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(54) Autothermal cracking process for producing olefins

(57) The present invention relates to a process for the production of olefins, and in particular, a process for the production of olefins, which comprises
a) contacting a paraffinic hydrocarbon containing feed and an oxygen-containing gas with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability at a gas hourly space velocity of at least 100,000 hr^{-1}, a pressure of at least 10 barg and a temperature of at least 750°C to produce a product stream comprising olefins and unreacted oxygen,
b) quenching the product stream by contacting with a quenchant, said contacting occurring within a residence time of less than 50 milliseconds from the front face of the catalyst until contact with the quenchant, to produce a quenched product stream comprising olefins and unreacted oxygen,
c) passing the quenched product stream from step (b) to one or more heat recovery steps in which it is cooled to a temperature of less than 300°C, and
d) subsequently passing the product stream to a contacting tower wherein it is contacted with one or more liquid streams to remove hydrocarbons having 6 or more carbon atoms, and optionally oxygenates, and produce a gaseous product stream at a temperature of less than 100°C,
and wherein the concentration of oxygen in the cooled product stream at the entrance of the contacting tower in step (d) is between 50 and 750 ppm by volume.

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Description

[0001] The present invention relates to a process for the production of olefins, and in particular, a process for the production of olefins by autothermal cracking of a paraffinic hydrocarbon containing feed.

[0002] Autothermal cracking is a route to olefins in which a hydrocarbon feed is mixed with oxygen and passed over an autothermal cracking catalyst. Combustion is initiated on the catalyst surface and the heat required to raise the reactants to process temperature and to carry out the endothermic cracking process is generated in situ. The product stream from the autothermal cracking process typically produces a gaseous stream comprising one or more olefins, hydrogen, carbon monoxide and carbon dioxide. Such a process is described, for example, in EP 0332289 B1; EP 0529793 B1; EP 0709446 A1 and WO 00/14035.

[0003] The product stream exits the catalyst bed at high temperature, typically in excess of 750°C. Especially at high pressure, it is necessary to quench the product stream exiting the catalyst to minimise gas-phase reactions and maintain olefin selectivity. This is described, for example, in EP 0529793 B1.

[0004] The quenching results in a product stream which is still at high temperatures, typically in excess of 500°C, and it is further advantageous to cool this stream further whilst recovering as much of the heat as possible, prior to subsequent separations.

[0005] The product stream exiting the autothermal cracking catalyst may also comprise unreacted oxygen. In particular, oxygen at the catalyst outlet is known to have advantages in preventing coke formation on the catalyst. Generally the art, where it discloses the presence of oxygen downstream of the catalyst, teaches relatively high amounts of oxygen should be present, especially more than 1000ppm, and usually significantly higher. Oxygen further downstream can however be detrimental and must normally be removed before subsequent treatment. WO 2004/033598, for example, describes a process for the removal of oxygen from a product stream comprising olefins, hydrogen and carbon monoxide, and in particular, from the product stream of an autothermal cracking process. In particular, the oxygen is typically present in an amount of at least 1000ppm and a catalyst is used to reduce the oxygen to relatively low levels, typically to levels below 10 ppm.

[0006] It has now been found, however, that it is advantageous to maintain some, but specifically not too much, oxygen throughout the quenching, cooling and initial treatment steps for the product stream from an autothermal cracking process. In particular, by careful selection of the amount of oxygen present downstream of the catalyst coke formation is minimised upstream whilst fouling is minimised downstream without compromising the optimum cooling and separations steps.

[0007] Thus, in a first embodiment, the present invention provides a process for the production of olefins, which process comprises

a) contacting a paraffinic hydrocarbon containing feed and an oxygen-containing gas with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability at a gas hourly space velocity of at least 100,000 hr^{-1}, a pressure of at least 10 barg and a temperature of at least 750°C to produce a product stream comprising olefins and unreacted oxygen,

b) quenching the product stream by contacting with a quenchant, said contacting occurring within a residence time of less than 50 milliseconds from the front face of the catalyst until contact with the quenchant, to produce a quenched product stream comprising olefins and unreacted oxygen,

c) passing the quenched product stream from step (b) to one or more heat recovery steps in which it is cooled to a temperature of less than 300°C
and

d) subsequently passing the product stream to a contacting tower wherein it is contacted with one or more liquid streams to remove hydrocarbons having 6 or more carbon atoms, and optionally oxygenates, and produce a gaseous product stream at a temperature of less than 100°C,
and wherein the concentration of oxygen in the cooled product stream at the entrance of the contacting tower in step (d) is between 50 and 750 ppm by volume.

