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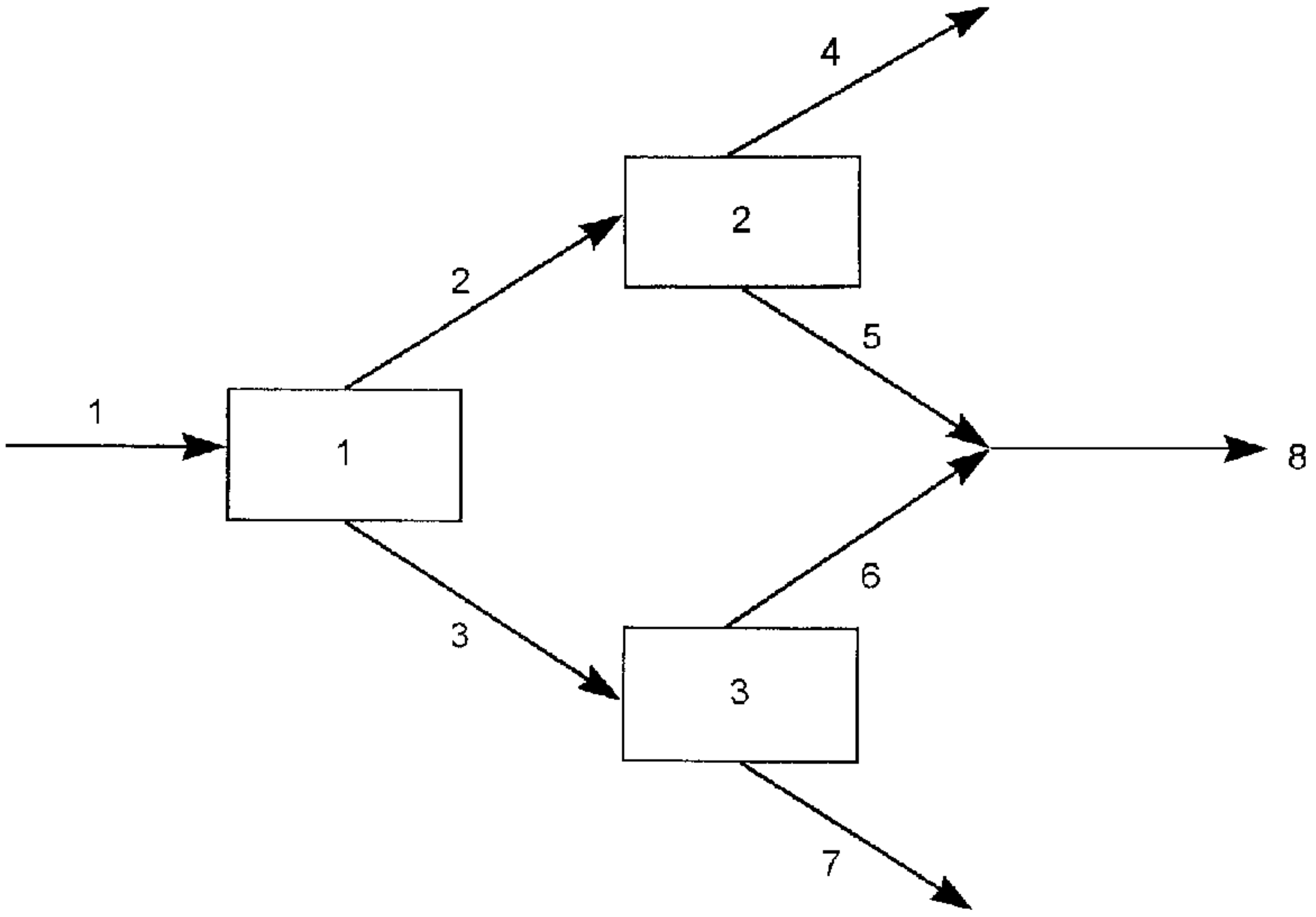
(54) Titre : PROCEDE DE SEPARATION D'OLEFINES DE COMPOSES SATURES
(54) Title: PROCESS FOR SEPARATING OLEFINS FROM SATURATED COMPOUNDS



(57) **Abrégé/Abstract**:

Process for treating feedstock comprising saturated hydrocarbons, internal olefins, and alpha olefins, comprising: (a) contacting feedstock with a linear polyaromatic compound to form reaction mixture comprising first linear polyaromatic compound-olefin adducts and saturated hydrocarbons; (b) separating first olefin adducts from the saturated hydrocarbons in the reaction mixture to form first olefin adduct stream and first saturated hydrocarbon stream; s(i) contacting at least a portion of first saturated hydrocarbon stream with a linear polyaromatic compound to form a reaction mixture comprising second linear polyaromatic compound-olefin adduct and saturated hydrocarbons; s(ii) separating said second olefin adduct from reaction mixture to form second olefin adduct stream and second saturated hydrocarbon stream, wherein concentration of saturated hydrocarbons in second saturated hydrocarbon stream is enriched over concentration of saturated hydrocarbons in first saturated hydrocarbon stream, and concentration of the saturated hydrocarbons in first saturated hydrocarbon stream is enriched over concentration of saturated hydrocarbons in feedstock; s(iii) optionally dissociating second olefin adducts to form first linear polyaromatic compounds and first olefin composition; s(iv) optionally separating linear polyaromatic compound from first olefin composition; and composition produced by said process.

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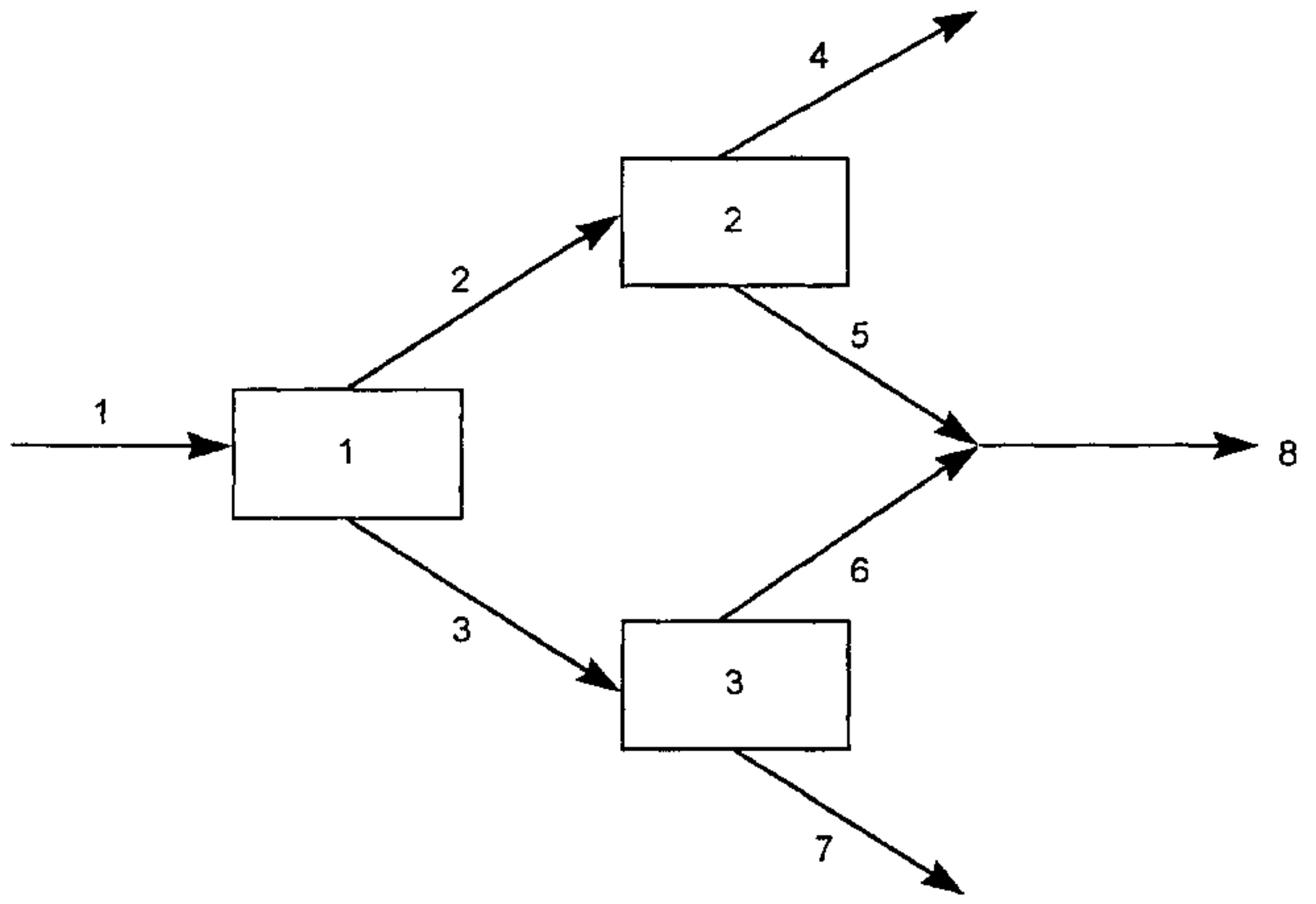
(54) Title: PROCESS FOR SEPARATING OLEFINS FROM SATURATED COMPOUNDS



(57) Abstract: Process for treating feedstock comprising saturated hydrocarbons, internal olefins, and alpha olefins, comprising: (a) contacting feedstock with a linear polyaromatic compound to form reaction mixture comprising first linear polyaromatic compound-olefin adducts and saturated hydrocarbons; (b) separating first olefin adducts from the saturated hydrocarbons in the reaction mixture to form first olefin adduct stream and first saturated hydrocarbon stream; s(i) contacting at least a portion of first saturated hydrocarbon stream with a linear polyaromatic compound to form a reaction mixture comprising second linear polyaromatic compound-olefin adduct and saturated hydrocarbons; s(ii) separating said second olefin adduct from reaction mixture to form second olefin adduct stream and second saturated hydrocarbon stream, wherein concentration of saturated hydrocarbons in second saturated hydrocarbon stream is enriched over concentration of saturated hydrocarbons in first saturated hydrocarbon stream, and concentration of the saturated hydrocarbons in first saturated hydrocarbon stream is enriched over concentration of saturated hydrocarbons in feedstock; s(iii) optionally dissociating second olefin adducts to form first linear polyaromatic compounds and first olefin composition; s(iv) optionally separating linear polyaromatic compound from first olefin composition; and composition produced by said process.

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PROCESS FOR SEPARATING OLEFINS FROM SATURATED COMPOUNDS

The present invention relates to a process for separating olefins from saturated hydrocarbons followed by separating linear alpha olefins and internal olefins from a saturated hydrocarbon stream and from an olefin stream.

