

METHOD FOR REDUCING TEMPERATURE IN THERMAL
CRACKING OF HYDROCARBONS

The present invention generally relates to processes for the thermal cracking of hydrocarbons and, specifically, to a method for saving energy in the thermal cracking of hydrocarbons.

5 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
10 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,
15 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,
20 a mixture of saturated hydrocarbons containing ethane, propane, butane, pentane and naphtha is converted to a mixture of olefinic compounds containing ethylene, propylene, butenes, pentenes, and naphthalene. Olefinic compounds are an important class of industrial
25 chemicals. For example, ethylene is a monomer or comonomer for making polyethylene and other polymers. Other uses of olefinic compounds are well known to

CASE: 33277

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.

The process for thermally or pyrolytically cracking saturated hydrocarbons to an olefin end-product is highly energy intensive. Typically, 70 to 95 percent of the total energy cost of operating a cracking process unit or olefins plant is fuel consumed in the cracking furnaces of such cracking process unit. Generally, depending upon the molecular weight of the feedstock and the desired feed conversion, the energy consumption per pound of olefin produced by a cracking process unit can range from about 7000 Btu per pound olefin produced upwardly to about 15,000 Btu per pound olefin produced. Typical olefin plants have annual olefin production capacities ranging upwardly to one billion pounds and, in some instances, more than one billion pounds. Thus, the energy requirements for operating an olefins plant constitute a major element in the cost of operating and producing cracked olefins. Because the fuel requirements for operating a cracking furnace are so large, even a small incremental improvement in the energy requirements to produce an olefin end-product can result in large cost savings in the per unit production cost of the olefins.

It is thus an object of this invention to provide an improved process for cracking saturated hydrocarbons to produce olefinic end-products.

Another object of this invention is to provide a method for improving the energy efficiency of a cracking process without loss of product yield.

A still further object of this invention is to provide a method of reducing the required cracking temperature to crack a hydrocarbon feed stream without

a loss in the percent conversion of the hydrocarbon feed stream to olefin end-product.

In accordance with one aspect of the invention, the tubes of a pyrolytic cracking furnace are treated with a composition containing a tin compound and a silicon compound to provide treated tubes. The treated tubes are utilized in the cracking of hydrocarbons under cracking conditions. Due to the use of the treated tubes, the cracking temperature that provides for a given feed conversion is below the cracking temperature required to achieve the given feed conversion when untreated tubes of a pyrolytic cracking furnace are used.

Another aspect of the invention includes a method of reducing a required cracking temperature for a given feed conversion in the operation of a cracking furnace of a thermal cracking process for cracking a hydrocarbon stream. The cracking furnace is equipped with a cracking tube having a surface. The method includes contacting the surface of the cracking tube with a composition comprising a tin compound and a silicon compound so as to provide a treated cracking tube. A hydrocarbon feed stream is charged to the treated cracking tube, which is maintained at a temperature so as to provide a cracking temperature below that required for the given feed conversion when the untreated cracking tube is used.

A final aspect of the invention includes a method of reducing energy consumption for a given feed conversion in the operation of a thermal cracking process for cracking a hydrocarbon stream. The method includes adding to the hydrocarbon stream in an amount effective for enhancing feed conversion for a given cracking temperature a composition comprising a tin compound and a silicon compound. The enhanced feed conversion at the given cracking temperature permits the reduction of the cracking temperature. This

reduction in cracking temperature results in a reduction in fuel or energy consumption.

Other objects and advantages of the invention will be apparent from the description of the invention and the appended claims thereof as well as from the
5 detailed description of the drawing in which:

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

10 FIG. 2 includes plots of the cracking tube coil outlet temperatures at a substantially fixed ethane conversion for an untreated cracking tube and a cracking tube treated in accordance with the novel methods described herein.

15 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-
20 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
25 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
30 standard testing methods of the American Society of Testing Materials (ASTM).

