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(71) Applicant: **Linde Aktiengesellschaft**

80331 München (DE)

(72) Inventors:

- **Schreiner, Bernhard, Dr.**
82041 Oberhaching (DE)
- **Gusberti, Ambrogio**
81669 München (DE)

(74) Representative: **Gellner, Bernd**

Linde AG
Legal Services Intellectual Property
Dr.-Carl-von-Linde-Strasse 6-14
82049 Pullach (DE)

(54) **Oxycombustion process for heating a feedstock**

(57) The invention relates to a method for treating a feed containing hydrocarbons with hydrogen wherein a fuel is combusted in a furnace by means of one or more burners, said feed is preheated by indirect heat exchange with the reaction products and/or the reaction heat from the combustion of said fuel to obtain a preheated feed,

said preheated feed is passed in a reactor containing a catalyst and said preheated feed is treated with hydrogen in said reactor and wherein said fuel is combusted in a reaction with an oxidant comprising more than 21 % by volume of oxygen.

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Description

[0001] The invention relates to a method for treating a feed containing hydrocarbons with hydrogen wherein a fuel is combusted in a furnace by means of one or more burners, said feed is preheated by indirect heat exchange with the reaction products and/or the reaction heat from the combustion of said fuel to obtain a preheated feed, said preheated feed is passed in a reactor containing a catalyst and said preheated feed is treated with hydrogen in said reactor.

[0002] Since the early 1950s several influences have triggered the development of various hydrotreating processes. The increased production of high-sulfur crude oils and consequently the need to remove sulfur compounds from oil fractions, more stringent product specifications because of environmental requirements, and the production of increased quantities of cracked material from conversion processes boosted the installation of adequate hydrotreating capacities in refineries. Hydrotreating plants represent the highest capacities of all secondary refining processes worldwide.

[0003] The term hydrotreatment shall mean a catalytic process wherein a hydrocarbons containing feed is reacted with hydrogen. This reaction may especially be used to purify the feed stream from nitrogen and/or sulfur or to crack heavy hydrocarbons into simpler molecules such as light hydrocarbons by breaking of carbon-carbon bonds. One important example of hydrotreating is the removal of sulfur components (hydrosulphurization or HDS) by reaction with hydrogen in the presence of a suitable catalyst, to form hydrogen sulfide. The hydrogen sulfide is removed from the process gas stream using a solvent (e.g., amine) wash and is then converted into elemental sulfur in a Claus plant.

[0004] Hydrotreating processes are applied to achieve the following objectives:

- Removal of sulfur, nitrogen, oxygen, and arsenic compounds from reformer feedstock (naphtha) to prevent poisoning of the platinum catalysts in the reformers. Hydrogenation of the unsaturated hydrocarbons of cracked naphtha to minimize coking of the reformer catalysts.
- Increase in the thermal stability of jet fuels. Additionally, an improvement of the smoke point can be aimed at by (partial) hydrogenation of aromatics.
- Removal of sulfur compounds from middle distillates (gas oils) to achieve blending qualities for diesel fuels and light heating oil. Unsaturated hydrocarbons in cracked gas oils are hydrogenated to improve the color stability and reduce the coking tendency of the products.
- Removal of sulfur, nitrogen, and metal compounds from catalytic cracking feedstock (vacuum gas oils, atmospheric residues) to limit the catalyst deactivation by nitrogen and metals, and to yield lower sulfur contents in the cracked products.

- Reduction of the sulfur content of heavy fuel oils.
- Hydrogenation of diolefins in pyrolysis gasoline (originating from ethylene production plants) to avoid the formation of gum which deteriorates the stability of these gasoline.
- Improvement of odor, color, and oxidation stability of lubricating oils by hydrofinishing (mild hydrotreating). Dearomatization and removal of sulfur, nitrogen, and oxygen compounds by deep hydrogenation (high-pressure hydrotreating) of lubricating oils

[0005] The present invention is related to the above mentioned processes in general and in particular to the removal of sulfur, nitrogen and metal compounds contained in the treated hydrocarbon containing feeds in particular within a refinery. The invention is also related to hydrocracking, whereby low weight hydrocarbons are produced by cracking long-chained hydrocarbons.