Many industrial processes produce olefin/saturated hydrocarbon streams that are mixtures of olefins, saturated hydrocarbons, and oxygenates. Olefins are frequently used in the manufacture of polymers such as polyethylene, as drilling mud additives, or as intermediates for the production of oil additives and detergents. Some industrial processes manufacture olefin streams by oligomerizing ethylene over an alpha olefin catalyst to produce mixtures of alpha and internal olefins having a broad range of carbon numbers. However, these streams rely on the use of ethylene as a feedstock material, which adds a significant cost to the manufacture of the olefin. On the other hand, the Fischer-Tropsch (FT) process starts with an inexpensive feedstock, syngas, generally derived from natural gas, coal, coke, and other carbonaceous compounds, to make oligomers comprised of olefins, aromatics, saturates, and oxygenates.

The FT process, however, is not very selective to the production of olefins. While reaction conditions and catalysts can be tuned to manufacture a stream rich in the desired species within the FT product stream, a large percentage of the FT stream contains other types of compounds which must be separated from the olefins, which olefins are purified, and then sold into different markets. For example, a typical commercial FT stream will contain a mixture of saturated hydrocarbons having a broad spectrum of molecular weights, olefins, aromatics, and oxygenates such as organic carboxylic acids, alcohols, ethers, esters, ketones and aldehydes. All these compounds must be separated from the crude FT stream before a particular composition may be offered commercially. To further complicate the separation operation, the FT stream contains compounds having a wide spectrum of carbon numbers, as well as a wide variety of olefins, ranging from C_2-C_{200} species, internal linear olefins, alpha linear olefins, internal branched olefins, alpha branched olefins, and cyclic olefins, many of which have similar molecular weights. Separating and isolating these species is no easy task. Conventional distillation methods are frequently inadequate to separate species having closely related boiling points.

Various processes have been proposed to efficiently separate the different species in a FT stream with sufficient purity that a particular composition is acceptable in the intended application. These processes for separating out different species in a FT stream include the use of molecular sieves, which are restricted to a feed having an average carbon number range which is more limited than a composition containing a broad spectrum of average carbon numbers ranging from C_5-C_{20}, the use of exchange resins, the use of super-fractionaters often operated at high pressure, and the use of oligomerization catalysts or etherification techniques to alter the boiling points of the species in the FT stream. Many reactive methods for separating species in a FT stream do not, however, selectively react with olefins while simultaneously rejecting paraffins.

US Patent No. 4,946,560 describes a process for the separation of internal olefins from alpha olefins by contacting a feedstock with an adducting compound such as anthracene to form an olefin adduct, separating the adduct from the feedstock, dissociating the olefin adduct through heat to produce anthracene and an olefin composition enriched in alpha olefin, and separating out the anthracene from the alpha olefin. This reference does not suggest the desirability or the capability of anthracene to separate olefins from saturated hydrocarbons in a first step, or further separate the linear alpha olefins from the saturated hydrocarbons removed in the first step along with separating linear alpha olefins from an olefin stream removed in the first step.

Once olefins are separated from saturated hydrocarbons, it would also be desirable to purify the removed saturated hydrocarbons and extract as much remaining olefin from the removed saturated hydrocarbon as possible.

As used throughout the specification and claims, the words, " first, second, third, etc" are meant only to distinguish one feed, composition, compound, or reaction zone, etc., from a different feed, composition, compound, reaction zone, etc., and are not meant to designate a particular sequence. For ease of tracking of a particular stream and for convenience sake only, olefin streams have been assigned the letter "o," alpha olefin streams have been assigned the letters "ao," internal olefin streams have been assigned the letters "io," and saturated compound streams have been assigned the letter "s." Their presence does not imply a particular order, sequence, or ascribe a meaning to the description and claim language, nor does a letter's absence in a claim or embodiment imply that a process step or composition not expressly mentioned is not required or implicit in the embodiment or claim. Where no spelled number or assigned letter is present, its use is not deemed necessary since other compounds, composition, steps, or reaction zones are not identically expressed in the embodiment or claim. Their absence or presence do not modify or ascribe a particular meaning, other than to differentiate from other identically expressed compounds, compositions, steps, reaction zones, etc in the embodiment or claim.

The present invention relates to a process for separating and isolating species, particularly in a FT stream. There is provided a process for treating a feedstock comprising saturated hydrocarbons, internal olefins, and alpha olefins, comprising:

(a) contacting the feedstock with a linear polyaromatic compound in a first reaction zone under conditions effective to form a reaction mixture comprising first linear polyaromatic compound-olefin adducts and saturated hydrocarbons;

(b) separating said first olefin adducts from the saturated hydrocarbons in the reaction mixture to form a first olefin adduct stream and a first saturated hydrocarbon stream;

s(i) contacting at least a portion of the first saturated hydrocarbon stream with a linear polyaromatic compound in a second reaction zone under conditions effective to form a reaction mixture comprising second linear polyaromatic compound-olefin adducts and saturated hydrocarbons;

s(ii) separating said second olefin adducts from the reaction mixture in the second reaction zone to form a second olefin adduct stream and a second saturated hydrocarbon stream, wherein the concentration of the saturated hydrocarbons in the second saturated hydrocarbon stream is enriched over the concentration of saturated hydrocarbons in the first saturated hydrocarbon stream, and the concentration of the saturated hydrocarbons in the first saturated hydrocarbon stream is enriched over the concentration of saturated hydrocarbons in the feedstock;

s(iii) optionally dissociating said second olefin adducts to form first linear polyaromatic compounds and a first olefin composition;

s(iv) optionally separating the first linear polyaromatic compounds from said first olefin composition;

The present invention preferably further comprises:

o(i) dissociating said first olefin adducts to form second linear polyaromatic compounds and a second olefin composition comprising alpha olefins and internal olefins;

o(ii) optionally separating the second linear polyaromatic compounds from said second olefin composition;

ao(i) contacting the second olefin composition with a linear polyaromatic compound in a third reaction zone under conditions effective to form a reaction mixture comprising linear polyaromatic compound-alpha olefin adducts and internal olefins;

ao(ii) separating said alpha olefin adducts, and optionally unreacted linear polyaromatic compounds as well, from the reaction mixture in the third reaction zone to form an alpha olefin adduct stream and an internal olefin stream;

ao(iii) dissociating the alpha olefin adducts to form linear polyaromatic compounds and an alpha olefin composition;

ao(iv) optionally separating the linear polyaromatic compounds from said alpha olefin composition;

whereby the concentration of alpha olefins in the alpha olefin composition is enriched over the concentration of alpha olefins in the second olefin composition, and the concentration of alpha olefins in the second olefin composition is enriched over the concentration of alpha olefins in the feedstock.

The feed stream to be treated comprises at least olefins and saturated hydrocarbons. The class of saturated hydrocarbons as used herein includes at least a paraffin. The class of saturated hydrocarbons may also include other molecules such as cycloparaffins.

An olefin means any compound containing at least one carbon-carbon double bond. The olefins may be linear, branched, conjugated, contain multiple double bonds anywhere along the chain, substituted, unsubstituted, contain aryl or alicyclic groups, or contain heteroatoms. The olefins may contain aryl moieties along with an aliphatic or cycloaliphatic moiety within the same compound, or may consist solely of an aliphatic, cycloaliphatic, or cycloaliphatic with aliphatic moieties on the compound. Preferably, the olefin is an aliphatic compound.

The olefin may be branched or linear. Examples of branching include alkyl, aryl, or alicyclic branches. The number of unsaturation points along the chain is also not limited. The olefin may be a mono-, di-, tri-, etc. unsaturated olefin, optionally conjugated. The olefin may also contain acetylenic unsaturation.

An alpha olefin is an olefin whose double bond is located on both of α and β carbon atoms. An α carbon atom is any terminal carbon atom, regardless of how long the chain is relative to other chain lengths in a molecule. The alpha olefin may be linear or branched. Branches or functional groups may be located on double bond carbon atoms, on carbon atoms adjacent to the double bond carbon atoms, or anywhere else along the carbon backbone. The alpha olefin may also be a polyene, wherein two or more points of unsaturation may be located anywhere along the molecule, so long as at least one double bond is in the alpha position.

An internal olefin is an olefin whose double bond is located anywhere along the carbon chain except at any terminal carbon atom. The internal olefin may be linear or branched. The location of a branch or substitution on the internal olefin is not limited. Branches or functional groups may be located on the double bond carbon atoms, on carbon atoms adjacent to the double bond carbon atoms, or anywhere else along the carbon backbone.

The olefin may also be substituted with chemically reactive functional groups. These types of compounds include those identified as oxygenates. Examples of chemically reactive functional groups are carboxyl, aldehyde, keto, thio, ether, hydroxyl, and amine. The number of functional groups on a molecule is not limited. The functional groups may be located anywhere along the carbon backbone.

The feedstock is generally produced by commercial processes such as the oligomerization of ethylene, optionally followed by isomerization and disproportionation. Alternatively, the feedstock may be produced by the Fischer-Tropsch process, which typically contains a high proportion of paraffins. A Fischer-Tropsch process catalytically hydrogenates carbon monoxide to produce compositions containing aliphatic molecular chains. Other processes for making feedstocks which may contain mixtures of olefins and paraffins include the dehydrogenation of paraffin, such as those made by the 'Pacol' (trade mark) processes of UOP, and the cracking of waxes. The most preferred feedstock is that obtained from a Fischer-Tropsch (FT) synthesis.

FT catalysts and reaction conditions can be selected to provide a particular mix of species in the reaction product stream. For example, the particular catalyst and reaction conditions may be tuned to enhance the amount of olefins and decrease the amount of paraffins and oxygenates in the stream. Alternatively, the catalyst and reaction conditions may be tuned to enhance the amount of paraffins and decrease the amount of olefins and oxygenates in the stream.

Generally, the reaction conditions will vary depending on the type of equipment employed. The FT reaction temperatures vary from 100°C to 500°C, an inlet gas pressure to the reactor from atmospheric to 10.3 MPa (1500 psig), and an H2/CO ratio from 0.5:1 to 5:1, preferably from 1.8:1 to 2.2:1, and gas hourly space velocity ranging from 1 to 10,000 v/v/hour. A variety of reactor vessel configurations can be used, including a fluidized(entrained) bed, a fixed bed, and a slurried bed. The temperature in these beds can be adjusted by those of ordinary skill to optimize the formation of FT products, including hydrocarbons, and particularly, olefins and types of olefins. To illustrate without limitation, in fluidized (entrained) bed(s), the temperature of reaction is generally high- e.g. ranging from 280° to 350°C, preferably 310° to 340°C. If a fixed bed reactor(s) is used, the reaction temperature is generally ranges from 200°C to 250°C, preferably from 210° to 240°C, and when a slurry bed reactor(s) is used, the temperature is generally within the range of 190°C to 270°C.

