(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 May 2001 (31.05.2001)

PCT

(10) International Publication Number
WO 01/38459 A1

(51) International Patent Classification[7]: C10G 9/20

(21) International Application Number: PCT/US00/32061

(22) International Filing Date:
21 November 2000 (21.11.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/444,941 22 November 1999 (22.11.1999) US

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *With international search report.*
— *Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/38459 A1

(54) Title: METHOD FOR IMPROVING THERMAL CRACKING PROCESS AND PRODUCT YIELDS THEREFROM

(57) Abstract: A method and a system are disclosed for improving thermal cracking of heavy hydrocarbons by measuring the asphaltene colloidal stability and/or the amount of coke of the bottoms fraction of the product. If the parameters are outside of predetermined limits, the operating conditions are adjusted in response to the determination.

METHOD FOR IMPROVING THERMAL CRACKING PROCESS AND PRODUCT YIELDS THEREFROM

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method for improved thermal cracking, such as visbreaking, on-purpose coking or delayed coking, of hydrocarbons, particularly heavy hydrocarbons.

2. Background of the Invention

While many catalytic cracking processes for converting hydrocarbons are widely used, a number of thermal cracking processes are still of significant importance in both the chemical and the refining industries. A thermal cracking or conversion process is a process, which, by using thermal energy, *i.e.* heat and temperature, converts or cracks larger hydrocarbon molecules, particularly those having boiling points higher than about 350°C, into smaller ones. For example, high boiling, heavy and lower valued residues from an oil refinery or chemical plant may be converted into lower boiling, light or intermediate and higher valued product cuts. Examples of commonly practiced thermal cracking reactions include, visbreaking, hydrocracking (cracking reaction in the presence of added hydrogen), and various on-purpose coking or delayed coking processes.

Primarily due to the high temperatures and other demanding reaction conditions used to effect thermal crackings and the facts that the feedstocks are quite heavy and the light products have higher hydrogen content, most thermal cracking operations are prone to severe fouling problems, including coking. Visbreaking is such an example.

Visbreaking is a thermal cracking reaction, in which heavy hydrocarbon feedstocks such as resids with high viscosity are fed into a reactor at a temperature high enough to cause these feedstocks to break down into smaller ones. The liquid product stream usually exhibits lower viscosity, or otherwise referred to as being visbroken. This product can be used as fuel oil. In response to the market demand, visbreaking today has the added importance of obtaining a maximum of conversion of heavy materials into middle and light distillate fractions products such as naphtha and gas oil. Gas oil and naphtha are useful as components for transportation fuel. This trend in the market place is particularly obvious in Europe and most other industrialized countries.

In a typical visbreaking plant, the charge (feedstock) is fed to and becomes preheated in a train of heat exchangers. This preheated charge is then sent to a furnace (or cracking unit) for the intended thermal cracking. The furnace is normally one or a plurality of tubes or reactors. The products from cracking pass through a fractionation column to separate the products. The tar from the cracking reaction is separated and removed from the bottom of the fractionation column and sent to one or more heat exchangers to recover some of the heat content, which may be used for preheating the charge.

In some operations there is a "soaker" unit between the furnace and the fractionation column to provide additional time for additional cracking to take place and/or for some of the initial cracking products to undergo additional reactions prior to separation. Unlike the furnace tubes, there is usually no additional heat input to the soaker. Because the cracking reactions are endothermic reactions and heat losses, the outlet temperature of a soaker, without heat input, is usually lower than the furnace outlet temperature by about 20 to 30°C. The residence time in a soaker is usually in the range of from about 10 minutes to about 30 minutes. The pressure in a

soaker is usually in the range of from about 3 bar (300 kPa) to about 20 bar (2 MPa).

The thermal cracking units (or furnaces) are normally operated at a temperature in the range of from about 420°C to about 500°C and a pressure in the range of from about 3 bar (300 kPa) to about 20 bar (2 MPa). When a charge of a vacuum or atmospheric distillation residue is used as the feedstock, the operating temperature of the furnace is close to the low end of the temperature range if there is a soaker between the furnace and the fractionation column. A temperature near the high end of the range is preferred if there is no soaker.

Primarily due to the constraints of reaction temperature, residence time, and thermal cracking reaction kinetics, a thermal cracking unit, such as a visbreaking unit, is normally sized for a desired level of conversion of the feedstock at a desired flow rate. The term "conversion" is used herein to mean the combined weight % of both the light distillate and the middle distillate, including gaseous products, naphtha and gas oil, relative to the total weight of the charge to the furnace.

Typically, the products recovered from the fractionation column have the following distribution of components: about 3 wt% to about 10 wt% of light distillates; about 10 wt% to about 20 wt% middle distillates; and about 70 wt% to 85 wt% of tar as heavy residue, which is removed from the bottom of the fractionation column. All of these weights are based on the weight of the feedstock.

Typical feedstocks to a visbreaking unit comprise of heavy bottom products from upstream atmospheric or vacuum distillation units or plants. The fouling characteristics of a particular feedstock under the visbreaking conditions are often the most important controlling factors in operating a

visbreaking unit. These characteristics tend to dictate the visbreaking temperature, which, in turn and at a particular flow rate, controls the conversion level of the charge and the yields of the desired light fractionations. Because the conversions are usually below 20 wt%, even an increase of just one wt% in conversion may have a significant impact on process economics and profitability.

