Microcarbon Residue Yield and Heteroatom Partitioning
Between Volatiles and Solids for Whole Vacuum Resids and
Their Liquid Chromatographic Fractions

Topical Report

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ABSTRACT

Five petroleum >1000° F resids were separated into compound type fractions using liquid chromatography. The coking tendency of each compound type was assessed using the micro-carbon residue (MCR) test (ASTM D 4530). Heteroatom (N, S, Ni, V) partitioning between MCR solids versus volatiles was determined through analysis of the starting fractions and the corresponding MCR solids.

The weighted sum of MCR solid yields over all compound types in a given resid was typically in good agreement with the MCR yield of the whole resid. This finding agrees with prior studies indicating coke yield to be an additive property. Sulfur partitioning was also an additive property, was predictable from MCR yield, and was nearly independent of the initial form (sulfide, thiophenic, sulfoxide) present. Nitrogen and nickel partitioning were nonadditive and therefore composition dependent. Partitioning of vanadium into solids was essentially quantitative for all resids and their fractions.

MCR solid yield was generally dependent only on H/C ratio. However, there is some evidence indicating secondary dependence on hydrocarbon structure; i.e., that naphthenic rings reduce MCR in proportion to H/C by virtue of their effective hydrogen transfer properties. Deposition of N and Ni into MCR solids over the fractions was often appreciably less than that of the whole resids, thereby indicating that interaction among various compound types was required for maximum incorporation of those elements into coke.

INTRODUCTION

Coke formation is inherent in many refining processes applied to petroleum resids, heavy oils and tar sand bitumens. The standard laboratory method for assessing coking tendency is determination of microcarbon residue (MCR, ASTM D 4530), which provides comparable results to the older Ramsbottom and Conradson carbon residue procedures. Results from laboratory carbon residue determinations correlate well with actual coke made in refining processes, including delayed coking (1,2)* and catalytic cracking (3). However, additional factors, including asphaltene and heteroatom content, must be considered to adequately correlate coking propensity with feedstock characteristics under hydroprocessing conditions (4).

Carbon residue yield correlates well with feedstock hydrogen content or H/C atomic ratio (5). This finding agrees with kinetic studies indicating a higher rate of coke formation with increasing feedstock aromaticity (6). Coke formation largely occurs through free radical polymerization of aromatics (7,8). Coke precursors may be formed via thermal or catalytic cracking reactions which cleave alkyl groups to form aryl radicals, or through abstraction of aryl hydrogens to form radicals (6,7). Heteroatoms such as N, Ni and V are often preferentially incorporated into coke because their presence activates a given molecule toward radical formation (8-10).

Because of its free radical mechanism, coke formation is basically a bimolecular process. Since the probability of bimolecular interaction is much greater in a liquid rather than gaseous phase, incompletely volatilized materials (e.g., asphaltenes) make a disproportionately large contribution to coke yield (7). The low volatility of high molecular weight fractions explains their high coking tendency better than alternate concepts based on claims of large condensed polyaromatic structures in petroleum heavy ends. Recent evidence suggests an upper limit of approximately six condensed rings per asphaltene molecule, with the average ring number near three (11). Preoxidation increases coke yield (12), perhaps via lowering volatility.

Catalysts and other solid substrates, including coke itself, can influence the extent of carbonization of the various compound types present. For example, substitution of iron-rich particles for coke as the solid substrate in fluidized or fixed bed coking processes can increase the yield and alter selected properties of the resulting liquids (13,14). An analogous effect may explain the decreased coke yield of Athabasca bitumen in the presence of sand (12). Pure acridine has a higher coking tendency than pure anthracene in the absence of catalysts, while the reverse is true in the presence of cracking or HDS catalysts (15). When present together, acridine interacts with the catalyst surface to actually inhibit anthracene coking. Relative deposition of sulfur and nitrogen into coke depends significantly on the available surface area of a given substrate; metal deposition and overall coke yield are much less affected and are governed primarily by reaction temperature (10).

Coke morphology depends both on feedstock characteristics and operating conditions. For example, the tendency of petroleum resids to form shot coke, an undesirable form of coke, during delayed coking increases with feedstock aromaticity and heteroatom content (16). This trend is consistent with the increased rate of coking, noted above, with these same feedstock parameters. The crystallinity of carbon deposited on metal surfaces depends on the catalytic activity of the metal, operating conditions, and the feedstock (17). Since coke is largely considered to be a low-value by-product in petroleum refining, relatively little effort has been devoted toward optimization of any process for improving the quality of coke produced.

*Numbers in parentheses refer to items in the list of references at the end of this report.

Synergistic effects in carbonization are rare. Typically, the coke or MCR yield from a combined stream is an additive property, i. e., simply the weighted average of the individual feedstocks (5). However, this generalization has not been tested with regard to the various compound classes within a given sample. In addition, the relative partitioning of sulfur, nitrogen and metals into carbon residue versus volatiles as a function of their initial chemical form has not been investigated. In the present work, five nominal 1000° F+ resids were separated into nine compound types using liquid chromatographic methods. These fractions were used to determine whether MCR yield was additive within compound types from a given resid, as well as the relative coking tendencies and heteroatom partitioning (volatiles versus solids) behavior of each compound type.

EXPERIMENTAL SECTION

Inspection properties of the five resids selected appear in table 1. The materials selected cover a wide range of MCR yield and heteroatom content. Two of the resids (Wilmington and Maya) were generated in-house via thin-film distillation; the others were obtained from refineries. All represent straight-run products.