[0006] According to the prior art the feed containing hydrocarbons is preheated in a furnace comprising one or more burners. The feed is preheated by indirect heat exchange with the reaction products from the combustion of a fuel and/or with the reaction heat. Gaseous or liquid hydrocarbons are used as fuel and combusted with air in one or more burners.

[0007] The preheated feed is then passed to a reactor where it is treated with hydrogen in the presence of a suitable catalyst. The reaction of the hydrocarbons with the hydrogen requires a certain temperature to accomplish the desired hydrogenation reaction. The design of the furnace and the burner or burners is usually set up in a way that the feed is heated to a temperature sufficient for the downstream hydrogenation reaction.

[0008] With time the performance of the catalyst decreases. In order to compensate for this decrease the temperature of the hydrocarbon feed can be increased. Further, in cases when the feed composition changes an increase in the preheating temperature might be necessary.

[0009] In the prior art such a temperature increase is achieved by burning more fuel which in turn has to be accomplished by the addition of more oxidant. Thus, the amount of combustion air has to be increased. However, sometimes the amount of combustion air which can be supplied to the burners is limited in particular by the limits of the blower which provide the air or by the design limit of the burners or by the furnace which does not allow additional gas flow.

[0010] The object of the present invention is to provide a method of the above mentioned type which ensures a flexible and easy adjustment of the preheat temperature and thereby the hydrogenation reaction temperature.

[0011] The object is solved by the features of claim 1. Advantageous embodiments of the invention are claimed by the dependent claims.

[0012] The inventive method for treating a feed containing hydrocarbons with hydrogen comprises the following steps:

A fuel is combusted in a furnace by means of one or more burners. The fuel is combusted in a reaction with an oxidant comprising more than 21 % by volume of oxygen, for example with oxygen-enriched air, technical oxygen or pure oxygen. The term technical oxygen shall in particular include an oxidant with an oxygen content of at least 90% by volume, at least 95% by volume or at least 98 % by volume.

[0013] Said combustion of the fuel is carried out in a furnace upstream of the reactor where the actual treatment of the hydrocarbon containing feed with hydrogen is carried out. In the furnace the feed is preheated by indirect heat exchange with the reaction products and/or the reaction heat from the combustion of the fuel. As a result a preheated feed of hydrocarbons is obtained.

[0014] That preheated feed is then passed to a downstream reactor containing a suitable catalyst. In the reactor the preheated feed is treated with hydrogen in the presence of said catalyst.

[0015] According to the invention the fuel is combusted in a reaction with oxygen enriched air, technical oxygen or pure oxygen. The use of oxygen as claimed ensures an easy adjustment of the preheating temperature and thereby the temperature in the downstream reactor (hydrogenation temperature). Only a small amount of additional oxygen provided to the combustion increases the preheating temperature. The design limits of the burner/s or the blower/compressor do no longer limit the preheating temperature. The use of oxygen as claimed increases the combustion temperature or in particular the temperature of the flame and not necessarily the size of the flame.

[0016] Additionally the throughput of the hydrocarbon feed can be raised because of the increased amount of heat provided by the oxygen enriched combustion according to the invention. Therefore the whole capacity of the process and the plant is increased by minor investments.

[0017] According to an embodiment of the invention oxygen, preferably technical oxygen, is mixed with combustion air directly at or in the burner/s to generate oxygen enriched air. This embodiment is the easiest way to benefit on the inventive thought. Only very little changes to an existing process and existing equipment are required. The flame temperature could be sensitively regulated by the amount of oxygen mixed into the combustion air.

[0018] In general, the temperature of the preheated feed and thereby the hydrogenation temperature in the reactor is controlled by the amount of said oxidant comprising more than 21 % by volume of oxygen supplied to the combustion reaction of the fuel. Preferably, the amount of oxidant is controlled in such a manner that a reaction temperature between 280°C and 480°C is achieved at the inlet of the reactor.

[0019] It is also possible to introduce the additional amount of oxygen directly into the combustion zone. The

combustion zone shall mean the zone or region where the fuel and the oxidant leaving the burner react with each other. The oxidant provided to the burner as such can be air, oxygen-enriched air or oxygen. In this case an additional oxidant stream, preferably technical oxygen or pure oxygen, is injected directly into the combustion zone. The additional oxidant mixes with the fuel and the oxidant supplied to the burner and thereby increases the total oxygen content for the combustion of the fuel.