The pyrolytic cracking of a higher molecular weight hydrocarbons to a lower molecular weight hydrocarbons can be referred to as conversion. The
35 terms "conversion", "feed conversion", and similar such terminology, as used throughout this specification, are defined as the ratio of the difference between the mass

of saturated hydrocarbons charged to a cracking zone and the mass of unconverted saturated hydrocarbons leaving, as an effluent, such cracking zone divided by the mass of saturated hydrocarbons charged to the cracking zone. The numerical value for conversion can be reported as a fraction (ratio) or as a percentage. Conversion can also be reported on an individual compound basis such as, for example, ethane conversion, propane conversion, butane conversion, and the like.

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 the 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 run 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 hydrocarbon 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, however, 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 the 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

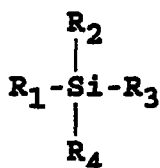
cracking tube. The outside wall temperature of the cracking tube can, thus, be higher than the cracking temperature and possibly substantially higher due to heat transfer considerations. Typical pressures within the cracking zone will generally be in the range of from about 5 psig to about 25 psig and, preferably from 10 psig to 20 psig.

The inventive method includes the treatment or treating of the tubes of a cracking furnace by contacting the surface of such tubes with a feed conversion enhancing composition. The use of the feed conversion enhancing composition provides for or induces an increase in the conversion of the hydrocarbon feedstock to a cracking furnace for a given cracking temperature. This enhancement in feed conversion permits the reduction in the cracking temperature below that required to give the feed conversion which results from utilizing untreated cracker tubes. The feed conversion enhancing composition is a combination or mixture of tin and silicon, thus the composition will comprise, consist essentially of, or consist of tin and silicon.

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

Examples of some inorganic silicon compounds that can be used include the halides, nitrides, hydrides, oxides and sulfides of silicon, silicic acids and alkali metal salts thereof. Of the inorganic silicon compounds, those which do not contain halogen are preferred.

Examples of organic silicon compounds that may be used include compounds of the formula



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wherein R_1 , R_2 , R_3 , and R_4 are selected independently from the group consisting of hydrogen, halogen, hydrocarbyl, and oxyhydrocarbyl and wherein the compound's bonding may be either ionic or covalent.

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The hydrocarbyl and oxyhydrocarbyl radicals can have from 1-20 carbon atoms which may be substituted with halogen, nitrogen, phosphorus, or sulfur. Exemplary hydrocarbyl radicals are alkyl, alkenyl, cycloalkyl, aryl, and combinations thereof, such as alkylaryl or

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alkylcycloalkyl. Exemplary oxyhydrocarbyl radicals are alkoxide, phenoxide, carboxylate, ketocarboxylate and diketone (dione). Suitable organic silicon compounds include trimethylsilane, tetramethylsilane,

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tetraethylsilane, triethylchlorosilane, phenyltrimethylsilane, tetraphenylsilane, ethyltrimethoxysilane, propyltriethoxysilane, dodecyltrihexoxysilane, vinyltriethoxysilane, tetramethoxyorthosilicate, tetraethoxyorthosilicate, polydimethylsiloxane, polydiethylsiloxane,

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polydihexylsiloxane, polycyclohexylsiloxane, polydiphenylsiloxane, polyphenylmethylsiloxane, 3-chloropropyltrimethoxysilane, and 3-aminopropyltriethoxysilane. At present

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hexamethyldisiloxane is preferred. Organic silicon compounds are particularly preferred because such compounds are soluble in the feed material and in the diluents which are preferred for preparing pretreatment solutions as will be more fully described hereinafter. Also, organic silicon compounds appear to have less of a tendency towards adverse effects on the cracking process than do inorganic silicon compounds.

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Any suitable form of tin may be utilized in the feed conversion enhancing composition comprising

tin and silicon. 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(isooctylmercaptoacetate) 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. At present tetrabutyltin is preferred. Again, as with silicon, organic tin compounds are preferred over inorganic compounds. Any of the listed sources of tin may be combined with any of the listed sources of silicon to form the feed conversion enhancing composition comprising tin and silicon.

The feed conversion enhancing composition can have any molar ratio of tin to silicon which suitably provides for the cracker tube treatment or enhanced cracker feed conversion as required hereunder. Generally, however, the molar ratio of tin to silicon of the composition can be in the range of from about 1:100 to about 100:1. Preferably, the molar ratio can be from about 1:10 to about 10:1 and, most preferably, it can be from 1:4 to 4:1.