The scheme for liquid chromatographic (LC) separations is shown in figure 1. Separation into strong acids (SA), weak acids (WA), strong bases (SB), weak bases (WB) and neutrals (N) was accomplished using nonaqueous ion exchange (NIE) chromatography. Subfractionation of neutrals into polar-neutrals (PN), sulfides (SUL), saturated hydrocarbons (SAT) and neutral-aromatics (NAR) was performed using the indicated sequence of HPLC methods. Details of the separation methodology and descriptions of typical compositions of each fraction appear elsewhere (18). Elemental composition was determined for all fractions and the corresponding MCR solids. Methodology for these analyses has also been described (18).

Deposition of hetero-atoms into the MCR solid versus volatiles was expressed as the weight fraction partitioning into the two phases:

$$F_s(X) = \frac{(\text{wt}\% X_s)(\text{MCR})}{(\text{wt}\% X_i)(100)} \quad 1)$$

$$F_v(X) = 1 - F_s \quad 2)$$

F_s, F_v = wt fraction of a given element, X, partitioning into the MCR solids and volatiles, respectively

wt % X_s = wt % of the element X in the MCR solids

MCR = yield of MCR solids, wt %

wt % X_i = wt % X present initially in the whole resid or chromatographic fraction

RESULTS

Table 2 shows mass balances from LC separations. The resids are listed in the same order as in table 1, which corresponds to increasing MCR yield from left to right. The increase in combined yield of strong acid plus strong base fractions from left to right in table 2 correlates roughly with that for MCR yield for whole resids in table 1. As shown in subsequent tables, these fractions generally provide the highest MCR yield for each series of fractions from a given resid.

TABLE 1. - Inspection properties for petroleum resids employed in carbonization study

Sample Name Origin	Brass River ^c Nigeria	Lagomedio Venezuela	Wilmington California	Maya Mexico	Merey Venezuela
Sample No.	3054	3064	1694	1741	3063
Boiling Range,					
°F	>1000	>950	>1000	>930	>950
°C	>535	>510	>535	>500	>510
Elemental Content, wt%					
C	86.32	84.54	84.40	82.81	84.52
H	11.89	11.43	10.23	9.82	10.10
N	0.36 (0.34) ^d	0.48	1.30	0.67	0.81
S	0.58 (0.62)	2.64	2.66	5.17	3.70
O ^a	0.85	0.91	1.41	1.53	0.87
H/C, Atomic Ratio,	1.641	1.611	1.444	1.413	1.424
Metal Content, ppm w/w					
Ni	15 (14.6)	36	177	107	150
V	7.1 (8.9)	361	124	567	596
Fe	18	6.8	123	16	14
Specific Gravity (60°F)	0.956	0.984	1.039	1.049	1.049
API Gravity	16.5	12.3	4.7	3.4	3.4
Microcarbon Residue (MCR), wt%	5.89 (5.9)	14.1	20.0	26.2	28.1
MCR Nitrogen Content, wt% ^b	1.94	1.77	3.29	1.97	2.33
MCR Sulfur Content, wt% ^b	0.77	4.17	1.56	6.50	4.13

^aBy difference.^bWt% of MCR solids.^cResid from crude blend into Sweeny Refinery, Phillips Petroleum Co. Contains predominantly Brass River crude, with minor amounts of other sweet crudes.^dData in parentheses courtesy of Phillips Petroleum Co.

Figure 1. Scheme for liquid chromatographic (LC) separation of > 1000° F resid

TABLE 2. - Separation mass balances (weight percent)^a

Sample Name Origin	Brass River Nigeria	Lagomedio Venezuela	Wilmington California	Maya Mexico	Merey Venezuela
Sample No.	3054	3064	1694	1741	3063
Boiling Range					
°F	>1000	>950	>1000	>930	>950
°C	>535	>510	>535	>500	>510
Strong Acids	5.2±0.5	8.1±0.3	11.2	17.8±1.2	17.2±0.6
Weak Acids	5.9±0.7	6.3±0.4	15.5	8.1±0.1	8.8±0.7
Strong Bases	5.0±0.3	5.2±0.1	11.7±0.3	10.3±0.1	13.0±0.1
Weak Bases	4.6±0.4	6.5±0.7	9.4±0.1	8.4±0.6	11.2±0.7
Neutrals	81.6±1.8	73.5±0.3	54.5±1.3	54.3±1.2	50.1±0.6
Polar-neutrals	1.9±0.3	2.8±1.0	10.7±0.7	3.5±0.5	4.6±0.6
Sulfides	4.5±0.7	8.9±0.2	10.7±1.0	9.4±0.8	8.2±1.1
Saturates	26.2±3.5	20.3±1.0	5.0±0.3	6.1±0.8	5.6±0.1
Neutral-aromatics	47.3±3.2	39.7±0.6	28.2±1.0	32.4±0.9	29.5±0.2
Total Recoveries					
NIE separation	102.3	99.6	102.3	98.9	100.3
Subfractionation					
of neutrals ^b	79.9	71.7	54.6	51.4	47.9

^aUncertainties shown are average deviations from duplicate determinations.

^bWhole resid basis. Compare with yield of neutrals.

Tables 3-7 provide a breakdown of elemental analyses and MCR testing of individual fractions from each resid. Balances for each major element and MCR yield over the initial NIE LC separation into acidic, basic and neutral types and subsequent LC subfractionation of neutrals were calculated from fraction yields in table 2 and the corresponding data for the individual fractions. The resulting balances were generally in good agreement (relative variation ≤10 percent) with data determined directly on the corresponding whole materials (whole resid in the case of NIE LC, whole neutrals for neutral subtypes). In the case of H/C, N and S data, this exercise simply indicates quantitative recovery of each element over the LC separations, which is in agreement with the quantitative mass recoveries indicated earlier in table 2. However, for MCR yield, this finding carries greater significance since it shows that coke yield, as reflected by MCR, is an additive property over the various compound types within a given resid.

