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Mass Resolving Power Requirement for Molecular Formula Determination of Fossil Oils

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Supporting Information

ABSTRACT: Ultrahigh-resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has been demonstrated to be capable of resolving doublets with mass difference of an electron. However, this resolving power can still be insufficient for positively identifying all of the overlapping species in petroleum and other fossil oils. To look into the ultimate resolving power required, we investigated all possible overlaps in molecular masses of monoisotopic, ^{13}C- and ^{34}S-containing hydrocarbon and heterocompound species that are commonly found in petroleum. Among homologous series containing up to 3 heteroatoms and with up to 30 double bond equivalences, it was found that over 80% even-mass and 50% odd-mass series have overlapping series with mass differences less than an electron mass of 0.458 mDa (458 μDa). Previously introduced nominal mass series are recommended to use as additional means of differentiating the overlapping series. However, the ultimate resolving power required for resolving all possible overlaps is 0.1 mDa, less than the mass of an electron. This should be one of the goals for developing future mass spectrometers with higher resolving power.

1. INTRODUCTION

Composition of complex fossil resources, petroleum, coal, and shale oils, has been expressed by z-series (or double bond equivalence, DBE) and carbon numbers based on the molecular formulas determined from accurate mass measurement.[1] We have reported the importance of including the valence of atoms to obtain accurate DBE.[2] However, without knowing the valence, we can only use a general expression of DBE with an understanding of its possible errors.[2]

Ultrahigh-resolution mass spectrometry has been used to obtain accurate masses with high accuracy.[3] Recent developments in Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) enable us to resolve doublets with mass difference of an electron.[4] In this paper, the use of mass defects for the determination of molecular formulas of the components is reviewed. The resolving power required for overlapping compound series is studied. A very significant number of the overlaps are found to have mass differences less than the mass of an electron. Metal-containing species, such as metalloporphyrins, are not in the scope of current studies.

In previous papers, we reported the use of a mass scale based on the mass of a methylene ($^{12}CH_2$) group as exactly 14 (14.000000), generally known as Kendrick mass scale in honor of Ted Kendrick's publication in 1963,[5] rather than ^{12}C as exactly 12 (12.000000) to yield a single value of mass defect within a given homologous series regardless of the carbon number of the molecule.[6] We also introduced the nominal mass series, z*, for compensating for the measurement errors in a double-focusing magnetic sector mass spectrometer having resolving power less than 100 000.[6] However, the mass measurement errors can be narrowed down to less than 1 millidalton (mDa) by using FT-ICR MS,[3] thus, increasing the confidence in the molecular formula determination based on accurate masses measured. Hence, data averaging using the nominal homologous series for high-resolution sector instruments has become unnecessary. However, as will be discussed below the nominal mass series would be useful for differentiating overlapping compound series that are difficult to resolve by accurate mass measurement alone.

2. RESULTS AND DISCUSSION

Mass defect is defined as accurate mass minus nominal mass, where the nominal mass of a molecule is the sum of nominal masses of constituent atoms. For example, the accurate and nominal masses of the monoisotopic (only the most abundant isotopes of the elements, such as ^{12}C and ^{1}H, are considered as monoisotopic) benzene are 78.0470 and 78 daltons (Da), respectively, on the ^{12}C mass scale. The mass defect from the nominal mass is defined as 0.0470 Da or 47 millidaltons (mDa). On the ^{12}C mass scale, the mass defects of the benzene homologous series vary with the number hydrogen atoms. For example, the mass defects of methyl (C_7), dimethyl (C_8), and trimethyl (C_9) benzenes are 62.6, 78.3, and 93.9 mDa, respectively. On the other hand, the accurate masses of the C_6–C_9 benzenes based on the $^{12}CH_2$ = 14.000000 mass scale are 77.9598, 105.9598, 119.9598, and 133.9598 Da, respectively. They all have the same mass defect of −40.2 mDa. Similarly, all of the other benzenes have the same mass defect on the $^{12}CH_2$ = 14.000000 mass scale regardless of the numbers of carbon and hydrogen atoms. For example, a hypothetic benzene molecule of 500 carbons ($C_{500}H_{994}$) also has the $^{12}CH_2$ mass defect of −40.2 mDa although the monoisotopic species becomes insignificant compared to the species containing ^{13}C isotope.[7] The monoisotopic nominal mass is calculated to be 6994, rather than 7002 on the ^{12}C mass scale. The sum of nominal masses of the atoms in $C_{500}H_{994}$ is also 6994. Hence, the accurate mass should be converted from the ^{12}C scale to "Kendrick" scale before rounding off for the nominal mass. It is recommended that the mass

