

APPARATUS AND METHOD FOR DETERMINING AND CONTROLLING
THE HYDROGEN-TO-CARBON RATIO OF A PYROLYSIS
PRODUCT LIQUID FRACTION

5 Field of the Invention

The invention relates to a method and apparatus for determining the hydrogen-to-carbon ratio of a liquid hydrocarbon. Another aspect of the invention relates to a method and apparatus for controlling the severity of
10 pyrolysis cracking processes.

Background of the Invention

A number of processes for the refining and processing of hydrocarbons require knowledge of the ratio of hydrogen-to-carbon in either the hydrocarbons being processed and/or
15 produced. Once such process is the production of olefins, in particular lower olefins, by the thermal cracking of hydrocarbon feedstocks.

The thermal cracking, or pyrolysis, of a hydrocarbon feedstock to prepare olefins is a known technique in the art.
20 The process is operated on a commercial scale to produce olefins, for example ethylene and propylene, in large quantities. A common process for commercial application is one in which the hydrocarbon feedstock is passed through one or more tubes or coils which define a thermal cracking zone
25 of a pyrolysis furnace. Heat input is provided by means of burners.

The properties of the hydrocarbon feedstock and the conditions under which the thermal cracking takes place determine the nature and contents of the product. In
30 general, it is desirable to operate the thermal cracking process so as to minimize the degree of coking. The depth of cracking or degree of conversion in the thermal cracking process is referred to as the cracking severity. The level of coking generally increases as the severity of the thermal

cracking increases, until a point is reached at which the level of coke becomes unacceptable. This point is often referred to as the maximum cracking severity, and often represents an optimum point combining a high olefin yield
5 with an acceptable length of time for which the furnace may be operated before the build up of coke requires the furnace to be shut down for decoke.

In the production of olefins on a commercial scale it is often highly desirable to be able to operate the thermal
10 cracking process at or as close as possible to the maximum cracking severity. A number of indicators of cracking severity have been determined for use in controlling commercial thermal cracking processes. Examples of such indicators include the cracking severity index, of use in
15 naphtha cracking, and the molecular collision parameter, used in the thermal cracking of gasoil. Other indicators include the outlet temperature of the thermal cracking tube or coil, and the hydrogen content of the liquid products of the cracking process. A parameter commonly employed in the
20 manufacture of ethylene is the propylene-to-methane ratio (PMR) or the ethylene-to-methane ratio (EMR) of the gaseous product of the thermal cracking process. However, the sensitivity of these indicators to factors such as changes in the hydrocarbon feedstock and to the reliability of the
25 product sampling techniques give rise to problems when using these indicators as part of a thermal cracking process control system.

Accordingly, there is a need for an indicator of cracking severity which is not sensitive to such process
30 parameters as feedstock quality fluctuations and which may be readily incorporated into a process control system. B. P. Ennis et al. ("High Temperature-Low Contact Time Pyrolysis Process," Symposium Series 43, Institute of Chemical

Engineers, Harrogate, Eng., June 1975) describe a steam
pyrolysis process for the thermal cracking of a wide range of
naphtha fractions. Ennis et al. state that a particularly
valuable index of pyrolysis severity is the hydrogen-to-
5 carbon atomic ratio in the pyrolysis gasoline product or C_5
and heavier (C_{5+}) products. Ennis et al. describe this as
being a measure of the degree of dehydrogenation of the
liquid phase and the resulting tendency for coke formation.
Since the calculated hydrogen-to-carbon ratio of the C_{5+}
10 products depends only on the predicted yield of C_4 and
lighter components and the hydrogen-to-carbon ratio of the
feed, Ennis et al. claim that this severity indicator is an
excellent means of comparing selectivity at the same depth of
cracking for various pyrolysis reactors or feedstocks.

15 While Ennis et al. suggest the use of hydrogen-to-carbon
ratio of the C_{5+} products to be a useful indicator of cracking
severity, there is no disclosure made of how this parameter
is to be measured or how it may be used to control a thermal
cracking process on a commercial scale. Heretofore, the
20 ratio of hydrogen-to-carbon in the liquid (C_{5+}) hydrocarbon
product of a thermal cracking process has been difficult to
determine. Typically, in a commercial thermal cracking
process, it is calculated on the basis of an analysis of the
hydrocarbon feedstock and the gaseous (C_4-) products, usually
25 obtained after a detailed feed characterization followed by a
simulation of the cracking conditions using a model.
However, none of the options available are practical if the
hydrogen-to-carbon ratio is to be used as a control
parameter.