The appropriate N and S data in tables 3-7 were substituted into equation 1 in order to obtain weight fractions of each element in MCR volatiles (F_V) versus solids (F_S). Results from those calculations are summarized in tables 8 and 9 for N and S, respectively. Balances for F_V and F_S , analogous to those indicated in earlier tables, also appear in tables 8 and 9.

TABLE 3. - Properties of LC fractions and MCR solids from Brass River >1000° F resid (3054)

	Fraction			MCR Yield (wt %)	MCR	
	H/C Ratio	N (wt %)	S (wt %)		N (wt %)	S (wt %)
Whole resid	1.641	0.36	0.58	5.89	1.94	0.77
Strong acids	1.425	0.54	0.61	20.5	1.53	0.98
Weak acids	1.408	1.12	0.75	18.4	2.32	0.76
Strong bases	1.352	2.53	0.91	28.1	2.54	0.86
Weak bases	1.557	1.66	1.61	17.6	2.56	0.78
Neutrals	1.738	0.134	0.53	3.01	0.62	0.76
Balance over NIE	1.676	0.40	0.61	6.82	-	-
Polar-neutrals	1.547	0.88	2.12	19.5	2.45	1.13
Sulfides	1.613	0.51	3.70	13.2	2.46	2.15
Saturates	1.933	<0.001	0.01	0.1	-	-
Neutral-aromatics	1.597	0.148	0.40	3.76	0.91	0.68
Balance over Neutral subtypes	1.707	0.137	0.50	2.8	-	-

TABLE 4. - Properties of LC fractions and MCR solids from Lagomedio >950° F resid (3064)

	Fraction			MCR Yield (wt %)	MCR	
	H/C Ratio	N (wt %)	S (wt %)		N (wt %)	S (wt %)
Whole resid	1.611	0.48	2.64	14.1	1.77	4.17
Strong acids	1.185	1.26	3.31	45.4	2.25	4.06
Weak acids	1.308	1.45	2.94	34.1	2.53	3.54
Strong bases	1.218	1.78	3.66	46.9	2.22	4.41
Weak bases	1.428	1.41	3.21	27.9	2.05	4.17
Neutrals	1.682	0.086	2.16	5.50	0.79	3.50
Balance over NIE	1.577	0.44	2.45	14.2	-	-
Polar-neutrals	1.522	0.35	4.25	20.1	1.58	4.39
Sulfides	1.592	0.15	5.29	12.5	0.80	5.31
Saturates	1.985	<0.01	0.02	<0.1	-	-
Neutral-aromatics	1.597	0.092	2.43	7.0	0.44	4.64
Balance over Neutral subtypes	1.703	0.083	2.17	6.2	-	-

TABLE 5. - Properties of LC fractions and MCR solids from Wilmington >1000° F resid (1694)

	Fraction			MCR Yield (wt %)	MCR	
	H/C Ratio	N (wt %)	S (wt %)		N (wt %)	S (wt %)
Whole resid	1.444	1.30	2.66	20.0	3.29	1.56
Strong acids	1.283	1.16	2.36	25.6	2.79	1.61
Weak acids	1.316	1.60	2.18	33.9	2.55	1.44
Strong bases	1.359	2.97	3.05	37.1	3.34	1.43
Weak bases	1.519	2.20	3.32	22.4	3.02	1.48
Neutrals	1.570	0.58	2.80	11.8	1.99	1.67
Balance over NIE	1.471	1.22	2.73	21.0	-	-
Polar-neutrals	1.509	1.08	4.13	21.6	1.74	1.58
Sulfides	1.561	0.90	5.01	18.4	3.26	2.85
Saturates	1.893	<0.001	0.01	<0.1	-	-
Neutral-aromatics	1.495	0.43	1.66	9.5	1.84	0.91
Balance over Neutral subtypes	1.547	0.61	2.65	12.7	-	-

TABLE 6. - Properties of LC fractions and MCR solids from Maya >930° F resid (1741)

	Fraction			MCR Yield (wt %)	MCR	
	H/C Ratio	N (wt %)	S (wt %)		N (wt %)	S (wt %)
Whole resid	1.413	0.67	5.17	26.2	1.97	6.50
Strong acids	1.139	1.43	6.00	49.4	2.16	7.01
Weak acids	1.315	1.41	4.69	31.2	1.89	5.86
Strong bases	1.147	1.86	6.00	49.5	2.74	7.04
Weak bases	1.394	1.18	6.15	27.7	2.58	6.45
Neutrals	1.565	0.165	4.20	10.5	0.69	5.82
Balance over NIE	1.410	0.75	4.92	24.7	-	-
Polar-neutrals	1.548	0.43	5.82	17.7	1.35	5.64
Sulfides	1.485	0.30	6.86	20.3	1.19	6.91
Saturates	1.971	<0.001	0.02	<0.1	-	-
Neutral-aromatics	1.561	0.091	3.77	8.9	0.47	5.63
Balance over Neutral subtypes	1.595	0.142	4.03	10.5	-	-

TABLE 7. - Properties of LC fractions and MCR solids from Merey >950° F resid (3063)

