolite comprises MFI zeolite. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the zeolite comprises a silicalite catalyst having a zeolite silica to alumina molar ratio of greater than 250. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrogen mol% in the cracking reactor is no more than 90. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrogen partial pressure in the cracking reactor is between 62 kPa (9 psia) and 345 kPa (50 psia). An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrogen to hydrocarbon mole ratio at an inlet to the cracking reactor is at least 2:1. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the ratio of olefins to paraffins of C_4-

hydrocarbons is at least 1 in the cracked effluent stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the naphtha feed stream has a T5 boiling point in a range of 0°C to 82°C and a T95 boiling point in a range of 20°C to 215°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising introducing a naphtha feed stream into a naphtha splitter column to produce at least two streams, the first stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 25°C to 82°C and the second stream having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C; passing the second stream to a naphtha hydrotreating reactor to produce a hydrotreated naphtha stream; and wherein reforming the naphtha stream comprises reforming the hydrotreated naphtha stream.

[0076] A second embodiment of the invention is a process for making aromatics and light olefins comprising reforming a naphtha stream in a reforming unit under reforming conditions to produce a reformer effluent stream comprising aromatic compounds and aliphatic compounds, wherein at least a portion of the aromatic compounds contain alkyl groups; taking a cracking feed stream from the reformer effluent stream; heating the cracking feed stream to at least 500°C and passing the cracking feed stream at a temperature of at least 500°C to a cracking reactor comprising a catalyst including a zeolite having pore size greater than 5 Angstroms; providing at least 50 mol% hydrogen to the cracking reactor to preserve the cracking catalyst against deactivation while maintaining the hydrogen partial pressure in the cracking reactor is between 62 kPa (9 psia) and 345 kPa (50 psia); and selectively cracking the aliphatic compounds and selectively dealkylating the alkyl groups on the aromatic compounds in the presence of the cracking catalyst in the cracking reactor under cracking conditions to cracked and dealkylated olefins and the aromatic compounds in a cracked reformer effluent stream, wherein the cracked olefins comprise at least one of ethylene, propylene, and butylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the hydrogen mol% in the cracking reactor is no more than 90. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising separating the cracked reformer effluent stream into an aromatic lean fraction comprising the cracked olefins and an aromatic rich fraction comprising the aromatic compounds; and passing the aromatic rich fraction to an aromatics complex. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the hydrogen to hydrocarbon mole ratio at an inlet to the cracking reactor inlet is at least 2:1. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the cracking conditions include at least one of a temperature in the range of 500°C to 700°C, a pressure in a range of 30 kPa (g) to 750 kPa (g), a hydrogen to C_{5+} hydrocarbon mole ratio at an inlet to the cracking reactor of at least 0.5:1 to 6:1, and a weight hourly space velocity (WHSV) of 0.1 hr^{-1} to 4 hr^{-1}. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising introducing a naphtha feed stream into a naphtha splitter column to form at least two streams, the first stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 20°C to 82°C and the second stream having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C; passing the second stream to a naphtha hydrotreating reactor producing a hydrotreated naphtha stream; and wherein reforming the naphtha stream comprises reforming the hydrotreated naphtha stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising introducing a naphtha feed stream into a naphtha hydrotreating reactor to produce a hydrotreated naphtha stream; passing the hydrotreated naphtha stream to a naphtha splitter column to produce at least two streams, the first hydrotreated stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 25°C to 82°C and the second hydrotreated stream having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C; and wherein reforming the naphtha stream comprises reforming the second hydrotreated stream.

[0077] A third embodiment of the invention is a process for making aromatics comprising taking a cracking feed stream boiling in the naphtha range comprising aromatic compounds and aliphatic compounds, wherein at least a portion of the aromatic compounds contain alkyl groups; heating the cracking feed stream to at least 500°C and passing the cracking feed stream at a temperature of least 500°C to a cracking reactor comprising a cracking catalyst including a zeolite with having a pore size greater than 5 Angstroms; providing at least 60 mol% to 90 mol% hydrogen to the cracking reactor to preserve the cracking catalyst against deactivation; selectively cracking the aliphatic compounds and selectively dealkylating the alkyl groups on the aromatic compounds in the presence of the cracking catalyst in the cracking reactor under cracking conditions to cracked olefins and aromatic compounds in a cracked effluent stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein the hydrogen partial pressure in the cracking reactor is between 62 kPa (9 psia) and 345 kPa (50 psia). An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the third embodiment in this paragraph wherein the hydrogen to hydrocarbon mole ratio at an inlet to the cracking reactor is at least 2:1.