[0008] In the present invention, oxygen is present throughout the catalyst, in the reactor immediately downstream of catalyst, in the quench and during heat recovery. In particular, oxygen is present during the "higher temperature" steps where it aids in preventing coking. In addition oxygen is also present in the subsequent contacting tower i.e. no oxygen removal need be applied prior to the contacting tower.

[0009] In the present invention, a specific range of oxygen is maintained in the entrance to the contacting tower, with a minimum of 50ppm oxygen and a maximum of 750 ppm oxygen.

[0010] Generally in the art, many experiments are operated at essentially complete oxygen conversion on the catalyst. In processes where the presence of oxygen downstream of the catalyst is disclosed, the general teachings are that relatively high amounts of oxygen should be present, especially more than 1000ppm, usually significantly higher. In these cases, WO 2004/033598 teaches that oxygen removal is required.

[0011] Further, although the teaching of WO 2004/033598 is silent on a specific location for oxygen removal, the general teaching would be that oxygen is detrimental to the downstream processing and therefore to remove essentially all of the oxygen prior to the downstream processing. However, it has now been found that prior to the contacting tower any attempt to treat the product stream to remove oxygen catalytically as in WO 2004/033598 would be prone to result in further cooling of the product stream and condensation of the heavy hydrocarbons in the product stream.

[0012] The specific range of the present invention however has been found to have the advantages of reducing coke formation in the upstream processing whilst avoiding the cost and complexity of providing any oxygen removal such as described in WO 2004/033598 prior to the contacting tower.

[0013] It has been found that at the levels of the present invention the amount of oxygen is sufficient to prevent coking in the upstream steps, but the amount of fouling encountered in the contacting tower is minimised. This means no oxygen removal is required upstream of the contacting tower. In particular, the product stream from the quench may be passed directly to the heat recovery steps, and the product stream from the heat recovery steps may be passed directly to the contacting tower, by which is meant that the respective streams may be passed to the subsequent steps without intermediate treatment. This provides a simpler and more efficient (in terms of heat recovery) process.

[0014] In addition, in a further aspect of the present invention, at the levels of oxygen in the present invention it has also been found that it is not necessary to remove oxygen prior to subsequent downstream processing steps. In particular it has been found that amine-based carbon dioxide removal systems can tolerate such levels of oxygen without significant degradation (and without specific additives to prevent degradation) even when based on short chain alkanolamines, especially ethanolamines, and glycolamines.

[0015] In contrast, oxygen has previously been linked to alkanolamine degradation (e.g. Rooney et al. Hydrocarbon Processing, July 1998, p. 109-113), and higher levels of oxygen would be generally expected to result in amine degradation without specific selection of oxygen-tolerant amines, such as hindered amines, or inclusion of specific additives to protect the amines, both of which are generally much more costly and/or complicated to operate. It has now been found that a more efficient overall treatment process may be achieved by allowing some oxygen to remain in the product stream from the autothermal cracking reaction when it is passed to the amine-based carbon dioxide removal system. This has the advantage that where oxygen is present in the autothermal cracking product stream an oxygen removal system may not be required prior to carbon dioxide removal.

[0016] Thus, in this further aspect of the present invention, the gaseous product stream at a temperature of less than 100°C which exits the contacting tower, and whilst still containing 50 to 750 ppm oxygen, is subsequently passed to an amine-based carbon dioxide removal step. Preferably the amine-based carbon dioxide removal step utilises one or more unhindered alkanolamines, especially alkanolamines having no substituents (alkanol or other) of more than 4 carbon atoms, and preferably one or more amines selected from ethanolamines and glycolamines, such as monoethanol amine, diethanol amine and diglycolamine.

[0017] In the most preferred embodiment of this aspect of the present invention, no specific oxygen removal step, for example no catalytic oxygen removal step, such as of the type described in WO 2004/033598, is provided at any point in the process.