30 Accordingly, there is a need for a method of determining
the hydrogen-to-carbon ratio of a liquid hydrocarbon fraction
which may be readily incorporated in a commercial process
control system.

Summary of the Invention

In a pyrolysis process in which a known amount of a hydrocarbon feed containing a known amount of tracer gas, a hydrocarbon feed carbon content and a hydrocarbon feed hydrogen content, is charged to a pyrolysis furnace operated under pyrolysis cracking process conditions to yield a pyrolysis product wherein said pyrolysis product comprises a liquid fraction and a gas fraction, wherein said liquid fraction comprises a liquid fraction hydrogen content and a liquid fraction carbon content to thereby provide a liquid fraction hydrogen-to-carbon ratio, and wherein said gas fraction comprises a gas fraction tracer gas concentration, a gas fraction hydrogen content and a gas fraction carbon content, the invention provides a method for determining said liquid fraction hydrogen-to-carbon ratio comprising the steps of:

(a) determining said hydrocarbon feed hydrogen content and said hydrocarbon feed carbon content;

(b) determining said gas fraction hydrogen content and said gas fraction carbon content; and,

(c) determining said liquid fraction hydrogen-to-carbon ratio by

subtracting the determined value for said gas fraction hydrogen content from the determined value for said hydrocarbon feed hydrogen content to give said liquid fraction hydrogen content,

subtracting the determined value for said gas fraction carbon content from the determined value for said hydrocarbon feed carbon content to give said liquid fraction carbon content, and

calculating the value for said liquid fraction hydrogen-to-carbon ratio.

Also, a method is provided for controlling said pyrolysis cracking process conditions, said method comprises the steps of:

5 (a) determining, preferably by use of near infrared spectrometry, a first measured value of said hydrocarbon feed hydrogen content and a second measured value of said hydrocarbon feed carbon content;

10 (b) determining, preferably by use of mass spectrometry, a third measured value of said gas fraction hydrogen content and a fourth measured value of said gas fraction carbon content;

(c) computing a first calculated value for said liquid fraction hydrogen-to-carbon ratio;

15 (d) comparing said first calculated value to a desired value for said liquid fraction hydrogen-to-carbon ratio to generate a differential value; and

(e) controlling said pyrolysis cracking process conditions in response to said differential value.

20 In addition, an apparatus is provided for thermally cracking a known amount of a hydrocarbon feed containing a known amount of tracer gas, a hydrocarbon feed hydrogen content and a hydrocarbon feed carbon content, said apparatus comprising:

25 pyrolysis furnace means defining a thermal cracking zone operated under pyrolysis cracking process conditions, which include a thermal cracking zone temperature, said pyrolysis furnace means provides for cracking said hydrocarbon feed to produce a pyrolysis product comprising a liquid fraction and a gas fraction;

30 first analyzer means for determining the hydrogen content of said hydrocarbon feed and for determining the carbon content of said hydrocarbon feed;

second analyzer means for determining the tracer gas concentration of said gas fraction and for determining the hydrogen concentration of said gas fraction and for determination the carbon concentration of said gas fraction;
5 and

computation means for determining the hydrogen-to-carbon ratio of said liquid fraction by using the determined hydrogen content of said hydrocarbon feed and the determined carbon content of said hydrocarbon feed as determined by said
10 first analyzer means, and the determined hydrogen concentration of said gas fraction and the determined carbon concentration of said gas fraction as determined by said second analyzer means.

Brief Description of the Drawings

15 FIG. 1 is a schematic representation of one embodiment of the inventive pyrolysis process system and system for determining and controlling the hydrogen-to-carbon ratio of the liquid fraction of a pyrolysis product.