A higher conversion level requires a higher operating temperature in the cracking unit, a longer residence time (i.e. lower flow rate) or both. However, the higher the operating temperature is, the higher the fouling is. Therefore, it is important to prevent or at least to minimize fouling inside the thermal cracking or visbreaking furnace and elsewhere in the system while maintaining as high a conversion as possible. A proper balance between operating conditions and fouling rates will allow longer operating time and produce more desired products before the cracking unit and other parts of the plant have to be shut down for cleanups, maintenance or repairs. Due to the chemistry involved and the nature of the feedstocks, it is generally believed that it is not possible to achieve total elimination of fouling from a thermal cracking reaction of heavy hydrocarbons such as visbreaking.

In view of the correlation between the charge conversion level and the cracking temperature, it is desirable to use as high a temperature as possible to maximize conversion. Accordingly, it is desirable to have a method that provides reliable measurements regarding the severity of fouling in the cracking reactor. The collected data from such measurements can be used to maintain the temperature, thus conversion, as high as possible while keeping the degree of fouling within an acceptable range.

The present invention provides such a method with short response times in measuring two parameters to allow quick adjustments of the reaction conditions for optimizing the conversion-fouling profile of the thermal cracking

reaction, particularly a visbreaking reaction. The present invention also provides a method, which is automated to make adjustments of cracking, including visbreaking, conditions to maximize conversion while keeping fouling within acceptable levels.

In an on-purpose coking or delayed coking process, a heavy carbon feed from different sources including visbreaking and other thermal cracking reactions is converted into coke products. It would be desirable to be able to control the bottoms fraction of the product from a reaction such as visbreaking to optimize the yield or other properties of the coke products from one or more coker or delayed coker.

SUMMARY OF THE INVENTION

One object of the present invention is to provide a method for improved thermal cracking of heavy hydrocarbons, such as visbreaking of vacuum distillation residue (resid), atmospheric distillation residue, crude oil, FCC (fluid catalytic cracking) slurry oil and mixtures thereof. The method comprises cracking the heavy hydrocarbons in a unit under first conditions effective to produce a product, separating the product into a light fraction and a bottoms fraction, measuring a parameter, such as asphaltene colloidal stability and/or amount of coke particles, of the bottoms fraction, making a determination of whether the parameter is outside of a limit, and adjusting the first conditions in response to the determination.

The present invention also relates to a system for conducting improved thermal cracking of heavy hydrocarbons. The system comprises a cracking unit comprising a cracking furnace, including a plurality of furnace tubes to crack the heavy hydrocarbons under first conditions effective to produce a product, a separation unit such as a fractionation column to separate the product into a light fraction and a bottoms fraction, at least one sensor to measure at least one parameter such as asphaltene colloidal stability and/or

amount of coke particles, at least one processor to make a determination if the at least one parameter is outside of a limit, and at least one controller to adjust the first conditions in response to the determination.

Another object of the present invention relates to a method for and a system of converting the bottoms fraction from a thermal cracking unit such as visbreaker into desired coke products in at least one coker or at least one delayed coker.

BRIEF DESCRIPTIONS OF THE DRAWINGS

Figure 1 depicts a block diagram showing the layout of equipment within the embodiments of the instant invention regarding how the parameters of the bottoms fraction of a visbreaking product are measured.

Figure 2 shows a typical correlation between infrared stability index (ISI, milliliters of heptane per gram of 1:1 toluene diluted tar residue) and cracking reaction severity.

Figure 3 shows a typical diagram representing number of coke particles per unit volume of diluted tar residue (about 1:20,000 v/v dilution in an aromatic solvent) as a function of cracking reaction severity.

One having ordinary skill in the art understands that the drawings are used for illustration purposes only and they do not represent all of the possible variations of the method, the system or both as embodied by the present invention.

DETAILED DESCRIPTIONS OF THE INVENTION

The present invention provides a method for and a system of performing an improved thermal cracking, such as visbreaking, of heavy hydrocarbons by (a) monitoring fouling, particularly propensity of precipitation of asphaltenes or aggregation of asphaltene colloids and coking of the bottoms fraction of the cracking product, and (b) adjusting the cracking

conditions in response to the data collected during monitoring. The object is to maximize conversions of heavy hydrocarbons and at the same time keeping fouling (such as asphaltene precipitation and/or coking or coke formation) within acceptable and/or predetermined limits.

The invention also relates to an improved coking process, including thermal coking and delayed coking processes. The bottoms fraction composition is adjusted so that it becomes a better feedstock for a downstream coker(s) or delayed coker(s), which are operated at a realtively high temperature.

Two separate parameters corresponding to fouling are independently monitored and measured in the present invention, particularly for visbreaking of vacuum and/or atmospheric distillation resids type thermal cracking reactions. The data collected from the measurements are compared with predetermined limits to determine if the thermal cracking conditions (a) may be changed or adjusted to achieve a higher conversion or (b) need to be modified to reduce fouling. The predetermined limits may be set by past experience or data collected in the same, similar or related operations, published results, results from conducting additional laboratory experiments, theoretical calculations, modeling, updates of existing model, and combinations thereof.