The catalyst used in the FT process is any known in the art, but preferably from among molybdenum, tungsten, and Group VIII compounds, including iron, cobalt, ruthenium, rhodium, platinum, palladium, iridium, osmium, combinations of the foregoing, combinations with other metals, and each being in the free metal form or as alloys, or as an oxide or carbide or other compound, or as a salt. Iron based and cobalt based catalysts have found common commercial use, and ruthenium has gained importance as a metal for the catalyst which favours the formation of high melting waxy species under high pressure conditions. Those skilled in the art will recognize which catalysts and combinations will favour the manufacture of desired species in the FT reaction composition. For example, fused iron containing a promoter such as potassium or oxides on a silica, alumina, or silica-alumina support are known as FT synthetic catalysts. Another example is the use of cobalt metal. Cobalt has the advantage of producing less methane during synthesis over the older nickel based catalysts, and produces a wide spectrum of species. With the proper selection of supports, promoters, and other metal combinations, the cobalt catalyst can be tuned to manufacture a composition rich in the desired species. Other catalysts, such as iron-cobalt alloy catalysts, are known for their selectivity toward olefins under certain process conditions.

The catalysts may be fused or precipitated, or sintered, cemented, impregnated, kneaded or melted on to a suitable support.

The catalysts may also contain promoters to promote the catalyst's activity, stability, or selectivity. Suitable promoters include alkali or alkaline earth metals, in free or combined form as an oxide, hydroxide, salt, or combinations thereof.

A FT stream generally contains virtually no sulphur or nitrogen compounds, which may be deleterious to other catalysts which derivatize the olefins or catalyze the reaction of olefins in other oligomerization or polymerization processes. Regardless of the method used, however, the FT process is not very selective to a particular species, and yields a wide variety of species within a composition.

The linear polyaromatic compound used in the process of the invention, however, is particularly well adapted for the separation of olefins from saturated hydrocarbons in a FT stream in the presence of oxygenates since oxygenates do not significantly impair the performance of the linear polyaromatic compound.

While reference is made to a FT stream, it is to be understood that any stream made by any process containing olefins and saturated hydrocarbons are suitable feedstocks for the process of the present invention. Most crude FT streams contain from 5 wt.% to 95 wt.% olefins, the remainder being saturated hydrocarbons comprising paraffins and cycloparaffins, and optionally other compounds such as aromatics optionally containing saturated or unsaturated alkyl branches, and oxygenates, based on the weight of all ingredients in the feedstock stream to the process of the invention.

The preferred amount of olefins present in the FT stream ranges from 15 wt.% to 70 wt.%, based on the weight of the FT stream. The amount of linear alpha olefin in the FT stream is not limited, but preferably ranges from 15 wt.% to 65 wt.%, based on the weight of the FT stream. The amount of other olefins, including branched alpha olefins and internal olefins, both linear and branched, is also not limited, but preferably ranges from 1 wt.% to 55 wt.%, more preferably from 5 wt.% to 45 wt.%, based on the weight of the FT stream. The amount of paraffin in most FT streams ranges from 5 wt.% to 95 wt.% based on the weight of all ingredients in the feedstock. In some FT streams, the FT catalyst is tuned to enhance the olefin concentration and decrease the paraffin concentration. In these streams, the amount of paraffin generally ranges from 5 to 65 wt.% of the stream. In other FT streams where the FT catalyst is tuned to enhance the amount of paraffin, the amount of paraffin in the stream ranges from 65 wt.% to 95 wt.%. The amounts of other compounds in a FT stream, such as oxygenates and aromatics, make up most of the remainder of the FT stream, and are generally present in amounts ranging from 5 wt.% to 40 wt.%. Minor amounts of other by-products and impurities, less than 5 wt.%, may be present in most FT streams.

The feedstock may be a processed FT stream which has been fractionated and/or purified by a conventional distillation, extraction, or other separation operation to obtain a desired carbon number cut, including a composition containing a mixture of carbon numbers or a single carbon cut composition, and to remove high and low boiling compounds, including olefins, paraffins, aromatics, and oxygenates from the crude stream. When the separation operation is conducted by distilling the reaction mixture containing the adduct, it is preferred that the feedstock used in the process of the invention contain an average carbon number ranging from C_5-C_{20} and wherein the predominant olefin species in the feedstock is within the range of C_5-C_{20}, inclusive. The linear polyaromatic compound efficiently separates the saturated hydrocarbons from the olefins when the average carbon number of the feedstock and the predominant olefinic species is within this range, inclusive. When the average carbon number of the feedstock exceeds C20, the polyaromatic compound-olefin adduct boils at a lower temperature than many of the species in the C20 +

feedstock composition, thereby leaving these high boiling species in the reaction mixture bottoms containing the adduct. Accordingly, the particular linear polyaromatic compound and the particular feedstock composition should be so selected that the linear polyaromatic compound-olefin adduct composition in the reaction mixture boils at a higher temperature than the amount of unreacted paraffin species in the feedstock one desires to separate. Therefore, the feedstock stream is preferably one which contains an average carbon number ranging from 5 to 20, and more preferably ranging from 6 to 18, and wherein the predominant olefin species is within these ranges, inclusive. These types of FT streams are generally processed by one of the techniques identified above to substantially remove cuts containing ingredients below or exceeding the range of C_5-C_{20}.

In addition to mixtures of olefins within this range, one may also employ what are known as single carbon cuts of olefins as feedstocks, wherein the single cut is within this range. For example, the feedstock employed may be a single C_6, C_8, C_9, C_{10}, C_{11}, C_{12}, C_{14}, or C_{16} carbon cut. These carbon cuts have utility as comonomers for polyethylene, poly alpha olefins, alpha olefin sulfonates, and as drilling fluids.

In the event that one desires to employ a feedstock outside the range of C_5-C_{20} , other separation techniques can be used to separate the adduct from the unreacted reaction mixture, including the selection of higher boiling polyaromatic compounds and/or other separation techniques such as liquid/liquid extraction or crystallization. These techniques, of course, can also be used with feedstocks within the range of C_5-C_{20}, inclusive.

The linear polyaromatic compound is utilized in the process of the present invention to form the adduct with the olefins in the feed stream. As used herein, "linear polyaromatic compound" refers to a linear polyaromatic compound having at least three fused aromatic rings, which may be unsubstituted or substituted and possess similar adducting properties as the unsubstituted molecule, and mixtures thereof. The linearity should extend to all three of the fused rings if a three fused ring compound is used and to at least four consecutively fused cyclic rings if a four or more fused ring compound is used. The linear polyaromatic compound also refers to mixtures of compounds containing as one of their ingredients the linear polyaromatic compound, including but not limited to coal tars, anthracene oil, and any crude mixtures containing cuts separated from naphthalene. The linear polyaromatic compound also includes aromatic molecules linked together by a bridging group, such as a hydrocarbon chain, an ether linkage, or a ketone group-containing chain so long as at least three fused rings are present in a linear arrangement; as well as those containing a heteroatom which do not interfere in the separation of olefins from saturated hydrocarbons.

The linear polyaromatic compound has a preferential selectivity toward adducting with linear alpha olefin compounds, and secondly with other olefins, and last with paraffins, with which the compound is virtually unreactive under any operating condition outside of cracking conditions. The linear polyaromatic compound of choice is one which has a selectivity for linear alpha olefin compounds over other olefins greater than 1:1 by mole, preferably 2:1 or more, more preferably 4:1.

Non-limiting examples of the linear polyaromatic compound include anthracene, 2,3-benzanthracene, pentacene, and hexacene. Suitable examples of substituents in substituted linear polyaromatic compounds include, but are not limited to, lower alkyl, e.g., methyl, ethyl, butyl; halo, e.g., chloro, bromo, fluoro; nitro; sulphato; sulphonyloxy; carboxyl; carbo-lower-alkoxy, e.g., carbomethoxy, carbethoxy; amino; mono- and di-lower-alkylamino, e.g., methylamino, dimethylamino, methylethylamino; amido; hydroxy; cyano; lower-alkoxy, e.g., methoxy, ethoxy; lower-alkyanoyloxy, e.g., acetoxy; monocyclic aryls, e.g., phenyl, xylyl, tolyl, benzyl, etc. The particular substituent size, their number, and their location, should be selected so that they are relatively inert under the reaction conditions and not so large as to block the formation of the Diels-Alder adduct. Suitable substituted linear polyaromatic compounds can be determined by routine experimentation. Examples of suitable linear polyaromatic compounds include 9,10-dimethylanthracene, 9,10-dichloroanthracene, 9-methylanthracene, 9-acetylanthracene, 9-(methylaminomethyl)anthracene, 2-chloroanthracene, 2-ethyl-9,10-dimethoxyanthracene, anthrarobin, and 9-anthryl trifluoromethyl ketone. The preferred linear polyaromatic compounds are substituted or unsubstituted anthracene and/or benzanthracene, particularly unsubstituted anthracene and 2,3-benzanthracene.

In a preferred embodiment of the present invention wherein the linear polyaromatic compound at each step comprises anthracene, said linear polyaromatic compound will comprise anthracene having a purity of 75% or more.

In a first reaction zone in step a), the feedstock composition, preferably a FT feedstock stream having an average carbon number ranging from C_6-C_{18}, is contacted with a linear polyaromatic compound. In the second reaction zone, the saturated hydrocarbon stream removed from the first reaction zone is also contacted with a linear polyaromatic compound. In each reaction zone, the Diels-Alder adduct forming reaction is carried out in a conventional fashion. Examples of suitable equipment in which the reactions are carried out include a continuously stirred tank reactor, configured as a single unit, or units in parallel or in series, wherein feedstock or an olefin composition, and linear polyaromatic compound, are added continuously to a stirred tank to form a liquid reaction mixture under heat, and the reaction mixture is continuously withdrawn from the stirred tank. Alternatively, the reaction may be carried out in a plug flow reactor or a series of plug flow reactors, a bubble column, or in a batch reactor.

The feedstock and olefin composition adducting reactions are typically carried out over a range of temperatures from 150° to 290°C, preferably from ~~about~~ 200° to 280°C, and most preferably from 240° to 265°C. The adduction reaction temperature may exceed 290°C so long as the temperature is below the boiling point of the olefin under the reaction conditions. Pressures typically run from atmospheric pressure to 100 atmospheres. The reactions can be carried out in the gas phase under vacuum or liquid phase or mixed gas-liquid phase, depending on the volatility of the feedstock, but generally in the liquid phase.