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Table 1. Kendrick Mass Defects of Saturated Hydrocarbons

C#	H#	DBE	^{12}C mass	K mass	KMD	m*	z*	representative compound series
1	4	0	16.0313	16.0134	0.0134	16	−12	alkanes
5	10	1	70.0783	70.0000	0.0000	70	−14	1-ring naphthenes
9	16	2	124.1252	123.9866	−0.0134	124	−2	2-ring naphthenes
13	22	3	178.1722	177.9732	−0.0268	178	−4	3-ring naphthenes
17	28	4	232.2191	231.9598	−0.0402	232	−6	4-ring naphthenes
21	34	5	286.2661	285.9464	−0.0536	286	−8	5-ring naphthenes
25	40	6	340.3130	339.9330	−0.0670	340	−10	6-ring naphthenes
29	46	7	394.3600	393.9196	−0.0804	394	−12	7-ring naphthenes
33	52	8	448.4069	447.9062	−0.0938	448	−14	8-ring naphthenes

Table 2. Kendrick Mass Defects of Benzene *para*-Condensed Series

C#	H#	DBE	^{12}C mass	K mass	KMD	m*	z*	representative compounds
6	6	4	78.0470	77.9598	−0.0402	78	−6	benzenes
10	8	7	128.0626	127.9196	−0.0804	128	−12	naphthalenes
14	10	10	178.0783	177.8794	−0.1206	178	−4	phenanthrenes/anthracenes
18	12	13	228.0939	227.8392	−0.1608	228	−10	chrysenes
22	14	16	278.1096	277.7990	−0.2010	278	−2	picenes
26	16	19	328.1252	327.7588	−0.2412	328	−8	benzopicenes
30	18	22	378.1409	377.7186	−0.2814	378	−14	dibenzopicenes/trinaphthythene
34	20	25	428.1565	427.6784	−0.3216	428	−6	tribenzopicenes
38	22	28	478.1722	477.6382	−0.3618	478	−12	tetrabenzopicenes

Table 3. Kendrick Mass Defects of mono-*cata*-Condensed Series Benzene *para*-Condensed Series

C#	H#	DBE	^{12}C mass	K mass	KMD	m*	z*	representative compounds
8	6	6	102.0470	101.9330	−0.0670	102	−10	indenes (see text)
12	8	9	152.0626	151.8928	−0.1072	152	−2	acenaphthalenes
16	10	12	202.0783	201.8526	−0.1474	202	−8	pyrenes
20	12	15	252.0939	251.8124	−0.1876	252	−14	benzopyrenes
24	14	18	302.1096	301.7722	−0.2278	302	−6	dibenzopyrenes
28	16	21	352.1252	351.7320	−0.2680	352	−12	benzonaphthopyrenes
32	18	24	402.1409	401.6918	−0.3082	402	−4	dinaphthopyrenes
36	20	27	452.1565	451.6516	−0.3484	452	−10	benzodinaphthopyrenes

Table 4. Kendrick Mass Defects of Di-*Cata*-Condensed Series of Benzene *Para*-Condensed Series

C#	H#	DBE	^{12}C mass	K mass	KMD	m*	z*	representative compounds
14	8	11	176.0626	175.8660	−0.1340	176	−6	diacenaphthalenes
18	10	14	226.0783	225.8258	−0.1742	226	−12	acepyrenes
22	12	17	276.0939	275.7856	−0.2144	276	−4	anthanthrenes
26	14	20	326.1096	325.7454	−0.2546	326	−10	peropyrenes/rubicenes
30	16	23	376.1252	375.7052	−0.2948	376	−2	pyranthrenes
34	18	26	426.1409	425.6650	−0.3350	426	−8	dibenzperopyrenes
38	20	29	476.1565	475.6248	−0.3752	476	−14	benzonaphthoperopyrenes

calibration, such as the masses of perfluorobutylamine and perfluorokerosene calibrants, be based on the $^{12}CH_2$ = 14.000000 mass scale for immediate recognition of the compound type of the components to facilitate the analysis of complex hydrocarbon mixtures and the molecular formula search by computer.

