METHOD FOR IMPROVING LIQUID YIELD DURING THERMAL CRACKING OF HYDROCARBONS

Field of the Invention

The present invention relates to methods and compositions for improving liquid yields during thermal cracking of hydrocarbons, and more particularly relates, in one embodiment, to methods and compositions for improving liquid yields during thermal cracking of hydrocarbons by introducing an additive into the hydrocarbon.

Background of the Invention

Many petroleum refineries utilize a delayed coking unit to process residual oils. Delayed coking is a process for obtaining valuable products from the otherwise poor source of heavy petroleum bottoms. Delayed coking raises the temperature of these bottoms in a process or coking furnace and converts the bulk of them to coke in a coking drum. The liquid in the coking drum has a long residence time to convert the resid oil to lower molecular weight hydrocarbons which distill out of the coke drum. Overhead vapors from the coking drum pass to a fractionator where various fractions are separated. One of the fractions is a gasoline boiling range stream. This stream, commonly referred to as coker gasoline, is generally a relatively low octane stream, suitable for use as an automotive fuel with upgrading. The liquid products from this thermal cracking are generally more valuable than the coke produced. Delayed coking is one example of a process for recovering valuable products from processed oil using thermal cracking of heavy bottoms to produce valuable gas and liquid fractions and less valuable coke.

It would thus be desirable to provide a method and/or composition that would improve the yield of liquid hydrocarbon products from a thermal cracking process.

Summary of the Invention

Accordingly, it is an object of the present invention to provide a composition and method for improving the liquid yield from a thermal cracking

process. Thermal cracking processes to which the invention may be applied include, but are not necessarily limited to, delayed coking, flexicoking, fluid coking and the like.

It is another object of the present invention to provide a composition and method for improving liquid yield during delayed coking, flexicoking or fluid coking using a readily available additive.

In carrying out these and other objects of the invention, there is provided, in one form, a method for improving liquid yield during thermal cracking of a hydrocarbon that involves introducing a metal additive to a hydrocarbon feed stream, heating the hydrocarbon feed stream to a thermal cracking temperature, and recovering a hydrocarbon liquid product. The metal additive can be a metal overbase or metal dispersion.

In another non-limiting embodiment of the invention, there is provided a refinery process that concerns a coking operation which includes introducing a metal additive to a coker feed stream, heating the coker feed stream to a thermal cracking temperature and recovering a hydrocarbon liquid product. Again, metal additive can be a metal overbase or metal dispersion or a combination thereof.

Brief Description of the Drawings

FIG. 1 is a chart of percent liquid yield results for Examples 1-5 using thermal cracking on a HTFT hydrocarbon stream;

FIG. 2 is a chart comparing liquid yield increases of Examples 2-4 with blank (1) (Example 1) of FIG. 1;

FIG. 3 is a chart comparing liquid yield increases of Examples 2-4 with blank (2) (Example 5) of FIG. 1; and

FIG. 4 is a chart of percent liquid yield results for Examples 6-10 using thermal cracking on a HTFT hydrocarbon stream.

Detailed Description of the Invention

It has been discovered that the use of overbase additives or metal dispersions improves liquid yield during the thermal cracking of a hydrocarbon, such as a thermal coking process. Any approach to increase the liquid yield during coke production will have a significant value to the operator.

It is expected that the method and additives of this invention would be useful for any hydrocarbon feed stream that is to be thermally cracked, such as in a coking application, including, but not necessarily limited to, coker feed streams, atmospheric tower bottoms, vacuum tower bottoms, slurry from an FCC unit, visbreaker streams, slops, and the like. As noted previously, thermal cracking processes to which the invention may be applied include, but are not necessarily limited to, delayed coking, flexicoking and fluid coking and the like.