Stoichiometric ratios or an excess of either olefin or linear polyaromatic compound can be used to form the adducts. The molar ratio of olefins to linear polyaromatic compound is preferably from 0.25:1 to 10:1. Preferably, a molar excess of linear polyaromatic compounds are used to ensure a complete and large recovery of all olefins in the first and subsequent adduction zones. However, in succeeding adducting reaction zones where greater selectivity towards forming adducts with linear alpha olefins are desired, the molar ratio of linear polyaromatic compounds to olefins may be moderated, desirably closer towards a 1.5:1 to 0.5:1 molar ratio of olefin to linear polyaromatic compound.

The residence time is for a time sufficient to adduct the desired amount of linear polyaromatic compound with the olefin. Typical residence times range from 30 minutes to 4 hours in a batch reaction.

An inert solvent can be utilized to dissolve the feedstock olefins or the linear polyaromatic compound or both in each of the adducting reactors. Preferred solvents are the hydrocarbon solvents which are liquid at reaction temperatures and in which the olefins, linear polyaromatic compound and olefin-linear polyaromatic compound adducts are soluble. Illustrative examples of useful solvents include the alkanes such as pentane, isopentane, hexane, heptane, octane and nonane; cycloalkanes such as cyclopentane and cyclohexane; and aromatics such as benzene, toluene, ethylbenzene and diethylbenzene. The amount of solvent to be employed can vary over a wide range without a deleterious effect on the reaction.

Preferably, the adducting reactions are carried out in the absence of a solvent, thereby improving the rate of reaction and avoiding the need for additional equipment and process steps for separating the solvent. After formation of the linear polyaromatic compound-olefin adduct in step (a), the adduct stream flows to a separation vessel effective for separating the saturated hydrocarbons from the linear polyaromatic compound-olefin adduct to form a saturated hydrocarbon stream and an olefin adducted stream in step (b). Due to the large molecular weight and structural difference between the adducts and the other ingredients in the reaction mixtures, such as saturated hydrocarbons and internal olefins, conventional separation techniques are quite suitable for removing the unreacted saturated hydrocarbons in step (b). For example, the saturated hydrocarbons in step (b) may be removed at the overhead or in fractions, by partial vacuum or flash distillation of the reaction mixture, while simultaneously withdrawing the liquid bottoms of the separation vessel comprising the adducts and unreacted linear polyaromatic compounds. It is desirable to raise the temperature at the bottom of the distillation column sufficient to retain the bottoms in liquid state, while keeping the temperature and residence time as low as possible to avoid dissociating the adducts. Suitable temperatures at the bottom of the separation vessel range from 210°C to 280°C, more preferably from 230°C to 270°C. While the pressure is not particularly limited, and the separation can be conducted under atmospheric pressure, it is preferred to conduct the separation under slight vacuum, e.g. 26.7 to 93.3 kPa (200 mmHg to 700 mmHg), to reduce the operating temperature and the residence time within the separation vessel. The residence time within the vessel should be short to avoid excessive dissociation of the adducts, such as from 1 to 30 minutes.

In step (b), the unreacted saturated hydrocarbon stream distillate includes paraffins and may include, if present in the feedstock composition, aromatics and oxygenates such as the alcohols, ketones, acids, along with internal and branched olefins which failed to adduct with the linear polyaromatic compound.

Alternatively, the adducts may be separated by cooling the reaction mixture until the adducts crystallize out, followed by filtration or centrifugation to remove the unreacted saturated hydrocarbons in step (b).

In most cases, any unreacted linear polyaromatic compound will separate out with the adducted olefin streams. Other ingredients, such as small amounts of higher molecular weight unreacted olefins, internal olefins, and branched olefins, may remain in the adducted olefin streams.

The process of the invention affords the flexibility for adjusting the recovery of a stream at each adducting and separation step to optimize the desired stream yield and concentration of species in the desired stream. For example, if one desires an alpha olefin stream highly concentrated in linear alpha olefin, the recovery of olefins from the feedstock will be moderate to avoid entraining excessive amounts of other olefins, part of which would otherwise be entrained in successive separations and dilute the linear alpha olefin concentration. Highly concentrating the linear alpha olefins, however, results in a lower linear alpha olefins stream yields than could be had if the recovery of olefin levels from the feedstock were set higher. On the other hand, if the linear alpha olefin stream yield is more desirable than attaining high concentrations of linear alpha olefins in the linear alpha olefin stream, then the recovery of olefins from the feedstock should be set a high level to ensure that larger quantities of olefins, including linear alpha olefins, are entrained in the olefin composition during the separation step, thereby resulting downstream in a larger alpha olefin stream yield, but at lower alpha olefin concentrations.

The recovery of a stream in a separation operation is determined by the molar ratio of linear polyaromatic compound to olefins, the adducting residence time, the temperature within the separation vessel, and most importantly, the residence time (rate of separation) of the reaction mixture in the separation vessel. To obtain a large olefin composition recovery, any one or a combination of the following variables are adjusted: a high linear polyaromatic compound to olefin molar ratio, e.g., >1, long residence times to ensure complete adduction, and moderate distillation temperatures to avoid dissociating the adducts. To obtain a smaller olefin composition recovery and highly concentrate the linear alpha olefins in the linear alpha olefin composition, any one or a combination of the following variables are adjusted: close to a 1:1 molar ratio or less, of linear polyaromatic compounds to olefins in the feedstock and shorter residence times to selectively adduct the linear alpha olefins in the feedstock. In either case, however, the concentration of the linear alpha olefin, or any other desired species, is enriched in the ultimate stream compared to the concentration of linear alpha olefin, or the other desired species, in the preceding composition treated and in the feedstock.

The rate of olefin recovery from the feedstock is not limited, and generally will depend upon the amount of olefin present in the feedstock. In one embodiment, the rate of recovery of olefin adducts from the first separation vessel, in moles/unit time, range from 0.10 to 0.40, more preferably from 0.15 to 0.35, each based upon a feedstock rate of 1.00. At these rates, from 40% to 100% of the olefins in the feedstock may be recovered into the olefin composition. In another embodiment, the rate of recovery ranges from 0.20 to 0.30, based upon a feedstock rate of 1.00.

In general, when a highly concentrated linear alpha olefin composition is desired, from 40% to 70% of the linear alpha olefins in the feedstock may be recovered into the olefin composition, and when the emphasis is on quantity of linear alpha olefin with a slight reduction in linear alpha olefin concentration in the linear alpha olefin stream, the recovery of olefins from the feedstock ranges from 70% to 100%. As noted above, in either case, the concentration of the desired species in the ultimate stream will be enriched over the concentration of the desired species in preceding feeds.

Based on the above as an example of optimizing the concentration or the quantity of linear alpha olefins in an alpha olefin stream, those of ordinary skill can set the rates of recovery and percentage of a desired species recovered at each separation step to optimize the concentration or quantity of other species in the feedstock one desires to recover.

When the saturated hydrocarbons are separated from the linear polyaromatic compound-olefin adduct in the separation vessel as a first saturated hydrocarbon stream, the first saturated hydrocarbon stream is enriched in its concentration of saturated hydrocarbons over the concentration of saturated hydrocarbons in the feedstock flowing to the first adduct reaction zone, and the concentration of olefins in the first saturated hydrocarbon stream is reduced over the concentration of olefins in the feedstock entering the first adduct reaction zone.

In the next step of the process, step s(i), the first saturated hydrocarbon stream comprising an enriched concentration of saturated hydrocarbons and a reduced concentration of linear alpha olefins and internal olefins, is contacted with linear polyaromatic compounds in a second adducting reaction zone under conditions effective to form a reaction mixture comprising second linear polyaromatic compound-olefin adducts and a second saturated hydrocarbon composition. Suitable reaction conditions and vessels include those used in the adducting reaction zone for the feedstock.

Once the second linear polyaromatic compound-olefin adduct has been formed in the second reaction zone in step s(i), the adduct stream flows to a separation vessel in step s(ii) effective for separating the second linear polyaromatic compounds-olefin adducts from the saturated hydrocarbons to form a second saturated hydrocarbon stream enriched in the concentration of saturated hydrocarbons over the concentration of saturated hydrocarbons in the first saturated hydrocarbons stream, and a second linear polyaromatic compound-olefin adduct stream.

Suitable methods and conditions for separating the second adducts from the second reaction mixture include any of the methods used to remove the adducted olefins from the reaction mixture in the first separation zone. Preferably, the second reaction mixture is distilled and a second saturated hydrocarbon stream is removed at the overhead of the distillation column, while the olefin adducts are removed from the column as a liquid bottoms stream. The second saturated hydrocarbon stream includes some internal olefins and alpha olefins, but in reduced concentrations over the concentration of these species in the first saturated hydrocarbon stream. However, the concentration of the saturated hydrocarbons in the second saturated hydrocarbon stream is enriched over their concentration in the first saturated hydrocarbon stream.

The second linear polyaromatic compound-olefin adducts in the second olefin adduct stream removed from step s(ii) are optionally, but preferably, dissociated in step s(iii) in a dissociation zone to form first linear polyaromatic compounds and a first olefin composition. The first olefin composition preferably comprises alpha olefins and internal olefins and is enriched in the concentration of said olefins over each of their concentrations in the first saturated hydrocarbon stream.

The dissociation process can be accomplished by feeding the adducted olefin stream to a dissociation vessel where the adducted olefin stream is heated and pyrolyzed at a temperature ranging from 200° to 500°C, preferably from 300° to 350°C, for a time sufficient to dissociate the adducts. The dissociation temperature can be further reduced below 200°C by stripping olefin gas as it is liberated using an inert gas. The pyrolysis frees the olefins from the linear polyaromatic compound. One or more dissociation vessels may be used in series to conduct the dissociation, and the dissociation vessels may also be operated under a partial vacuum up to superatmospheric pressures.

In an optional but preferable step s(iv), the linear polyaromatic compound may subsequently be separated from the resulting mixture by any conventional means, which may occur simultaneously with the pyrolysis operation in the same pyrolysis equipment, such as by vacuum or flash distilling off the olefins along with any impurities at the pyrolysis temperatures, and removing the linear polyaromatic compound as a bottoms from the dissociation zone. The dissociation vessel is operated under slight vacuum to lower the boiling point of the dissociated linear alpha olefin and at a temperature sufficient to dissociate the adduct. Other separation techniques include filtration and centrifugation.

Linear polyaromatic compounds that are removed from dissociation zones in the present invention may be recycled back to the first adducting reaction zone wherein the dissociated linear polyaromatic compounds become a source of the linear polyaromatic compounds used for the adducting reaction in the first adducting zone, or to a mixing zone wherein the feedstock, linear polyaromatic compound recycle, and some fresh linear polyaromatic compound are premixed prior to entering the adduct reaction zone.