[0018] Step (a) of the process of the present invention comprises contacting a paraffinic hydrocarbon containing feed and an oxygen-containing gas with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability at a gas hourly space velocity of at least 100,000 hr^{-1}, a pressure of at least 10 barg and a temperature of at least 750°C to produce a product stream comprising olefins and unreacted oxygen.

[0019] In step (a) the mixture of a hydrocarbon feed and a molecular oxygen-containing gas is autothermally cracked. Combustion of the hydrocarbon is initiated on the catalyst surface which generates the temperature necessary to carry out the endothermic cracking process.

[0020] The paraffinic hydrocarbon containing feed to the autothermal reactor in step (a) may be any suitable paraffinic hydrocarbon containing feedstock. Typically the paraffinic hydrocarbon has at least 2 carbon atoms, and is most preferably one or more of ethane, propane or butanes, although heavier paraffinic hydrocarbons may be used. The paraffinic hydrocarbon may be used substantially pure or may be in admixture with other hydrocarbons and optionally other materials, for example methane, nitrogen, carbon monoxide, carbon dioxide, and steam.

[0021] The molecular oxygen-containing gas is suitably either oxygen or air.

[0022] The hydrocarbon and oxygen-containing gas may be contacted with the catalyst bed in any suitable molar ratio, provided that the ATC product stream comprising olefins is produced. The preferred stoichiometric ratio of hydrocarbon to oxygen is 5 to 16, preferably, 5 to 13.5 times, preferably, 6 to 10 times the stoichiometric ratio of hydrocarbon to oxygen required for complete combustion of the hydrocarbon to carbon dioxide and water.

[0023] In a preferred embodiment, hydrogen is co-fed to the reaction. Combustion of hydrogen to generate heat reduces the amount of hydrocarbon combustion necessary, improving the selectivity of the process. Suitably, the molar ratio of hydrogen to oxygen is in the range 0.2 to 4, preferably, in the range 0.2 to 3.

[0024] The catalyst used may be any catalyst capable of supporting combustion beyond the fuel rich limit of flammability. The catalyst may comprise a Group VIII metal as its catalytic component. Suitable Group VIII metals include platinum, palladium, ruthenium, rhodium, osmium and iridium. Rhodium, and more particularly, platinum and palladium are preferred. Suitable catalysts may be based on promoted or modified Group VIII metals, such as described, for example, in WO 00/14035 and

WO 00/14037.

[0025] The catalyst may be unsupported, such as in the form of a metal gauze, but is preferably supported. Any suitable support material may be used, such as ceramic or metal supports, but ceramic supports are generally preferred. Where ceramic supports are used, the composition of the ceramic support may be any oxide or combination of oxides that is stable at high temperatures of, for example, between 600°C and 1200°C. The support material preferably has a low thermal expansion co-efficient, and is resistant to phase separation at high temperatures.

[0026] Suitable ceramic supports include cordierite, mullite, lithium aluminium silicate (LAS), alumina (e.g. α-Al_2O_3), stabilised zirconias, alumina titanate, niascon, and calcium zirconyl phosphate. The ceramic supports may be wash-coated, for example, with γ-Al_2O_3.

[0027] The support is preferably in the form of a foam or a honeycomb monolith.

[0028] The autothermal cracking reaction of step (a) is operated at a pressure of at least 10barg. Preferably the autothermal cracking reaction is operated at a pressure of between 15-40barg and advantageously between 20-30barg e.g. 25barg.

[0029] The subsequent quenching, cooling and contacting are advantageously operated at as close to the elevated pressure of step (a) as possible (some small drops in pressure inherently occur moving through the process). Thus, steps (b), (c) and (d) are each operated at a pressure of at least 10barg, preferably at a pressure of between 15-40barg and advantageously between 20-30barg e.g. 25barg.

[0030] The present invention is particularly relevant at these elevated pressures because of the requirements to rapidly quench to maintain olefin yield, to relatively rapidly subsequently cool to optimise heat recovery and to relatively rapidly remove heavy components (to avoid them condensing in an "uncontrolled" manner). Therefore, it has been found that oxygen removal prior to the contacting tower is particularly disadvantageous when operating at pressure. The present invention is also particularly relevant at elevated pressures because any potential detrimental effects of higher oxygen may be expected to be worse as pressure increases. This would again teach to remove any oxygen earlier, but as noted above earlier oxygen removal is disadvantageous.