Detailed Description of the Invention

20 The present invention provides a method for determining the hydrogen-to-carbon ratio of the liquid fraction of a pyrolysis product that is yielded from a thermal cracking zone of a pyrolysis cracking process unit. In a pyrolysis or thermal cracking process, a hydrocarbon feedstock is charged
25 to a pyrolysis or thermal cracking furnace whereby the hydrocarbon feed is subjected to pyrolytic or thermal cracking process conditions. A pyrolysis or cracked product is yielded from the pyrolysis furnace.

The hydrocarbon feedstock used in the thermal cracking
30 process of the present invention may be any of the hydrocarbons or hydrocarbon fractions used in conventional thermal cracking processes for the preparation of olefins. Suitable feedstocks range from C₄ fractions, such as butane,

C₅ fractions, such as pentane, as well as gasoline, naphtha, kerosene and gasoil fractions. Hydrocarbon feedstocks as heavy as vacuum gasoils may also be employed. The process of the present invention is particularly suitable for use with gasoline, naphtha, kerosene and heavy/vacuum gasoil fractions, with gasoline, naphtha and heavy/vacuum gasoil fractions being especially preferred feedstocks. The hydrocarbon feedstocks are readily produced, for example, by means of the conventional refining of crude oil. The hydrocarbon feedstock may consist of a single fraction mentioned hereinbefore or a mixture of the fractions.

An advantage of the process of this invention is that fluctuations in the composition and boiling point range of the hydrocarbon feedstock may occur and be accommodated by the control system. That is, the inventive method is particularly useful in determining and controlling the hydrogen-to-carbon ratio of the pyrolysis product liquid fraction even when there are fluctuations or changes in the composition or boiling point range of the hydrocarbon feedstock.

As earlier noted, the hydrocarbon feedstock is subjected to thermal cracking in a thermal cracking zone. Any suitable process arrangement and apparatus can be employed for the purposes of the present invention. A process regime commonly applied on a commercial scale employs tubular reactor coils installed in externally fired heaters. The hydrocarbon feedstock is fed to the tubular reactor coils which define the thermal cracking zone into which heat is supplied. Heating of the coils is typically provided by the combustion of a suitable fuel, such as a hydrocarbon oil or refinery gas. Suitable apparatus for carrying out the thermal cracking are well known in the art. For a general discussion of aspects of the thermal cracking of hydrocarbon feedstocks

to yield olefins, reference is made to Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 9, pages 400 to 411.

5 The operating conditions of the thermal cracking zone are dependent upon the specific design of the thermal cracking apparatus and the severity of cracking required. The hydrocarbon feedstock is heated in the thermal cracking zone until a temperature is reached at which the hydrocarbon molecules crack. The temperature required to effect cracking 10 will depend upon the composition and boiling point range of the feedstock. Typical temperatures for the thermal cracking, measured at the outlet of the thermal cracking zone, are in the range of from 750°C to 950°C, more preferably from 800°C to 900°C.

15 The process may be operated at any suitable pressure. The thermal cracking is preferably carried out at a pressure, measured at the outlet of the thermal cracking zone, in the range of from 100 kPa (1 bar) to 500 kPa (5 bar), more preferably from 100 kPa (1 bar) to 300 kPa (3 bar).

20 The flowrate at which the hydrocarbon feedstock is supplied to the thermal cracking zone will depend upon the specific design of the process apparatus. Within these constraints, any suitable flowrate may be employed. Typical flowrates of the hydrocarbon feedstock in commercial scale 25 units is in the range of from 10,000 kg/hr to 60,000 kg/hr, more preferably from 15,000 kg/hr to 50,000 kg/hr.

The residence time of the hydrocarbon feedstock in the thermal cracking zone will depend upon the apparatus design and the other process operating conditions. Typical 30 residence times for the hydrocarbon feedstock in the thermal cracking zone are in the range of from 0.05 seconds to 1.0 seconds, more preferably from 0.10 seconds to 0.50 seconds.

To aid the thermal cracking process, the hydrocarbon feedstock may be mixed with an inert diluent and the resulting mixture fed to the thermal cracking zone. A most suitable inert diluent is steam. The inert diluent is typically present in weight ratio of diluent-to-hydrocarbon of from 0.1 kg/kg to 1.0 kg/kg, more preferably from 0.3 kg/kg to 0.8 kg/kg.