In this paper we limit our discussions of mass defects for molecules of less than 30 double bond equivalences (DBE, the total number of double bonds and cyclic saturated rings plus twice the number of triple bonds to carbon) that are generally reported in the literature. The results can easily be extended to molecules of DBE > 30 for applications. For smaller molecules, only the most abundant isotopic species, that is, monoisotopic, ^{13}C and ^{34}S species, are considered. For larger molecules, species containing two ^{13}C isotopes would become significant in abundance to be included in the discussions. Other isotopic species, such as ^{2}H, ^{33}S, ^{17}O, and ^{15}N species, are generally found insignificant in fossil oils. Without specifications in isotopes, the molecules denoted are monoisotopic. For example, CH_4SO_2 denotes $^{12}C^{1}H_4{}^{32}S^{16}O_2$.

2.1. Hydrocarbons. The mass defects of hydrocarbon series are studied for saturated and aromatic compounds present in petroleum and other fossil oils. The saturated hydrocarbons found in petroleum are paraffins (alkanes and isoalkanes) and cycloparaffins (naphthenes) of single and multiple saturate rings (5- and/or 6-membered). The isomers of cycloparaffins, such as olefins, diolefins, cycloolefins, and multienes, are produced during refining processes, rarely present in natural resources as crude oils.[8] Table 1 shows carbon and hydrogen numbers, DBEs, accurate masses based on ^{12}C = 12.00000 scale (^{12}C mass) and $^{12}CH_2$ = 14.00000 scale (K mass), mass defects on the $^{12}CH_2$ scale (Kendrick mass defect, KMD), nominal mass after the round-off of

Table 5. Kendrick Mass Defects of Hydrocarbons As a Function of DBE

DBE	KMD	representative compound types
0	0.0134	alkanes (normal paraffins and isoparaffins)
1	0.0000	1-ring naphthenes/(olefins not found in crude oils)
2	−0.0134	2-ring naphthenes/(diolefins and cycloolefins not found in crude oils)
3	−0.0268	3-ring naphthenes (tricyclic terpanes)/adamantanes
4	−0.0402	4-ring naphthenes (steranes)/benzenes
5	−0.0536	5-ring naphthenes (hopanes)/indans/tetralins/diadamantanes
6	−0.0670	6-ring naphthenes/indenes
7	−0.0804	naphthalenes/triadamantanes
8	−0.0938	acenaphthenes/biphenyls
9	−0.1072	acenaphthalenes/fluororenes
10	−0.1206	phenanthrenes/anthacenes
11	−0.1340	diacenaphthalenes/cyclopentanophenanthrenes
12	−0.1474	pyrenes/terphenyls/fluoranthenes
13	−0.1608	chrysenes
14	−0.1742	acepyrenes/benzo[*ghi*]fluoanthenes
15	−0.1876	benzopyrenes/perylenes
16	−0.2010	picenes/corannulenes
17	−0.2144	anthanthrenes
18	−0.2278	dibenzopyrenes/benzoperylenes
19	−0.2412	benzopicenes/coronenes
20	−0.2546	peropyrenes/rubicenes
21	−0.2680	benzonaphthopyrenes
22	−0.2814	trinaphthythene/benzocoronenes
23	−0.2948	pyranthrenes
24	−0.3082	dinaphthopyrenes
25	−0.3216	tribenzopicenes/dibenzocoronenes
26	−0.3350	ovalenes
27	−0.3484	dinaphthopentacenes
28	−0.3618	decacylenes/tribenzocoronenes
29	−0.3752	dinaphthocoronenes
30	−0.3886	benzooctaphenes

Kendrick mass (m*), nominal mass z-series (z*), and representative compound series (with possible presence of other isomeric series) of saturated hydrocarbons. Cycloparaffins, or naphthenes, of greater than 6 rings are rarely reported in the literature. The representative molecules showing the numbers of carbon and hydrogen atoms on the left columns represent the smallest members of the respective homologous series.

To facilitate discussions of aromatic hydrocarbons we use hypothetical molecules derived from *para-* and *cata-*condensation series of benzene as basis to obtain all possible Kendrick mass defects of aromatic compounds.[9]

Table 2 lists accurate masses, mass defects, and z* numbers of benzene *para*-condensed series. Note that benzenes have the same mass defect as 4-ring naphthenes because both series have the same molecular formula of C_nH_{2n-6} where n is the number of carbon atoms This occurs for every additional *para*-condensed aromatic ring with corresponding three additional cycloparaffinic rings. For example, naphthalenes have the same general molecular formula of C_nH_{2n-12}, thus, the same mass defect of −80.4 mDa as 7-ring naphthenes.