[0078] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

[0079] In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS

What is claimed is:

1. A process for making aromatics comprising:

taking a cracking feed stream boiling in the naphtha range comprising aromatic compounds and aliphatic compounds, wherein at least a portion of the aromatic compounds contain alkyl groups;

passing the cracking feed stream at a temperature of at least 500°C to a cracking reactor comprising a cracking catalyst including a zeolite with a maximum pore diameter of greater than 5 Angstroms;

adding at least 60 mol% hydrogen to the cracking reactor to preserve the cracking catalyst against deactivation;

selectively cracking the aliphatic compounds and selectively dealkylating the alkyl groups on the aromatic compounds in the presence of the cracking catalyst in the cracking reactor under cracking conditions to cracked olefins and aromatic compounds in a cracked effluent stream.

2. The process of claim 1 further comprising reforming a naphtha stream in a reforming unit under reforming conditions to produce a reformer effluent stream and taking said cracking feed stream from said reformer effluent stream.

3. The process of claim 1 wherein the zeolite comprises MFI zeolite.

4. The process of claim 1 wherein the zeolite comprises a silicalite catalyst having a zeolite silica to alumina molar ratio of greater than 250.

5. The process of claim 1 wherein the hydrogen mol% in the cracking reactor is no more than 90.

6. The process of claim 1 wherein the hydrogen partial pressure in the cracking reactor is between 62 kPa (9 psia) and 345 kPa (50 psia).

7. The process of claim 1 wherein the hydrogen to hydrocarbon mole ratio is at least 2:1 at an inlet to the cracking reactor.

8. The process of claim 1 wherein the ratio of olefins to paraffins of C_{4-} hydrocarbons is at least 1 in the cracked effluent stream.

9. The process of claim 1 wherein the naphtha feed stream has a T5 boiling point in a range of 0°C to 82°C and a T95 boiling point in a range of 20°C to 215°C.

10. The process of claim 1 further comprising:

introducing a naphtha feed stream into a naphtha splitter column to produce at least two streams, the first stream having a T5 boiling point in a range of 0°C to 34°C and a T95 boiling point in a range of 25°C to 82°C and the second stream having a T5 boiling point in a range of 20°C to 82°C and a T95 boiling point in a range of 140°C to 215°C;

passing the second stream to a naphtha hydrotreating reactor to produce a hydrotreated naphtha stream; and

wherein reforming the naphtha stream comprises reforming the hydrotreated naphtha stream.