The pyrolysis product yielded from the thermal cracking zone of the pyrolysis process generally comprises a liquid fraction and a gas fraction. The liquid fraction of the pyrolysis product comprises predominantly hydrocarbons having five or more carbon atoms per molecule and the gas fraction of the pyrolysis product comprises predominantly those hydrocarbons having four or less carbon atoms per molecule and gaseous compounds including carbon monoxide, carbon dioxide, hydrogen sulfide, hydrogen and helium.

The invention includes the introduction or addition of a known amount of an inert tracer gas to the hydrocarbon feedstock being charged to the pyrolysis furnace of the process. Any inert gas that can suitably serve as a tracer by passing through the pyrolysis cracking zone unchanged can be used in the invention. Examples of such suitable tracer gas include those selected from the group consisting of helium, argon, nitrogen, and neon. These are suitable, primarily, because they have low solubility in the liquid fraction of the pyrolysis product. The preferred tracer gas for use in the invention is helium. The tracer gas may be introduced in quantities ranging from 100 ppm by volume to 1000 ppm by volume, particularly 100 ppm by volume to 500 ppm by volume.

Essentially all of the tracer gas introduced with the hydrocarbon feed to the pyrolysis furnace can be recovered along with the gas fraction of the pyrolysis product; and,

because the amount of tracer gas introduced into the hydrocarbon feedstock and the amount of hydrocarbon feedstock are both known, the proportion of the pyrolysis product that is the gas fraction can readily be determined by measuring the concentration of tracer gas that is in the gas fraction. The proportion of the pyrolysis product that is the gas fraction may be determined by dividing the value for the known amount of tracer gas introduced into the hydrocarbon feedstock by the measured value for the tracer gas concentration in the gas fraction.

The use of the tracer gas permits the on-line analysis of the pyrolysis product gas fraction using conventional analyzer means for analyzing the gas fraction of the pyrolysis product. Suitable on-line analyzers can include, for example, gas chromatographs and mass spectrometers.

To analyze the gas fraction, a sample of the pyrolysis product is cooled and the gas fraction and liquid fraction are separated. The gas fraction can then be analyzed using suitable analyzer means to determine its tracer gas concentration and hydrogen-to-carbon ratio, through the component analyses of the gas fraction. As described above, the value for the tracer gas concentration permits a determination of the proportion of the pyrolysis product that is the gas fraction and with the measured value for the hydrogen-to-carbon ratio of the gas fraction, the combination of such information can be used to determine the hydrogen content of the gas fraction and the carbon content of the gas fraction.

In the inventive method, the hydrogen-to-carbon ratio of the liquid fraction of the pyrolysis product is determined indirectly by determining the hydrogen and carbon contents of the gas fraction by the method described above and determining, using any suitable analyzer means, the hydrogen

and carbon contents of the hydrocarbon feed to the pyrolysis unit and, then, calculating the difference between the gas fraction hydrogen and carbon contents and the hydrogen feed hydrogen and carbon contents to provide values for the amounts of hydrogen and carbon that are in the liquid fraction of the pyrolysis product.

Any suitable analyzer means for determining the hydrogen content of the hydrocarbon feed and for determining the carbon content of the hydrocarbon feed can be used. The preferred means or method of analyzing the hydrocarbon feed include the use of any conventional near infrared (NIR) analysis techniques or the use of conventional nuclear magnetic resonance (NMR) analytical techniques. The preferred analytical technique is NIR analysis. It is understood herein that the hydrogen content of the hydrocarbon feed is analyzed by the NIR or NMR analytical techniques with the carbon content being determined by difference. ~~Also, the sulfur content of the hydrocarbon can additionally be measured and used in determining the carbon content.~~

The use of NIR spectrometric techniques provides certain advantages such as allowing for the quick and direct online analysis of the hydrocarbon feed. The values for the hydrocarbon feed hydrogen content and the hydrocarbon feed carbon content obtained through the use of the online analyzer can be used in the determination by any suitable computation means of the liquid fraction hydrogen content and the liquid fraction carbon content. The liquid fraction hydrogen-to-carbon ratio is determined by using the information relating to the hydrogen and carbon contents of the hydrocarbon feed and the gas fraction of the pyrolysis product obtained by use of the above-described analysis techniques and computing values for the liquid fraction

hydrogen content and the liquid fraction carbon content. Having these values permits the calculation of the hydrogen-to-carbon ratio of the pyrolysis product liquid fraction. Any suitable means or method can be used to perform the
5 computations, but it is preferred to use computer means such as conventional computer systems.