	Fraction			MCR Yield (wt %)	MCR	
	H/C Ratio	N (wt %)	S (wt %)		N (wt %)	S (wt %)
Whole resid	1.424	0.81	3.70	28.1	2.33	4.13
Strong acids	1.126	1.58	3.86	52.1	2.53	4.12
Weak acids	1.292	1.32	3.46	35.4	2.75	3.59
Strong bases	1.159	1.90	3.82	48.5	2.74	4.22
Weak bases	1.331	1.37	3.90	34.7	2.77	3.91
Neutrals	1.561	0.24	3.22	11.3	1.34	3.84
Balance over NIE	1.385	0.91	3.51	27.9	-	-
Polar-neutrals	1.461	0.51	4.87	24.7	1.42	5.00
Sulfides	1.551	0.32	5.41	19.5	1.34	5.52
Saturates	1.950	<0.01	0.03	<0.1	-	-
Neutral-aromatics	1.533	0.16	2.78	10.4	0.67	4.14
Balance over Neutral subtypes	1.578	0.20	3.11	12.1	-	-

TABLE 8. - Partitioning of nitrogen into MCR volatiles (v) versus solids (s) (wt fraction N)^a

Resid Boiling range, °F	Brass River >1000		Lagomedio >950		Wilmington >1000		Maya >930		Merey >950	
	F _V	F _S	F _V	F _S	F _V	F _S	F _V	F _S	F _V	F _S
Whole resid	0.68	0.32	0.48	0.52	0.49	0.51	0.23	0.77	0.19	0.81
Strong acids	0.42	0.58	0.19	0.81	0.38	0.62	0.25	0.75	0.17	0.83
Weak acids	0.52	0.38	0.40	0.60	0.46	0.54	0.58	0.42	0.26	0.74
Strong bases	0.72	0.28	0.42	0.58	0.58	0.42	0.27	0.73	0.30	0.70
Weak bases	0.73	0.27	0.59	0.41	0.69	0.31	0.39	0.61	0.30	0.70
Neutrals	0.86	0.14	0.49	0.51	0.59	0.41	0.56	0.44	0.37	0.63
Balance over NIE	0.81	0.19	0.46	0.54	0.56	0.44	0.46	0.54	0.31	0.69
Polar Neutrals	0.46	0.54	0.09	0.91	0.65	0.35	0.44	0.56	0.31	0.69
Sulfides	0.36	0.64	0.33	0.67	0.33	0.67	0.19	0.81	0.18	0.82
Saturates	-	-	-	-	-	-	-	-	-	-
Neutral-aromatics	0.77	0.23	0.66	0.34	0.59	0.41	0.54	0.46	0.56	0.44
Balance over Neutral subtypes ^b	0.82	0.18	0.69	0.31	0.59	0.41	0.52	0.48	0.52	0.48

^aSee equations 1 and 2.^bCalculated assuming F_V for saturates = 1.00.

TABLE 9. - Partitioning of sulfur into MCR volatiles (v) versus solids (s) (wt fraction S)^a

Resid Boiling range, °F	Brass River >1000		Lagomedio >950		Wilmington >1000		Maya >930		Merey >950	
	F _V	F _S	F _V	F _S	F _V	F _S	F _V	F _S	F _V	F _S
Whole resid	0.92	0.08	0.78	0.22	0.88	0.12	0.67	0.33	0.69	0.31
Strong acids	0.67	0.33	0.44	0.56	0.83	0.17	0.42	0.58	0.44	0.56
Weak acids	0.81	0.19	0.59	0.41	0.78	0.22	0.61	0.39	0.63	0.37
Strong bases	0.73	0.27	0.43	0.57	0.83	0.17	0.42	0.58	0.46	0.54
Weak bases	0.91	0.09	0.64	0.36	0.90	0.10	0.71	0.29	0.65	0.35
Neutrals	0.96	0.04	0.91	0.09	0.93	0.07	0.85	0.15	0.87	0.13
Balance over NIE	0.92	0.08	0.81	0.19	0.88	0.12	0.70	0.30	0.70	0.30
Polar Neutrals	0.90	0.10	0.78	0.22	0.92	0.08	0.83	0.17	0.75	0.25
Sulfides	0.92	0.08	0.88	0.12	0.90	0.10	0.80	0.20	0.80	0.20
Saturates	-	-	-	-	-	-	-	-	-	-
Neutral-aromatics	0.94	0.06	0.87	0.13	0.95	0.05	0.87	0.13	0.85	0.15
Balance over Neutral subtypes ^b	0.96	0.04	0.90	0.10	0.94	0.06	0.87	0.13	0.85	0.15

^aSee equations 1 and 2.^bCalculated assuming F_V for saturates = 1.00.

Balances for S partitioning over LC fractions (table 9) agree well with those for the corresponding whole materials, thereby indicating that S partitioning, like MCR yield, is an additive property. However, those for N (table 8) generally do not agree with results for the whole materials, thereby indicating that N partitioning is composition dependent. This difference in behavior between S and N is consistent with the higher strength of C-N compared to C-S bonds, and the previously noted tendency of N to activate molecules toward radical formation. Other workers observed a significant dependence for N partitioning on vapor residence time in delayed coking, but very little for S (13).