There are a number of parameters may be monitored and/or measured to provide the needed data for adjusting the thermal cracking reaction operating conditions. Examples of such parameters include, but are not limited to the stability of asphaltene/asphaltene colloids in the bottoms product exiting the cracking units, the viscosity of the bottoms fraction, the pour point of the bottoms fraction, the amount of coke particles in the bottoms fraction, the chemical composition of the bottoms fraction, combinations thereof and others.

A preferred first parameter measures the precipitation and/or a propensity for such precipitation of asphaltenic compounds, collectively referred to herein as asphaltenes, on the surface of the heat exchangers, the furnace or furnace tubes, the soaker (if there is one in the system), or other parts of the system. (*See* **Figure 2**)

Most of typical visbreaking feedstocks comprise asphaltenes, paraffinic compounds, aromatic compounds and minor amounts of various other compounds, including heteroatom-containing compounds. Typical asphaltenes are dark brown to black-colored amorphous solids with complex structures, relatively high molecular weight and relatively low hydrogen content. In addition to carbon and hydrogen in the composition, asphaltenes also contain nitrogen, oxygen and sulfur species or compounds.

Typically, asphaltenes have some solubilities and/or exist in stabilized colloidal form in the crude oil, atmospheric distillation resid, vacuum distillation resid, mixtures thereof or in certain organic solvents like carbon disulfide. However, asphaltenes are essentially insoluble in solvents like light naphthas, which are the major products from thermal cracking reactions like visbreaking. Consequently, asphaltenes have a tendency of precipitating and/or aggregating out of the thermal cracking products and depositing on the surface of the equipment or pipes because the naphtha content in the cracking product is higher than that originally present in the feedstock charge prior to undergoing thermal cracking or visbreaking or on-purpose coking or delayed coking.

A preferred second parameter monitors and measures the degree or severity of dehydrogenations, both thermal and catalytic dehydrogenations, which take place during a thermal cracking reaction such as visbreaking. Severe dehydrogenation reactions lead to highly carbonaceous materials like coke. This coke formation phenomenon is also referred to herein as coking. Coking generally becomes much more severe when the thermal cracking temperature is above a certain temperature, usually between about 400°C

and about 500°C, which depends on the feed and operating conditions and equipment. (*See* **Figure 3**) It should be mentioned that the number of carbon particles in a feed (charge) itself generally remains fairly constant when coming from a particular source.

These carbonaceous materials or cokes are insoluble in the liquid phase and tend to adhere to the surface of the furnace, thus creating a fouling layer. Any coke which does not stick to the furnace surface is carried through the process, exits with the bottom tar products. It is observed that such carbonaceous materials generally appear in fine particulate forms with a wide range of particle sizes and size distributions. The data collected in the measurement of the second parameter are related to the number of coke or carbon particles within a unit volume of oil, i.e. the bottoms fraction of the product of the thermal cracking reaction. The measurement usually determines only those particles smaller than about 30 microns (μ) in diameter, more often only those smaller than about 20μ and larger than about 1μ per milliliter of a diluted bottoms fraction (tar). It is usually convenient, but not necessarily required, to use a dilution ratio of 20,000, *i.e.* 5μl of tar diluted with 100ml of solvent. Particles smaller than about 1μ are typically disregarded for the purposes of this invention.

These two measurements of the first and the second parameters may be carried out independently or in concert, simultaneously or sequentially, and combinations thereof. The data collected from the measurements may be used to monitor, control or adjust operating conditions of the furnace tube and/or the soaker, if present, either independently or together, depending on the feedstock charge, the reaction conditions, the equipment of the system and the desired outcome.

The data collected from the measuring and/or analytical instrument are sent to one or more data processing units or processors, which are either on-site, at a remote location or both. The processor(s), such as computers, can

compare the data with a limit or set of limits to determine whether the collected data are outside of the limits. The determinations are used to adjust, if needed, the thermal cracking reaction operating conditions, including, but not limited to thermal cracking temperature, furnace outlet temperature (also referred to herein as reactor outlet temperature interchangeably), pressure, residence time, flow rate of the heavy hydrocarbons, injection of additives and combinations thereof. Operating conditions related to a soaker, if there is one used in the system, may be adjusted in accordance with the determinations as well. These operating conditions of a soaker include, but are not limited to, residence time of the product in the soaker, if and what gas or gas mixtures to be injected into the soaker, the flow rate(s) of the gas(es), the temperature(s) of the gas(es), the quantity of the gas(es) and combinations thereof. (*infra*)

The processors or computers are capable of issuing commands to the controllers of the various operating conditions in accordance with one or more models. It is within the embodiment of the present invention to use the data collected to modify, refine or refresh the set of reference data and/or the models continuously, intermittently, at a preset interval, upon a triggering point or event or a combination thereof. The one or more models may be updated or modified online or off-line, continuously or periodically. It is also possible to house one or more of the processors with one or more of the analytical instrument or one or more of the various controllers. Various processors and/or computers may be on-site, at a remote location or both.

Alternatively, the collected data may be used directly to adjust all of the operating conditions mentioned herein and particularly those in the preceding paragraph, if needed. There may be one or more models used for the method or system in deciding if and how the changes or adjustments are to be made. This is conditioned on the fact that the controllers of those operating conditions are capable of receiving the data or commands directly.