[0020] In a preferred embodiment that additional oxidant is supplied to the combustion zone via the pilot burner. Many burners comprise a pilot burner in order to provide a flame to ignite said burner. According to this embodiment the pilot burner is not only used to ignite the burner but also to provide additional oxygen to the combustion zone when the burner is operating.

[0021] Advantageously the preheating temperature of the feed and thereby the hydrogenation temperature in the reactor is enhanced in a certain time period prior to a regular shutdown of the plant, wherein the hydrogenation method is operated, to deactivate the catalyst earlier.

[0022] In the prior art the catalyst load of the hydrogenation reactor is changed periodically. Usually the changes are correlated with the deactivation of the catalyst but the change date is usually influenced by organizational reasons in particular in case of a shut-down of the whole complex. According to a preferred embodiment of the invention the preheating temperature and thereby the reaction temperature is enhanced in a certain period before a shut-down of the plant. The enhanced reaction temperature leads to a higher performance of the catalyst related to an earlier deactivation. In this embodiment the reaction temperature is adjusted in a way, that the catalyst reaches its deactivation (End Of Run) state at the same time as the regular shut-down is planned. The higher performance in the certain time period before the regular shut-down is the great benefit of this embodiment.

[0023] The performance of the catalysts used in the hydrotreatment reaction decreases with time. In order to compensate for this decrease it is possible to reduce the flow of the feed stream. However, this would mean reduced output from the hydrogenation reactor. In a preferred embodiment of the invention the temperature of the feed stream to the reactor is increased by increasing the oxygen content of the oxidant reacting with the fuel. Thereby, the run time of the catalyst can be increased in order to counterbalance the deterioration of the catalyst.

[0024] Preferably the amount of oxygen is regulated in way, that a reaction temperature of 330 °C to 340 °C in the hydrogenation reactor is achieved, which leads to a high performance of the catalyst and thereby high conversion rates. Thereby a deep desulphurization is achieved, sufficient to produce so called "clean fuels". For instance Dimethyldibenzothiophene is only converted at elevated temperatures and pressures. Such a conversion is on the other hand essential to gain sulfur content of 10 ppmw maximum in the desulphurized feed.

[0025] The invention is preferably used in a hydrotreatment process wherein said treatment of the hydrocarbon feed with hydrogen shall reduce the content of sulphur and / or nitrogen of the hydrocarbons in the feed. Such treatments are often referred to as hydrodesulphurization or HDS and as hydrodenitrogenation or HDN. According to the invention the preheating temperature and thereby the hydrogenation temperature can be adjusted in an easy way and over a large range.

[0026] The purification of the hydrocarbon feed from sulphur or nitrogen takes place in so-called HDS units or HDN units. The hydrocarbon feed, for example raw gasoil, reacts with the hydrogen over the catalyst to remove sulphur and/or nitrogen from the hydrocarbons.

[0027] The feed to these HDS units or HDN units can comprise naphta. Naphta is an intermediate distillation product from petroleum refineries boiling in a certain range and containing certain hydrocarbons. Naphta shall in particular mean the fraction of hydrocarbons which boil between 30 °C and 200 °C. It consists of a complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms. The naphta feed purified in the inventive manner can then be used as clean fuel.

[0028] The invention can also be used to remove sulphur and/or nitrogen from a hydrocarbon feed comprising kerosene and / or petroleum diesel. Kerosene and petroleum diesel are also intermediate products from the fractional distillation of petroleum. Kerosene has a boiling point between 150 °C and 275 °C and comprises a mixture of carbon chains that typically contain between six and 16 carbon atoms per molecule. Petroleum diesel, also called petrodiesel, or fossil diesel is produced from the fractional distillation of crude oil between 200 °C and 350 °C, resulting in a mixture of carbon chains that typically contain between 8 and 21 carbon atoms per molecule.

[0029] Another preferred field of application of the invention is the treatment of a hydrocarbon feed with hydrogen in order to crack the hydrocarbon molecules. Such a process is also referred to as hydrocracking. Hydrocracking is a catalytic cracking process in the presence of gaseous hydrogen wherein longer-chain carbon molecules are broken down into short chain carbon molecules. The products of this process are saturated hydrocarbons. Major products from hydrocracking are for example jet fuel and diesel. Similar to the products of the above-described hydrodesulphurization process all these products have a very low content of sulfur and other contaminants.