Figure 2 shows correlations of H/C ratio (tables 3-7), F_S(N) (table 8) and F_S(S) (table 9) with MCR yield for the five whole resids. In each case, an approximately linear relationship is obtained. Parameters from regression analysis of each data set are shown in Appendix A. The Wilmington resid results are somewhat atypical in that they fall below the indicated least-squares fitted line for all three correlations. This behavior may in turn reflect unusual compositional features of that crude. For example, prior mass spectrometric analyses of saturate fractions from 370-535° C distillates indicated that the distribution for Wilmington maximized at 4-ring compounds (steroidal configuration), whereas those from other crudes maximized at 0-ring (*n*-paraffins, isoparaffins) or 1-ring (alkylcyclopentanes, alkylcyclohexanes) and progressively decreased with increasing ring number (19). In any case, the inexactness of correlations in figure 2 and in others discussed below generally reflect subtle effects of chemical structure rather than experimental error.

Figures 3-7 are analogous to figure 2, but show results for LC fractions from each of the five resids. Correlations obtained for whole resids (figure 2) are superimposed as dashed lines on each figure for comparison. Correlations for H/C ratio versus MCR yield for LC fractions agree substantially with those from the whole resids in each case (see appendix), which reinforces the earlier conclusion that MCR yield is an additive property relating only to the relative abundance of H versus C.

Figure 2. Correlation of coking parameters for straight-run vacuum resid.

Figure 3. Correlation of coking parameters for Brass River Fractions. Corresponding correlations for the whole resids (dashed lines, see figure 2) are superimposed.

Figure 4. Correlation of coking parameters for Lagomedio Fractions. Corresponding correlations for the whole resids (dashed lines, see figure 2) are superimposed.

Figure 5. Correlation of coking parameters for Wilmington Fractions. Corresponding correlations for the whole resids (dashed lines, see figure 2) are superimposed.

Figure 6. Correlation of coking parameters for Maya Fractions. Corresponding correlations for the whole resids (dashed lines, see figure 2) are superimposed.

Figure 7. Correlation of coking parameters for Merey Fractions. Corresponding correlations for the whole resids (dashed lines, see figure 2) are superimposed.

As seen by the close agreement in correlations between LC fractions and whole resids, sulfur partitioning is generally independent of chemical form (e.g., sulfide versus thiophenic) and other structural aspects. However, the lower slope for the Wilmington fraction correlation, which also fits the result for the whole Wilmington resid quite well (figure 5), indicates that sulfur partitioning is not completely independent of structure. Even in the case of Wilmington, however, the initial form of sulfur (e.g., NAR = predominantly thiophenic, SUL = predominantly sulfide, PN = predominantly sulfoxide) had little effect on the proportion found in the MCR solids versus volatiles. The latter is largely a function of the MCR solid yield. The previously noted agreement in table 8 for calculated balances versus whole materials also indicates that sulfur partitioning is an additive rather than composition dependent property.

Nitrogen partitioning for LC fractions showed a much lower dependence on MCR solid yield than for the whole resids. This difference is quite evident in the decreased slopes of lines for fractions in figures 3-7, compared to that for the whole resids, which is superimposed on each figure. This disparity in correlations for LC fractions versus whole resids, coupled with the previously mentioned lack of agreement between balance versus whole F_V and F_S data in table 8, clearly demonstrates a compositional dependence for N deposition into coke. Interestingly, the sulfide fraction consistently deposits a high proportion of N into solids in relation to its MCR yield. This may relate to the structure of N compounds present in that fraction, or it may point to a synergistic interaction between S and N during coking, which results in a greater proportion of N being incorporated into the solid phase.

Figures 8 and 9 show the relationships between N and S contents, respectively, of LC fractions and whole resids versus that of the corresponding MCR solids. N is almost universally enriched in the MCR solids relative to the starting material, whereas the behavior of S is quite variable. The considerable data scatter in these figures shows the superiority of prior correlations which have MCR solid yield factored in (figures 2-7).

Tables 10-14 list Ni and V contents of NIE LC fractions and the corresponding MCR solids for each resid. Ni and V breakdowns were not determined for neutral subtypes (saturates, neutral-aromatics, etc.). Balances for Ni and V over the fractions typically agree well with results for the whole resid in the case of Ni, but indicate recoveries ranging from 98 to as low as 86 weight percent in the case of V. Ni and V are present in each chromatographic fraction, but their relative concentration in neutrals is significantly lower owing to dilution by bulk nonmetal containing constituents such as saturated hydrocarbons. Ni and V are substantially enriched in MCR solids owing to nearly quantitative partitioning, as indicated in tables 15 and 16.

Fractions of Ni found in MCR solids [$F_S(\text{Ni})$] range from 0.82 to 1.07, as shown in table 15. Since the theoretical maximum for $F_S(\text{Ni})$ is one, results greater than 1.00 reflect experimental error. Consideration of all data ≥ 1.00 resulted in an estimate of error of ± 0.05 , at a 95 percent confidence level. Thus, all $F_S(\text{Ni})$ data in the table ≥ 0.95 should be interpreted as 1.00, and all $F_V(\text{Ni})$ data between 0 and 0.05 are effectively zero. Within these constraints of probable experimental error, only about one-half of the fractions/whole resids may be stated as having released measurable quantities of Ni into the MCR volatiles. As for N, balances for Ni over LC fractions typically do not agree with those of the corresponding whole resid, thereby indicating that Ni partitioning is composition dependent.

Fractions of V found in MCR solids [$F_S(\text{V})$] range from 0.83 to 1.08, as shown in table 16. Estimation of error at the 95 percent confidence level for V as done above for Ni yielded a result of ± 0.08 . Thus, all $F_S(\text{V})$ data ≥ 0.92 should be interpreted as 1.00 and all $F_V(\text{V})$ data between 0 and 0.08 are effectively zero. Since only one set of data, that for Maya weak bases, lies outside the above error limits, the only conclusions drawn from the table is that V very effectively partitions into solids under the conditions of the MCR test.