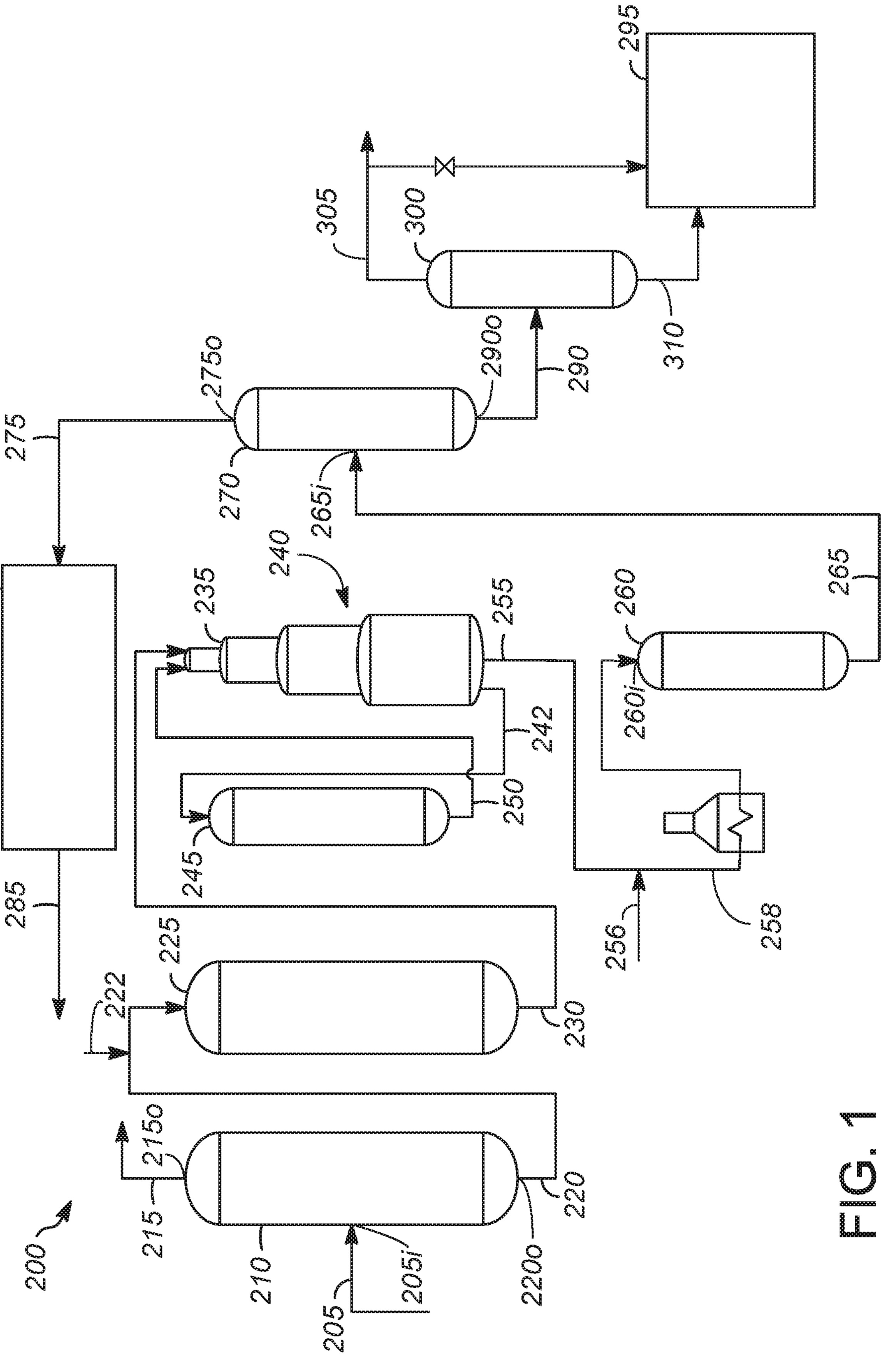
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FIG. 1