[0031] Step (a) is operated at a temperature of at least 750°C. For avoidance of doubt, this temperature, as used herein, is the temperature at the exit of the catalyst (catalyst exit temperature). Suitably the catalyst exit temperature is in the range 750°C to 1200°C. Preferably, the autothermal cracking step is carried out at a catalyst exit temperature of at least 850°C, more preferably in the range 850°C to 1050°C and, most preferably, in the range 850°C to 1000°C.

[0032] The hydrocarbon feed and the molecular oxygen-containing gas are fed to the autothermal cracker in admixture under a Gas Hourly Space Velocity (GHSV) of at least 100,000 hr^{-1}. Preferably, the GHSV exceeds 200,000 hr^{-1}, especially greater than 1,000,000 hr^{-1}. The most preferred gas hourly space velocity is a pressure dependent gas hourly space velocity, usually of greater than 10,000 h^{-1} $barg^{-1}$, preferably greater than 20,000 h^{-1} $barg^{-1}$ and, most preferably, greater than 100,000 h^{-1} $barg^{-1}$. For example, at 20 barg pressure, the gas hourly space velocity is most preferably greater than 2,000,000 h^{-1}.

[0033] In the present invention, the autothermal cracking reaction in step (a) is operated such that less than 100% oxygen conversion is obtained. This is achieved by controlling the severity of reaction, for example, by control of the hydrocarbon to oxygen ratio and the space velocity. The conversion of oxygen is also a strong function of the time until the reaction is quenched, which necessitates the relatively rapid quenching of the product stream from step (a) in step (b) according to the process of the present invention.

[0034] In contrast, without the rapid introduction of the product stream to the quench according to the present invention, continued reaction of in the gas phase (at the pressures according to the present invention) may rapidly reduce the concentration of any oxygen present to well below 50 ppm. For comparison, without a quench step (b) it is believed that the residual oxygen level obtained will generally be less than 10ppm.

[0035] Without wishing to be bound by theory, thereafter any changes in oxygen in the product stream are believed to be relatively slow compared to those at the higher temperature pre-quenching, although it is still advantageous to cool relatively quickly in the one or more heat recovery steps of step (c) to maximise heat recovery.

[0036] In a particular embodiment of the present invention, the concentration of oxygen in the cooled product stream at the entrance of the contacting tower or a parameter corresponding thereto is specifically used as a control parameter for the autothermal cracking process to maintain the concentration of oxygen at the entrance to the contacting tower in the desired range (e.g. 50 to 750 ppm). By this is meant that the concentration of oxygen or the corresponding parameter is determined and any variations from the desired range are reacted to by changing the severity of the reaction to maintain the concentration of oxygen at the entrance to the contacting tower in the desired range, typically by adjusting the hydrocarbon to oxygen ratio and/or the space velocity.

[0037] In this embodiment, the concentration of oxygen in the cooled product stream at the entrance of the contacting tower may be measured and used directly, for example by use of a suitable oxygen analyser, or the concentration of oxygen in the cooled product stream at the entrance of the contacting tower may be calculated from measurements made elsewhere in the process which can be related to the concentration of oxygen at the entrance of the contacting tower, for example measurement at the exit to the contacting tower. (Little if any change in oxygen is expected in the contacting tower under normal operation.)

[0038] Alternatively, a parameter corresponding to the concentration of oxygen in the cooled product stream at the entrance of the contacting tower may be used as the control parameter. Examples of such "corresponding parameters" include the concentration of oxygen downstream of the entrance to the contacting tower, for example at the exit to the contacting tower, since, as previously noted, little if any change in oxygen is expected in the contacting tower under normal operation, and so this measurement can readily be used instead

[0039] Surprisingly, it has been found that the minimum value of 50ppm of oxygen at the entrance to the contacting tower can be used to minimise coking upstream over a range of elevated pressure and other reaction conditions. In particular, as the reaction conditions are varied a number of factors may affect the severity of the reaction. As O/C ratio or pressure increase, for example, the minimum amount of oxygen required at the catalyst exit to prevent coking of the catalyst also tends to increase. However, at these higher severity conditions the amount of gas phase reaction prior to quenching also increases, which has been found to result in a similar minimum oxygen level being obtained downstream. This means that the minimum downstream oxygen concentration of at least 50ppm according to the present invention may be used, over a wide range of conditions, to ensure that coking of the catalyst is minimised even though the oxygen at the catalyst exit may vary significantly.