Suitable metal additives for use in this invention include, but are not necessarily limited to, magnesium overbases, calcium overbases, aluminum overbases, zinc overbases, silicon overbases, barium overbases, strontium overbases, cerium overbases and mixtures thereof, as well as dispersions. These overbases and dispersions are soluble in hydrocarbons, even though it is generally harder to get these additives dispersed in hydrocarbon as contrasted with aqueous systems. In one non-limiting embodiment of the invention, the metal additive contains at least about 1 wt% magnesium, calcium, aluminum, zinc, silicon, barium, cerium or strontium. In one alternative embodiment, the additive contains about 5 wt% metal, in another non-limiting embodiment, the amount of metal or alkali earth metal is at least about 17 wt%, and in a different alternate embodiment, at least about 40 wt%. Processes for making these metal overbases and dispersion materials are known. In one non-limiting embodiment, the metal overbase is made by heating a tall oil with magnesium hydroxide. In another embodiment the overbases are made using aluminum oxide. In another embodiment dispersions are made using magnesium oxide or aluminum oxide.

Dispersions and overbases made using other metals would be prepared similarly. In one non-limiting embodiment the target particle size of these dispersions and overbases is about 10 microns or less, alternatively about 1 micron or less. It will be appreciated that all of the particles in the additive are not of the target size, but that a "bell-shaped" distribution is obtained so that the average particle size distribution is 10μ or less, or alternatively 1μ or less.

In further detail, the metal dispersions or complexes useful in the present invention may be prepared in any manner known to the prior art for preparing overbased salts, provided that the overbase complex resulting therefrom is in the form of finely divided, and in one non-limiting embodiment, submicron particles which form a stable dispersion in the hydrocarbon feed stream. Thus, one non-restrictive method for preparing the additives of the present invention is to form a mixture of a base of the desired metal, *e.g.*, $Mg(OH)_2$, with a complexing agent, *e.g.* a fatty acid such as a tall oil fatty acid, which is present in a quantity much less than that required to stoichiometrically react with the hydroxide, and a non-volatile diluent. The mixture is heated to a temperature of about 250-350°C, whereby there is afforded the overbase complex or dispersion of the metal oxide and the metal salt of the fatty acid.

The above described method of preparing the overbase complexes of the present invention is particularly set forth in U.S. Pat. No. 4,163,728, wherein for example, a mixture of $Mg(OH)_2$ and a carboxylic acid complexing agent is heated at a temperature of about 280-330°C in a suitable non-volatile diluent.

Complexing agents which are used in the present invention include, but are not necessarily limited to, carboxylic acids, phenols, organic phosphorus acids and organic sulfur acids. Included are those acids which are presently used in preparing overbased materials (*e.g.* those described in U.S. Pat. Nos. 3,312,618; 2,695,910; and 2,616,904) and constitute an art-recognized class of acids. The carboxylic acids, phenols, organic phosphorus acids and organic sulfur acids which are oil-soluble *per se*, particularly the oil-

soluble sulfonic acids, are especially useful. Oil-soluble derivatives of these organic acidic substances, such as their metal salts, ammonium salts, and esters (particularly esters with lower aliphatic alcohols having up to six carbon atoms, such as the lower alkanols), can be utilized in lieu of or in combination with the free acids. When reference is made to the acid, its equivalent derivatives are implicitly included unless it is clear that only the acid is intended. Suitable carboxylic acid complexing agents which may be used herein include aliphatic, cycloaliphatic, and aromatic mono- and polybasic carboxylic acids such as the naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids and alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally are long chain acids and contain at least eight carbon atoms and in one non-limiting embodiment at least twelve carbon atoms. The cycloaliphatic and aliphatic carboxylic acids can be saturated or unsaturated.

The metal additives acceptable for the method of this invention also include true overbase compounds where a carbonation procedure has been done. Typically, the carbonation involves the addition of CO_2, as is well known in the art.

It is difficult to predict in advance what the proportion of the overbase additive of this invention should be in the hydrocarbon feed stream that it is applied to. This proportion depends on a number of complex, interrelated factors including, but not necessarily limited to, the nature of the hydrocarbon fluid, the temperature and pressure conditions of the coker drum or other process unit, the amount of asphaltenes in the hydrocarbon fluid, the particular inventive composition used, etc. It has been discovered that higher levels of asphaltenes in the feed require higher levels of additive, that is, the level of additive should correspond to and be directly proportional to the level of asphaltenes in the feed. Nevertheless, in order to give some sense of suitable proportions, the proportion of the overbase additive of the invention may be applied at a level between about 1 ppm to about 1000 ppm, based on the hydrocarbon fluid. In another non-limiting embodiment of the invention,

the upper end of the range may be about 500 ppm, and alternatively up to about 300 ppm. In a different non-limiting embodiment of the invention, the lower end of the proportion range for the overbase additive may be about 50 ppm, and alternatively, another non-limiting range may be about 75 ppm.