Figure 8. Correlation of nitrogen content (wt. %) of whole resids and their fractions ("initial") versus that of the resulting MCR solids. The dotted line corresponds to a 1:1 correlation.

Figure 9. Correlation of sulfur content (wt. %) of whole resids and their fractions ("initial") versus that of the resulting MCR solids. The dotted line corresponds to a 1:1 correlation.

TABLE 10. - Metal content (ppm w/w) of LC fractions and MCR solids from Brass River >1000° F resid (3054)

	MCR Yield (wt %)	Fraction		MCR	
		Ni	V	Ni	V
Whole Resid	5.89	15	7.1	208	119
Strong Acids	20.5	55	41	230	204
Weak Acids	18.4	23	16	122	86
Strong Bases	28.1	64	39	221	142
Weak Bases	17.6	50	19	264	111
Neutrals	3.01	6.5	1.5	202	48
Balance	6.82	15	7.0	-	-

TABLE 11. - Metal content (ppm w/w) of LC fractions and MCR solids from Lagomedio >950° F resid (3064)

	MCR Yield (wt %)	Fraction		MCR	
		Ni	V	Ni	V
Whole Resid	14.1	36	361	261	2600
Strong Acids	45.4	171	1610	382	3670
Weak Acids	34.1	50	645	141	2000
Strong Bases	46.9	171	1220	344	2660
Weak Bases	27.9	104	679	297	2420
Neutrals	5.5	6.5	43	90	705
Balance	14.2	38	311	-	-

TABLE 12. - Metal content (ppm w/w) of LC fractions and MCR solids from Wilmington >1000° F resid (1694)

	MCR Yield (wt %)	Fraction		MCR	
		Ni	V	Ni	V
Whole Resid	20.0	177	124	770	581
Strong Acids	25.6	209	157	590	602
Weak Acids	33.9	182	159	537	497
Strong Bases	37.1	248	144	670	386
Weak Bases	22.4	244	127	946	546
Neutrals	11.8	123	87	856	724
Balance	21.0	167	118	-	-

TABLE 13. - Metal content (ppm w/w) of LC fractions and MCR solids from Maya >930° F resid (1741)

	MCR Yield (wt %)	Fraction		MCR	
		Ni	V	Ni	V
Whole Resid	26.2	107	567	408	2170
Strong Acids	49.4	247	1210	472	2310
Weak Acids	31.2	90	708	268	2310
Strong Bases	49.5	320	1070	550	1990
Weak Bases	27.7	110	532	424	1590
Neutrals	10.5	24	229	228	1030
Balance	24.7	108	558	-	-

TABLE 14. - Metal content (ppm w/w) of LC fractions and MCR solids from Merey >950° F resid (3063)

	MCR Yield (wt %)	Fraction		MCR	
		Ni	V	Ni	V
Whole Resid	28.1	150	596	483	2220
Strong Acids	52.1	276	1120	541	2330
Weak Acids	35.4	116	673	322	1760
Strong Bases	48.5	309	1200	591	2500
Weak Bases	34.7	177	766	521	2390
Neutrals	11.3	35	129	310	1140
Balance	27.9	135	555	-	-

TABLE 15. - Partitioning of nickel into MCR volatiles (v) versus solids (s) (wt fraction Ni)

Resid Boiling range, °F	Brass River >1000		Lagomedio >950		Wilmington >1000		Maya >930		Merey >950	
	F _v	F _s	F _v	F _s	F _v	F _s	F _v	F _s	F _v	F _s
Whole Resid	0.18	0.82	-	1.02	0.13	0.87	0	1.00	0.10	0.90
Strong Acids	0.14	0.86	-	1.01	0.28	0.72	0.06	0.94	-	1.02
Weak Acids	0.02	0.98	0.04	0.96	0	1.00	0.07	0.93	0.02	0.98
Strong Bases	0.03	0.97	0.06	0.94	0	1.00	0.15	0.85	0.07	0.93
Weak Bases	0.07	0.93	0.20	0.80	0.13	0.87	-	1.07	-	1.02
Neutrals	0.06	0.94	0.24	0.76	0.18	0.82	0	1.00	0	1.00
Balance	0.06	0.94	0.19	0.81	0.14	0.86	0.03	0.97	0.01	0.99

TABLE 16. - Partitioning of vanadium into MCR volatiles (v) versus solids (s) (wt fraction V)

Resid Boiling range, °F	Brass River >1000		Lagomedio >950		Wilmington >1000		Maya >930		Merey >950	
	F _v	F _s	F _v	F _s	F _v	F _s	F _v	F _s	F _v	F _s
Whole Resid	0.01	0.99	-	1.02	0.06	0.94	0	1.00	-	1.05
Strong Acids	-	1.02	-	1.03	0.02	0.98	0.06	0.94	-	1.08
Weak Acids	0.01	0.99	-	1.06	-	1.06	-	1.02	0.07	0.93
Strong Bases	-	1.02	-	1.02	0	1.00	0.08	0.92	-	1.01
Weak Bases	-	1.03	0.01	0.99	0.04	0.96	0.17	0.83	-	1.08
Neutrals	0.04	0.96	0.10	0.90	0.02	0.98	0.09	0.91	0	1.00
Balance	0.03	0.97	0.07	0.93	0.01	0.99	0.08	0.92	-	1.02

An attempt was also made to determine Fe partitioning between MCR volatiles and solids. This task was subsequently abandoned because of excessive data scatter attributed to inhomogeneity of Fe (particulate forms) in both whole resid/fractions and the MCR solids, and analytical contamination problems. To the extent determinable from the available data, Fe appeared to partition mostly into the MCR solids, as was the case for Ni and V.

