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SIMULATION DISTILLATION BY COMPREHENSIVE
TWO-DIMENSIONAL GAS CHROMATOGRAPHY

BACKGROUND OF THE INVENTION

[0001] The present invention relates to the characterization of a petroleum or refinery stream.

[0002] Since distillation is a fundamental separation process for the petroleum refining industry, it is essential to be able to characterize a crude oil or refinery stream based on its boiling behavior in the refinery units. Lab scale distillations are relatively slow and costly. Thus, simulated distillation by gas chromatography (GC) has been widely used in the petroleum industry to predict boiling yield. It is an important tool to provide information for parameter setting of the distillation process during refining.

[0003] GC Simulated Distillation as practiced in prior art uses a non-polar column (that elutes the molecules based on boiling point) and a flame ionization detector. However, recent developments in GC technology has advanced the separation from conventional one-dimensional (1D) separation (such as boiling point) to comprehensive two-dimensional (2D) separation (such as boiling point and polarity). Comprehensive two-dimensional gas chromatography (2DGC or GCxGC) technique can be applied to simulated distillation. If a hydrocarbon detector such as flame ionization detector (FID) is used, the most significant advantage is that the total yield curve and sub-total yields of each compound class such as saturates, one-ring aromatics, two-ring aromatics, and three aromatics can be determined. If an element-selective detector such as a sulfur chemiluminescence detector (SCD) is used, the sulfur compound classes such as mercaptan/sulfide/thiophene, benzothiophene, and dibenzothiophene) can be

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determined in addition to the total yield. Likewise a nitrogen specific detector (with 2DGC) could be used to determine the boiling yields of the individual classes of nitrogen containing molecules such as aliphatic amines, pyrrols, indoles, and carbazoles.

SUMMARY OF THE INVENTION

[0004] This invention describes a method to perform a simulation of distillation by comprehensive two-dimensional gas chromatography and convert the result to a simulation of distillation with total yield and sub-total yield of pre-defined compound classes as a function of boiling point. The new 2D (2DGC or GCxGC) simulated distillation results will provide more information than traditional 1D simulation distillation results especially in the yield of different compound class. The most direct impact of these results will be in determining the value of the crude oil and / or the refinery streams. This invention could also be of particular value to provide a tool to help the refining industry meet new more restrictive regulations limiting levels of sulfur (and nitrogen) levels in distillate products.

[0005] The steps of the present invention characterize a petroleum stream based on its boiling behavior. This method includes the steps of separating the petroleum stream with a two-dimensional gas chromatograph to determine polarity as a function of temperature, and then integrating the two-dimensional gas chromatograph at a given temperature to determine signal intensity.

BRIEF DESCRIPTION OF THE FIGURES

[0006] Figure 1 shows a GCxGC chromatogram of a hydrocarbon mixture in the diesel temperature boiling range.

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[0007] Figure 2 shows the simulated distillation curve based on the compound class separated in Figure 1.

[0008] Figure 3 shows the GCxGC chromatogram of the sulfur containing sample as in Figures 1 and 2.

[0009] Figure 4 shows the simulation distillation curve of the sample based on the compound class separated in Figure 3.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Experiment Instrumentation and Conditions

[0010] The 2D GC (GC×GC) system is peagus 4D manufactured by LECO corp. (St. Josph, Michigan, USA) consists of an Agilent 6890 gas chromatograph (Agilent Technology, Wilmington, DE) configured with inlet, columns, and detectors. A split/splitless inlet system with an 100-vial tray autosampler was used. The two-dimensional capillary column system utilizes a non-polar first column (BPX-5, 30 meter, 0.25mm I.D., 1.0 µm film), and a polar (BPX-50, 3 meter, 0.25mm I.D., 0.25µm film), second column. Both capillary columns are the products of SGE Inc. Austin, TX. A dual jet thermal modulation assembly based on Zoex technology (Zoex Corp. Lincoln, NE) which is liquid nitrogen cooled "trap-release" dual jet thermal modulator is installed between these two columns. A flame ionization detector (FID) and a sulfur chemilumescence detector (SCD) (GE analytical Inc.) are used for the signal detection. A 1.0 microliter sample was injected with 75:1 split at 300°C from Inlet. Carrier gas is flow at 1.0 ml per minute. The oven was programmed from 60°C with 0-minute hold and 3°C per minute increment to 300°C with 0-minute hold. The total GC run time was 80 minutes. The modulation period was 10

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seconds. The sampling rate for the detector was 100Hz. After data acquisition, it was processed for qualitative and quantitative analysis by the LECO software package that came with the instrument. The display-quality chromatogram was accomplished by converting data to a two-dimensional image that was processed by a commercial program ("Transform" (Research Systems Inc. Boulder, CO)). The two-dimensional image was further treated by "PhotoShop" (Adobe System Inc. San Jose, CA) to generate publication-ready images. The simulation distillation conversion was done by exporting the digital data to a Excel file and simulated distillation curves were generated by summing the related Excel cells. The temperature calibration was done by using a normal paraffin mixture to generate the reference retention time under the same experimental conditions.