Again, the models may be modified either online or off-line, continuously or periodically.

The first parameter measures and monitors the precipitation of asphaltenes and/or the stability asphaltene colloids, i.e. propensity for forming precipitates in a particular mixture. All of these different asphaltene precipitation mechanisms are usually difficult and time-consuming to be quantified individually. Accordingly, they are collectively referred to herein as asphaltene colloidal stability. There are several ways of carrying out this measurement to determine asphaltene colloidal stability. Examples include flocculation ratio method (FR), peptisation index (PV, i.e. peptisation value) and other methods such as the so-called Martin Bailey method (MB), hot filtration test (HFT), Shell hot filtration test, ASTM D-1661, ASTM D-4870 and UOP 1174 methods. These methods generally rely on the capability of paraffinic fluids to cause asphaltenes to separate out of a mixture. As already discussed, asphaltenes are insoluble in most light naphthas. Most of these methods are rather complex operations. They can be time-consuming with long response time/cycle and it is not unusual to encounter frequent reproducibility problems.

For the present invention, it is preferred to use a method of determining the infrared stability index (ISI) as a measure of asphaltene colloidal stability. This ISI measurement is accomplished by using a system comprising an automatic titrator, a near infrared (NIR) probe and a data processor. A first volume amount of a sample, such as a heavy tar residue from a visbreaking reactor (furnace) is obtained. This sample is then diluted with a fixed volume amount of a suitable aromatic solvent, such as benzene, toluene, xylenes, C_9 to C_{10} aromatics and mixtures thereof to form a mixture. The volume of the_aromatic solvent to the volume of the tar residue is in the range of from about 10 to 1 to about 1 to 10, preferably in the range of from about 1 to 1 to about 1 to 5.

A paraffinic solvent, such as light naphtha, butane, pentane, hexane, heptane, mixtures and others, is then added to this mixture, with the help of the automatic titrator or other suitable equipment, to dose and measure the amount needed to induce flocculation in and the infrared stability index of the mixture. A flocculation point is reached when detectable aggregation occurs in the sample because the paraffinic solvent is actually used as an "anti-solvent." This point is also the end point of the titration. A heptane such as n-heptane is a preferred paraffinic solvent. While butanes and pentanes may be more sensitive than heptane, their lower boiling points and the corresponding higher vapor pressures make the actual titration operation more difficult.

This "infrared stability index" or ISI can be determined by a method such as light absorbance and/or scattering using at least one light source and at least one probe, such as an NIR probe. Infrared (about 25μm to about 2.5μm) or visible light (about 750 nm to about 400 nm) sources may also be used. NIR means the light has a wavelength in the range of from about 2.5 μm to about 750 nm. NIR, near-infrared, method is preferred for measuring absorbance or light scattering of dark colored mixtures or solutions. In the probe, the absorbance and/or scattering at one or more wavelengths may be monitored at the same time.

The ratio of the volume of the paraffinic solvent to the first volume of the sample is defined as the "first parameter" for purposed of this invention. If this first parameter, measured by ISI in the examples below, decreases below a certain value, it is an indication that the asphaltenes and/or asphaltene colloids are becoming too unstable and any precipitation and/or aggregation will become unacceptable to the thermal cracking or visbreaking reaction operator. The severity of the cracking unit needs to be moderated. Cracking conditions such as cracking temperature, furnace outlet temperature and/or residence times may be lowered. Conversely, if the first

parameter is much higher than the value, the severity of the cracking unit may be increased to increase conversion of the feed. Depending on the unit, the feed and other operating conditions, this value or limit may vary. In the examples below (*infra*), the predetermined limit is set at about 1.75, preferably about 1.70.

The data of the first parameter may be used directly or it can be recorded and stored in a processor to be further analyzed, compared and used to issue commands to alter, adjust or modify one or more thermal cracking (including visbreaking) operating conditions, including those conditions related to the soaker operation, if one is used in the system. The first parameter may also be used in concert with the second parameter (*infra*) to determine any changes or adjustments of one or more of the operating conditions.

The infrared stability index is determined in the following manner. As the transparent paraffinic solvent is added to the mixture containing the tar residue and the aromatic solvent, optical absorbance decreases and the incident light transmitted increases. This increase continues until a point where the asphaltenes and/or asphaltene colloids begin to precipitate and/or form aggregates out of the entire mixture. This is the flocculation point determined by the end point of measuring infrared stability index. This precipitation or aggregation is a result of the fact, as discussed earlier, that asphaltenes and/or the asphaltene colloids are practically insoluble in paraffinic solvents. The scattering and/or absorbance of light would cause the transmitted light intensity to decrease again. The decrease will continue as more paraffinic solvent is added because more asphaltenes will precipitate out of the system.

Independent of or in conjunction with the infrared stability index measurement and the associated flocculation point determination as discussed in the preceding paragraphs, the number of carbon or coke

particles is determined. Prior to the measurement, the tar residue is diluted with a larger amount of aromatic solvent. The total volume of the aromatic solvent to the volume of the tar residue is generally in the range of from about 1,000,000 to 1 to about 1 to 1, preferably from about 100,000 to 1 to about 5 to 1.