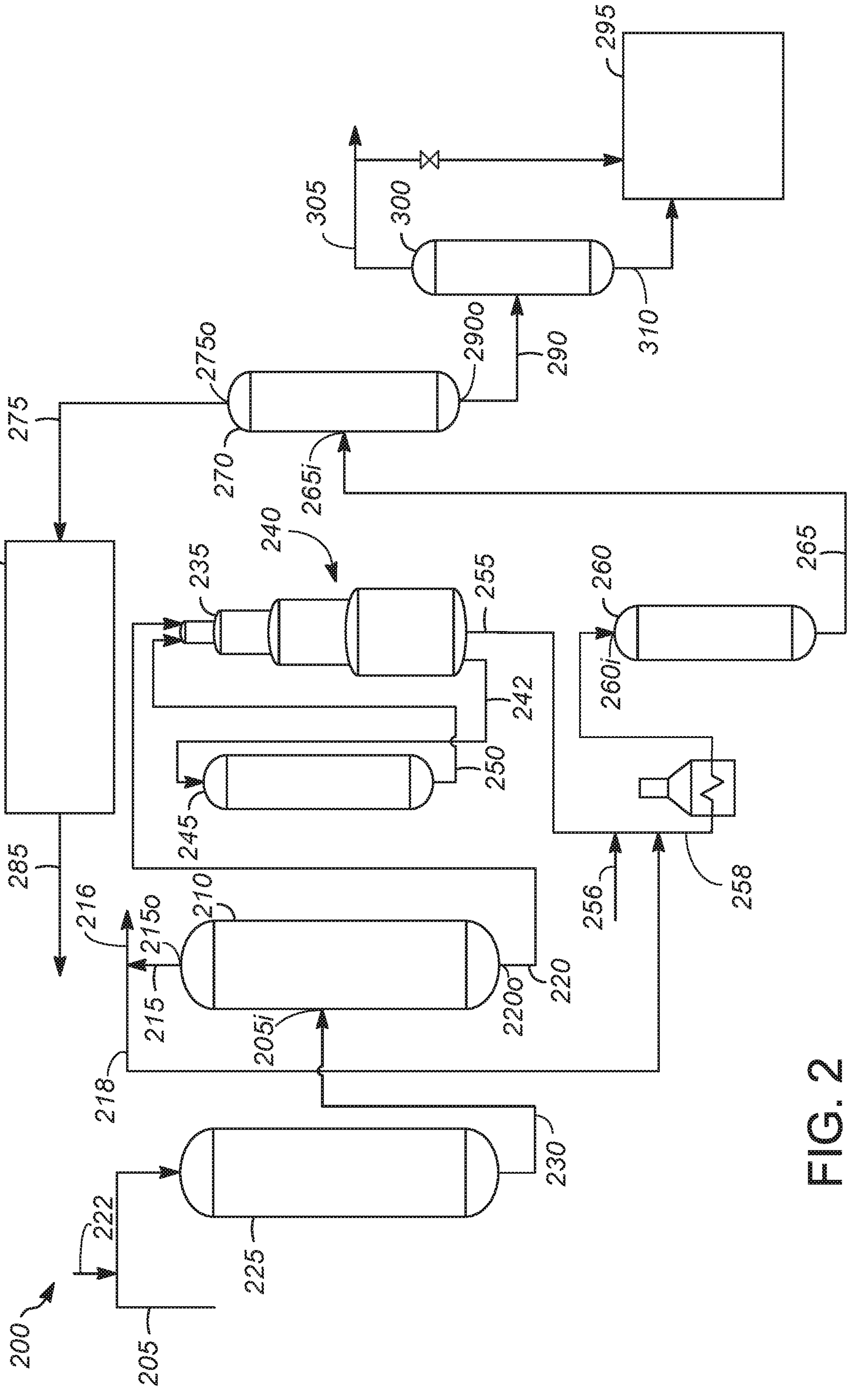
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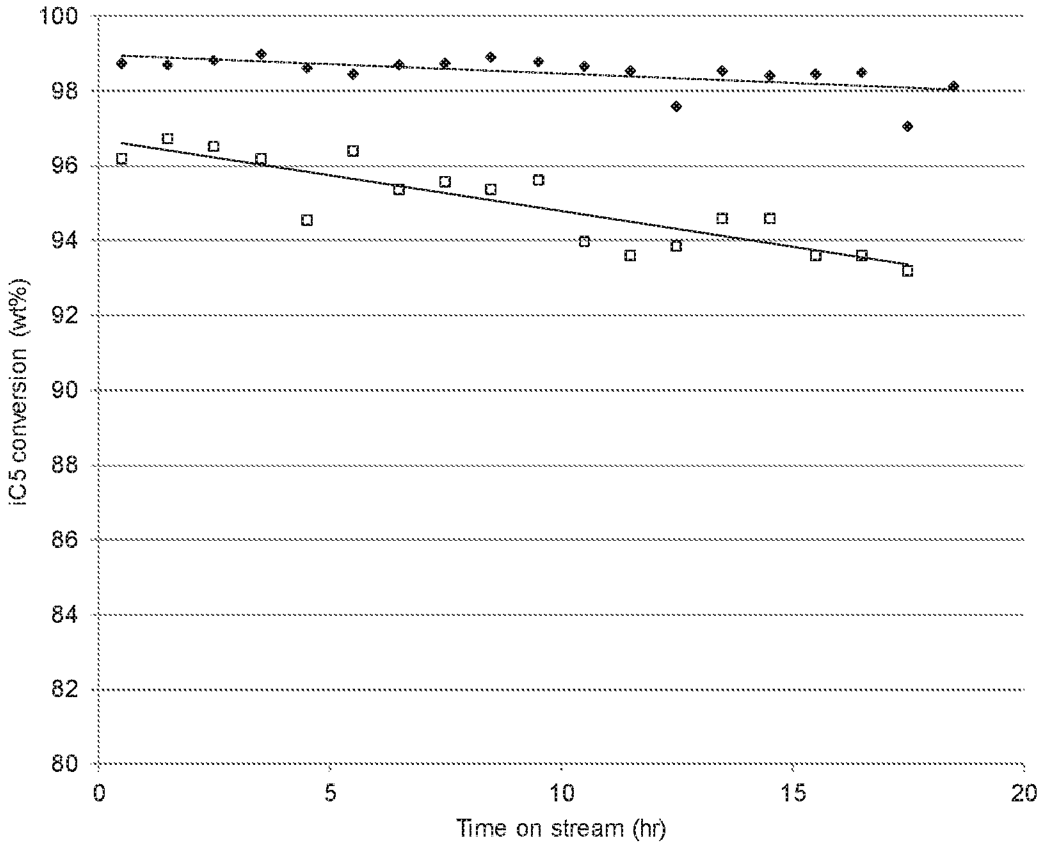
FIG. 2

