METHOD FOR PROMOTING THE SPALLING OF COKE PRODUCED DURING THE THERMAL CRACKING OF HYDROCARBONS

The present invention relates to processes for the thermal cracking of hydrocarbons. More specifically, the present invention relates to a method for promoting the spalling of coke produced during the pyrolytic cracking of hydrocarbons.

In a process for producing an olefin compound, a fluid stream containing a saturated hydrocarbon such as ethane, propane, butane, pentane, naphtha, or mixtures of two or more thereof is fed into a thermal (or pyrolytic) cracking furnace. A diluent fluid such as steam is usually combined with the hydrocarbon feed material being introduced into the cracking furnace.

Within the furnace, the saturated hydrocarbon is converted into an olefinic compound. For example, an ethane stream introduced into the cracking furnace is converted into ethylene and appreciable amounts of other hydrocarbons. A propane stream introduced into the furnace is converted to ethylene and propylene, and appreciable amounts of other hydrocarbons. Similarly, a mixture of saturated hydrocarbons containing ethane, propane, butane, pentane ad naphtha is converted to a mixture of olefinic compounds containing ethylene, propylene, butenes, pentenes, and naphthalene. Olefinic compounds are an important class of industrial chemicals. For example, ethylene is a monomer or comonomer for making polyethylene and other polymers.

Other uses of olefinic compounds are well known to those skilled in the art.

As a result of the thermal cracking of a hydrocarbon, the cracked product stream can also contain appreciable quantities of hydrogen, methane, acetylene, carbon monoxide, carbon dioxide, and pyrolytic products other than the olefinic compounds.

During the thermal or pyrolytic cracking of hydrocarbons, a semi-pure carbon which is termed as "coke" is formed. The coke formed in the cracking process normally deposits upon the surfaces of the cracking tubes of the pyrolytic cracking furnace of such process. The accumulation of coke upon the surfaces of the cracking tubes ultimately requires the shutdown of the cracking furnace in order to burn off the coke deposits. The accumulation of coke deposits necessitates the periodic shutdown of the cracking furnace due to the excessive pressure drop across the cracking furnace tubes and the higher furnace temperatures required as a result of the thermal insulating properties of the deposited coke.

Compositions known as antifoulants have been used to inhibit the formation and deposition of coke upon the surfaces of cracking furnace tubes and on the metal surfaces of downstream heat exchangers and other process equipment. In spite of the inhibition in the formation of coke by use of such antifoulants, the coke buildup during the cracking of hydrocarbons still occurs but at a slower rate. It can be desirable for there to be minimal buildup or deposition of coke upon the cracker tube surfaces. A reduction in coke accumulation on the cracking tubes will increase the run length of a cracking furnace between shutdowns and thereby improve the cracking operation.

In accordance with the present invention, spalling of coke produced during the pyrolytic cracking of a hydrocarbon stream is promoted by passing the

hydrocarbon stream through a tube of a pyrolytic cracking furnace operated under suitable cracking conditions to thereby produce a cracked product stream. An antifoulant containing tin but having a substantial absence of silicon is added to the hydrocarbon stream in an amount sufficient to promote the spalling of coke produced during the pyrolytic cracking of the hydrocarbon stream.

Another aspect of the invention includes contacting an antifoulant containing tin but having a substantial absence of silicon with a tube of a pyrolytic cracking furnace under suitable treatment conditions to thereby provide a treated tube. A hydrocarbon stream is passed through the treated tube which is operated under suitable cracking conditions to thereby produce a cracked product stream having therein spalled coke.

The invention will now be described with reference to the accompanying drawings in which:

FIG. 1 is a schematic diagram representing the portion of an ethylene cracking process that includes pyrolytic cracking furnace means and other elements of the novel process;

FIG. 2 is a bar chart showing the amount of coke spalled during ethane cracking from an HK4M alloy tube treated with dimethylsulfide, tin, or a tin/silicon mixture; and

FIG. 3 is a bar chart showing the amount of coke spalled during ethane cracking from an HP Modified alloy tube treated with dimethylsulfide, tin, or tin/silicon.