EXAMPLE 1

[0011] GCxGC or 2DGC-FID chromatogram of a hydrocarbons mixture in the diesel temperature boiling range.

[0012] Figure 1 shows the GCxGC (or 2DGC) of the hydrocarbon mixture boiling in diesel temperature range. The figure shows separation of saturated hydrocarbons from 1, 2 and 3 ring aromatic hydrocarbons.

[0013] The X-axis can be converted from retention time in Figure 1 to temperature in Figure 2. The X-axis in figure 1 is the first column retention time. As described previously, the first column (of the GCxGC) is a non-polar column. The elution of the non-polar column is based on the boiling point of the compounds. A separated n-paraffin mixture (for example, from n-hexane (C₆) to n-Tetracontane (C₄₀)) is prepared. This mixture is analyzed with GCxGC at the same condition as running simulated distillation sample. A chromatogram with

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only n-paraffins will be obtained and each n-paraffin has a unique retention time. Because the boiling point of each n-paraffin is well known, the retention time of each n-paraffin can be exchanged with that specific temperature. The other retention time between each n-paraffin can be interpolated based on the assumption of the linear response of retention time and temperature. With this temperature calibration experiments and interpolation, the X-axis (retention time axis) can be converted to an axis with temperature labeled (a temperature axis).

[0014] The flame ionization detector (FID) signal intensity can be converted to weight percentage of sample analyzed. The FID signal intensity is direct proportional to the number of carbon atoms in the component detected. For the hydrocarbon only component, this signal intensity is directly reflected to the relative weight of that specific component. By normalizing the relative signal intensity (relative weight), the signal intensity can be converted to weight percentage (single FID intensity divided by total FID signal intensities in a chromatogram).

[0015] The black lines in Figure 1 divide the region of different compound classes. The GCxGC chromatogram is a display of three dimensional data. All the data along Y-axis can be summarized by compound class region and summed up in each X-axis position. After calibration with the normal paraffin compound mixture, the X-axis retention time can be converted to temperature. The plot of accumulated compound class weight percentage (summarized compound class intensity followed by converting the FID signal intensities to weight percentage) along the temperature scale, the simulated distillation curve can be generated. Figure 2 is the simulated distillation curve based on the separation of the sample in Figure 1.

EXAMPLE 2

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[0016] If a sulfur chemiluminescence detector (SCD) is attached to a GCxGC (or 2DGC) or integrated with existing flame ionization detector, the breakdown of sulfur species by compound class or type can be determined. Similarly, as described above for the hydrocarbon (FID) detector signal, the sulfur signal from the 2DGC can be used to generate simulated distillation curves for individual sulfur molecular types.

[0017] The signal intensity of the sulfur chemiluminescence detector (SCD) can be converted to mole percentage of sample analyzed. The SCD signal intensity is direct proportional to the number of sulfur atoms in the component detected. For the sulfur atom containing hydrocarbons, most of them only have one sulfur atom in each component, this signal intensity is direct reflect to the relative mole of that specific component. By normalize the relative signal intensity (relative mole), the signal intensity can be converted to mole percentage (single SCD intensity divided by total SCD signal intensities in a chromatogram).

[0018] Figure 3 shows the sulfur containing compound GCxGC (or 2DGC) chromatogram of the same sample as in Figure 1 and 2. The sulfur compound classes in Figure 3 are labeled as follows: MST = mercaptan/sulfide/thiophene, BT = benzothiophene, and DBT = dibenzothiophene. The plot of accumulated compound class mole percentage along the temperature scale can generate the simulated distillation curve.

[0019] Figure 4 shows the simulation distillation curve of the sample generated based on the compound class separated in the Figure 3.

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[0020] The new 2DGC (or GCxGC) simulated distillation technology will provide more information than traditional 1D simulation distillation result especially in the yield of different compound class. The most direct impact of these results will indicate the value of the crude oil or the refinery streams.

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CLAIMS:

1. A method to simulate distillation of a petroleum stream by comprehensive two-dimensional gas chromatography comprising:
 - a) separating said petroleum stream with a two-dimensional gas chromatograph to determine polarity as a function of temperature,
 - b) integrating the two-dimensional gas chromatograph at a given temperature to determine signal intensity as a function of temperature.
2. The method of claim 1 wherein said temperature is first dimension retention time and said polarity is second dimension retention time.
3. The method of claim 2 where first dimension retention time is boiling point.
4. The method of claim 1 wherein the signal intensity is weight percent.
5. The method of claim 1 wherein said signal intensity is mole percent.
6. The method of claim 4 wherein said integrating step gives the weight percent of saturates, one-ring aromatics, two-ring aromatics and three-ring aromatics in the petroleum feedstream.

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7. The method of claim 5 wherein said integrating step gives the mole percent of non-carbon elements containing compounds.

8. The method of claim 7 wherein the non-carbon elements containing compounds include sulfur containing compounds.