FIG. 3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96
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84
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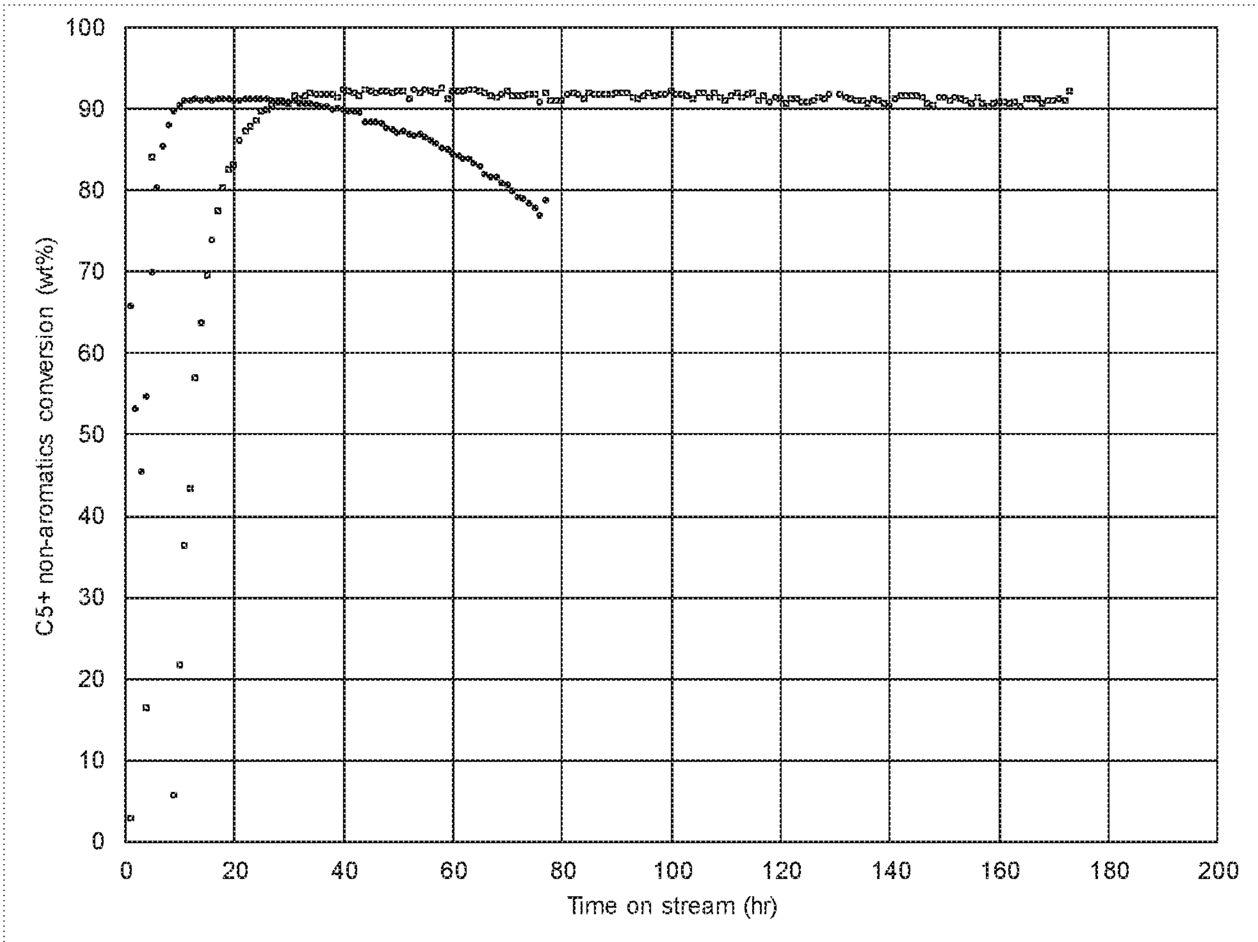
Time on stream (hr)