The first olefin adduct stream, preferably removed from the separation vessel in step (b) as a liquid bottoms stream, is dissociated in step o(i) in a dissociation zone to form second linear polyaromatic compounds and a second olefin composition. The equipment and processing conditions for conducting the dissociation of the first olefin adduct stream may be the same equipment and processing conditions used to dissociate the second olefin adduct stream.

In an optional step o(ii), the linear polyaromatic compound is separated from the resulting reaction mixture by any conventional means, in the manner described previously in optional step s(iv).

The second olefin composition, whether separated or in a mixture with the dissociated linear polyaromatic compounds, is now enriched in the concentration of olefins over the concentration of olefins in the feedstock. Since the linear polyaromatic compound exhibits a preference towards adducting with linear alpha olefins, the linear alpha olefin concentration in the olefin composition is enriched over the concentration of linear alpha olefins present in the feedstock, based on the weight of all ingredients in the feedstock and the olefin composition. In the case that the feedstock comprises branched olefins, the concentration of branched olefins in the second olefin composition may be reduced over the concentration of branched olefins in the feedstock. In the event that the olefin composition is not separated from the linear polyaromatic compounds prior to feeding the olefin composition to the alpha olefin adducting reaction zone, the concentration of the ingredients in the olefin composition exclusive of the weight and amount of linear polyaromatic compounds, is enriched over the concentration of olefins in the feedstock composition. Further, the concentration of saturated hydrocarbons and the concentration of paraffins in the olefin composition is reduced over that of the feedstock.

In the next step of the process, step ao(i), the second olefin composition is contacted with linear polyaromatic compounds in a third reaction zone under conditions effective to form a reaction mixture comprising linear polyaromatic compound-alpha olefin adducts and internal olefins. Suitable reaction conditions and vessels include those used in the first reaction zone for the feedstock. Since the second olefin composition used as the feed is essentially, if not completely, free of saturated hydrocarbons which would otherwise have an effect of diluting a feedstock, the conversion of olefins in the second olefin composition toward linear polyaromatic compound-linear alpha olefin adducts is higher than the conversion of the feedstock toward linear polyaromatic compound-linear alpha olefin adducts. The preferential selectivity of the linear polyaromatic compound toward linear alpha olefins makes possible the separation between the linear alpha olefins and other species in the olefin composition, such as linear internal olefins, branched internal olefins, and branched alpha olefins.

Once the linear polyaromatic compound-linear alpha olefin adduct has been formed in the third reaction zone in step ao(i), the third adduct stream flows to a third separation vessel in step ao(ii) effective for separating the internal olefins and other unreacted olefins from the linear polyaromatic compound-alpha olefin adducts to form an internal olefin stream and an alpha olefin adduct stream. Suitable methods and conditions for separating the adducts from the reaction mixture include any of the methods used to remove the adducted olefins from the reaction mixture in the first separation zone. Preferably, the reaction mixture is distilled and the internal olefin stream is removed at the overhead of the distillation column, while the linear alpha olefin adducts are removed from the column as a liquid bottoms stream. The separated unreacted internal olefin stream distillate contains some linear internal olefins, branched internal olefins, and branched alpha olefins. The concentration of the linear internal olefins, branched internal olefins, and branched alpha olefins in the internal olefin stream is enriched over the concentration of these olefins in the second olefin composition and in the feedstock.

The rate of recovery of linear alpha olefin adducts in the separation vessel of step ao(ii) is also variable and not limited. In general, the percentage of linear alpha olefin recovered from the olefin composition is set such that from a total of 30 to 60% linear alpha olefins are recovered into the alpha olefin stream, based upon the amount of linear alpha olefin present in the feedstock. If emphasis is placed upon recovering larger amounts of linear alpha olefin into the alpha olefin stream, the percentage of linear alpha olefin recovered from the olefin composition is set such that from a total of greater than 60% to 95% linear alpha olefins based upon the amount of alpha olefins in the feedstock are recovered into the alpha olefin stream.

The linear polyaromatic compound-alpha olefin adducts in the alpha olefin adduct stream removed from step ao(ii) are dissociated in step ao(iii) in a dissociation zone to form linear polyaromatic compounds and an alpha olefin composition. Suitable methods and conditions for dissociating the adducts in the alpha olefin adduct stream include any of the methods mentioned as suitable for dissociating the adducts in the first olefin adduct stream. This stream is enriched in the concentration of linear alpha olefin over the concentration of linear alpha olefin in the second olefin composition. The alpha olefin composition comprises a high concentration of linear alpha olefins, and minor amounts of other olefins such as linear internal olefin, branched internal olefin, and branched alpha olefins. The concentration of these other olefins are reduced in the linear alpha olefin composition over the concentration of these other olefins in the olefin composition. The concentration of linear alpha olefins in the alpha olefin composition is preferably at least 90 wt.%, more preferably at least 95 wt.%, based on the weight of all ingredients in the alpha olefin stream.

Optionally, and preferably, in step ao(iv), the alpha olefin composition is separated and isolated from the dissociated linear polyaromatic compounds. The alpha olefin composition at this step, is removed from the dissociation vessel to form an alpha olefin stream. The alpha olefins may be removed from the dissociation vessel through the overhead of a cracking vessel operated under slight vacuum and at a temperature sufficient to vaporize the alpha olefins and dissociate the adducts. More preferably, the removal of alpha olefins is carried out in the same vessel used to carry out the dissociation reaction in step ao(iii).

If desired, the internal olefin stream may be combined with the second olefin stream, and used for any of the purposes identified below where a high concentration of alpha olefin is not critical to the particular application. Alternatively, a portion or the whole of combined internal olefin stream/second olefin stream, or a portion or the whole of the individual second olefin stream and/or internal olefin stream can be recycled back to the feedstock feed entering the first adducting reaction zone.

For purposes of measuring the percentage reduction of a species in a stream, the concentration (all concentrations determined on the basis of the total weight of all ingredients present in the stream in question) of the species or series of species in question contained in the product stream is subtracted from the concentration of the species or series of species in question contained in the predecessor stream in question, the difference then divided by the concentration of the same species in the predecessor stream multiplied by 100. For purposes of measuring the % enrichment of a species in a stream, the concentration of the species or series of species in the predecessor or feedstock stream is subtracted from the concentration of species or series of species in question contained in the product stream, the difference then divided by the concentration of those same species present in the predecessor feedstock stream and multiplied by 100. For purposes of adding together a series of species, the sum total of the series in the predecessor stream is added, and then the sum total of the species in the product stream are added. The total in the product stream is then compared to the total in the predecessor stream to determine whether the total of the series in the product stream was enriched or reduced over the sum total in the predecessor stream. The appropriate calculation mentioned above is then applied depending on whether the series in the product stream were reduced or enriched.

The concentration of all olefins in the first saturated hydrocarbon stream is preferably reduced through the process of the invention by at least 15%, more preferably at least 30%, most preferably at least

40%, over the concentration of all the olefins in the feedstock.

Since the linear polyaromatic compound is more selective towards adducting with linear alpha olefins relative to other olefins, the concentration of linear alpha olefins in the first saturated hydrocarbon stream in another embodiment are reduced by at least 30%, more preferably by at least 40%, most preferably by at least 50%, over the concentration of linear alpha olefins present in the feedstock stream.

The concentration of saturated hydrocarbons in the first saturated hydrocarbon stream is enriched over the concentration of saturated hydrocarbons in the feedstock stream. The concentration is preferably enriched by at least 5%, more preferably by at least 10%, most preferably by at least 20%, and can be enriched by 100-400%, especially when the concentration of saturated hydrocarbon in the feedstock is low. Generally, the degree of enrichment of saturated hydrocarbon in the saturated hydrocarbon stream varies inversely with the concentration of the saturated hydrocarbons in the particular feedstock employed.

The concentration of saturated hydrocarbons in the second olefin composition is preferably reduced through the process of the invention in only one pass by at least 80%, more preferably by at least 90%, most preferably by at least 95% over the concentration of saturated hydrocarbon in the feedstock, and most preferably by 100%.

The concentration of linear alpha olefins in the second olefin composition is enriched over the concentration of linear alpha olefins present in the feedstock stream. The concentration of linear alpha olefins present in the second olefin composition is preferably enriched by at least 30%, more preferably by at least 40%, most preferably by at least 60%, over the concentration of linear alpha olefins present in the feedstock composition. The process of the invention can achieve concentrations of linear alpha olefin in the olefin composition higher than 80 wt.%, more preferably at least 90 wt.%.

Further, the concentration of all olefins in the second olefin composition is enriched over the concentration of all olefins in the feedstock stream. The degree of olefin enrichment varies inversely with the concentration of olefins present in the feedstock. Preferably, the concentration of all olefins in the second olefin composition is enriched by at least 40%, preferably by at least 60%.

The process of the present invention is capable of separating olefins from saturated hydrocarbons in a feedstock consisting essentially of saturated hydrocarbons and olefins, resulting in a concentration of olefins in the olefin composition ranging from 90% to 100%.

The process of the present invention enriches the concentration of saturated hydrocarbons in the second saturated hydrocarbon stream relative to both the first saturated hydrocarbon stream and the feedstock. The degree of enrichment in the second saturated hydrocarbon stream relative to the first saturated hydrocarbon stream is preferably at least 5%, more preferably at least 10%. In general, the degree of enrichment will not be extremely high at this stage since the first adduction and separation highly concentrates the amount of saturated hydrocarbon in the first saturated hydrocarbon stream.

The concentration of internal olefins in the second saturated hydrocarbon stream is generally reduced by at least 20% over the concentration of internal olefins in the first saturated hydrocarbon stream.

The first olefin composition and second olefin stream are enriched in linear alpha olefins over the concentration of linear alpha olefins in the first saturated hydrocarbon stream and in the feedstock, preferably by at least 50%, more preferably by at least 100%.

The concentration of internal olefins is also enriched in the first olefin composition and second olefin stream over the concentration of internal olefins in the first saturated hydrocarbon stream, preferably by at least 20%, more preferably by at least 50%.

The concentration of linear alpha olefins in the alpha olefin composition is enriched over the concentration of linear alpha olefins in the second olefin composition and in the feedstock. The concentration of linear alpha olefins in the alpha olefin composition is preferably enriched over the concentration of linear alpha olefins in the second olefin composition by at least 15%, more preferably by at least 20%, most preferably by at least 30%. The concentration of all other olefins in the alpha olefin stream is preferably reduced, collectively, by at least 20%, more preferably by at least 30%, most preferably by at least 40%, over the concentration of all other olefins collectively in the second olefin composition. Specifically, the concentration of branched olefins in the alpha olefin stream may be reduced by 60%, more preferably by 75%, and as high as 90% over the concentration of the branched olefins in the feedstock and the second olefin composition.