The mono-*cata*-condensed series of benzene *para*-condensed series are listed in Table 3.[9] C_8H_6 is a hypothetical molecule for conveniently showing the "first" member of the benzene mono-*cata*-condensed series. However, the first member of this homologous series actually found in petroleum is indene with a formula of C_9H_8.

Table 4 lists di-*cata*-condensed series of benzene *para*-condensed series. The first member derived from benzene is $C_{10}H_6$ which has not been found in the petroleum systems. We start this di-*cata*-condensed series from diacenaphthalenes for collecting the homologous series mass defects database.

The KMDs of naphthenoaromatic (or hydroaromatic) hydrocarbons, including indans/tetralins (DBE = 5 as 5-ring naphthenes) and acenaphthenes (DBE = 8 as 8-ring naphthenes), are also included in Tables 1−4. Biphenyls and terphenyls have KMDs of −93.8 and −147.4 mDa, similar to 8-ring naphthenes (or acenaphthenes) and pyrenes, respectively, of equivalent DBEs.

The KMD of a hydrocarbon can be obtained from DBE by eq 1.

$$\mathrm{KMD} = -\,0.0134 \times \mathrm{DBE} + 0.0134 \tag{1}$$

Table 5 lists the KMDs of hydrocarbons as a function of DBE, with representative compound types that are commonly found in crude oils. Olefins, diolefins, and cycloolefins are normally not found in crude oils; however, they can be formed in the refinery processes that apply heat.[10]

The nominal mass (m*) and KMD can be readily obtained from the accurate mass measured. Hence the DBE and the numbers of carbon and hydrogen atoms of a given hydrocarbon can be calculated from eqs 2−4.

$$\mathrm{DBE} = -\,(\mathrm{KMD} - 0.0134)/0.0134 \tag{2}$$

$$\mathrm{C\#} = (\mathrm{m}^* - (2 - 2\mathrm{DBE}))/14 \tag{3}$$

$$\mathrm{H\#} = \mathrm{m}^* - \mathrm{C\#} \times 12 \tag{4}$$

2.2. Heteroatom Containing Compounds (Heterocompounds).

Fossil resources contain components having heteroatoms in the molecules. The heteroatoms in petroleum are mostly sulfur, with lesser amounts of nitrogen, oxygen, and metals. The number and amounts of heteroatoms increase with boiling point. In heavy oils and vacuum residues, the multitude of heteroatoms in molecules renders the determination of elemental composition of the molecules difficult.

Tables 6 and 7 list the KMDs as a function of DBE for heterocompounds containing one sulfur and oxygen atom, respectively. Many low DBE compound series, such as alcohols, ethers, aldehydes, and ketones, are not found in crude oils, but can be produced in petrochemical processes. They are listed as references. It should be noted that the differences in mass defect between sulfur compounds and corresponding oxygen compounds of 3 DBEs greater are less than an electron mass, 0.5 mDa. For example, the KMD of thiophenes (DBE = 3) of −90.4 mDa is less than 0.5 mDa from that of benzofurans (DBE = 6) of −89.9 mDa. The resolving power required for differentiating these two compound series is >1 000 000 at 500 Da and >500 000 at 250 Da. Thus, KMD alone is not sufficient for elemental composition determination from instruments not reaching the required resolving power or the mass measurement errors being greater than 0.5 mDa. To compensate for these deficiencies, we use nominal mass series, z*, along with KMD because DBE can only be known after the molecular formula is determined.[6] Nominal mass series, z*, is defined as the modulus, or remainder, of the nominal mass m* divided by 14 minus 14. It was previously introduced to resolve problems of using KMDs for molecular formula determination from accurate mass measurement of double-focusing sector mass spectrometers that have limited resolving power of