In another aspect of the invention, the determined value for the hydrogen-to-carbon ratio for the pyrolysis product liquid fraction can be used as an indicator of the cracking
10 severity and in the control of the thermal cracking furnace. It is recognized that the correlation between thermal cracking zone severity and liquid fraction hydrogen-to-carbon ratio is inverse and that an increase in the thermal cracking zone severity will result in a decrease in the hydrogen-to-
15 carbon ratio of the pyrolysis product liquid fraction and that a decrease in the thermal cracking zone severity will result in an increase in the hydrogen-to-carbon ratio of the pyrolysis product liquid fraction.

It is desirable to operate the thermal cracking furnace
20 so as to provide a liquid fraction hydrogen-to-carbon ratio of as close to one (1.0), on a molar basis, as is economically feasible; but, generally, the liquid fraction hydrogen-to-carbon ratio should be controlled to within the range of from 1.01 to 1.5 and, more typically, it is
25 controlled to within the range of from 1.02 to 1.2 and, most typically, from 1.05 to 1.1, on a molar basis. Typical hydrocarbon-to-carbon ratios for a hydrocarbon feed to a pyrolysis cracking unit are in the range of from 1.6 to 2.5, more typically from 1.7 to 2.2 and, most typically, from 1.8
30 to 2.0, on a molar basis.

In the control of the pyrolysis cracking process conditions there is a predetermined desired thermal cracking severity as represented by a desired hydrogen-to-carbon ratio

for the pyrolysis product liquid fraction. To control the pyrolysis process, a comparison is made between the desired liquid fraction hydrogen-to-carbon ratio and the actual liquid fraction hydrogen-to-carbon ratio, as determined in accordance with the inventive method described herein, to provide a differential value. The pyrolysis process conditions are adjusted in response to any differences between the desired and actual hydrogen-to-carbon ratio values.

The differential value can be defined as the difference in the hydrocarbon-to-carbon ratio as determined by subtracting the actual value for the liquid fraction hydrocarbon-to-carbon ratio from the desired value for the liquid fraction hydrocarbon-to-carbon ratio. A negative differential value will require increasing the pyrolysis process cracking severity and a positive differential value will require decreasing the pyrolysis process cracking severity.

While a number of pyrolysis process operating conditions can impact the severity of the thermal cracking conditions, one typical process parameter that is controlled in response to the differential value in hydrogen-to-carbon ratio is the cracking temperature within the thermal cracking zone. The thermal cracking zone temperature is related to and can be monitored by measurement of the temperature of the pyrolysis product at the outlet of the thermal cracking zone. The thermal cracking zone temperature can be controlled by adjusting the firing rate of the burners of the pyrolysis furnace.

Now referring to FIG. 1, presented is a simplified schematic representation of a pyrolysis process system 10 for thermally cracking a hydrocarbon feed. A hydrocarbon feedstock is charged, at a known rate, by way of conduit 12

to cracking furnace tubes or coils 14 of pyrolysis or thermal cracking furnace 16. A diluent steam stream may be introduced into the hydrocarbon feedstock of conduit 12 by way of conduit 17. Thermal cracking furnace 16 is equipped
5 with cracking furnace tubes or coils 14 and burners 18. Thermal cracking furnace 16 defines a heating zone and provides means for thermally cracking the hydrocarbon feed. Cracking furnace tubes or coils 14 define a pyrolysis or thermal cracking zone and provide means for receiving the
10 hydrocarbon feed for heat input into the hydrocarbon feed. Burners 18 define a combustion zone and provide means for combusting a fuel to generate heat for input into the thermal cracking zone defined by cracking furnace tubes or coils 14.

Fuel is introduced to burners 18 through conduit 20.
15 Interposed in conduit 20 is control valve 22, which provides means for controlling the rate of fuel input into burners 18 to thereby control the heat input to the thermal cracking zone defined by cracking furnace tubes or coils 14.