The concentration of internal olefins in the internal olefin composition is enriched over the concentration of internal olefins in the second olefin composition and in the feedstock. The concentration of internal olefins in the internal olefin composition is preferably enriched over the concentration of internal olefins in the second olefin composition by at least 10%, more preferably by at least 15%, and generally up to 40%. The concentration of branched olefins in the internal olefin composition is preferably enriched by at least 30%, more preferably by at least 50%, most preferably by at least 70%. The concentration of linear alpha olefins in the internal olefin stream is preferably reduced by at least 20%, more preferably by at least 30% over the concentration of linear alpha olefin in the second olefin composition.

The present invention will now be described by way of example with reference to the single figure of the accompanying drawing, which is a block flow diagram of the process of the present invention. Adduction, separation, and dissociation steps occur in each of the individual blocks 1, 2, and 3, and lines 1-8 represent the feed and product streams into and from each block.

Block 1 represents the first adduction zone, separation zone, and dissociation zone. Block 2 represents the second adduction zone, separation zone, and dissociation zone. Block 3 represents the third adduction zone, separation zone, and dissociation zone.

Line 1 represents the composition of the feedstock, line 2 represents the composition of the first saturated hydrocarbon stream, line 3 represents the second olefin composition stream, line 4 represents the second saturated hydrocarbon stream, and line 5 represents the composition of the first olefin composition stream, line 6 represents the internal olefin composition, line 7 represent the linear alpha olefin composition, and line 8 represents an embodiment wherein the second olefin stream and the internal olefin stream are combined.

The modelled mass balances tabulated below prophetically illustrate one of the embodiments of the present invention wherein the recovery of a high concentration of linear alpha olefins in the olefin composition, and recovery of internal olefins and alpha olefins from the first saturated hydrocarbon stream is desirable. Table A tabulates the mass balance based upon the quantity of each species in a feed and product stream, while Table B presents a mass balance based upon the concentration of each species in a feed and product stream. Table A results are reported as moles/unit time, and Table B results are reported as a mole percent composition in each stream. The mass balances are on a calculated basis to illustrate the concept of the present invention, and are based upon the use of anthracene as the linear polyaromatic compound and upon the assumptions noted below Table B.

Table A

	1	2	3	4	5	6	7
Paraffins (linear/branched)	0.15	0.15	0.00	0.15	0.00	0.00	0.00
Saturated alkyl aromatics	0.15	0.15	0.00	0.15	0.00	0.00	0.00
Saturated oxygenates	0.15	0.15	0.00	0.15	0.00	0.00	0.00
Linear alpha olefins	0.20	0.06	0.14	0.00	0.06	0.06	0.08
Linear 2-olefins	0.10	0.05	0.05	0.01	0.05	0.03	0.02
2-methyl 1-olefins	0.25	0.22	0.03	0.11	0.11	0.02	0.00
Total	1.00	0.79	0.21	0.57	0.21	0.11	0.10

Table B

	1	2	3	4	5	6	7
Paraffins (linear/branched)	15%	19%	0%	26%	0%	0%	0%
Saturated alkyl aromatics	15%	19%	0%	26%	0%	0%	0%
Saturated oxygenates	15%	19%	0%	26%	0%	0%	0%
Linear alpha olefins	20%	8%	66%	1%	27%	51%	82%
Linear 2-olefins	10%	7%	22%	1%	22%	27%	16%
2-methyl 1-olefins	25%	28%	12%	20%	51%	22%	2%

Assumptions:

Block 1 recovery set at 70% of the Linear Alpha Olefins in stream 1. Block 2 recovery set at 95% of the Linear Alpha Olefins and 63% of all the olefins contained in stream 2. Block 3 recovery set at 60% of the Linear Alpha Olefins contained in stream 3. Equilibrium is assumed at each stage. Assume the equipment is capable of perfect rejection of saturated hydrocarbons, aromatics, and oxygenates. The ratio of equilibrium constants between linear alpha olefins and linear 2-olefins is set at 2.7. The ratio of equilibrium constants between linear alpha olefins and 2-Methyl 1-Olefins is set at 20. In block 1, the percentage of linear 2-olefin extracted from block 1 is 46%, and of the 2-methyl 1-olefin is 10%. In block 2, 88% of the linear 2-olefins are extracted, and 49% of the 2-methyl 1-olefin are extracted, each based upon the amount of material entering block 2.

The mass balances tabulated below prophetically illustrate another embodiment of the present invention wherein the recovery of higher quantities, albeit at lower concentrations relative to the embodiment above, of linear alpha olefins in the linear alpha olefin stream is desirable. Table C tabulates the mass balance based upon the quantity of each species in a feed and product stream, while Table D presents a mass balance based upon the concentration of each species in a feed and product stream. The mass balances are on a calculated basis to illustrate the concept of the present invention, and are based upon the use of anthracene as the linear polyaromatic compound and upon the assumptions noted below Table D.

Table C

	1	2	3	4	5	6	7
Paraffins (linear/branched)	0.15	0.15	0.00	0.15	0.00	0.00	0.00
Saturated alkyl aromatics	0.15	0.15	0.00	0.15	0.00	0.00	0.00
Saturated oxygenates	0.15	0.15	0.00	0.15	0.00	0.00	0.00
Linear alpha olefins	0.20	0.03	0.17	0.00	0.03	0.04	0.13
Linear 2-olefins	0.10	0.03	0.07	0.00	0.03	0.03	0.04
2-methyl 1-olefins	0.25	0.19	0.06	0.10	0.09	0.05	0.01
Total	1.00	0.71	0.29	0.56	0.15	0.12	0.17

Table D

	1	2	3	4	5	6	7
Paraffins (linear/branched)	15%	21%	0%	26%	0%	0%	0%
Saturated alkyl aromatics	15%	21%	0%	27%	0%	0%	0%
Saturated oxygenates	15%	21%	0%	27%	0%	0%	0%
Linear alpha olefins	20%	4%	58%	0%	19%	35%	75%
Linear 2-olefins	10%	5%	23%	1%	19%	26%	21%
2-methyl 1-olefins	25%	28%	19%	18%	63%	39%	4%

Assumptions:
Block 1 recovery set at 85% of the Linear Alpha Olefins in stream 1. Block 2 recovery set at 95% of the Linear Alpha Olefins and 59% of all the olefins contained in stream 2. Block 3 recovery set at 75% of the Linear Alpha Olefins contained in stream 3. Equilibrium is assumed at each stage. Assume the equipment is capable of perfect rejection of saturated hydrocarbons, aromatics, and oxygenates. The ratio of equilibrium constants between linear alpha olefins and linear 2-olefins is set at 2.7. The ratio of equilibrium constants between linear alpha olefins and 2-Methyl 1-Olefins is set at 20. In block 1, the percentage of linear 2-olefin and 2-methyl 1-olefin extracted from block 1 is 68% and 22% respectively. In block 2, the percentage of the linear 2-olefins and 2-methyl 1-olefin extracted are 88% and 49%, respectively, each based upon the amount of material entering block 2.

An advantage of a Fischer-Tropsch stream is that it contains a mixture of both even and odd carbon, and the process of the present invention produces a stream having even and odd carbon number olefin species at very low to zero amount of saturated hydrocarbons, with high concentrations of linear alpha olefins. The process of the present invention can also provide a Fischer-Tropsch olefin composition having a mixture of internal olefins and/or branched olefins, and linear alpha olefins with low amounts of saturated hydrocarbons.

In one embodiment, the process of the present invention provides a composition, preferably Fischer-Tropsch derived, comprising odd and even numbered olefins, and the composition has an average carbon number ranging from C_5 to C_{20}, preferably C_6 to C_{18}, or more preferably in the C_6 to C_{12} range, comprising:

a) at least two linear alpha olefin species having different carbon chain lengths;

b) the two most predominant (on a mole basis) linear alpha olefin species of said at least two linear alpha olefin species are each within the range of C_5 to C_{20}, or in the case of using a C_6 to C_{18} feedstock, within that range, or in the case of using a C_6 to C_{12} feedstock, within that range, inclusive;

c) said two most predominant linear alpha olefin species are present in an amount of at least 20 wt%, preferably at least 30 wt.%, more preferably at least 40 wt.%, based on the weight of the olefins in the composition;

d) cumulatively, the total amount of linear alpha olefins present in the composition within said range, inclusive, is at least 40 wt.%, preferably at least 60 wt.%, more preferably at least 70 wt.%, and even 90 wt.% or more, based on the weight of the olefins in the composition;

e) one or more odd numbered olefins within said range present in an amount of at least 10 wt.%, preferably at least 20 wt.%, more preferably at least 30 wt.%, and even 40 wt.% or more, cumulative;

f) a cumulative amount of aromatics, saturated hydrocarbons, and oxygenates of 10 wt.% or less, preferably 5 wt.% or less, more preferably 2 wt.% or less, still more preferably 1 wt.% or less, most preferably 0.5 wt.% or less, each based on the weight of the composition; and preferably

g) 6 wt.% or less of branched olefins having branching at the C2 or C3 position relative to the most proximate double bond, more preferably 4 wt.% or less, based on the weight of the composition.

The above mentioned composition preferably has as one of the two most predominant olefin species an odd carbon number linear alpha olefin.

The present invention further provides a composition, preferably Fischer-Tropsch derived, having an average carbon number ranging from C_6 to C_{18} comprising at least two linear alpha olefin species having different carbon chain lengths within said range, inclusive, at least 50 wt.% of linear alpha olefins, where the composition has a most predominant olefin species represented by n carbon numbers, wherein the next most predominant olefin species has either n+1 or n-1 carbon numbers; and wherein said composition comprises 10 wt.% or less, preferably 2 wt.% or less of saturated hydrocarbons; and preferably wherein said composition has branched olefins containing branching at the C_2 or C_3 positions, relative to the most proximate double bond, in an amount of 6 wt.%, more preferably 4 wt.% or less, based on the weight of the composition.

The present invention further provides a process for contacting a linear polyaromatic compound with a feedstock composition comprising linear alpha olefins, internal olefins, and saturated hydrocarbons, separating the olefins from the saturated hydrocarbons in the feedstock composition to form an olefin stream and a saturated hydrocarbon stream, subsequently contacting a linear polyaromatic compound with the saturated hydrocarbon stream comprising linear alpha olefins and internal olefins, and separating the internal olefins and linear alpha olefins from the saturated hydrocarbons in the saturated hydrocarbon stream to form a second saturated hydrocarbon stream and an olefin composition, whereby the concentration of each of internal olefins and linear alpha olefins in the olefin composition is enriched over the concentration of each of internal olefins and linear alpha olefins in the feedstock and in the olefin stream.