FIG. 4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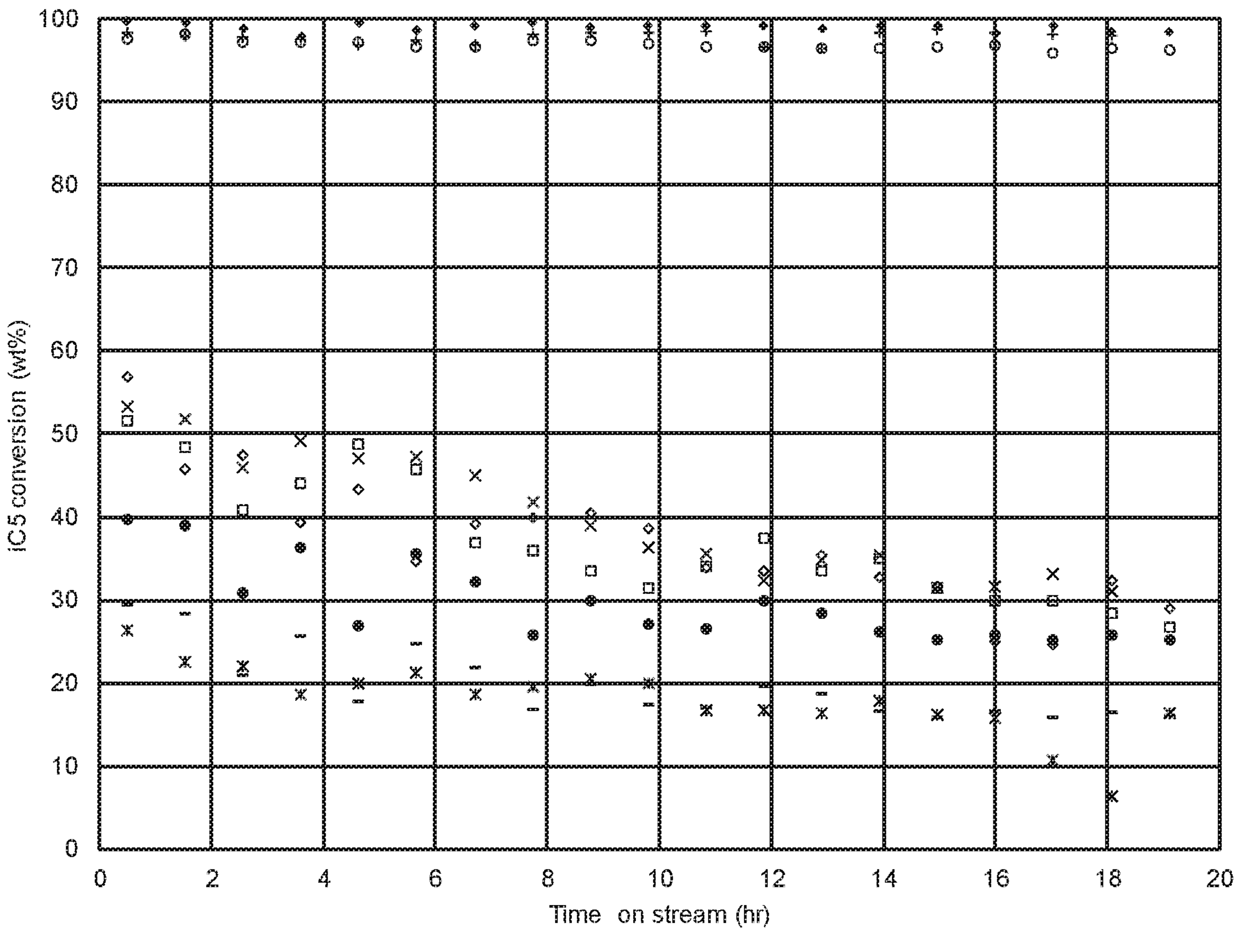
200
Time on stream (hr)