[0040] In step (b) of the process of the present invention the product stream is quenched by contacting with a quenchant, said contacting occurring within a residence time of less than 50 milliseconds from the front face of the catalyst until contact with the quenchant. As used herein, this residence time is a nominal residence time calculated using the measured catalyst exit temperature and reactor pressure, and based on the volume of product stream (whilst allowing for volume occupied by the bed). For the purposes of this calculation and this residence time as defined herein, therefore, it is assumed that the product stream is formed and the temperature rises effectively instantaneously on entry to the catalyst.

[0041] Step (b) produces a quenched product stream comprising olefins and unreacted oxygen.

[0042] Any suitable quenchant may be used. The quenchant may be a gas or a liquid. The quenchant may be an inert quenchant or may be a reactive quenchant, for example, a hydrocarbon, especially an alkane or mixture of alkanes which could crack to produce olefin. When the quenchant is gas it is preferably an inert gas. Preferably the quenchant is a liquid e.g. water.

[0043] The quenchant, such as water, is usually injected at a pressure higher than the pressure of the gaseous product stream, such as 100 barg, and is usually injected at a temperature of between 100-400°C and preferably between 200-350°C e.g. 300°C. Injecting the quenchant at high pressure and high temperature ensures that a large proportion of the quenchant instantaneously vaporizes at the reactor pressure and therefore provides a very rapid temperature drop in the gaseous product stream.

[0044] The product stream is preferably quenched on exiting the catalyst to a temperature at least 100°C below the catalyst exit temperature. Preferably, the autothermal cracking step (a) is carried out at a catalyst exit temperature of at least 850°C and the product stream is quenched on exiting the catalyst such that the temperature of the product stream is reduced to less than 750°C. Preferably, the contacting of the quenchant with the product stream occurs within a residence time of less than 25 milliseconds from the front face of the catalyst until contact with the quenchant.

[0045] The quench system preferably comprises one or more more quench tubes into which the product stream is passed and wherein it is contacted with the quenchant, such as described in PCT/GB2006/004800.

[0046] In particular, each quench tube preferably has a length, L, a diameter, D, and at least one quenchant inlet per tube which inlet passes quenchant into the tube from the side of said tube, and wherein,

[0047] D is between 0.04 and 0.10 m and L/D is at least 5.

[0048] D is preferably between 0.04 and 0.08m.

[0049] L/D is preferably at least 10. Preferably, L/D is less than 15.

[0050] By "passes quenchant into the tube from the side of said tube" is meant that the quenchant is introduced at an angle, suitably at least 30°, especially at least 45°, and preferably approximately 90°, compared to the longitudinal axis of the quench tube. This provides better mixing, and hence more rapid cooling, than a quenchant inlet injecting quenchant along the axis of the quench tube i.e. in parallel to the general direction of flow through the tube.

[0051] Preferably, two to four quenchant inlets are provided per quench tube, suitably spaced approximately equidistantly around the quench tube.

[0052] Each quenchant inlet may comprise a single nozzle or a number of nozzles, for example 2 to 7 nozzles. Typically, they will be close packed to minimise the size of the inlet nozzle arrangement.

[0053] In use, each quench tube may be defined by an inlet end, at the end to which the stream to be quenched is introduced and an outlet end at the other end. The quenchant inlet (at least the first nozzle where more than one nozzle is provided per inlet) is generally provided in the portion of each quench tube closest to the inlet end, so that the quenchant can be contacted with the stream to be cooled as quickly as possible after it enters the quench tube.

[0054] Typically at least 2 tubes are provided, usually at least 3. Preferably, the number of tubes is less than 20, more preferably less than 10.

[0055] The quenched product stream will comprise one or more mono-olefins, unreacted oxygen, carbon monoxide and carbon dioxide. The one or more olefins typically comprise ethene, propene, butene and higher olefins. In addition, the product stream will generally also comprise hydrogen, water, oxygenates, alkanes, such as methane, and heavier hydrocarbons, especially those having 6 or more carbon atoms, such as aromatics.