The process of the present invention advantageously provides an olefin composition which is highly concentrated in olefins, wherein the concentration of olefins in the olefin composition may be at least 90% and up to 100% olefin purity in the olefin composition. The process of the present invention also provides for the recovery of an olefin composition from a first saturated hydrocarbon stream, which olefin composition is enriched in both linear alpha olefins and internal olefins.

The olefin composition of the present invention is useful as a component in drilling fluids, to react with elemental sulphur to make sulphurized products as extreme pressure agents in metal working fluids, as a co-monomer for the polymerization of polyethylene, as an intermediate in making poly alpha olefins (PAO) used as a lubricant, as a chlorination feed to make polychlorinated hydrocarbons in PVC applications, to react with hydrogen sulphides to make primary and secondary mercaptans as pharmaceutical intermediates and as additives to modify the properties of rubber, as solvents, and as a precursor for the manufacture of plasticizer alcohols and detergent range alcohols and surfactants, which may be derivatized into detergent range sulphates or alkoxysulphates for laundry liquids and powders, dishwashing powders and liquids, bar soap, shampoo, liquid hand soap, and hard surface cleaners.

~~The ranges and limitations provided in the present specification and claims are those which are believed to particularly point out and distinctly claim the present invention. It is, however, understood that other ranges and limitations that perform substantially the same function in substantially the same manner to obtain the same or substantially the same result are intended to be within the scope of the present invention.~~

The present invention will now be illustrated by reference to the following Examples.

EXAMPLE

A Fischer-Tropsch stream comprised of the composition set forth in Table 1 was used as a feedstock. The FT composition was derived by passing syngas over a FT catalyst and subsequently distilling products in the boiling point range of hexyl to undecyl hydrocarbons. This composition was used as the feed. Hydrocarbons in the C_7-C_{10} range were the most abundant.

0.14 moles of anthracene having a 95% purity and 62.5 g of the feedstock were placed in an autoclave. The total olefin content of the charged feed was about 0.15 moles (19.8g), for an olefin/anthracene molar ratio of 1.1:1. The autoclave was sealed and then purged with nitrogen. The autoclave was heated to 255°C for 5.6 hours to form the Diels-Alder adduct between the olefin and the anthracene. The autoclave contents were stirred during heating.

Once the reaction was complete, the autoclave was cooled to 20°C. The product mixture was transferred to a glass flask and the unreacted olefin, saturated hydrocarbons, and unreacted oxygenates were removed by distillation as Sat.Str. 1. The composition of Sat.Str. 1 was determined by gas chromatographic analysis.
The material remaining in the flask consisted of some entrained saturated hydrocarbons, unreacted anthracene, and the anthracene-olefin adduct. The flask and its contents were then heated to a temperature ranging from 310-350°C to dissociate the adduct to anthracene and Olefin 1 product described in Table 1 below. Olefin 1 product was separated and isolated from the anthracene by distillation. 9.3 g of Olefin 1 product was recovered, of which 8.7 grams was olefin. The composition of Olefin 1 product was determined by gas chromatographic analysis.

The results indicate that Sat.Str. 1 is enriched in saturated hydrocarbons (alkanes) over the concentration of saturated hydrocarbons in the feedstock stream, by 24%. The concentration of alpha olefin in the Sat.Str. 1

stream was reduced by 55% over the concentration of alpha olefin in the feedstock.

Olefin 1 product is greatly enriched in alpha olefin content and overall olefin content over the concentration of alpha olefin and overall olefin content in the feedstock stream. Olefin 1 product is enriched in alpha olefin content by 202%, and in overall olefin content, was enriched by 197% ([(88.21 + 5.77) - (27.18 + 4.43)]/(27.18 + 4.43) x 100).

Further, the concentration of saturated hydrocarbon (alkane) in Olefin 1 stream was greatly reduced; by 95%. The presence of saturated hydrocarbons in Olefin 1 product is due to its incomplete removal upon distillation of the unreacted material from the adduct before the dissociation step.

TABLE 1

SEPARATION OF SATURATED HYDROCARBONS FROM OLEFINS

Composition	Total Weight (g)	Alkanes (wt.%)	Internal Olefins (wt.%)	Alpha Olefins (wt.%)	Oxygenates (wt.%)	Unknowns (wt.%)
Feedstock	62.5	63.8	4.43	27.18	3.06	1.45
Sat. Str. 1	44.3	78.25	4.6	12.23	3.01	0.91
Olefin 1	9.3	3.31	5.77	88.21	2.0	0.81

The concentration of saturated hydrocarbons in Sat.Str. 1 stream was enhanced, and the concentration of internal olefins in the Sat.Str. 1 stream was decreased, by separating a portion of the internal olefins in Sat.Str. 1 stream from the saturated hydrocarbons.

44.3 g of Sat.Str. 1 containing 7.5 g (0.059 moles) of olefin was treated with 0.034 moles of anthracene for 6 hours at 255°C in the equipment noted above. The molar ratio of olefin to anthracene was 1.7:1. 30.24 g of unreacted material was removed by distillation as Sat.Str. 2 stream. The bottoms of the distillation column was thermally dissociated at 310-350(C as described above. 1.67 g of the resulting Olefin 2 internal olefin stream was removed by distillation from the dissociated anthracene. Each of Sat.Str. 2 and Olefin 2 were analyzed by gas chromatography. The results are reported in Table 2.

Sat.Str. 2, compared to the feedstock stream Sat.Str. 1, was enriched in alkanes by 7.3%. The concentration of internal olefin in Sat.Str. 2, compared to the feedstock Sat.Str. 1 stream, was increased by 31%.

Olefin 2 was enriched in internal olefins and in alpha olefins over the concentration of each olefin in the feedstock Sat.Str. 1 stream. The internal olefin enrichment was about 98%, and the alpha olefin enrichment was about 570%.

TABLE 2

SEPARATION OF INTERNAL OLEFINS FROM SATURATED HYDROCARBONS

Composition	Total Weight (g)	Alkanes (wt.%)	Internal Olefins (wt.%)	Alpha Olefins (wt.%)	Oxygenates (wt.%)	Unknowns (wt.%)
Sat. Str. 1 Feedstock	44.3	79.25	4.6	12.23	3.01	0.91
Sat. Str. 2	30.24	85.04	6.03	6.54	1.63	0.76
Olefin	1.67	6.80	9.11	82.0	1.26	0.83

The Olefin 1 product was also treated in the following manner to enhance the concentration of alpha olefin. 0.055 moles of anthracene having a 95% purity and 9.3 g of the Olefin 1 product were placed in an autoclave. The total olefin content of the charged feed was about 0.068 moles (8.7g), for an olefin/anthracene molar ratio of 1.2:1. The autoclave was sealed and then purged with nitrogen. The autoclave was heated to 255°C for 6 hours to form the Diels-Alder adduct between the olefin and the anthracene. The autoclave contents were stirred during heating.

Once the reaction was complete, the autoclave was cooled to 20°C. The product mixture was transferred to a glass flask and the unreacted olefin, saturated hydrocarbons, and unreacted oxygenates were removed by distillation as Internal Olefin product. The composition of Internal Olefin product was determined by gas chromatographic analysis, and reported below in Table 3.

The material remaining in the flask consisted of some unreacted anthracene and the anthracene-olefin adduct. The flask and its contents were then heated to a temperature ranging from 250-280°C to dissociate the adduct to anthracene and Alpha Olefin product described in Table 3 below. Nitrogen gas was swept over the anthracene-olefin adduct during the dissociation step to facilitate olefin removal and recovery. Alpha Olefin product was separated and isolated from the anthracene by distillation. 2.6 g of Alpha Olefin product was recovered. The composition of Alpha Olefin product was determined by gas chromatographic analysis.

TABLE 3

SEPARATION OF LINEAR ALPHA OLEFINS FROM THE OLEFIN 1 PRODUCT

Composition	Total Weight (g)	Alkanes (wt.%)	Internal Olefins (wt.%)	Alpha Olefins (wt.%)	Oxygenates (wt.%)	Unknowns (wt.%)
Olefin 1 Feedstock	9.3	3.31	5.77	88.21	2.0	0.81
Alpha Olefin Comp.	2.61	0.00	2.88	96.93	0.05	0.14
Internal Olefin Comp.	1.78	8.12	12.25	78.53	0.9	0.2

Alpha Olefin product, compared to the feedstock stream Olefin 1, was enriched in alpha olefin by 10%. The concentration of internal olefin in Alpha Olefin product, compared to the feedstock Olefin 1 stream, was decreased by 50%.

Internal Olefin product was enriched in internal olefins over the concentration of internal olefins in the Olefin 1 feedstock by 112%.

CLAIMS

1. A process for treating a feedstock comprising saturated hydrocarbons, internal olefins, and alpha olefins, comprising:

(a) contacting the feedstock with a linear polyaromatic compound in a first reaction zone under conditions effective to form a reaction mixture comprising first linear polyaromatic compound-olefin adducts and saturated hydrocarbons;

(b) separating said first olefin adducts from the saturated hydrocarbons in the reaction mixture to form a first olefin adduct stream and a first saturated hydrocarbon stream;

s(i) contacting at least a portion of the first saturated hydrocarbon stream with a linear polyaromatic compound in a second reaction zone under conditions effective to form a reaction mixture comprising second linear polyaromatic compound-olefin adduct and saturated hydrocarbons;

s(ii) separating said second olefin adducts from the reaction mixture in the second reaction zone to form a second olefin adduct stream and a second saturated hydrocarbon stream, wherein the concentration of the saturated hydrocarbons in the second saturated hydrocarbon stream is enriched over the concentration of saturated hydrocarbons in the first saturated hydrocarbon stream, and the concentration of the saturated hydrocarbons in the first saturated hydrocarbon stream is enriched over the concentration of saturated hydrocarbons in the feedstock;

s(iii) optionally dissociating said second olefin adducts to form first linear polyaromatic compounds and a first olefin composition;

s(iv) optionally separating the first linear polyaromatic compound from said first olefin composition.

