

STABLE CARBON ISOTOPE ANALYSIS OF COPROCESSING MATERIALS

Michael S. Lancet, Richard A. Winschel, Francis P. Burke
CONSOLIDATION COAL COMPANY
Research & Development
4000 Brownsville Road
Library, PA 15129

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INTRODUCTION

The purpose of obtaining stable carbon isotope analyses of coprocessing products is to determine the amount of coal (or petroleum) carbon that is present in any reaction product. This *carbon-sourcing* of distillate fractions, soluble resid, and insoluble organic matter, etc. is useful in modeling reactions, and evaluating synergistic effects if they exist. A complete description of the method outlined in this paper, including all experimental details and calculation methods can be found in Reference 1.

Basic Method of Application

In general, the ratio of the two stable isotopes (carbon-12 and carbon-13) differs by small but measurable amounts for different natural hydrocarbons like coal and petroleum. The isotope ratio is reported in units of parts-per-thousand (per mil) difference from a standard. For example, Pittsburgh seam coal has a carbon isotope ratio of about -24 per mil. Cold Lake bitumen has a carbon isotope ratio of about -30 per mil. If we analyze a physical mixture of the two and it has a carbon isotope ratio of, say, -26 per mil, we can use a simple mixing equation to calculate that $(-24 - (-26))/(-24 - (-30)) \times 100 = 33.3\%$ of the carbon in the mixture is petroleum carbon or, alternatively, that 66.7% is coal carbon. The precision and accuracy of the method are adequate for mixtures of practical interest (2).

Selective Isotopic Fractionation

Actual coprocessing, however, involves considerable bond breaking. Because $^{12}\text{C} - ^{12}\text{C}$ bonds are slightly weaker than $^{13}\text{C} - ^{12}\text{C}$ bonds, the lighter products, particularly the C_1 x C_4 gases, are slightly enriched in ^{12}C relative to the feed. The heavier products are slightly enriched in ^{13}C . At high conversion conditions (1), this selective isotopic fractionation becomes significant and must be accounted for. The simple physical mixing equation tends to under-account for the isotopically heavier component (usually the coal) in the lighter product fractions, and to over-account for it in the heavier fractions.

PROCEDURES

Sampling and Analysis Procedures

Practical application of stable carbon isotope analysis requires that the coal and petroleum have sufficiently different carbon isotope ratios. In general, a difference of at least 2 per mil is necessary, but a difference of 4 per mil is preferable, particularly if selective isotopic fractionation is expected. With careful attention to sampling and analysis procedures, it is possible to achieve analytical reproducibility (difference between repeat analyses) of about 0.2 per mil routinely. Therefore, the inherent accuracy of the method is about 5% (relative). Without

adequate attention to sampling and analysis procedures it is possible to encounter reproducibility errors of 1 per mil or more, rendering the application essentially useless. The biggest problem appears to be homogeneity for residual samples (i.e., nondistillate oils), although gas samples also are a problem. For viscous liquids and tar samples, the best approach is to homogenize the residual samples by melting, mixing, freezing (in liquid nitrogen), grinding, and remixing, then supplying a small (~1g) aliquot of the sample to the analyst. All isotope analyses were performed at least in duplicate, and an additional replicate analysis was obtained when those results differed by more than 0.2 per mil. Secondary standards similar to the analyzed material should be analyzed routinely to assure accuracy. The standard NBS 22 was analyzed 79 times during this work, giving a standard deviation of 0.04 per mil.

Correcting for Selective Isotopic Fractionation

Selective isotopic fractionation is the most significant problem in applying carbon isotope analysis to carbon-sourcing of coprocessing products. Attempts have been made to account for isotopic fractionation by doing "blank" runs in which the petroleum is processed alone (3). However, it is impossible to do a coal-only run at coprocessing conditions, without the use of a vehicle solvent, and this would require further correction. Ignoring the isotopic fractionation of the coal is convenient; however, we found (1) that higher-rank coals, in particular, undergo significant isotopic fractionation. It is also impractical to do a petroleum-only run and a coal-only run for each coprocessing run. Therefore, we sought a correction method that could be applied for the most common cases in which correction factors from blank runs are unavailable.