The feed conversion enhancing composition is utilized in the treatment of the surfaces of the cracking tubes of a cracking furnace. The composition is contacted with surfaces of the cracking tubes either by pretreating the cracking tubes with the composition prior to charging the tubes with a hydrocarbon feed or by adding the composition to the hydrocarbon feed in an amount effective for enhancing feed conversion for a given cracking temperature.

Any method can be used which suitably treats the tubes of a cracking furnace by contacting such tubes with the feed conversion enhancing composition under suitable treatment conditions to thereby provide treated tubes. The treated tubes will provide for a lower required cracking temperature for a given cracker feed conversion.

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 feed conversion enhancing composition can then be admixed with the steam being charged to the cracker tubes. The feed conversion enhancing composition can be admixed with the steam as either a neat liquid or as a mixture of the feed conversion enhancing composition with an inert diluent. It is preferred, however, to first vaporize either the neat liquid or the mixture prior to its introduction into or admixing with the steam. The amount of feed conversion enhancing composition admixed with the steam can be such as to provide a concentration of the feed conversion enhancing composition in the steam in the

range of from about 1 ppmw to about 10,000 ppmw, preferably, from about 10 ppmw to about 1000 ppmw and, most preferably, from 20 to 200 ppmw.

5 The admixture of steam and feed conversion enhancing composition is contacted with or charged to the cracker tubes for a period of time sufficient to provide for treated tubes, which when placed in cracking service, will require a cracking temperature for a given feed conversion below that for untreated
10 tubes. 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
15 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 feed conversion enhancing composition is directly admixed with the
20 hydrocarbon cracker feed, it can be added in such an amount to be effective in enhancing the feed conversion above that which occurs when no feed conversion enhancing composition is added. Due to the memory effect resulting from the application of the feed
25 conversion enhancing composition, 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 feed conversion enhancing composition in the hydrocarbon cracker feed
30 during treating of the cracker tubes can be in the range of from about 1 ppmw to about 10,000 ppmw, preferably, from about 10 ppmw to about 1000 ppmw and, most preferably, from 20 to 200 ppmw.

Now referring to FIG. 1, there is illustrated
35 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 feed conversion enhancing 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 effluent from cracking furnace 12 passes downstream through conduit 24. To provide for the heat energy necessary to operate cracking furnace 12, fuel gas is conveyed through conduit 26 to burners 28 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 feed conversion enhancing composition is conveyed to cracking furnace 12 feed stream through conduit 30 and admixed prior to the resulting mixture entering cracking furnace 12. Interposed in conduit 30 is heat exchanger 32 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.

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EXAMPLE

This example demonstrates the energy savings of a tube treated with tin and silicon compared to an

untreated tube.

A 1.52" I.D. HP-Modified tube that was 12 feet in length was treated with 500 ppmw dimethylsulfide for four hours at 1250°F.

5 Dimethylsulfide was introduced with 26.4 lb/hr steam and 3.5 lb/hr nitrogen at 400°F. and 40 psig several feet upstream of an electric furnace which enclosed the reactor tube. The feed rate was then changed to 25.3 lb/hr ethane and 7.6 lb/hr steam at 12 psig and the
10 temperatures in the furnace were brought up to cracking conditions in a period of one hour. Residence time in the reactor tube was held at 270 milliseconds. The dimethylsulfide injection was reduced to 125 ppmw at twenty hours after the ethane charge was introduced and
15 injection was continued for the remainder of the 56 hour test run. The steady-state coil outlet temperature was maintained at 1770°F. to hold ethane conversion constant at 67% throughout the test run.