After the dilution, the number of coke particles is measured. The number of coke particles smaller than about 20 microns and larger than about 1 micron per unit volume of the residue is defined as the second parameter for the feed, the thermal cracking unit and operating conditions of the examples of the present invention. Similar to ISI, this particle size limit may vary from unit to unit, reaction to reaction and/or feed to feed, depending on the charge (feed), the operating conditions, the operating experience, data collected, baseline information, the particle analyzer used and many other parameters or combinations. The particle-count measurements can be accomplished by using various particle size analyzers. One example is a light-scattering particle size analyzer equipped with a He-Ne (helium-neon) laser light source and the associated electronics.

This second parameter or the corresponding data collected can be used directly or it can be recorded and stored in a processor (such as a computer) to be further analyzed, compared and used to issue commands to alter, adjust or modify one or more thermal cracking (including visbreaking) operating conditions, including those conditions related to the soaker operation, if one is used in the system. This second parameter may also be used in concert with the first parameter (*supra*) to determine any changes or adjustments of one or more of the operating conditions.

For a visbreaking reaction, it is generally preferred to keep the number of coke particles (carbonaceous materials smaller than about 20 microns) per unit volume of the tar residue below a level or reference or limit. If the number of the second parameter is much below this limit, it is possible to

raise these parameters to increase conversion of the charge. If the parameter is much higher than the limit, it may be necessary to adjust the operating conditions as described in the preceding paragraph, including lowering cracking temperature, lowering FOT and/or decreasing residence time. Too much coke formation indicates that excessive dehydrogenation is occurring in the cracking reaction and this is not desirable. From experience, there also may be coke particles greater than about 20 microns in size. The number is generally low and it is usually difficult to correlate the number with thermal cracking reaction performance of a particular cracking unit.

For both the first and the second parameters, the measured and collected data are normally stored in the analytical instrument and/or separate on-site or remote processors or computers. The data are then compared with the respective references with one or more computer models in order to determine whether any of the operating conditions need to be changes. If changes or adjustments of the operating conditions are needed in accordance with the differences and/or models analyzing the data, proper command signals are sent to various controllers, which in turn change the conditions, such as temperature, flow rate, pressure, gas injection rate in a soaker and others as disclosed herein.

There are a number of ways of setting up the references. One way is to pre-select acceptable limits from past operating experience. Another way may employ theoretical, empirical or semi-empirical methods to calculate the references. It is also possible to use a continuous update method by incorporating the data collected. Certainly, one can use a combination of these different methods in setting the reference points for the first parameter and the second parameter. One or more (computer) models may be used. These models may be related to setting up the reference points, comparison of the collected data with the reference points, issuing commands to controllers in the system in response to the results of the comparisons, and

combinations thereof. It is possible to use different processors or computers for different aspects, provided that there is the communication among the processors, analytical instrument, operating condition controllers, and/or other instrument or equipment as needed.

Regardless of the way the references or reference points are determined or selected, if these limits are exceeded (lower in infrared stability index or higher in coke particle count), operating conditions are changed to bring the parameters back to within acceptable ranges. If the data fall far short of the limit(s), the reaction is then not producing high enough conversions. The operating conditions are then changed to increase the conversion of heavy hydrocarbon charge (feedstock) while maintaining the one or, preferably, both parameters within the limits.

It is also within the embodiment of the present invention to integrate the measurements of both parameters into a single system. **Figure 1** shows such an integrated system. The system according to Figure 1 operates as follows:

Control box **30** generates an electrical signal, which is transmitted to a near-infrared (NIR) probe **10**. NIR probe **10** transduces the electrical signal into an optical signal, which is transmitted into the oil (e.g. a sample of a tar residue from a visbreaker dissolved in an aromatic solvent). The same probe, or optionally a separate sensor **20**, detects and measures the changes in intensity of the optical signal at a fixed path length. If there is increasing in the number of asphaltene particles per unit volume of the oil phase, the intensity decreases.

Control box **30** amplifies and transmits the detected signal to automated titrator **40**, which doses a clear and transparent paraffinic solvent to the "oil" in a volume that is inversely proportional to the change in signal voltage. The data related to the volume added by titrator **40** is sent to

processor or computer **50**. As the paraffinic solvent is added to the oil, the optical resistance of the oil decreases. As a result, the NIR light incident upon the detector increases. The addition or dosing continues until a infrared stability index is reached, *i.e.* the asphaltenes or asphaltenic components begin to precipitate out of the oil phase. At his infrared stability index, the optical resistance starts to increase and the detector will detect decreasing light.

These changes in optical resistance as detected by the detector are transmitted to processor or computer **50**. The data are stored and analyzed. Furthermore, the data are plotted against the volume of the paraffinic solvent added by automated titrator **40**. The infrared stability index is determined and the ratio of the volume of the paraffinic solvent to the volume of oil at the infrared stability index is determined. This is the data for the first parameter. This collected data may be used alone or in combination with the data collected for the second parameter to adjust or change the thermal cracking reaction operating conditions and/or the operating conditions of the soaker, if one such unit is used.