Table 6. Kendrick Mass Defects of Mono-Sulfur Compounds

DBE	KMD	C	H	S	^{12}C mass	K mass	m*	z*	representative compounds
0	−0.0502	1	4	1	48.0034	47.9498	48	−8	mercaptans/sulfides
1	−0.0636	4	8	1	88.0347	87.9364	88	−10	thiophanes/cyclic sulfides
2	−0.0770	4	6	1	86.0190	85.9230	86	−12	dihydrothiophenes/dicyclic sulfides
3	−0.0904	4	4	1	84.0034	83.9096	84	−14	thiophenes
4	−0.1038	6	6	1	110.0190	109.8962	110	−2	thiophenols/naphthenothiophenes
5	−0.1172	7	6	1	122.0190	121.8828	122	−4	cyclopentenothiophenes
6	−0.1306	8	6	1	134.0190	133.8694	134	−6	benzothiophenes
7	−0.1440	10	8	1	160.0347	159.8560	160	−8	naphthalenethiol
8	−0.1574	12	10	1	186.0503	185.8426	186	−10	diphenylsulfides
9	−0.1708	12	8	1	184.0347	183.8292	184	−12	dibenzothiophenes
10	−0.1842	14	10	1	210.0503	209.8158	210	−14	naphthenodibenzothiophenes
11	−0.1976	14	8	1	208.0347	207.8024	208	−2	fluoroenothiophenenes
12	−0.2110	16	10	1	234.0503	233.7890	234	−4	benzonaphthothiophenes
13	−0.2244	17	10	1	246.0503	245.7756	246	−6	pyrenothiophenes
14	−0.2378	18	10	1	258.0503	257.7622	258	−8	acenaphthobenzothiophenes
15	−0.2512	20	12	1	284.0660	283.7488	284	−10	dinaphthothiophenes
16	−0.2646	22	14	1	310.0816	309.7354	310	−12	acenaphthonaphthothiophenes
17	−0.2780	22	12	1	308.0660	307.7220	308	−14	benzopyrenothiophenes
18	−0.2914	24	14	1	334.0816	333.7086	334	−2	naphthophenanthrothiophenes
19	−0.3048	24	12	1	332.0660	331.6952	332	−4	anthanthrenothiophenes
20	−0.3182	26	14	1	358.0816	357.6818	358	−6	benzoperylenothiophenes
21	−0.3316	26	12	1	356.0660	355.6684	356	−8	corenenothiophenes
22	−0.3450	28	14	1	382.0816	381.6550	382	−10	peropyrenothiophenes
23	−0.3584	30	16	1	408.0973	407.6416	408	−12	benzonaphthopyrenothiophenes
24	−0.3718	30	14	1	406.0816	405.6282	406	−14	benzocoronenothiophenes
25	−0.3852	32	16	1	432.0973	431.6148	432	−2	pyranthrenothiophenes
26	−0.3986	34	18	1	458.1129	457.6014	458	−4	dinaphthopyrenothiophenes
27	−0.4120	34	16	1	456.0973	455.5880	456	−6	dibenzocoronenothiophenes
28	−0.4254	36	18	1	482.1129	481.5746	482	−8	dibenzperopyrenothiophenes

Table 7. Kendrick Mass Defects of Mono-Oxygen Compounds

DBE	KMD	C	H	O	^{12}C mass	K mass	m*	z*	representative compounds
0	−0.0095	1	4	1	32.0262	31.9905	32	−10	alcohols/ethers[a]
1	−0.0229	2	4	1	44.0262	43.9771	72	−12	tetrahydrofurans/aldehydes/ketones
2	−0.0363	4	6	1	70.0419	69.9637	70	−14	dihydrofurans/cyclic ketones
3	−0.0497	4	4	1	68.0262	67.9503	68	−2	furans
4	−0.0631	6	6	1	94.0419	93.9369	94	−4	phenols/naphthenofurans
5	−0.0765	7	6	1	106.0419	105.9235	106	−6	benzaldehydes/cyclopentenofurans
6	−0.0899	8	6	1	118.0419	117.9101	118	−8	benzofurans
7	−0.1033	10	8	1	144.0575	143.8967	144	−10	naphthols
8	−0.1167	12	10	1	170.0732	169.8833	170	−12	diphenylethers
9	−0.1301	12	8	1	168.0575	167.8699	168	−14	dibenzofurans
10	−0.1435	14	10	1	194.0732	193.8565	194	−2	naphthenodibenzofurans
11	−0.1569	14	8	1	192.0575	191.8431	192	−4	fluoroenofurans
12	−0.1703	16	10	1	218.0732	217.8297	218	−6	benzonaphthofurans
13	−0.1837	17	10	1	230.0732	229.8163	230	−8	pyrenofurans
14	−0.1971	18	10	1	242.0732	241.8029	242	−10	acenaphthobenzofurans
15	−0.2105	20	12	1	268.0888	267.7895	268	−12	dinaphthofurans
16	−0.2239	22	14	1	294.1045	293.7761	294	−14	acenaphthonaphthofurans
17	−0.2373	22	12	1	292.0888	291.7627	292	−2	benzopyrenofurans
18	−0.2507	24	14	1	318.1045	317.7493	318	−4	naphthophenanthrofurans
19	−0.2641	24	12	1	316.0888	315.7359	316	−6	anthanthrenofurans
20	−0.2775	26	14	1	342.1045	341.7225	342	−8	benzoperylenofurans
21	−0.2909	26	12	1	340.0888	339.7091	340	−10	corenenofurans
22	−0.3043	28	14	1	366.1045	365.6957	366	−12	rubicenofurans
23	−0.3177	30	16	1	392.1201	391.6823	392	−14	benzonaphthopyrenofurans
24	−0.3311	30	14	1	390.1045	389.6689	390	−2	benzocoronenofurans
25	−0.3445	32	16	1	416.1201	415.6555	416	−4	pyranthrenofurans
26	−0.3579	34	18	1	442.1358	441.6421	442	−6	dinaphthopyrenofurans
27	−0.3713	34	16	1	440.1201	439.6287	440	−8	dibenzocoronenofurans
28	−0.3847	36	18	1	466.1358	465.6153	466	−10	dibenzperopyrenofurans
29	−0.3981	38	20	1	492.1514	491.6019	492	−12	benzooctacenofurans
30	−0.4115	38	18	1	490.1358	489.5885	490	−14	decacyclenofurans