DISCUSSION

The approximately linear relationship between coke make, as approximated by MCR solid yield, and hydrogen abundance, as expressed by H/C ratio, is in accordance with previously proposed mechanisms for coke formation via aryl radicals, which were discussed in the introductory section. Thus, the probability of a given aryl radical to react with another aromatic moiety to form coke or a coke precursor, versus molecular hydrogen or other hydrogen rich moiety such as a cycloalkane to form liquid product, should in fact relate directly to hydrogen abundance. Bunker has shown that coke formation can be virtually eliminated during pyrolysis in a hydrogen atmosphere, which demonstrates the fundamental impact of hydrogen availability on coke yield (7,20,21).

Minor negative deviations from average H/C versus MCR correlations in figures 2-7, such as that for the whole Wilmington resid (figure 2) or Wilmington neutral-aromatic or strong acid fractions (figure 5), probably reflect better than average hydrogen donor capabilities for those materials, which causes decreased coke yield in proportion to overall H/C ratio. This may relate to a higher relative abundance of naphthenic forms of aliphatic hydrogen in each case. For example, Wilmington is known to contain a higher concentration of naphthenic acids than many crudes (22,23), which would contribute to the naphthenic character of its strong acid fraction. This observation, coupled with the previously mentioned naphthenic composition of its saturated hydrocarbon fraction, builds a case for the naphthenic character of the Wilmington resid as a whole. Thus, a trend towards slightly lower MCR yield in proportion to H/C is indicated for naphthenic as compared to paraffinic feedstocks. Loss of hydrogen from naphthenic rings is favored over loss from acyclic paraffins because of the difference in stability of products from each; i.e. aromatics compared to olefins.

As reflected by R² terms listed in the appendix, linear correlations for MCR yield versus H/C ratio for Brass River and Wilmington resid fractions (figures 3 and 5, respectively) exhibit significantly greater data scatter than those for the other resids. It is unlikely that data for those resids are less precise; rather, a greater structural dependence for MCR yield is implied. For example, the potential effect of naphthenic character in reducing coking discussed

above may be partly responsible for the observed variation. It is interesting to note that both of these resids contain a higher concentration of Ni than V (table 1), whereas the reverse is true for the other resids, and generally, for the bulk of known crude oils. The Ni/V ratio can have geochemical significance; it may also relate to aspects of hydrocarbon structure impacting coking behavior.

As with carbon, incorporation of sulfur into MCR solids is largely nonselective, depending solely on MCR yield to a good approximation. The proportionally greater incorporation of S into MCR solids with increasing solid yield is intuitive. A common misconception among refiners is that S in coke is derived primarily from that present in aromatic (thiophenic) forms in the feedstock. For all resids, deposition of S into solids was largely independent of the form (sulfide, thiophenic, or sulfoxide) present initially.

However, as was also the case for carbon, S partitioning appears to exhibit smaller secondary dependences on composition. For example, MCR solids from Wilmington are depleted in S relative to the corresponding fraction, whereas those from Maya and Lagomedio are generally enriched (figure 9). This difference in partitioning between resids could relate to variations in their sulfur distribution as a function of boiling point or aromaticity. That is, the least volatile or most aromatic species present, which have the highest probability for forming coke as discussed earlier, may be deficient in S in the case of Wilmington and enriched for Maya and Lagomedio. In addition, there is a slight preference for incorporation of thiophenic forms of sulfur compared to sulfide forms. This preference is evident in the consistent positioning of points for neutral-aromatic fractions (thiophenic S) above least square fitted lines in figures 3-7 and those for sulfide fractions below the line, for example. Thus, S partitioning is not completely independent of chemical form(s) present, but the magnitude of the effect is close to experimental error.

As with S, the initial chemical form of N exerted minimal impact on its partitioning behavior, except that there appeared to be a slight preference for incorporation of acidic forms of N (primarily pyrrolic and amide types) over basic types (azaarenes). An interesting feature of nitrogen partitioning is the relatively smooth increase in $F_S(N)$ with MCR solid yield for whole resids (figure 2) compared to widely fluctuating data for LC fractions from a given resid. This plus the overall decrease in $F_S(N)$ calculated over the fractions compared to the whole resid (except for Lagomedio, see table 8) suggests specific interactions among nitrogen compounds of different type during coking of whole resids. For example, acidic and basic N compounds could combine in the whole resid to maximize N partitioning into MCR solids, whereas such interaction is not possible in the case of MCR testing of individual LC fractions. The high degree of partitioning into solids observed for N present in sulfide fractions, and the Lagomedio polar-neutral fraction, may also result from specific interactions between N and S compounds in those cases. Alternately, the N compounds in those fractions, which constitute a very small proportion of the total N present, may simply possess high coking tendencies which are obscured when either the whole resid or whole neutral fraction is subjected to the MCR test.

The composition dependency for N partitioning provides a basis for its control via blending or use of additives. If sufficient information on the nature of the interactions between N compounds were available, it should be possible to maximize N deposition into solids, for example, via optimization of appropriate ratios of N types in the feedstock.