In a similar way, particle analyzer **60** is used to determine the number of coke particles per unit volume of oil in the oil sample wherein the particles are smaller than a predetermined size. This size limit is usually between about 1 micron and 20 mincrons. Coke or carbonaceous materials are not soluble in the organic solvent used to dilute the tar residue. Typical organic solvents include benzene, toluene, the xylenes, C_9 or C_{10} aromatics such as pseudocumene and mixtures thereof. It is known that the number of aromatic solvent insoluble particles increases after the thermal cracking reaction. In other words, a thermal cracking reaction such as a visbreaking reaction generates such coke particles. The amount of coke particles in the tar residue has been known to correlate with the amount of coking taking place inside the cracking furnace or furnace tubes.

The number of particles measured in this manner is the collected data for the second parameter. This collected data may be used alone or in combination with the data collected for the first parameter to adjust or change the thermal cracking reaction operating conditions and/or the operating conditions of the soaker, if one is used. As shown below in the example, the furnace outlet temperature is an operating parameter that may be controlled in response to the collected data of the first parameter, the second parameter or both to maximize conversion within acceptable limits of asphaltene precipitation/asphaltene colloid aggregation and coking.

To one skilled in the art, a number of variations are possible and suitable for the present invention. For example, the system may be integrated. The various signals, feedbacks and commands may be generated, stored, compared with references or calculated with one or more models by different processors or computers or modules, which may be part of any of the analytical equipment disclosed herein. In addition, the entire system can be automated. Alternatively, it may be preferred to automate only part of the system.

The term "heavy hydrocarbon" as used herein means generally the type of hydrocarbon feedstock or charge or petroleum fluid that contains asphaltene and/or asphaltene colloids and is regularly subjected to thermal cracking or visbreaking in the refining and chemical industries. The structures and compositions of a heavy hydrocarbon are very complex and there could be heteroatom-containing compounds present. Commonly detected heteroatoms include, but are not limited to, oxygen, nitrogen, sulfur and mixtures thereof. _Examples of heavy hydrocarbons include vacuum distillation residue (or resid), atmospheric distillation residue, crude oil, FCC slurry oil and mixtures thereof.

If a soaker is used in the visbreaking system, it is also within the embodiment to use substantially non-reactive gases such as nitrogen, steam

or mixtures thereof inside the soaker, particularly in the vicinity of the bottom and the side walls thereof. Independent from and/or in concert with adjusting the operating conditions of the visbreaking unit, the data collected from measuring the two parameters also may be used to adjust the injection of such substantially non-reactive gas or gas mixtures in the soaker. For instance, the quantity, injection rate, injection location, gas temperature and combinations thereof may be adjusted in response to the data. It is preferred to use steam. [*see* US 5,925,236].

The following example was carried out to illustrate certain embodiments of the present invention. The furnace outlet temperature was the operating parameter controlled by the collected data of the first and the second parameters. One having ordinary skill in the art would appreciate the teachings of the example and the associated data with respect to the disclosures as well as the claims of the present invention and realize that many other modifications or variations can be made within the scope and spirit of the present invention.

Example 1

The example was carried out in a visbreaker unit located in a refinery. A sample of vacuum residue was charged to the unit at a rate in the range of from about 65 to about 95 cubic meters per hour (m^3/h). Typical furnace outlet temperatures (FOT) were in the range of from about 455°C to about 465°C. Conversions of the feed was about 15.4 wt%. In other words, the light fraction of the product stream is 15.4 wt% of the charge and the bottoms fraction of the product stream constitutes the balance.

As the severity of the thermal cracking process, visbreaking, increases the value of the first parameter decreases, and the value of the second parameter increases. In order to optimize the cracking severity in accordance with the present invention, the FOT was increased until the first

parameter fell to a predetermined value of 1.7, or until the second parameter rose to a predetermined value of 2500. For an average operation, the flow rate was slightly lower at 87.1 m^3/h. The first parameter was about 1.86 and the second parameter was about 444.

The optimization or improvement of the process was performed in several steps during an eleven-hour period. (*see* **TABLE** below) The objective was to operate the thermal cracking to achieve as high a conversion as possible while maintaining both the first parameter and the second parameter within acceptable levels, which represent acceptable asphaltene precipitation, particularly before and after cracking, and coking, particularly during cracking, respectively.

At the start of the optimization of the visbreaking process, *i.e.* at time of 0.00 hour, FOT was about 462.5°C and the flow rate was about 89.4 m^3/h. The first parameter was about 1.87 and the second parameter, about 408. The conversion remained steady at about 15.4 wt%. These were not too different from those values observed for an average operation.

At time of 5:00 hour, the temperature of the visbreaking reaction was raised so FOT became 464.0°C. The flow rate was 88.6 m^3/h. The first parameter decreased to about 1.75 and at the same time the second parameter increased to 693. The conversion was much higher at 17.6 wt%. The temperature, FOT, was allowed to go up to 465.5°C at a flow rate of 90.3 m^3/h. While the conversion went to 18.2 wt%, it was at the expense of the first parameter decreasing to the predetermined limit of 1.70 and the second parameter increasing substantially to 1540. Further increasing FOT to 466°C at a flow rate of 80.0 m^3/h, resulted in an even higher conversion of 21.3 wt%. Both the first parameter and the second parameter were outside of the predetermined limits. The first parameter was 1.53 and the second parameter, 5351. These levels were not acceptable. Accordingly, the conditions were changed at this time to lower FOT.

These results are presented below in the **TABLE**.