[a] Not found in crude oils.

Table 8. Kendrick Mass Defects of Mono-Nitrogen Compounds

DBE	KMD	C	H	N	^{12}C mass	K mass	m*	z*	representative compounds
0	0.0075	1	5	1	31.0422	31.0075	31	−11	amines
1	−0.0059	5	11	1	85.0891	84.9941	99	−13	piperidines/cyclic amines
2	−0.0193	2	3	1	41.0265	40.9807	41	−1	nitriles
3	−0.0327	4	5	1	67.0422	66.9673	67	−3	pyrroles
4	−0.0461	5	5	1	79.0422	78.9539	79	−5	pyridines/anilines
5	−0.0595	8	9	1	119.0735	118.9405	119	−7	indoles
6	−0.0729	7	5	1	103.0422	102.9271	117	−9	benzonitriles/indolines
7	−0.0863	9	7	1	129.0578	128.9137	129	−11	quinolines/isoquinolines
8	−0.0997	11	9	1	155.0735	154.9003	155	−13	azabiphenyls
9	−0.1131	12	9	1	167.0735	166.8869	167	−1	carbazoles
10	−0.1265	13	9	1	179.0735	178.8735	179	−3	acridines/phenanthridines
11	−0.1399	14	9	1	191.0735	190.8601	191	−5	5H-benzo[def]carbazoles
12	−0.1533	15	9	1	203.0735	202.8467	203	−7	azapyrenes
13	−0.1667	17	11	1	229.0891	228.8333	229	−9	azachrysenes
14	−0.1801	17	9	1	227.0735	226.8199	227	−11	azabenzo[ghi]fluoanthrenes
15	−0.1935	19	11	1	253.0891	252.8065	253	−13	azabenzopyrenes/azatriphenylenes
16	−0.2069	19	9	1	251.0735	250.7931	251	−1	azacorannulenes
17	−0.2203	21	11	1	277.0891	276.7797	277	−3	azaanthanthrenes
18	−0.2337	23	13	1	303.1048	302.7663	303	−5	azadibenzopyrenes
19	−0.2470	23	11	1	301.0891	300.7530	301	−7	azacoronenes
20	−0.2604	25	13	1	327.1048	326.7396	327	−9	azarubicenes
21	−0.2738	27	15	1	353.1204	352.7262	353	−11	azabenzonaphthopyrenes
22	−0.2872	27	13	1	351.1048	350.7128	351	−13	azabenzocoronenes
23	−0.3006	29	15	1	377.1204	376.6994	377	−1	azapyranthrenes
24	−0.3140	31	17	1	403.1361	402.6860	403	−3	azadinaphthopyrenes
25	−0.3274	31	15	1	401.1204	400.6726	401	−5	azadibenzocoronenes
26	−0.3408	33	17	1	427.1361	426.6592	427	−7	azadibenzoperopyrenes
27	−0.3542	35	19	1	453.1517	452.6458	453	−9	azabenzooctaphenes
28	−0.3676	35	17	1	451.1361	450.6324	451	−11	azadecacyclenes
29	−0.3810	37	19	1	477.1517	476.6190	477	−13	azabenzonaphthoperopyrenes