A pretreatment of six hours with 100 ppmm tetrabutyltin and 50 ppmm hexamethyl disiloxane at
20 temperatures from 1200°F. to 1500°F. and 40 psig was done on the same tube described above. This mixture was also injected at the same location as the dimethylsulfide with 26.4 lb/hr steam and 3.5 lb/hr
25 nitrogen. The feed was then changed to 25.3 lb/hr ethane and 7.6 lb/hr steam and the temperatures in the furnace were brought up to cracking conditions in a period of one hour. Residence time in the reactor tube was held at 270 milliseconds. Four hours after
30 the ethane charge was brought in, the concentration of the tin/silica mixture was reduced to 50 ppmm tetrabutyltin and 25 ppmm hexamethyl disiloxane. Eight hours after the ethane charge was brought in, the injection of the tin/silica mixture was discontinued
35 for the remainder of the 103 hour test run. The steady state coil outlet temperature was maintained at 1615°F. to hold ethane conversion constant at 67% throughout

the test run. This is 155°F. lower than the test run with the untreated tube which clearly demonstrates the energy savings that can be obtained by treating an ethane pyrolysis tube with a tin/silica composition.

5 Selected data points obtained from the two test runs described in this Example are presented in Table I. These data are presented in the plot of FIG. 2. A comparison of the data obtained from the two test runs shows the benefit of a significantly reduced coil outlet temperature that results from the use of the novel cracker tube treatment method.

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TABLE I			
Comparative Data for Conventional Dimethylsulfide (DMS) Treatment of Cracker Tubes Versus the Inventive Treatment of Cracker Tubes With Tin/Silicon (Sn/Si) Compound			
Run Time (Hrs)	DMS Run	Sn/Si Run	Difference
0	1575	1650	-75
5	1671	1639	32
10	1738	1626	112
11	1768	1621	147
15	1766	1620	146
20	1772	1616	156
25	1772	1614	158
30	1775	1612	163
35	1772	1612	160
40	1775	1615	150
45	1774	1612	162
50	1777	1613	164
55	1777	1614	163

Reasonable variations and modifications are possible by those skilled in the art within the scope of the described invention and the appended claims.



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- 17 -
C L A I M S

1. A method of reducing a cracking temperature required for a given feed conversion in the operation of a cracking furnace of a thermal cracking process for cracking a hydrocarbon stream within a cracking tube in said furnace, which comprises

(a) contacting the internal surface of said cracking tube with a composition comprising a tin compound and a silicon compound;

(b) charging said hydrocarbon stream to said cracking tube during or after said contacting; and

(c) maintaining said given feed conversion at a cracking temperature below the cracking temperature which would have been required to achieve said given feed conversion if step (a) had not been practiced.

2. A method according to claim 1, wherein said tin compound is an organotin compound and said silicon compound is an organosilicon compound.

3. A method according to claim 1 or 2, wherein in said composition the molar ratio of said tin compound to said silicon compound is in the range of from 1:100 to 100:1.

4. A method according to any one of the preceding claims, wherein the contacting step further includes utilizing said composition in an admixture with steam at a concentration in the range of from about 1 ppmw to about 10,000 ppmw.

5. A method according to any one of the preceding claims, wherein the contacting step is conducted at a temperature in the range of from about 300°F. to 2000°F.

6. A method according to any one of the preceding claims, wherein the contacting step is conducted for a time period upwardly to about 12 hours.

7. A method according to any one of the preceding claims, wherein said organotin compound is tetrabutyltin and said organosilicon compound is hexamethyldisiloxane.

8. A method according to any one of the preceding

CASE: 33277

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- 18 -

claims, wherein said contacting is effected by adding the composition to said hydrocarbon stream in an amount effective for enhancing feed conversion for a given cracking temperature and thereafter, maintaining said given feed conversion at below the cracking temperature which would have been required to achieve said given feed conversion if step (a) had not been practiced to thereby reduce energy consumption.

9. A method according to claim 8, wherein said amount of said composition added to said hydrocarbon stream is such as to provide a concentration in the range of from 1 to 10,000 parts by weight of said composition per parts by weight of said hydrocarbon stream.

10. A method according to any one of claims 1-7, wherein the charging of said hydrocarbon stream to said cracking tube is effected after said contacting.

11. A method according to any one of the preceding claims, wherein the cracking temperature at which cracking is carried out is in the range of from 1200°F. to 2000°F.

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