TABLE

Time (h)	FOT (°C)	Flow rate (m^3/h)	First Parameter	Second Parameter	Conversions (%)
Average Operation					
	462.5	87.1	1.86	444	15.4
Optimization Starting Conditions					
0:00	462.5	89.4	1.87	408	15.4
Optimization Step 1 (Increase Temperature)					
5:00	464.0	88.6	1.75	693	17.6
Optimization Step 2 (Increase Temperature)					
11:00	465.5	90.3	1.70	1540	18.2
Optimization Step 3 (Decrease Temperature)					
24:00	466.0	80.0	1.51	5351	21.3

From the results in the **TABLE**, it can be seen that using the present invention can allow one to measure the changes of the performance of the visbreaking reaction and to maximize product yields without causing unreasonably high coke formation.

These parameters are determined by analytical methods and instrument that can be automated, it is within the embodiment of the present invention to use control units or processors to compare the data with one or more models to determine if the reactions are optimized. The decision is then transmitted to controls of the visbreaking unit to vary the reaction conditions such as temperature, residence time (flow rate), pressure and combinations thereof.

A number of theories and hypotheses discussed herein solely for easy understanding and better appreciation of the present invention by one skilled in the art. They are not intended to limit either the scope or the spirit the invention in any way. Similarly, the foregoing examples and any preferred embodiments are intended for illustration purposes only to demonstrate the embodied invention. They are not intended to limit the spirit or the scope of

the invention, which is described by the entire written disclosure herein and defined by the claims below.

CLAIMS

1. A method for improving thermal cracking of heavy hydrocarbons comprising:

cracking the heavy hydrocarbons in a unit under first conditions effective to produce a product comprising a light fraction and a bottoms fraction;

separating the light fraction from the bottoms fraction;

measuring a parameter of the bottoms fraction;

making a determination of whether the parameter is outside of a limit; and

adjusting the first conditions in response to the determination.

2. The method of claim 1, wherein the parameter is selected from the group consisting of asphaltene colloidal stability, amount of coke particles and a combination thereof.

3. The method of claim 2, wherein the thermal cracking is visbreaking.

4. The method of claim 3, wherein the heavy hydrocarbons are selected from the group consisting of crude oil, atmospheric distillation residue, vacuum distillation residue, FCC slurry oil and mixtures thereof.

5. The method of claim 2, wherein the first conditions comprise thermal cracking temperature, furnace outlet temperature, pressure, residence time and flow rate of the heavy hydrocarbons.

6. The method of claim 1, wherein the thermal cracking is visbreaking and the cracking unit further comprises a soaker operating under second conditions.

7. The method of claim 2, wherein the bottoms fraction is used as feedstock for at least one coker or at least one delayed coker.

8. The method of claim 7 further comprising adjusting the second conditions in response to the determination.

9. The method of claim 8, wherein

the thermal cracking is visbreaking;

the heavy hydrocarbons are selected from the group consisting of crude oil, atmospheric distillation residue, vacuum distillation residue, FCC slurry oil and mixtures thereof; and

the parameter is selected from the group consisting of asphaltene colloidal stability, amount of coke particles and a combination thereof.

10. A system for performing improved thermal cracking of heavy hydrocarbons, the system comprising:

a cracking unit comprising a cracking furnace to crack the heavy hydrocarbons under first conditions effective to produce a product;

a fractionation column to separate the product into a light fraction and a bottoms fraction;

at least one sensor to measure at least one parameter of the bottoms fraction

at least one processor to make a determination if the at least one parameter is outside of a limit; and

at least one controller to adjust the first conditions in response to the determination.

11. The system of claim 10, wherein the parameter is selected from the group consisting of asphaltene colloidal stability, amount of coke particles and a combination thereof.

12. The system of claim 10, wherein the thermal cracking is visbreaking and the heavy hydrocarbons are selected from the group consisting of crude oil, atmospheric distillation residue, vacuum distillation residue, FCC slurry oil and mixtures thereof.

13. The system of claim 11, wherein the first conditions comprise thermal cracking temperature, furnace outlet temperature, pressure, residence time and flow rate of the heavy hydrocarbons.

14. The system of claim 12 further comprising a soaker which operates under second conditions.

15. The system of claim 14, wherein the soaker has a substantially non-reactive gas injected in a vicinity of a location selected from its bottom, its side walls and combinations thereof and wherein the gas is selected from nitrogen, steam and a combination thereof.

16. The system of claim 14, wherein the at least one controller further adjusts the second conditions in response to the determination.

17. A system for performing improved thermal cracking of heavy hydrocarbons, the system comprising:

a cracking unit comprising a cracking furnace to crack the heavy hydrocarbons under first conditions effective to produce a product;

a fractionation column to separate the product into a light fraction and a bottoms fraction;

at least one sensor to measure at least one parameter of the bottoms fraction

at least one processor to make a determination if the at least one parameter is outside of a limit; and

at least one controller to adjust the first conditions in response to the determination.

at least one coker or delayed coker for converting the bottoms fraction.