A tracer gas, such as helium, is introduced through
20 conduit 24 at a known rate into the diluent steam stream 17 that combines with the hydrocarbon feed being charged to cracking furnace tubes or coils 14 through conduit 12. The pyrolysis product is withdrawn as an effluent from cracking furnace tubes or coils 14 through conduit 26. A sample of
25 the pyrolysis product is removed from conduit 26 for analysis by analyzer 28. Analyzer 28 provides means for analyzing the gas fraction of the pyrolysis product for the tracer gas concentration, the fraction that is hydrogen and the fraction that is carbon. To analyze the gas fraction of the pyrolysis
30 product, the pyrolysis product is first separated into its gas fraction and liquid fraction, with the gas fraction being analyzed by analyzer 28. The information generated by

analyzer 28 is provided to computer and controller 30 by line 32.

A sample of the hydrocarbon feed is removed from conduit 12 for analysis by analyzer 34. Analyzer 34 provides means
5 for measuring and determining the hydrogen and carbon content of the hydrocarbon feed. The information generated by analyzer 34 is provided to computer and controller 30 by line 36. Computer and controller 30 provides means for processing the input information to compute a value for the hydrogen-to-
10 carbon ratio of the liquid fraction of the pyrolysis product and, further, to provide means to control the cracking severity at which thermal cracking furnace 16 operates in response to changes in the liquid fraction hydrogen-to-carbon ratio.

15 To control the severity of the cracking process, a predetermined value, also referred to as a set point, for the desired hydrogen-to-carbon ratio for the liquid fraction is provided to computer and controller 30 by line 38. Computer and controller 30 processes the information provided by line
20 32, line 36 and line 38 to compute a value for the hydrogen-to-carbon ratio of the liquid fraction. A differential value between the actual hydrogen-to-carbon ratio of the liquid fraction and the desired hydrogen-to-carbon ratio of the liquid fraction is computed by computer and controller 30
25 with an output signal, representative of the differential value, being sent by line 40 to control valve 22. Control valve 22 is adjusted in response to the input signal from line 40 to thereby alter the heat input to thermal cracking furnace 16 and, thus, the cracking severity, to ultimately
30 provide a liquid fraction having the desired hydrogen-to-carbon ratio.

The following example represents a hypothetical calculation.

EXAMPLE

Known amounts:

Tracer helium gas: 268.5 g/hr

Hydrocarbon feed: 34931.4 kg/hr

5 Determination and Calculations:

Hydrocarbon feed composition: 13.86 wt% hydrogen,
86.04 wt% carbon

Hydrocarbon feed hydrogen content: 13.86 wt% of
34931.4 kg/hr = 4841.5 kg/hr

10 Hydrocarbon feed carbon content: 86.04 wt% of
34931.4 kg/hr = 30054.98 kg/hr

Concentration of helium in gas fraction: 80 ppmV
or 12.807 ppmw

Proportion of pyrolysis product that is the gas
15 fraction: $(268.5 \text{ g/hr}) / (12.807 \text{ ppmw}) = 20965.1 \text{ kg/hr}$

Gas fraction composition: 17.325 wt% hydrogen,
82.675 wt% carbon

Gas fraction hydrogen content: 17.325 wt% of
20965.1 kg/hr = 3632.20 kg/hr

20 Gas fraction carbon content: 82.675 wt% of 20965.1
kg/hr = 17332.90 kg/hr

Liquid fraction hydrogen content: 4841.5 kg/hr -
3632.20 kg/hr = 1209.30 kg/hr

Liquid fraction carbon content: 30054.98 kg/hr -
25 17332.90 kg/hr = 12722.08 kg/hr

Liquid fraction hydrogen-to-carbon ratio: $(1209.3 \text{ kg/hr}) / (12722.08 \text{ kg/hr}) = 0.095055$ on a weight basis,
 $(0.095055)(12) = 1.14$ on a molar basis.

Although this hypothetical calculation has been
30 calculated in terms of mass flow rates (in kg/hr), it can
also be calculated in terms of mass quantities (e.g. in kg)
i.e. without the time element.

While this invention has been described in terms of the presently preferred embodiment, reasonable variations and modifications are possible by those skilled in the art. Such variations and modifications are within the scope of the
5 described invention and the appended claims.