The partitioning behavior of Ni appears to be comparable to that of N; i.e., composition dependent. Given the low abundance of Ni compounds in each resid, interactions controlling Ni deposition into solids probably do not occur between two Ni compounds, but rather between Ni compounds and other types. It is tempting to attribute the sporadic partitioning (table 15) of Ni into MCR volatiles to the presence of significant quantities of porphyrinic or other volatile

Ni forms in selected whole resids and LC fractions. However, the fraction with the highest $F_V(\text{Ni})$, Wilmington strong acids, does not contain detectable levels of Ni or V porphyrins (24). Furthermore, $F_V(\text{Ni})$ for Wilmington weak bases (0.13) and neutrals (0.18) is out of proportion with the percent total Ni present in porphyrinic forms in those fractions (weak bases 18 percent, neutrals 79 percent) (24). Hence, visible spectroscopic determination of porphyrin content is a poor predictor of relative Ni volatility in the MCR test. Therefore, other compositional factors, such as N content, probably impact Ni partitioning to a greater extent than its initial chemical form in the resid.

As noted in the Results section, partitioning of V into MCR volatiles was generally too low to be accurately measured from the difference between V contents of starting materials versus MCR solids. Since porphyrinic forms of V are generally more abundant than those for Ni (24), the nearly quantitative deposition of V into solids indicates a similar conclusion to that for Ni, i.e., that the initial chemical form does not control coking behavior. Some forms of V exhibit appreciable volatility; distinct bimodal distributions of V as a function of atmospheric equivalent boiling point are typically observed (25). The observed lack of release of a significant proportion of more volatile V forms further substantiates the fundamental difference between coking, as approximated by the MCR procedure, versus controlled volatilization, as in distillation.

CONCLUSIONS

The compositional dependence of N and Ni partitioning, and potentially that for V had it been more easily measured, is consistent with the ability of each element to promote radical formation (8-10), and the greater sensitivity of those elements toward process conditions, as noted in prior work with small scale coking units (13). With the exception of compounds containing those elements, and other minor structural effects noted, the coking behavior of whole resids and each compound class contained within is largely defined by atomic composition, rather than detailed molecular structure. Thus, the compound class or functional group concepts are largely irrelevant to noncatalytic coking behavior, as approximated by the MCR test method. The additive nature of coke yield over fractions of a given whole resid is a logical consequence of its simple dependence on H/C ratio, since H/C ratio is itself an additive property. The linear relationship between sulfur partitioning and MCR yield is consistent with random substitution of sulfur for carbon in both solid and volatile products, according to the proportion of each product and the relative abundance of S versus C (S/C ratio).

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APPENDIX A

TABLE A-1. - Parameters from regression analyses of Figures 2-9

Figure	Data Set	Coordinates		Equation	m	b	R ²
		y	x				
2	Whole resids	H/C	MCR yield	$y = mx+b$	-0.0113	1.72	0.88
		F _s (N)	"	"	0.0214	0.182	0.92
		F _s (S)	"	"	0.0101	0.0219	0.68
3	Brass River fractions ¹	H/C	"	"	-0.0127	1.72	0.77
		F _s (N)	"	"	0.0082	0.258	0.17
		F _s (S)	"	"	0.0090	0.0077	0.58
4	Lagomedio fractions ¹	H/C	"	"	-0.0115	1.73	0.97
		F _s (N)	"	"	0.0041	0.497	0.13
		F _s (S)	"	"	0.0117	0.0212	0.98
5	Wilmington fractions ¹	H/C	"	"	-0.0087	1.64	0.55
		F _s (N)	"	"	0.0018	0.432	0.017
		F _s (S)	"	"	0.0054	-0.0011	0.79
6	Maya fractions ¹	H/C	"	"	-0.0111	1.69	0.98
		F _s (N)	"	"	0.0054	0.471	0.28
		F _s (S)	"	"	0.0116	0.0025	0.97
7	Merey fractions ¹	H/C	"	"	-0.0109	1.70	0.96
		F _s (N)	"	"	0.0046	0.571	0.32
		F _s (S)	"	"	0.0104	0.0109	0.99
8	N in feed vs. MCR solids	N _{initial}	N _{MCR}	"	0.711	-0.446	0.64
		"	"	$y = be^{mx}$	1.11	0.0735	0.81
		"	"	$y = b+m(\ln x)$	1.004	0.390	0.57
		"	"	$y = bx^m$	1.70	0.252	0.84
9	S in feed vs. MCR solids	S _{initial}	S _{MCR}	$y = mx+b$	0.691	0.969	0.72

¹Data for saturate fractions excluded from correlations.

Figure A-1. Figure 8 replotted to show fitted curves from each regression mode.

Figure A-2. Figure 9 with linear regression. ~~Figure 9~~ fitted line indicated.

ADDENDUM

Subsequent to this work, a statistical analysis was performed by workers at INTEVEP* to determine whether additional relationships (besides those stated in the report) existed between fraction composition and microcarbon residue yield. A description of their analysis and findings was presented in a separate report: Garcia, R.; Gedler, G.; Izquierdo, A.; Rodriguez, D. *Statistical Analysis on Coke Yields in Vacuum Resids as a Function of Compound Classes and Elemental Analysis*; Report INT-02578, 92; INTEVEP, S. A.: Los Teques, Venezuela, 1993; 37 pp. A summary of their findings is given below.

A linear combination of H/C ratio, vanadium and nitrogen content is a good model to explain coke yield, under non-catalytic conditions, as determined by MCR. Of all these factors, the H/C ratio has the most important contribution in agreement with work previously reported.

No evidence of the compound class influence came from this analysis. However due to the limitations in the set of data, further work should be carried out to confirm this conclusion.

The role of vanadium compounds on coke formation should equally be studied.

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