The process of this invention involves the pyrolytic cracking of hydrocarbons to produce desirable hydrocarbon end-products. A hydrocarbon stream is fed or charged to pyrolytic cracking furnace means wherein the hydrocarbon stream is subjected to a severe, high-temperature environment to produce cracked gases. The

hydrocarbon stream can comprise any type of hydrocarbon that is suitable for pyrolytic cracking to olefin compounds. Preferably, however, the hydrocarbon stream can comprise paraffin hydrocarbons selected from the group consisting of ethane, propane, butane, pentane, naphtha, and mixtures of any two or more thereof. Naphtha can generally be described as a complex hydrocarbon mixture having a boiling range of from about 180°F. to about 400°F. as determined by the standard testing methods of the American Society of Testing Materials (ASTM).

As an optional feature of the invention, the hydrocarbon feed being charged to pyrolytic cracking furnace means can be intimately mixed with a diluent prior to entering pyrolytic cracking furnace means. This diluent can serve several positive functions, one of which includes providing desirable reaction conditions within pyrolytic cracking furnace means for producing the desired reactant end-products. The diluent does this by providing for a lower partial pressure of hydrocarbon feed fluid thereby enhancing the cracking reactions necessary for obtaining the desired olefin products while reducing the amount of undesirable reaction products such as hydrogen and methane. Also, the lower partial pressure resulting from the mixture of the diluent fluid helps in minimizing the amount of coke deposits that form on the furnace tubes. While any suitable diluent fluid that provides these benefits can be used, the preferred diluent fluid is steam.

The cracking reactions induced by pyrolytic cracking furnace means can take place at any suitable temperature that will provide the necessary cracking to the desirable end-products or to give a desired feed conversion. The actual cracking temperature utilized will depend upon the composition of the hydrocarbon feed stream and the desired feed conversion.

Generally, the cracking temperature can range upwardly to about 2000°F. or greater depending upon the amount of cracking or conversion desired and the molecular weight of the feedstock being cracked. Preferably, however, the cracking temperature will be in the range of from about 1200°F. to about 1900°F. Most preferably, the cracking temperature can be in the range from 1500°F. to 1800°F.

The cracked hydrocarbon effluent or cracked hydrocarbons or cracked product stream from pyrolytic cracking furnace means will generally be a mixture of hydrocarbons in the gaseous phase. This mixture of gaseous hydrocarbons can comprise not only the desirable olefin compounds, such as ethylene, propylene, butylene, and amylene, but also, this cracked hydrocarbon stream can contain undesirable contaminating components that include both oxygenated compounds and acidic compounds and light ends such as hydrogen and methane.

The cracking furnace means of the inventive method can be any suitable thermal cracking furnace known in the art. The various cracking furnaces are well known to those skilled in the art of cracking technology and the choice of a suitable cracking furnace for use in a cracking process is generally a matter of preference. Such cracking furnaces are equipped with at least one cracking tube to which the hydrocarbon feedstock is charged or fed. The cracking tube provides for and defines a cracking zone contained within the cracking furnace. The cracking furnace is utilized to release the heat energy required to provide for the necessary cracking temperature within the cracking zone in order to induce cracking reactions therein. Each cracking tube can have any geometry which suitably defines a volume in which cracking reactions can take place and, thus, will have an inside surface. The term "cracking temperature" as used

herein is defined as being the temperature within the cracking zone defined by a cracking tube. The outside wall temperature of the cracking tube can, thus, be higher than the cracking temperature and possibly substantially higher due to heat transfer considerations. Typical pressures within the cracking zone will generally be in the range of from about 0 psig to about 100 psig and, preferably from 0 psig to 60 psig.

The inventive method provides for or promotes the spalling of coke produced during the pyrolytic cracking of a hydrocarbon stream. It has been discovered that the treatment or treating of the tubes of a cracking furnace with a tin compound only or, more specifically, with a composition having an absence of silicon but comprising tin, coke spalling is promoted. Coke spalling occurs when the coke formed in the cracking tubes during the cracking of hydrocarbon either fails to adhere to the tube surfaces thereby forming a layer of coke or when it is deposited upon the tube surfaces and thereafter chips, flakes or breaks off such surfaces.

Coke spalling for many cracking operations can be undesirable if the spalled coke results in damage or plugging of equipment located down stream from the cracking furnace. However, in situations where the downstream equipment can handle the fragments of spalled coke or, alternatively, where means is provided which can suitably remove the spalled coke contained in a cracked product stream, the promotion of coke spalling can result in increasing the length of time between decoking of the cracker furnace tubes; because, coke is removed from the tube surfaces by spalling, or it is prevented from depositing or adhering to the tube surfaces. By increasing the length of time between cracker tube decokings, the furnace production down time is reduced thereby

improving cracking furnace productivity and throughput. Thus, if the equipment used to process the cracker furnace product stream can handle the spalled coke without detriment, or, if suitable removal or separation means for removing at least a portion of the spalled coke contained in the cracked product stream can be provided, then coke spalling can be desired.