Table 9. Partial List of the KMDs for Monoisotopic Heterocompounds Containing 2 and 3 Heteroatoms

DBE	S_2	O_2	N_2	SO	NS	NO	SO_2	NO_2
0	−0.1139	−0.0325	0.0017	−0.0732	−0.0561	−0.0154	−0.0961	−0.0518
1	−0.1273	−0.0459	−0.0117	−0.0866	−0.0695	−0.0288	−0.1095	−0.0652
2	−0.1407	−0.0593	−0.0251	−0.1000	−0.0829	−0.0422	−0.1229	−0.0786
3	−0.1541	−0.0727	−0.0385	−0.1134	−0.0963	−0.0556	−0.1363	−0.0920
4	−0.1675	−0.0861	−0.0519	−0.1268	−0.1097	−0.0690	−0.1497	−0.1053
5	−0.1809	−0.0995	−0.0653	−0.1402	−0.1231	−0.0824	−0.1631	−0.1187
6	−0.1943	−0.1129	−0.0787	−0.1536	−0.1365	−0.0958	−0.1765	−0.1321
7	−0.2077	−0.1263	−0.0921	−0.1670	−0.1499	−0.1092	−0.1899	−0.1455
8	−0.2211	−0.1397	−0.1055	−0.1804	−0.1633	−0.1226	−0.2033	−0.1589
9	−0.2345	−0.1531	−0.1189	−0.1938	−0.1767	−0.1360	−0.2167	−0.1723
10	−0.2479	−0.1665	−0.1323	−0.2072	−0.1901	−0.1494	−0.2301	−0.1857
11	−0.2613	−0.1799	−0.1457	−0.2206	−0.2035	−0.1628	−0.2435	−0.1991
12	−0.2747	−0.1933	−0.1591	−0.2340	−0.2169	−0.1762	−0.2569	−0.2125
13	−0.2881	−0.2067	−0.1725	−0.2474	−0.2303	−0.1896	−0.2703	−0.2259
14	−0.3015	−0.2201	−0.1859	−0.2608	−0.2437	−0.2030	−0.2837	−0.2393
15	−0.3149	−0.2335	−0.1993	−0.2742	−0.2571	−0.2164	−0.2971	−0.2527
16	−0.3283	−0.2469	−0.2127	−0.2876	−0.2705	−0.2298	−0.3105	−0.2661
17	−0.3416	−0.2603	−0.2261	−0.3010	−0.2839	−0.2432	−0.3239	−0.2795
18	−0.3550	−0.2737	−0.2395	−0.3144	−0.2973	−0.2566	−0.3373	−0.2929
19	−0.3684	−0.2871	−0.2529	−0.3278	−0.3107	−0.2700	−0.3507	−0.3063
20	−0.3818	−0.3005	−0.2663	−0.3412	−0.3241	−0.2834	−0.3641	−0.3197
21	−0.3952	−0.3139	−0.2797	−0.3546	−0.3375	−0.2968	−0.3775	−0.3331
22	−0.4086	−0.3273	−0.2931	−0.3680	−0.3509	−0.3102	−0.3909	−0.3465
23	−0.4220	−0.3407	−0.3065	−0.3814	−0.3643	−0.3236	−0.4043	−0.3599
24	−0.4354	−0.3541	−0.3199	−0.3948	−0.3777	−0.3370	−0.4177	−0.3733
25	−0.4488	−0.3675	−0.3333	−0.4082	−0.3911	−0.3504	−0.4311	−0.3867

<100 000 associated with significant mass measurement errors. The averaging of measured masses of the same z* compensated for measurement errors and interferences of overlapping series, thus, improving the accuracy of molecular formula determination.[6] In the example above, the z* of thiophenes and benzofurans are −14 and −8, respectively. With the ambiguity in mass defect, the use of z* can assist in determining the elemental composition correctly.

The molecular weights of odd-number nitrogen atoms in the molecules are in odd numbers, hence, an odd z* value.