2. The process of claim 1 comprising:

o(i) dissociating said first olefin adducts to form second linear polyaromatic compounds and a second olefin composition comprising alpha olefins and internal olefins;

o(ii) optionally separating the second linear polyaromatic compounds from said second olefin composition;

ao(i) contacting the second olefin composition with a linear polyaromatic compound in a third reaction zone under conditions effective to form a reaction mixture comprising linear polyaromatic compound-alpha olefin adducts and internal olefins;

ao(ii) separating said alpha olefin adducts, and optionally unreacted linear polyaromatic compounds as well, from the reaction mixture in the third reaction zone to form an alpha olefin adduct stream and an internal olefin stream;

ao(iii) dissociating the alpha olefin adducts to form linear polyaromatic compounds and an alpha olefin composition;

ao(iv) optionally separating the linear polyaromatic compounds from said alpha olefin composition;

whereby the concentration of alpha olefins in the alpha olefin composition is enriched over the concentration of alpha olefins in the second olefin composition, and the concentration of alpha olefins in the second olefin composition is enriched over the concentration of alpha olefins in the feedstock.

3. The process of claim 1 or 2, wherein the feedstock is contacted with a linear polyaromatic compound at a temperature ranging from 150° to 290°C.

4. The process of any one of claims 1 to 3, wherein the feedstock comprises a stream derived from a Fischer-Tropsch process.

5. The process of any one of claims 1 to 4, wherein the feedstock comprises from 15 wt.% to 70 wt.% olefin, based on the weight of all ingredients in the feedstock.

6. The process of any one of claims 1 to 5, wherein the amount of paraffin ranges from 5 to 95 wt.% based on the weight of all ingredients in the feedstock.

7. The process of any one of claims 1 to 6, wherein the feedstock has an average carbon number ranging from C_5-C_{20} and wherein the predominant olefin species in the feedstock is within the range of C_5-C_{20}, inclusive.

8. The process of any one of claims 1 to 7, wherein the total concentration of olefins and the concentration of linear alpha olefins are enriched in the second olefin composition over the concentration of olefins and linear alpha olefins in the feedstock, and the concentration of saturated hydrocarbons are reduced in the second olefin composition over the concentration of saturated hydrocarbons in the feedstock.

9. The process of any one of claims 1 to 8, wherein the linear polyaromatic compound at each step comprises substituted or unsubstituted anthracene and/or benzanthracene.

10. A composition comprising odd and even numbered olefins, said composition having an average carbon number ranging from C_5 to C_{20} comprising:

a) at least two linear alpha olefin species having different carbon chain lengths;

b) the two most predominant (on a mole basis) linear alpha olefin species of said at least two linear alpha olefin species are each within the range of C_5 to C_{20}, inclusive;

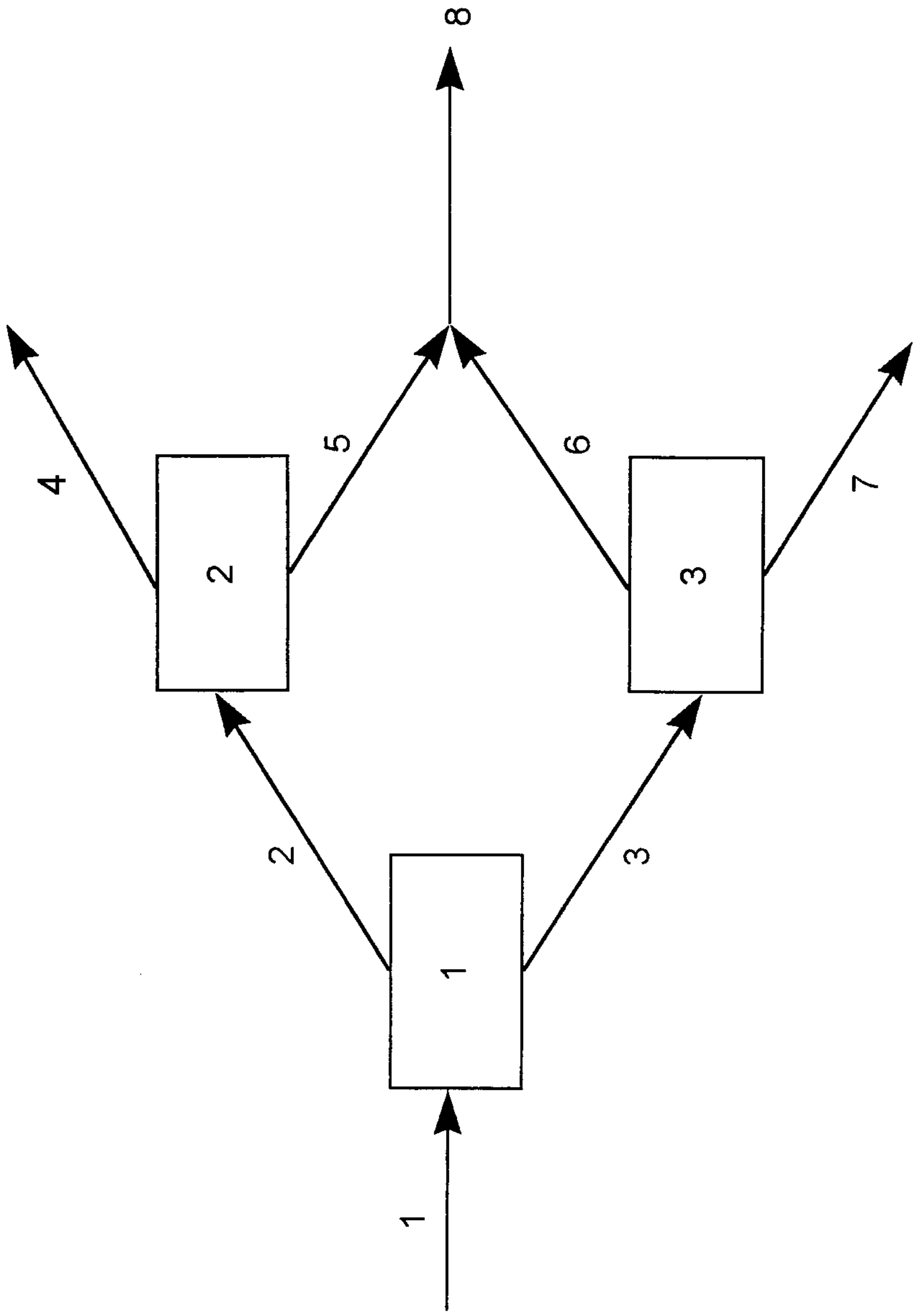
c) said two most predominant linear alpha olefin species are present in an amount of at least 20 wt%, based on the weight of the olefins in the composition;

d) cumulatively, the total amount of linear alpha olefins present in the composition within said range, inclusive, is at least 40 wt.%, based on the weight of the olefins in the composition;

e) one or more odd numbered olefins within said range present in an amount of at least 10 wt.%, cumulative;

f) a cumulative amount of aromatics, saturated hydrocarbons, and oxygenates of 10 wt.% or less, based on the weight of the composition; and optionally

g) 6 wt.% or less of branched olefins having branching at the C2 or C3 position relative to the most proximate double bond, based on the weight of the composition.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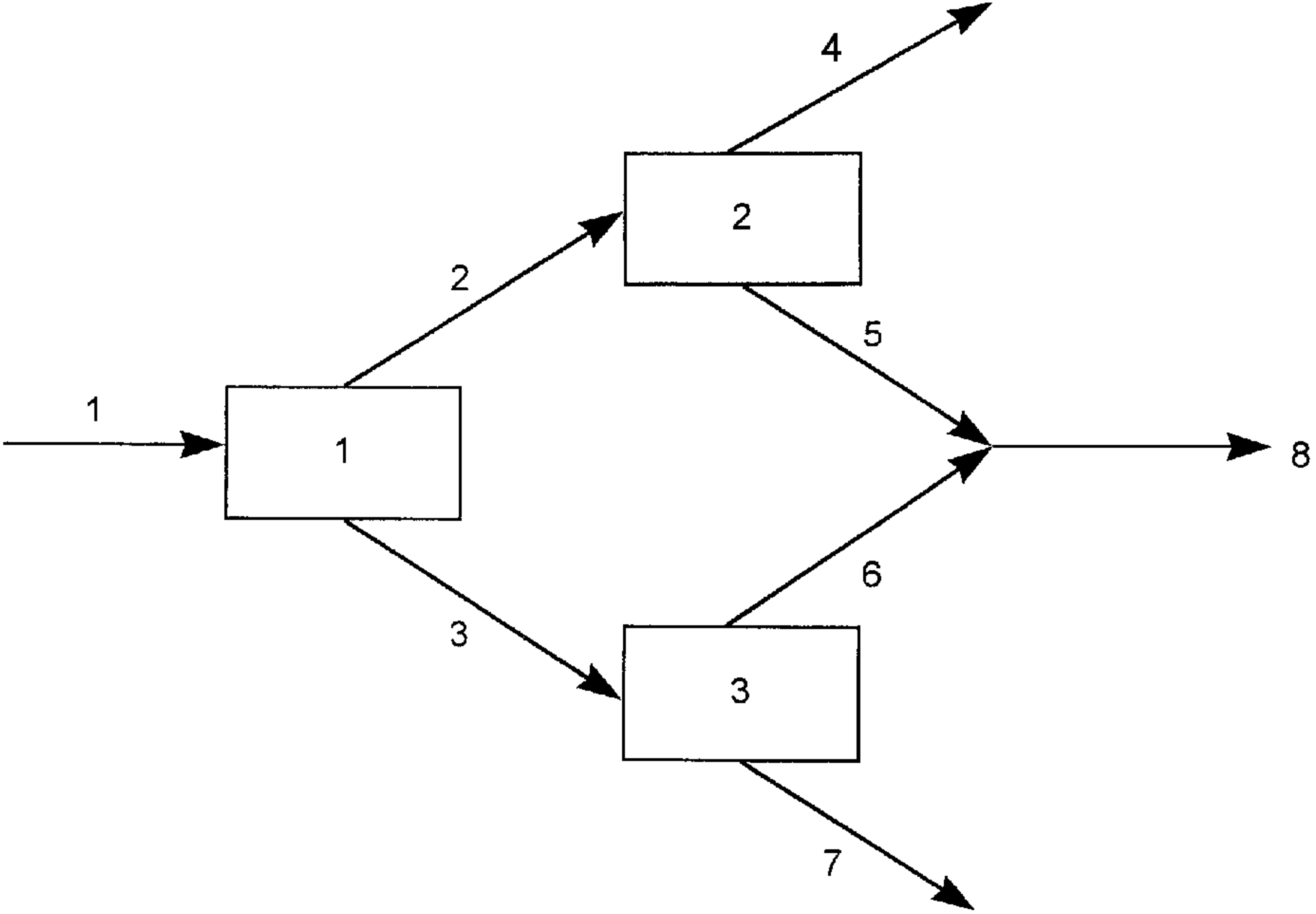
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