A critical aspect of the instant invention is the use of a composition having an absence of a silicon compound but comprising a tin compound. It has been discovered that the treatment of the tubes of a cracking furnace in accordance with the methods described herein with a tin compound only, as opposed to a compound containing both a tin compound and a silicon compound, unexpectedly promotes the spalling of coke. When a composition containing a combination of tin and silicon is used to treat cracker furnace tubes, on the other hand, excessive spalling of coke is not observed; rather, the formation and deposition of coke appears to be inhibited. Thus, by combining tin and silicon certain antifoulant benefits and properties are obtained that are different from those of an antifoulant containing a tin compound only or, alternatively, a material having an absence of silicon but comprising tin.

Any suitable form of tin may be utilized in the antifoulant composition having an absence of silicon and comprising tin. Elemental tin, inorganic tin compounds and organic tin compounds as well as mixtures of any two or more thereof are suitable sources of tin. The term "tin" generally refers to any one of these tin sources.

Examples of some inorganic tin compounds which can be used include tin oxides such as stannous oxide and stannic oxide; tin sulfides such as stannous sulfide and stannic sulfide; tin sulfates such as stannous sulfate and stannic sulfate; stannic acids

such as metastannic acid and thiostannic acid; tin halides such as stannous fluoride, stannous chloride, stannous bromide, stannous iodide, stannic fluoride, stannic chloride, stannic bromide and stannic iodide; tin phosphates such as stannic phosphate; tin oxyhalides such as stannous oxychloride and stannic oxychloride; and the like. Of the inorganic tin compounds those which do not contain halogen are preferred as the source of tin.

Examples of some organic tin compounds which can be used include tin carboxylates such as stannous formate, stannous acetate, stannous butyrate, stannous octoate, stannous decanoate, stannous oxalate, stannous benzoate, and stannous cyclohexanecarboxylate; tin thiocarboxylates such as stannous thioacetate and stannous dithioacetate; dihydrocarbyltin bis(hydrocarbyl mercaptoalkanoates) such as dibutyltin bis(isoocylmercaptoacetate) and dipropyltin bis(butyl mercaptoacetate); tin thiocarbonates such as stannous O-ethyl dithiocarbonate; tin carbonates such as stannous propyl carbonate; tetrahydrocarbyltin compounds such as tetramethyltin, tetraoctyltin, tetradodecyltin, and tetraphenyltin; dihydrocarbyltin oxides such as dipropyltin oxide; dibutyltin oxide, dioctyltin oxide, and diphenyltin oxide; dihydrocarbyltin bis(hydrocarbyl mercaptide)s such as dibutyltin bis(dodecyl mercaptide); tin salts of phenolic compounds such as stannous thiophenoxide; tin sulfonates such as stannous benzenesulfonate and stannous-p-toluenesulfonate; tin carbamates such as stannous diethylcarbamate; tin thiocarbamates such as stannous propylthiocarbamate and stannous diethyldithiocarbamate; tin phosphites such as stannous diphenyl phosphite; tin phosphates such as stannous dipropyl phosphate; tin thiophosphates such as stannous O,O-dipropyl thiophosphate, stannous O,O-dipropyl dithiophosphate and stannic O,O-dipropyl

dithiophosphate, dihydrocarbyltin bis(O,O-dihydrocarbyl thiophosphate)s such as dibutyltin bis(O,O-dipropyl dithiophosphate); and the like. Organic tin compounds are preferred over inorganic compounds. At present tetrabutyltin is most preferred.

The term "silicon" as used herein refers to silicon sources such as elemental silicon, inorganic silicon compounds and organic silicon compounds as well as mixtures of any two or more thereof.

The antifoulant composition described herein is utilized in the treatment of the surfaces of the cracking tubes of a pyrolytic cracking furnace. The composition is contacted with surfaces of the cracking tubes either by pretreating the cracking tubes with the antifoulant prior to charging the tubes with a hydrocarbon feed or by adding the antifoulant to the hydrocarbon feed in an amount effective for treating the cracker tubes.