[0056] In step (c), this stream is passed to one or more heat recovery steps in which it is cooled to a temperature of less than 300°C. Any suitable heat recovery steps may be used, but typically comprise one or more heat exchangers, especially at least one waste heat boiler.

[0057] Most preferably the product stream from the quench may be passed directly to the one or more heat recovery steps without any intermediate treatment. This maximises the potential heat recovery. Preferably, the product stream is passed into the first of the one or more heat recovery steps with a mean residence time of less than 100ms, and preferably with a maximum residence time of less than 100ms, said residence time being as measured from the exit of the quench and into the first of the one or more heat recovery steps. (This residence time can be readily calculated based on the measured temperature and pressure, and on the volume of the stream at this stage).

[0058] A particularly preferred heat recovery system is described in PCT/GB2007/002191.

[0059] Step (c) results in a cooled product stream at a temperature of less than 300°C. As noted previously, it is believed that any changes in the concentration of oxygen in the product stream at this stage are relatively slow compared to those at the higher temperature pre-quenching, and thus in the absence of any oxygen removal step between the heat recovery steps of step (c) and the subsequent contacting tower (as in the present invention) the stream exiting step (c) also comprises between 50 and 750 ppm by volume oxygen. No other product separation occurs during cooling, and hence the cooled product stream comprises all the components present in the quenched product stream and in essentially the same amounts, including oxygenates and hydrocarbons having 6 or more carbon atoms.

[0060] In step (d) of the process of the present invention, the cooled product stream at a temperature of less than 300 °C is passed to a contacting tower wherein it is contacted with one or more liquid streams to remove hydrocarbons having 6 or more carbon atoms, and optionally oxygenates, and produce a gaseous product stream at a temperature of less than 100°C.

[0061] Suitably, the one or more liquid streams include at least a first liquid hydrocarbon stream, which is preferably a stream of one or more hydrocarbons which are liquid at 40°C (at atmospheric pressure). The first liquid hydrocarbon stream may be a single (liquid) hydrocarbon. Preferably, however, a mixture of hydrocarbons is used. The hydrocarbon(s) preferably have a low volatility. Suitable mixtures are gasoline, diesel and gas oils, and mixtures having properties similar to such streams. (Hereinafter, reference to gasoline, diesel and gas oils, includes reference to mixtures having properties similar to such streams.)

[0062] The first liquid hydrocarbon stream preferably comprises, at least in part, hydrocarbons having 6 or more carbon atoms and produced in the autothermal cracking process itself which have been previously removed and can be recycled.

[0063] The first liquid hydrocarbon stream will absorb at least some of the hydrocarbons having 6 or more carbon atoms present in the cooled product stream. Typical hydrocarbons having 6 or more carbon atoms which may be present include paraffinic, aromatic and olefinic hydrocarbons, such as hexane, toluene, naphthalene and benzene. If not removed these components tend to accumulate in subsequent processing steps. The use of a first liquid hydrocarbon stream has the advantage that such components are generally more soluble in the first liquid hydrocarbon stream than in water, and, hence, are more effectively removed from the first gaseous stream than using water.

[0064] Preferably at least 80% of the hydrocarbons having 6 or more carbon atoms present in the cooled product stream from step (c) are removed in step (d).

[0065] In a preferred embodiment, step (d) also removes at least some of the oxygenates present in the cooled product stream from step (c). The oxygenates present typically comprise one or more of ethers, aldehydes, ketones, esters, carboxylic acids and alcohols.

[0066] Whilst the use of a first liquid hydrocarbon stream may remove some oxygenates, principally the "heavier" oxygenates, this oxygenate removal is preferably achieved by use of a first aqueous stream in the contacting tower. The first aqueous stream is preferably relatively clean water, by which is meant comprises at least 95wt% water, such as at least 98wt% water. The water is preferably substantially free of any components that would react or complex with carbon dioxide, since it is generally preferred to separate the carbon dioxide subsequent to the contacting tower. The water may, however, contain components which aid oxygenate removal, as long as such components do not react or complex with the carbon dioxide to any great extent under the conditions used in the contacting step.

[0067] Preferably, the process of step (d) of the present invention removes at least 80% by weight of the oxygenates present in the cooled product stream from step (c), preferably at least 95% by weight.