C L A I M S

1. In a pyrolysis process in which a known amount of a hydrocarbon feed containing a known amount of tracer gas, a hydrocarbon feed carbon content and a hydrocarbon feed hydrogen content, is charged to a pyrolysis furnace operated under pyrolysis cracking process conditions to yield a pyrolysis product wherein said pyrolysis product comprises a liquid fraction and a gas fraction, wherein said liquid fraction comprises a liquid fraction hydrogen content and a liquid fraction carbon content to thereby provide a liquid fraction hydrogen-to-carbon ratio, and wherein said gas fraction comprises a gas fraction tracer gas concentration, a gas fraction hydrogen content and a gas fraction carbon content, a method is provided for determining said liquid fraction hydrogen-to-carbon ratio comprising the steps of:

(a) determining said hydrocarbon feed hydrogen content and said hydrocarbon feed carbon content;

(b) determining said gas fraction hydrogen content and said gas fraction carbon content by determining said gas fraction tracer gas concentration, utilizing the thus determined gas fraction tracer gas concentration to determine the proportion of said pyrolysis product that is said gas fraction, and utilizing the thus determined proportion of said pyrolysis product that is said gas fraction in determining said gas fraction hydrogen content and said gas fraction carbon content; and,

(c) determining said liquid fraction hydrogen-to-carbon ratio by

subtracting the determined value for said gas fraction hydrogen content from the determined value for said hydrocarbon feed hydrogen content to give said liquid fraction hydrogen content,

subtracting the determined value for said gas fraction carbon content from the determined value for said hydrocarbon feed carbon content to give said liquid fraction carbon content, and

calculating the value for said liquid fraction hydrogen-to-carbon ratio.

2. A method as recited in claim 1 wherein:

said determining step (a) is performed either by near infrared spectrometry or by nuclear magnetic resonance;

said determining step (b) is performed either by mass spectrometry or by gas chromatography.

3. A method as claimed in claim 1 comprising the steps of:

(a) determining said hydrocarbon feed hydrogen content and said hydrocarbon feed carbon content;

(b) determining said gas fraction hydrogen content and said gas fraction carbon content;

(c) computing said liquid fraction hydrogen-to-carbon ratio by

using said gas fraction hydrogen content as determined by step (b) and said hydrocarbon feed hydrogen content as determined by step (a) to determine said liquid fraction hydrogen content;

using said gas fraction carbon content as determined by step (b) and said hydrocarbon feed carbon content as determined by step (a) to determine said liquid fraction carbon content; and,

computing said liquid fraction hydrogen-to-carbon ratio utilizing the above determined said liquid fraction hydrogen content and the above determined said liquid fraction carbon content.

4. A method as recited in claim 3 wherein:

determining step (a) is performed by use of near infrared spectrometry to provide a first measured value of said hydrocarbon feed hydrogen content and a second measured value of said hydrocarbon feed carbon content;

determining step (b) is performed by

determining by use of mass spectrometry a third measured value of said gas fraction tracer gas concentration;

utilizing said third measured value in computing a first calculated value of the proportion of said pyrolysis product that is said gas fraction; and

utilizing said first calculated value in combination with the mass spectrometric analysis of the hydrogen content and the carbon content of said gas fraction to give a fourth measured value of said gas fraction by hydrogen content and a fifth measured value of said gas fraction carbon content; and

computing step (c) is performed by

subtracting said fourth measured value from said first measured value to give a second calculated value for said liquid fraction hydrogen content;

subtracting said fifth measured value from said second measured value to give a third calculated value for said liquid fraction carbon content; and

computing a fourth calculated value for said liquid fraction hydrogen-to-carbon ratio by dividing said second calculated value by said third calculated value to give said liquid fraction hydrogen-to-carbon ratio.

5. A method as recited in any of claims 1-4, which method comprises the steps of:

(a) determining by use of near infrared spectrometry a first measured value of said hydrocarbon feed hydrogen content and a second measured value of said hydrocarbon feed carbon content;

(b) determining by use of mass spectrometry a third measured value of said gas fraction hydrogen content and a fourth measured value of said gas fraction carbon content;

(c) computing a first calculated value for said liquid fraction hydrogen-to-carbon ratio;

(d) comparing said first calculated value to a desired value for said liquid fraction hydrogen-to-carbon ratio to generate a differential value; and

(e) controlling said pyrolysis cracking process conditions in response to said differential value.