Any method can be used which suitably treats the tubes of a cracking furnace by contacting such tubes with the antifoulant under suitable treatment conditions to thereby provide treated tubes.

The preferred procedure for pretreating the tubes of the cracking furnace, includes charging to the inlet of the cracking furnace tubes a saturated or slightly superheated steam having a temperature in the range of from about 300°F. to about 500°F. The cracking furnace is fired while charging the tubes with the steam so as to provide a superheated steam which exits the tubes at a temperature exceeding that of the steam introduced into the inlet of the tubes. Generally, the steam effluent will have a temperature upwardly to about 2000°F. Thus, the treating temperature can be in the range of from about 300°F. to about 2000°F., preferably, from about 400°F. to about 1800°F. and, most preferably, from 500°F. to 1600°F. It is desirable for the steam to be charged to the

convection section of the cracking furnace, therefore, first passing through the convection section tubes followed by passing through the radiant section tubes.

The antifoulant can then be admixed with the steam being charged to the cracker tubes. The antifoulant can be admixed with the steam as either a neat liquid or as a mixture of the antifoulant with an inert diluent. In any event, it is preferred to vaporize or convert into an aerosol either the neat liquid or the mixture prior to its introduction into or admixing with the steam. The amount of antifoulant admixed with the steam can be such as to provide a concentration of the antifoulant in the steam in the range of from about 1 ppmm to about 10,000 ppmm, preferably, from about 10 ppmm to about 1000 ppmm and, most preferably, from 20 to 200 ppmm.

The admixture of steam and antifoulant is contacted with or charged to the cracker furnace tubes for a period of time sufficient to provide for treated tubes, which when placed in cracking service, will provide or promote an amount of coke spalling exceeding that which occurs when the antifoulant includes silicon. Such time period for pretreating the cracker tubes is influenced by the specific geometry of the cracking furnace including its tubes; but, generally, the pretreating time period can range upwardly to about 12 hours, and longer if required. But, preferably, the period of time for the pretreating can be in the range of from about 0.1 hours to about 12 hours and, most preferably, from 0.5 hours to 10 hours.

In the case where the antifoulant composition is directly admixed with the hydrocarbon feed to the cracking furnace, it can be added in such an amount to be effective in promoting the spalling of coke produced during the pyrolytic cracking of the hydrocarbon feed. Due to the memory effect resulting from the application of the antifoulant the mixing with the hydrocarbon

cracker feed is conducted intermittently as required but, preferably, for periods up to about 12 hours. The concentration of the antifoulant in the hydrocarbon cracker feed during treating of the cracking furnace tubes can be in the range of from about 1 ppmm to about 10,000 ppmm, preferably, from about 10 ppmm to about 1000 ppmm and, most preferably, from 20 to 200 ppmm.

Now referring to FIG. 1, there is illustrated by schematic representation cracking furnace section 10 of a pyrolytic cracking process system. Cracking furnace section 10 includes pyrolytic cracking means or cracking furnace 12 for providing heat energy required for inducing the cracking of hydrocarbons. Cracking furnace 12 defines both convection zone 14 and radiant zone 16. Respectively within such zones are convection coils as tubes 18 and radiant coils as tubes 20.

A hydrocarbon feedstock or a mixture of steam and such hydrocarbon feedstock is conducted to the inlet of convection tubes 18 by way of conduit 22 which is in fluid flow communication with convection tubes 18. During the treatment of the tubes of cracking furnace 12, the admixture of steam and the antifoulant composition can also be conducted to the inlet of convection tubes 18 through conduit 22. The feed passes through the tubes of cracking furnace 12 wherein it is heated to a cracking temperature in order to induce cracking or, in the situation where the tubes are undergoing treatment, to the required treatment temperature. The cracked product stream from cracking furnace 12 passes downstream through conduit 24 to separator 26 which defines a zone and provides means for removing at least a portion of the spalled coke contained in the cracked product stream. The spalled coke removed from the cracked product stream passes from separator 26 by way of conduit 28, and the cracked product stream having at least a portion of the spalled

coke contained therein removed therefrom passes from separator 26 by way of conduit 30.

To provide for the heat energy necessary to operate cracking furnace 12, fuel gas is conveyed through conduit 32 to burners 34 of cracking furnace 12 whereby the fuel gas is burned and heat energy is released.