[0068] In a preferred embodiment, step (d) comprises contacting the cooled product stream from step (c) with both a first hydrocarbon stream and a first aqueous stream. A most preferred contacting to remove both oxygenates and hydrocarbons having 6 or more carbon atoms is described in PCT/GB2006/004650.

[0069] The concentration of oxygen in the cooled product stream at the entrance of the contacting tower in step (d) is between 50 and 750 ppm by volume. Preferably, the concentration of oxygen is less than 500ppm by volume, and most preferably less than 350ppm by volume. Suitably the concentration of oxygen is at least 100ppm by volume.

Claims

1. A process for the production of olefins, which process comprises

a) contacting a paraffinic hydrocarbon containing feed and an oxygen-containing gas with a catalyst capable of supporting combustion beyond the normal fuel rich limit of flammability at a gas hourly space velocity of at least 100,000 hr^{-1}, a pressure of at least 10 barg and a temperature of at least 750°C to produce a product stream comprising olefins and unreacted oxygen,
b) quenching the product stream by contacting with a quenchant, said contacting occurring within a residence time of less than 50 milliseconds from the front face of the catalyst until contact with the quenchant, to produce a quenched product stream comprising olefins and unreacted oxygen,
c) passing the quenched product stream from step (b) to one or more heat recovery steps in which it is cooled to a temperature of less than 300°C
and
d) subsequently passing the product stream to a contacting tower wherein it is contacted with one or more liquid streams to remove hydrocarbons having 6 or more carbon atoms, and optionally oxygenates, and produce a gaseous product stream at a temperature of less than 100°C,
and wherein the concentration of oxygen in the cooled product stream at the entrance of the contacting tower in step (d) is between 50 and 750 ppm by volume.

2. A process as claimed in claim 1 wherein no specific oxygen removal is provided upstream of the contacting tower.

3. A process according to claim 1 or claim 2 wherein the quenched product stream from step (b) is directly to the heat recovery steps in step (c), and the product stream from the heat recovery steps in step (c) is passed directly to the contacting tower in step (d) without intermediate treatment.

4. A process according to any one of the preceding claims wherein no catalytic oxygen removal step is provided at any point in the process.

5. A process according to any one of the preceding claims wherein steps (b), (c) and (d) are each operated at a pressure of at least 10barg.

6. A process according to any one of the preceding claims wherein step (b) comprises a quench system which comprises one or more more quench tubes into which the product stream is passed and contacted with the quenchant.

7. A process according to any one of the preceding claims wherein the product stream is passed into the first of the one or more heat recovery steps with a mean residence time of less than 100 ms, said residence time being as measured from the exit of the quench and into the first of the one or more heat recovery steps.

8. A process according to any one of the preceding claims wherein step (d) comprises contacting the cooled product stream from step (c) with both a first hydrocarbon stream and a first aqueous stream.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 25 2567

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,Y	EP 0 529 793 A (BRITISH PETROLEUM CO PLC [GB]) 3 March 1993 (1993-03-03) * claims 1,7 * * page 3, lines 4-7,22-24,28-31,40-43 * -----	1-8	INV. C10G11/22 C10G70/04 C10G70/06 B01D53/14 B01D53/72
Y	WO 03/066551 A (BP CHEM INT LTD [GB]; BURNS ANDREW LINDSAY [GB]; GRIFFITHS DAVID CHARL) 14 August 2003 (2003-08-14) * claim 1; figure 1 * * page 6, lines 7-12 * * page 8, lines 30-33 * * page 10, lines 2-9,19-23 * * page 13, lines 16-32 * -----	1-8	
Y	EP 0 709 446 A (BP CHEM INT LTD [GB]) 1 May 1996 (1996-05-01) * claim 1 * * page 3, lines 23-27 * * page 4, lines 42-52 * -----	1-8	
A	US 4 125 568 A (THERIOT WALTER A ET AL) 14 November 1978 (1978-11-14) * claim 1 * -----	1,8	TECHNICAL FIELDS SEARCHED (IPC) C10G B01D
A	US 2 734 809 A (PETTYJOHN ELMORE ET AL) 14 February 1956 (1956-02-14) * claim 1; figure * -----	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	13 December 2007	Harf, Julien

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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