While the overbase additive can be fed to the coker feedstock, or into the side of the delayed coker, in one non-limiting embodiment of the invention, the additive is introduced as far upstream of the coker furnace as possible without interfering with other units. In part, this is to insure complete mixing of the additive with the feed stream, and to allow for maximum time to stabilize the oil and asphaltenes in the stream.

The thermal cracking of the hydrocarbon feed stream should be conducted at relatively high temperatures, in one non-limiting embodiment at a temperature between about 850°F (454°C) and about 1300°F (704°C). In another non-limiting embodiment, the inventive method is practiced at a thermal cracking temperature between about 900°F (482°C) and about 950°F (510°C).

A dispersant may be optionally used together with the overbase additive to help the additive disperse through the hydrocarbon feedstock. The proportion of dispersant may range from about 1 to about 500 ppm, based on the hydrocarbon feedstock. Alternatively, in another non-limiting embodiment, the proportion of dispersant may range from about 20 to about 100 ppm. Suitable dispersants include, but are not necessarily limited to, copolymers of carboxylic anhydride and alpha-olefins, particularly alpha-olefins having from 2 to 70 carbon atoms. Suitable carboxylic anhydrides include aliphatic, cyclic and aromatic anhydrides, and may include, but are not necessarily limited to maleic anhydride, succinic anhydride, glutaric anhydride, tetrapropylene succininc anhydride, phthalic anhydride, trimellitic anhydride (oil soluble, non-basic), and mixtures thereof. Typical copolymers include reaction products between these anhydrides and alpha-olefins to produce oil-soluble products. Suitable alpha olefins include, but are not necessarily limited to ethylene,

propylene, butylenes (such as n-butylene and isobutylene), C2-C70 alpha olefins, polyisobutylene, and mixtures thereof

A typical copolymer is a reaction product between maleic anhydride and an alpha-olefin to produce an oil soluble dispersant. A useful copolymer reaction product is formed by a 1:1 stoichiometric addition of maleic anhydride and polyisobutylene. The resulting product has a molecular weight range from about 5,000 to 10,000, in another non-limiting embodiment.

The invention will now be described with respect to certain more specific Examples which are only intended to further describe the invention, but not limit it in any way.

TABLE I – Materials Used in Experiments

Material Designation	Description
Additive A	Magnesium dispersion containing approximately 17 wt% magnesium
Additive B	Carboxylic anhydride / C_{20-24} alpha olefin copolymer dispersant
Additive C	Metal passivator
Additive D	Aluminum overbase made using sulfonic acid

Experimental High Temperature Fouling Test (HTFT) Procedure

Samples of heated coker feed were poured out in pre-weighed 100 mL beakers. The amount of the sample was weighed and recorded. Prior to a HTFT run, the preweighed beaker with coker feed was heated to about 400°F (204°C). The base of a Parr pressure vessel was preheated to about 250°F (121°C). For samples where Additive C was used, a metal coupon was pretreated with the Additive C. The coupon was then placed in a warmed oil sample. If Additive B or Additive A were to be added, it was done so as the feed was heated and had become liquid.

The HTFT sample was heated to the desired temperature, normally 890°F (477°C) to 950°F (510°C), dependent on the furnace outlet temperature in which the coker feed was processed. When the coker sample,

autoclave base, and HTFT furnace had all reached the appropriate test temperature, the sample beaker was placed into the autoclave base and the autoclave top was secured to the base. The closed vessel was then placed into the heated furnace. An automated computer-based test program then recorded the test elapsed time, sample temperature and autoclave pressure every 30 seconds throughout the test run. When the coker feed had reached the desired test temperature, liquid hydrocarbon and vapors were vented from the vessel at predetermined pressure levels until all available liquid/gas hydrocarbons were removed from the coker feed as coking occurs. This process was usually completed in seven to ten minutes after the coker feed test sample reached the set test temperature, *i.e.* 920°F (493°C). Upon cooling, the condensed liquid/gas hydrocarbon was measured to the nearest 0.5 mL and the weight of the liquid was recorded. The density of the liquid was recorded and the yield percentage was calculated.