The correction method (4,5) is based on the fact that isotopic fractionation will make the hydrocarbon gases isotopically lighter than the respective feed, often by a substantial amount (4-10 per mil relative to the feed). However, because the gas usually represents only a small portion of the carbon (5-10%), the non-gaseous products will differ from the feed by only 0.1 to 1.0 per mil. Therefore, the yield, isotope ratio and carbon content of the gas can be used to calculate the carbon isotope ratios of those portions of the feed coal and feed petroleum that report to the non-gaseous products.

It is not possible to determine from isotope analysis how the coal and petroleum individually fractionate. Overcoming this requires two assumptions. First, we assume that the gaseous carbon is produced from coal and petroleum carbon in equal proportion to their concentrations in the feed. Second, we assume that the degree of fractionation is the same for both feeds. That is, if the isotope balance requires that the gas is 4 per mil lighter than the total feed carbon, we assume that both the coal and petroleum each produce gas that is 4 per mil isotopically lighter than the respective feed carbon. The results of a sensitivity analysis (6) show that, for reasonable relaxations of these assumptions, relative errors are 5-10% if the feedstock pair has a sufficiently large difference in isotope ratio (>4 per mil). A third assumption is that the non-gaseous products from a particular feed all have the same isotope ratio. That is, that the coal-derived carbon in the naphtha has the same isotope ratio as the coal-derived carbon in the resid. In fact, there probably is some heterogeneity in the isotope ratios of the non-gaseous products, with the heavier products being isotopically heavier. This error is minimized by choosing feedstock pairs with large isotopic differences.

It is difficult to obtain valid data on gas samples. However, the carbon content and isotope ratio of the gas can be forced based on the feed analyses and analyses of the non-gas products. If valid gas data are available, they can be used.

EXAMPLE OF APPLICATION TO CONTINUOUS COPROCESSING SAMPLES

This section provides an example of the computations necessary to employ the standard method of correction. The data from five product samples and two feedstock samples from period 11 of Hydrocarbon Research Inc. (HRI) coprocessing Bench Run 238-1, also known as Bench Run No. 2, are used in this example. The feedstocks to this run were Westerholt coal (German bituminous) and Cold Lake vacuum still bottoms (VSB). The large difference, 5.5 per mil, between the isotope ratios of the two feedstocks make the Westerholt coal/Cold Lake VSB pair a good candidate for carbon sourcing via the stable carbon isotope method. The products obtained included initial boiling point (IBP) x 350°F, 350 x 650°F and 650 x 975°F distillates, 975°F+ pressure filter liquid (PFL) and tetrahydrofuran (THF) washed pressure filter cake (PFC). Operating conditions, conversions, and yields (Z) from Run 238-1 are given below. A 1:1 MF coal/petroleum ratio was used.

OPERATING CONDITIONS AND PROCESS PERFORMANCE
HRI Coprocessing Bench Run 238-1, Period 11

Conditions

Feedstock Ratio (dry coal/petroleum):	1
Nominal Pressure, psig:	2500
Temperature, °F (both stages):	810
Relative Space Velocity:	1.0

Process Performance

Coal Conversion (% MAF):	90
975 °F+ Resid Conversion (% MAF):	82

The input data required for the carbon sourcing calculation are the feed compositions, carbon and carbon isotope analyses of the feed components, and yields, carbon contents, and carbon isotope ratios of the product fractions. These are shown below. As noted above, we found it convenient to calculate the carbon content and isotope ratio of the carbonaceous gas because of problems with sample acquisition and analytical reliability. However, measured values may be used if available. In this example, the gas analyses are calculated by forcing the carbon and isotope analyses. The input data for the example case are given below:

<u>Feed Composition</u>	<u>wt % Feed</u>	<u>wt % Carbon</u>	<u>lb Carbon/ 100 lb feed</u>	<u>δ¹³C, per mil</u>
Coal (MF)	50.0	77.9	38.9	-24.30
Petroleum	<u>50.0</u>	<u>84.0</u>	<u>42.0</u>	<u>-29.84</u>
Total Feed	100	80.9	80.9	(a)

<u>Feed Composition</u>	<u>wt % Feed</u>	<u>wt % Carbon</u>	<u>lb Carbon/ 100 lb feed</u>	<u>δ¹³C, per mil</u>
C ₁ x C ₄ , CO ₂	12.4	(a)	(a)	(a)
IBP x 350°F	16.1	86.2	13.9	-27.39
350 x 650°F	32.1	87.0	27.9	-27.18
650 x 975°F	19.5	89.2	17.4	-26.12
975°F+ liquid	11.9	91.2	10.9	-25.61
PFC, THF-washed	8.0	66.1	5.3	-23.99
H ₂ Consumption	-4.5	-	-	-

(a) Not analyzed.

Based on the feed composition and coal and petroleum analyses, the isotope ratio of the total feed can be calculated as:

$$\delta^{13}\text{C}_{\text{feed}} = \frac{(-24.30)(38.90) + (-29.84)(42.00)}{80.9} = -27.18 \text{ per mil} \quad (1)$$

The carbon yield in the product gas is the difference between the feed carbon (80.9 lb) and the sum of the carbon in the other products (13.9+27.9+17.4+10.8+5.3), or 5.6 lb carbon, giving a gas carbon content of 5.6/12.4 x 100 or 45.1%. By forced isotope balance, the isotope ratio of the carbon in the carbonaceous gas is given by:

$$\delta^{13}\text{C}_{\text{gas}} = \frac{(80.9)(-27.18) - [(13.9)(-27.39) + (27.9)(-27.18) + (17.4)(-26.12) + (10.8)(-25.61) + (5.3)(-23.99)]}{5.6} = -36.0 \text{ per mil} \quad (2)$$

This illustrates the commonly observed effect of selective isotopic fractionation: the gas (-36.0 per mil) is isotopically lighter (more negative) than either of the feed components.

Based on the calculated carbon isotope ratio of the gas, the isotope ratio of the total non-gaseous product (distillates + resid + PFC) is calculated as:

$$\delta^{13}\text{C}_{\text{non-gas}} = \frac{(80.9)(-27.18) - (5.6)(-36.0)}{(13.9 + 27.9 + 17.4 + 10.8 + 5.3)} = -26.52 \text{ per mil} \quad (3)$$

We assume that the carbon in the product gas is produced from each feedstock in proportion to its carbon in the feed, or 2.7 and 2.9 lb carbon from the coal and petroleum, respectively. We also assume that the difference (X) between the isotope ratio of the coal and petroleum carbon and the gases they produce is the same. X, for each feed, is equal to the difference in the isotope ratio calculated for the product gas and that of the total feed:

$$X = -27.18 - (-36.0) = 8.82 \text{ per mil} \quad (4)$$

Then the carbon isotope ratios of the non-gas coal and petroleum carbons are calculated as:

$$\delta^{13}\text{C}_{\text{coal}} = \frac{(38.9)(-24.3) - (2.7)(-24.30 - 8.82)}{(38.9 - 2.7)} = -23.64 \text{ per mil} \quad (5)$$

$$\delta^{13}\text{C}_{\text{petr.}} = \frac{(42.0)(-29.84) - (2.9)(-29.84 - 8.82)}{(42.0 - 2.9)} = -29.19 \text{ per mil} \quad (6)$$

Actually, it was not necessary to calculate the isotope ratio of the gas. The correction to be applied to each of the non-gaseous feedstocks is the difference between the isotope ratio of the total feed (-27.18 from Equation 1) and the total non-gaseous product (-26.52 from Equation 3). These values differ from those of the original feedstocks by 0.66 per mil. Compared to the difference of 5.5 per mil in the coal and petroleum isotope ratios, this represents a relatively small correction. We have documented cases in which isotopic fractionation is more severe, and if feedstock pairs have closer isotope ratios, failure to correct for isotopic fractionation can lead to unacceptably large errors.