FIG. 5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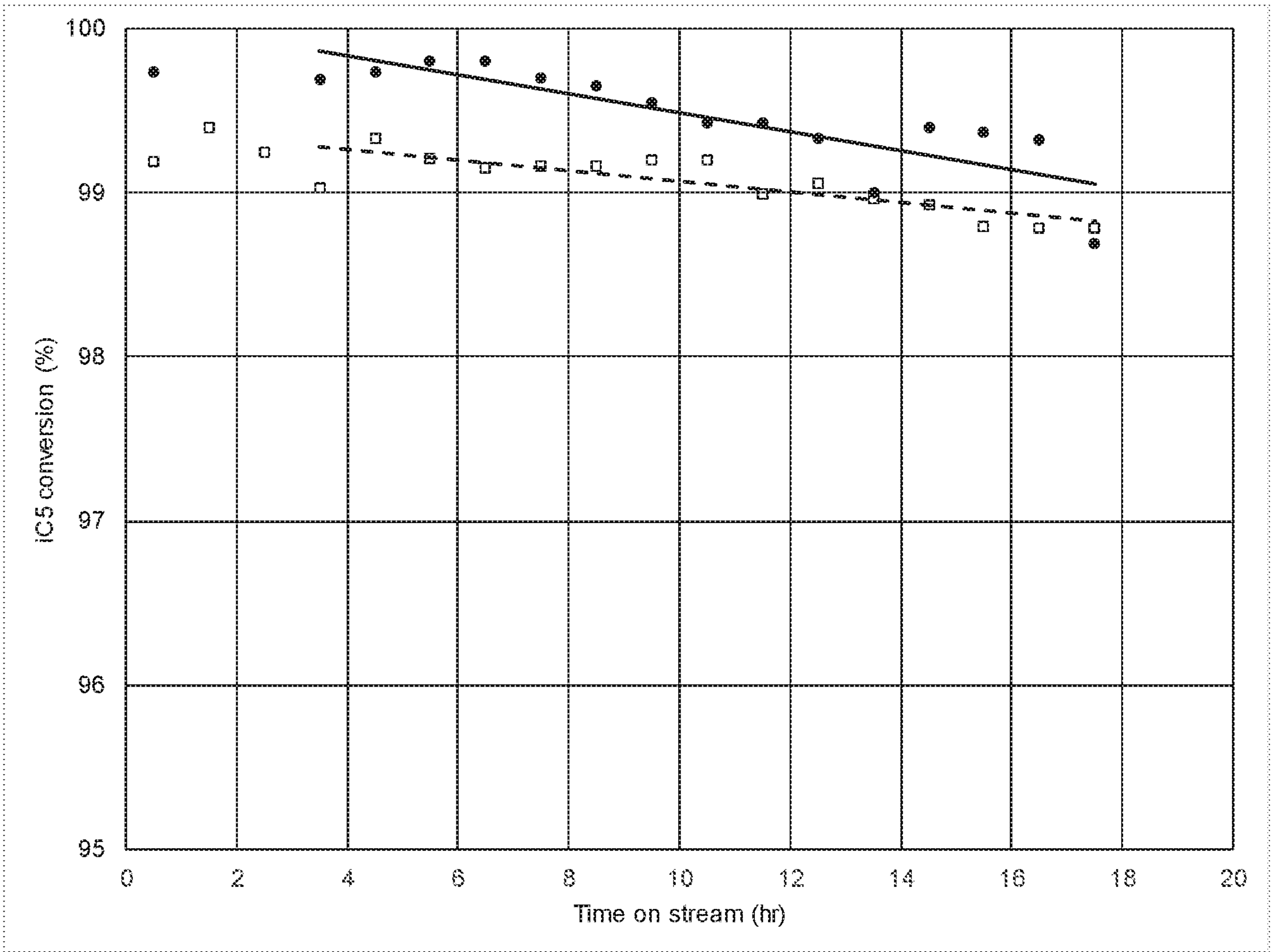
Time on stream (hr)

FIG. 6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Time on stream (hr)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2017/056040

A. CLASSIFICATION OF SUBJECT MATTER

C10G47/02 *(2006.01)*
C07C9/02 *(2006.01)*
C07C11/02 *(2006.01)*
C07C15/02 *(2006.01)*

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 47/02, C07C 9/02, 11/02, 15/02

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)

RUPAT, PAJ, ESP@cenet, USPTO, EAPATIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6160191 A (EXXON CHEMICAL PATENTS INC.) 12.12.2000	1-10
A	US 2015025283 A1 (EXXONMOBIL CHEMICAL PATENTS INC) 22.01.2015	1-10
A	US 2015251971 A1 (UOP LLC) 10.09.2015	1-10
A	US 6398947 B2 (EXXON MOBIL OIL CORPORATION) 04.06.2002	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 December 2017 (14.12.2017)	21 December 2017 (21.12.2017)

Name and mailing address of the ISA/RU:	Authorized officer
Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37	A.Sedov Telephone No. (8-495) 531-65-15