Results

Results for measuring the percent liquid yield are shown in FIG. 1. The data show that when magnesium overbase Additive A was included in the feed, the level of liquid yield (Examples 2-4) was consistently greater than that of the untreated samples (Examples 1 and 5). In determining the liquid yield increase, the amount of liquid added to the samples when adding additive was subtracted out, thereby making the calculated results conservative. It would be expected that any carrier solvent added would go with the gas fraction.

The increase in liquid yield in comparing samples with Additive A to those without Additive A ranges between 1.67 to 8.63. Liquid yield increases compared to blank (1) (Example 1) and blank (2) (Example 5) are shown in FIGS. 2 and 3, respectively.

Additional results are presented in FIG. 4 using the same heated coker feed as for Examples 1-5. Example 7 using Mg dispersion Additive A gave a yield % increase of 1.5% over a 34.1% yield of the blank of Example 6 to

35.6%. Example 8 using the Al overbase Additive D gave a yield % of 36.7%, which was 2.6% higher than the blank. Example 9 employing a 50/50 combination of Additive A and Additive D gave a liquid yield % of 36.0%, improved by 1.9% over the blank of Example 6. Finally, Example 10 used a 50/50 combination of Additive A and Additive D as in Example 9, but at one-half the treatment rate of Example 9. Example 10 gave a 35.6% liquid yield, which was 1.5% over the liquid yield % of the blank Example 6. These Examples thus demonstrate that the use of a combination of metal additives may improve liquid yield.

The economic value of the invention that a refinery would observe is subject to the level of liquid yield increase and the value of the quality of liquid obtained. It is expected that a conservative increase in using the overbase additives of the invention would improve the liquid yield by about 2.5%, which would be a significant contribution over the course of a year.

In the foregoing specification, the invention has been described with reference to specific embodiments thereof, and has been demonstrated as effective in improving liquid yields from thermal cracking of coker feedstock, as a non-limiting example. However, it will be evident that various modifications and changes can be made thereto without departing from the broader spirit or scope of the invention as set forth in the appended claims. Accordingly, the specification is to be regarded in an illustrative rather than in a restrictive sense. For example, specific crosslinked overbase additives, and combinations thereof with other dispersants, and different hydrocarbon-containing liquids other than those specifically exemplified or mentioned, or in different proportions, falling within the claimed parameters, but not specifically identified or tried in a particular application to improve liquid yield, are within the scope of this invention. Similarly, it is expected that the inventive compositions will find utility as yield-improving additives for other hydrocarbon-containing fluids besides those used in delayed coker units.

What is claimed is:

1. A method for improving liquid yield during thermal cracking of a hydrocarbon comprising:

introducing a metal additive to a hydrocarbon feed stream in an amount from 1 to 1,000 ppm, where the metal additive is selected from the group consisting of a metal overbase and a metal dispersion, consisting of a metal compound, where in the metal compound the metal is selected from the group consisting of magnesium, calcium, aluminum, silicon, cerium, barium, strontium, and mixtures thereof, where the metal additive contains at least 1 wt% metal;

heating the hydrocarbon feed stream to a thermal cracking temperature between 850°F (454°C) and 1300°F (704°C); and

recovering a hydrocarbon liquid product in an amount at least 1.5% increased over an identical method absent the metal additive.

2. The method of claim 1 where the hydrocarbon feed stream is a coker feed stream.

3. The method of any of the above claims further comprising introducing a dispersant to the hydrocarbon feed stream.

4. The method of any of the above claims, where the method is a refinery process comprising a coking operation, where the hydrocarbon feed stream is a coker feed stream.

5. The method of any of the above claims where the metal compound is selected from the group consisting of metal oxides, metal hydroxides and combinations thereof.

6. The method of any of the above claims where in the metal compound, the metal is selected from the group consisting of magnesium, aluminum, silicon, cerium, barium, strontium, and mixtures thereof.