[0030] In general, the invention provides a method for treating a hydrocarbon feed with hydrogen wherein the feed can be pre-heated in a controlled manner, in particular wherein the temperature of the hydrocarbon feed can be chosen according to the requirements of the subsequent reaction. The invention allows to compensate a decrease of the catalyst performance by increasing the feed temperature. That increase is achieved by increasing the oxygen content of the oxidant supplied to the burn-

er and/or the combustion reaction of the fuel.

Claims

1. Method for treating a feed containing hydrocarbons with hydrogen wherein:
 - a fuel is combusted in a furnace by means of one or more burners,
 - said feed is preheated by indirect heat exchange with the reaction products and/or the reaction heat from the combustion of said fuel to obtain a preheated feed
 - said preheated feed is passed in a reactor containing a catalyst and
 - said preheated feed is treated with hydrogen in said reactor **characterized in that**,
 - said fuel is combusted in a reaction with an oxidant comprising more than 21 % by volume of oxygen.
2. Method according to claim 1, **characterized in that** said fuel is combusted in a reaction with oxygen enriched air, technical oxygen or pure oxygen
3. Method according to claim 2, **characterized in that** said burner(s) is supplied with said fuel and with oxygen enriched air.
4. Method according to any of the previous claims, **characterized in that** said fuel and oxygen react in a combustion zone and wherein said oxidant is injected into said combustion zone.
5. Method according to claim 4, **characterized in that** said burner(s) comprises a pilot burner in order to provide a flame to ignite said burner and wherein said oxidant is supplied to the combustion zone via said pilot burner.
6. Method according to any of the previous claims, **characterized in that** the temperature of the preheated feed is controlled by the amount of oxygen, preferably technical oxygen, combusted with said fuel.
7. Method according to any of the previous claims, **characterized in that** the temperature of the preheated feed is increased when the performance of the catalyst decreases.
8. Method according to any of the previous claims, **characterized in that** the amount of oxidant is controlled in such a manner that a reaction temperature between 280°C and 480°C is achieved at the inlet of the reactor.

9. Method according to any of the previous claims,
characterized in that said treatment with hydrogen
is used to reduce the content of sulphur and / or
nitrogen of said hydrocarbons in said feed. 5
10. Method according to any of the previous claims,
characterized in that said hydrocarbons containing
feed comprises naphta. 10
11. Method according to any of the previous claims,
characterized in that said hydrocarbons containing
feed comprises kerosene. 15
12. Method according to any of the previous claims,
characterized in that said hydrocarbons containing
feed comprises petroleum diesel. 20
13. Method according to any of the previous claims,
characterized in that said treatment with hydrogen
is used for hydrocracking of said hydrocarbons in
said feed. 25

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EUROPEAN SEARCH REPORT

Application Number
EP 12 00 4044

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	HYDROCARBON PUBLISHING COMPANY: "REFINERY CO ₂ MANAGING STRATEGIES:TEHCNOLOGY SOLUTIONS TO REDUCE CARBON FOOTPRINT AND MEET BUSSINES SUSTAINABILITY GOALS", 30 April 2010 (2010-04-30), pages 1-26, XP002682361, Retrieved from the Internet: URL:http://www.hydrocarbonpublishing.com/ReportP/Report_Refinery_Co2_Management_Strategies.pdf	1-4,6, 8-10,13	INV. C10G35/00 C10G47/00
Y	* see page 17 from line 26 "oxycombustion" onwards to page 18, line 2. *	1-13	
Y	----- Fujisaki, Wataru et al.: "Thermal and NO _x Characteristics of High Performance Oxy Fuel Flames", Conference American Flame Research Committee, Baltimore, Maryland, September 30-October 2, 1996 2 October 1996 (1996-10-02), XP002682362, Retrieved from the Internet: URL:http://content.lib.utah.edu:81/cdm4/document.php?CISOROOT=/AFRC&CISOPTR=10631&REC=20 * the whole document * ----- -/--	1-13	
			TECHNICAL FIELDS SEARCHED (IPC)
			C10G
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 27 August 2012	Examiner Rumbo, Angel
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 P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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EUROPEAN SEARCH REPORT

Application Number
EP 12 00 4044

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC)
Place of search Munich		Date of completion of the search 27 August 2012	Examiner Rumbo, Angel
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 P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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