To complete the calculation, these corrected values are used in lieu of the original feedstock isotope ratios, to calculate the coal carbon contents of the non-gaseous products. For example, the coal carbon content of the IBP X 350 °F₂ distillate (-27.39 per mil) is given by:

$$\% \text{ Coal Carbon} = \frac{-29.19 - (-27.39)}{-29.19 - (-23.64)} \times 100 = 32.4\% \quad (7)$$

The remainder of the product compositions are calculated in a similar manner. The results are shown below.

<u>Product Fraction</u>	<u>% Coal Carbon</u>	<u>% Petroleum Carbon</u>
C ₁ x C ₄ , CO ₂	48.1	51.9
IBP x 350°F	32.4	67.6
350 x 650°F	36.2	63.8
650 x 975°F	55.4	44.6
975°F+ liquid	64.6	35.4
PFC, THF-washed	93.8	6.2

Conversions

Knowing the relative proportions of coal and petroleum carbon in the product fractions, it is possible to calculate the conversion of either feedstock to that fraction. This could be useful information in reaction modeling, or for investigating the possibility of feedstock synergisms. The conversions from this example are given below:

<u>Product Fraction</u>	<u>Conversion</u>	
	<u>% Coal Carbon</u>	<u>% Petroleum Carbon</u>
C ₁ x C ₄ , CO ₂	6.9	6.9
IBP x 350°F	11.6	22.3
350 x 650°F	26.0	42.4
650 x 975°F	24.7	18.5
975°F+ liquid	18.0	9.1
IOM	<u>12.7</u>	<u>0.8</u>
Total	99.9	100.0

Selectivity

The coal-conversion selectivity is simply the ratio of the percent coal carbon in a given product fraction to that in the feed (in this case 48.1%). A value greater than unity indicates that the coal carbon is preferentially converted to (or retained in) that product fraction. Selectivities for this example are given below.

<u>Product Fraction</u>	<u>Coal Carbon Selectivity</u>
IBP x 350°F	0.7
350 x 650°F	0.8
650 x 975°F	1.2
975°F+ liquid	1.3
PFC, THF-washed	2.0

These results indicate that the lower boiling distillates were preferentially produced from the petroleum, while the higher boiling distillates, resid and IOM were preferentially produced from the coal. Note that there is no information on

the gas. We assumed in correcting for selective isotopic fractionation that it was produced with equal selectivity from the coal and petroleum.

SUMMARY

It was demonstrated that, under appropriate circumstances, stable carbon isotope analysis can be an excellent method to determine the contributions of the individual feedstock to coal/petroleum coprocessing products and to follow the reaction pathways of the individual feedstocks. There are two primary considerations in applying this method: 1) the difference in the stable carbon isotopic compositions of the two feedstocks ($\delta^{13}\text{C}$), and 2) selective isotopic fractionation errors. An adequate difference in the isotope ratios of the coal and petroleum can be assured by selecting the appropriate coprocessing feedstocks. Selective isotopic fractionation is a consequence of the coprocessing process. It is affected by processing severity, and most coprocessing operations are at high enough severity to induce significant isotopic fractionation. Nevertheless, errors introduced by isotopic fractionation can be corrected, at least in some circumstances.

Even in those cases where the feedstocks are isotopically similar and where isotopic fractionation effects are significant but not corrected (worst case), the method provides data that are useful for discerning trends. However, for use of the method as a quantitative tool, it is important to maximize the difference in the isotope ratios of the coprocessing feedstocks and to follow good, careful sampling and analytical practices. This method allows one to examine the fate of the individual feedstocks through the coprocessing process.

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