6. A method as recited in claim 5 wherein:

determining step (b) is performed by

determining by use of mass spectrometry a fifth measured value of said gas fraction tracer gas concentration;

utilizing said fifth measured value in computing a second calculated value of the proportion of said pyrolysis product that is said gas fraction; and

utilizing said second calculated value in combination with the mass spectrometric analysis of the hydrogen content and the carbon content of said gas fraction to give said third measured value and said fourth measured value;

computing step (c) is performed by

subtracting said third measured value from said first measured value to give a third calculated value for said liquid fraction hydrogen content;

subtracting said fourth measured value from said second measured value to give a fourth calculated value for said liquid fraction carbon content; and

computing said first calculated value by dividing said third calculated value by said fourth calculated

value to give said liquid fraction hydrogen-to-carbon ratio;

comparing step (d) is performed by

subtracting said first calculated value from said desired value to give said differential value; and,

controlling step (e) includes increasing the severity of said pyrolysis cracking process conditions in response to a negative value for said differential value and decreasing the severity of said pyrolysis cracking process conditions in response to a positive value for said differential value.

7. A method as recited in claims 5 or 6 wherein said desired value for said liquid fraction hydrogen-to-carbon ratio on a molar basis is in the range of from 1.0 to 2.0, particularly from 1.01 to 1.5, more particularly from 1.02 to 1.2 and, most particularly, from 1.05 to 1.1.

8. A method as recited in any of claims 5-7 wherein said pyrolysis cracking furnace includes a thermal cracking zone; and,

wherein said pyrolysis cracking process conditions include a thermal cracking zone temperature which is representative of the severity of said pyrolysis cracking process whereby increases in said thermal cracking zone temperature provide for an increase in the severity of said pyrolysis cracking process conditions and decreases in said thermal cracking zone temperature provide for a decrease in the severity of said pyrolysis cracking process conditions; and,

controlling step (e) provides for maintaining said thermal cracking zone temperature in the range of from 750°C to 950°C by increasing said thermal cracking zone temperature in response to a negative value for said differential value and decreasing said thermal cracking

zone temperature in response to a positive value for said differential value.

9. A method as recited in any of claims 1-8, wherein the tracer gas is selected from the group consisting of helium, argon, nitrogen and neon; and, the tracer gas is present in an amount ranging from 100 ppm by volume to 1000 ppm by volume, particularly from 100 ppm by volume to 500 ppm by volume.

10. An apparatus for thermally cracking a known amount of a hydrocarbon feed containing a known amount of tracer gas, a hydrocarbon feed hydrogen content and a hydrocarbon feed carbon content, said apparatus comprising:

- a pyrolysis furnace defining a thermal cracking zone operated under pyrolysis cracking process conditions, which include a thermal cracking zone temperature, said pyrolysis furnace provides for cracking said hydrocarbon feed to produce a pyrolysis product comprising a liquid fraction and a gas fraction;

- a first analyzer for determining the hydrogen content of said hydrocarbon feed and for determining the carbon content of said hydrocarbon feed;

- a second analyzer for determining the tracer gas concentration of said gas fraction and for determining the hydrogen concentration of said gas fraction and for determination the carbon concentration of said gas fraction; and

- a computer for determining the hydrogen-to-carbon ratio of said liquid fraction by using the determined hydrogen content of said hydrocarbon feed and the determined carbon content of said hydrocarbon feed as determined by said first analyzer, and the determined tracer gas concentration of said gas fraction, the determined hydrogen concentration of said gas fraction

and the determined carbon concentration of said gas fraction as determined by said second analyzer.

11. An apparatus as defined in claim 10, further comprising:

comparing means for comparing the determined hydrogen-to-carbon ratio of said liquid fraction as determined by said computer to generate a differential value between a desired hydrogen-to-carbon ratio for said liquid fraction and the determined hydrogen-to-carbon ratio of said liquid fraction; and

a controller for adjusting said thermal cracking zone temperature in response to said differential value; and wherein

said first analyzer includes a near infrared analyzer; and,

said second analyzer includes a mass spectrometer.