During the treatment of convection tubes 18 and radiant tubes 20, the antifoulant composition is conveyed to cracking furnace 12 feed stream through conduit 36 and admixed prior to the resulting mixture entering cracking furnace 12. Interposed in conduit 36 is heat exchanger 38 which provides heat exchange means for transferring heat energy and to thereby vaporize the feed conversion enhancing composition.

The following example is provided to further illustrate the present invention.

EXAMPLE

The following two comparisons illustrate the promotion of coke spalling by the addition of a tin compound without the addition of a silicon compound.

An experimental ethane cracker equipped with a HK4M alloy tube feeding 44 lb/hr ethane and 13.2 lb/hr steam was fed 300 ppmw sulfur as dimethyl sulfide during cracking, a common treatment in current crackers. Conversion was kept constant at 65% and residence time at 120 milliseconds. Spalled coke collected after the reactor in a dead leg zone upon completion of the 70 hour run amounted to 4 grams/day. This same tube was treated with 100 ppmm tetrabutyl tin, without silicon, for six hours prior to charging ethane. Spalled coke collected after a 70 hour run amounted to 14.5 grams/day. In a separate run, the HK4M tube was treated with 100 ppmm each of tetrabutyltin and hexamethyldisiloxane for six hours prior to charging ethane. Spalled coke was collected over a 100 hour period at a rate of 2.5 grams/day.

Data for each of the three experimental runs with the HK4M tube are presented in FIG. 2. As can be observed from an analysis of the data, the tin only treatment provides for a significantly greater amount of coke spalling than does the tin/silicon or the dimethyl sulfide compounds.

An experimental ethane cracker equipped with HP Modified alloy tube feeding 25.3 lb/hr ethane and 7.6 lb/hr steam was fed 300 ppmw sulfur as dimethylsulfide during cracking. Conversion was kept constant at 67% and residence time was 270 milliseconds. Spalled coke collected after the reactor in a dead leg zone upon the completion of a 55 hour run amounted to a daily rate of 2 grams/day. This same tube was treated with tetrabutyltin, without silicon, for six hours prior to charging ethane. Spalled coke collected after a 65 hour run amounted to 24 grams/day, an increase of twelve times compared to the sulfur-treated run. In a separate run, the HP Modified tube was treated with 100 ppmm each of tetrabutyltin and tetraethylsilane for six hours prior to charging ethane. Spalled coke was collected over a three day period at a rate of 2 grams/day. Data for each of the three experimental runs are presented in FIG. 3. As can be observed from the data, the tin only treatment provides for a significantly greater amount of coke spalling than does the tin/silicon or the dimethylsulfide compounds.



C L A I M S

1. A method for promoting the spalling of coke produced during the pyrolytic cracking of a hydrocarbon stream, said method including passing said hydrocarbon stream through a tube of a pyrolytic cracking furnace operated under suitable cracking conditions to thereby produce a cracked product stream; and adding an antifoulant containing tin but having an absence of silicon to said hydrocarbon stream in an amount sufficient to promote the spalling of coke produced during the pyrolytic cracking of said hydrocarbon stream to thereby provide said cracked product stream having therein spalled coke.

2. A method according to claim 1, wherein the amount of said antifoulant added to said hydrocarbon stream is such as to give a concentration in said hydrocarbon stream in the range of from about 1 ppmm to about 10,000 ppmm.

3. A method of promoting the spalling of coke produced during the pyrolytic cracking of a hydrocarbon stream, said method including contacting an antifoulant containing tin but having an absence of silicon with a tube of a pyrolytic cracking furnace under suitable treatment conditions; and passing said hydrocarbon stream through the thus treated tube, said tube being operated under suitable cracking conditions to thereby produce a cracked product stream having therein spalled coke.

4. A method according to claim 3, wherein the antifoulant is used for contacting in an admixture with a diluent at a concentration in the range of from about 1 ppmm to about 10,000 ppmm.

5. A method according to claim 3 or 4, wherein the contacting is conducted at a temperature in the range of from about 300°F. to about 2000°F.

6. A method according to claim 5, wherein the contacting is conducted upwardly to about 12 hours.

7. A method according to any one of the preceding claims, which includes removing at least a portion of said

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spalled coke from said cracked product stream.

8. A method according to any one of the preceding claims, wherein the tin is an organotin compound.

9. A method according to claim 8, wherein said organotin compound is tetrabutyltin.