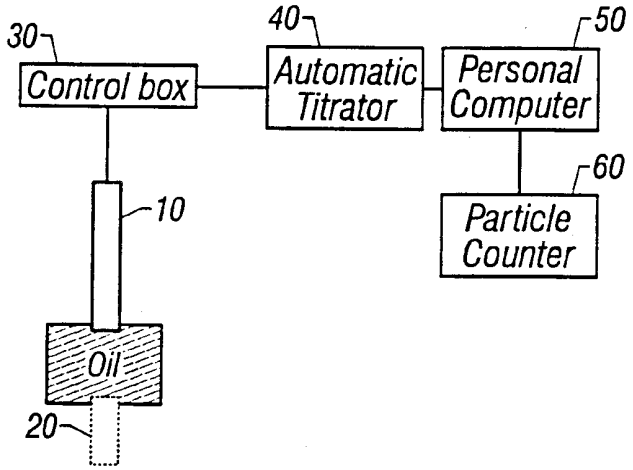

30
Control box
40
Automatic Titrator
50
Personal Computer
60
Particle Counter
10
Oil
20

FIG. 1

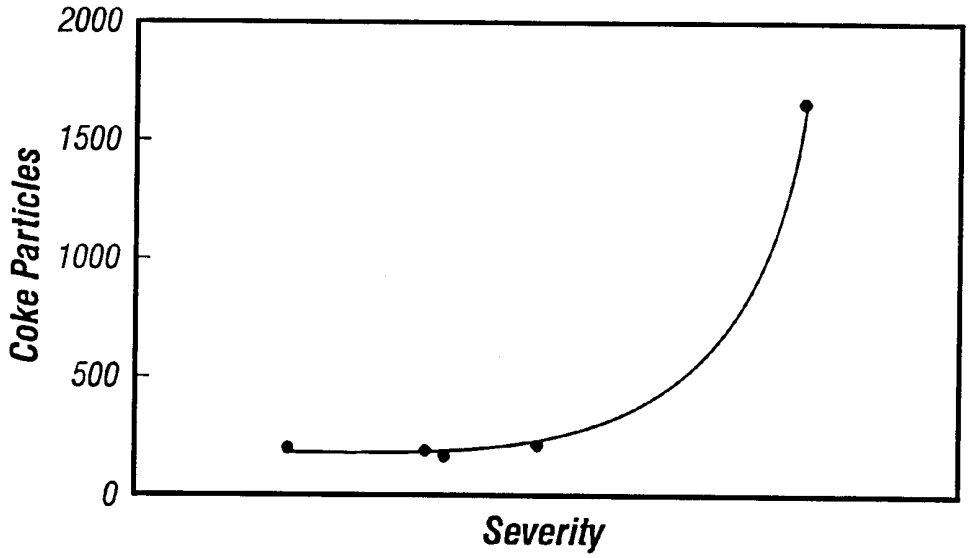

2000
1500
1000
500
0
Coke Particles
Severity

FIG. 2

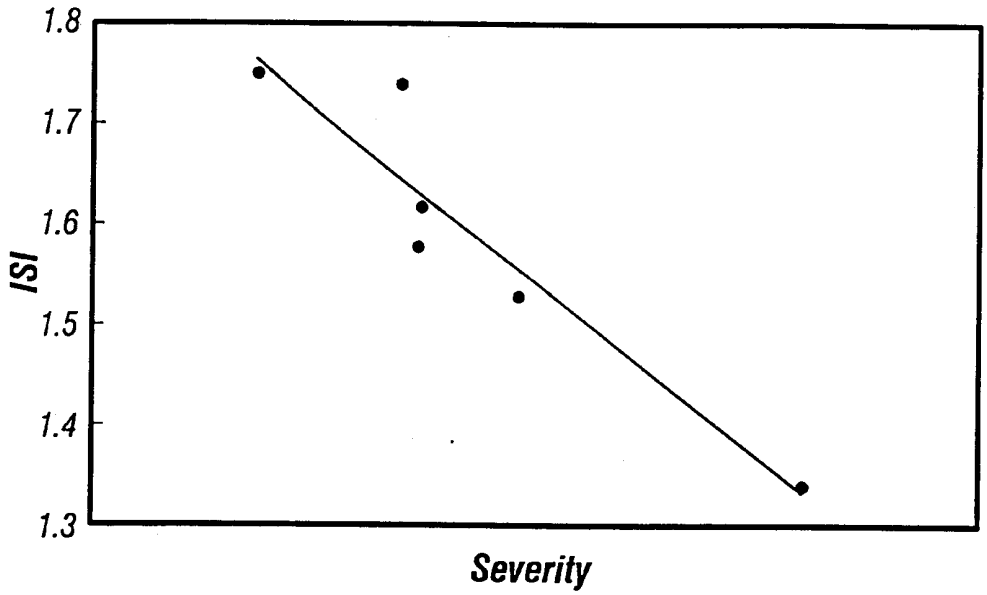


FIG. 3

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/US 00/32061

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G9/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 198133 Derwent Publications Ltd., London, GB; Class H04, AN 1981-59999D XP002161800 & SU 783 334 A (KUIB MOSC NEFTEKHIM), 30 November 1980 (1980-11-30) abstract ---	1-17
A	WO 98 17742 A (DOW CHEMICAL CO) 30 April 1998 (1998-04-30) -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 March 2001	19. 03. 2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Michiels, P

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat. .al Application No
PCT/US 00/32061

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
SU 783334 A	30-11-1980	NONE	
WO 9817742 A	30-04-1998	EP 0946677 A	06-10-1999