Table 10. Partial List of Sorted KMD's

type	DBE	KMD	z*
$^{13}C_2O_2$	6	−0.1084	−4
$^{34}SN_2$	3	−0.1086	−10
$^{13}C_2SO$	3	−0.1089	−10
O_3	4	−0.1090	−14
$^{13}CN_3$	8	−0.1091	−12
$^{13}C_2S_2$	0	−0.1094	−2
SO_2	1	−0.1095	−6

Table 11. Difference in KMDs of Overlapping Compound Types ("Even" and "Odd" Indicate *n* Even and Odd Masses)

	compound type 1				compound type 2			
KMD difference	type 1	DBE 1	KMD 1	z* 1	type 2	DBE 2	KMD 2	z* 2
<0.0 mDa/even	SO	4	−0.1268	−14	$^{34}S_2$	0	−0.1267	−14
	SO_2	4	−0.1497	−12	$^{34}S_2O$	0	−0.1497	−12
	S_2O	4	−0.1904	−10	$^{34}S_2S$	0	−0.1904	−10
	^{34}SSO	4	−0.1968	−8	$^{34}S_3$	0	−0.1968	−8
	N_2	10	−0.1323	−2	$^{13}C_2S_2O$	0	−0.1323	−14
<0.0 mDa/odd	$^{13}CS_2$	0	−0.1116	−3	$^{13}C_2N^{34}S$	4	−0.1117	−11
0.1 mDa/even	O_2	1	−0.0459	−10	$^{13}C_2S$	0	−0.0458	−6
	O_3	0	−0.0554	−6	$^{13}CN_3$	4	−0.0556	−4
	O_3	1	−0.0688	−8	$^{13}C_2SO$	0	−0.0687	−4
	O_4	1	−0.0918	−8	$^{13}C_2SO_2$	0	−0.0917	−2
	S_3	0	−0.1775	−14	$^{13}C_2N_2O$	12	−0.1776	−4
	SO_2	1	−0.1095	−6	$^{13}C_2S_2$	0	−0.1094	−2
	^{13}CNO	8	−0.1204	−10	^{34}SS	0	−0.1203	−2
	$^{13}CNOS$	8	−0.1840	−6	$^{34}SS_2$	0	−0.1839	−12
	$^{13}C_2S_2$	3	−0.1496	−8	$^{34}S_2O$	0	−0.1497	−12
0.1 mDa/odd	NO_2	1	−0.0518	−9	$^{13}C_2NS$	0	−0.0516	−5
	$^{13}CO_3$	0	−0.0532	−5	$^{13}C_2N_3$	4	−0.0533	−1
0.2 mDa/even	HC	2	−0.0134	−2	^{13}CNO	0	−0.0132	−8
	S	2	−0.0770	−12	$^{13}CNOS$	0	−0.0768	−4
	S_2	0	−0.1139	−4	$^{13}C_2O_4$	3	−0.1141	−8
	S_3	0	−0.1775	−14	^{34}S	9	−0.1773	−10
	O	13	−0.1837	−8	$^{34}SS_2$	0	−0.1839	−12
	^{13}CN	2	−0.0170	−14	$^{13}C_2N_2O$	0	−0.0168	−8
	$^{13}CN_3$	5	−0.0689	−6	$^{13}C_2SO$	0	−0.0687	−4
	$^{13}CN_3$	8	−0.1091	−12	$^{13}C_2S_2$	0	−0.1094	−2
	$^{34}SN_2$	0	−0.0684	−4	$^{13}C_2O_2$	3	−0.0682	−12
	$^{34}SO_2$	0	−0.1026	−2	$^{13}C_2HC$	9	−0.1027	−14
0.2 mDa/odd	N	2	−0.0193	−1	$^{13}CN_2O$	0	−0.0190	−9
	N_3	5	−0.0712	−5	^{13}CSO	0	−0.0709	−5
	N_3	8	−0.1114	−11	$^{13}CS_2$	0	−0.1116	−3
	^{13}CHC	2	−0.0112	−1	$^{13}C_2NO$	0	−0.0109	−7
	^{13}CO	2	−0.0341	−13	$^{13}C_2NO_2$	0	−0.0339	−7
	$^{13}CS_3$	0	−0.1753	−13	$^{13}C^{34}S$	9	−0.1750	−9
0.3 mDa/even	HC	5	−0.0536	−8	^{13}CNS	0	−0.0539	−6
	HC	10	−0.1206	−4	^{34}SS	0	−0.1203	−2
	S	5	−0.1172	−4	^{13}CS2N	0	−0.1175	−2
	S	10	−0.1842	−14	^{34}SS2	0	−0.1839	−12
	S_3	0	−0.1775	−14	^{13}CN	14	−0.1778	−10
	^{34}S	0	−0.0567	−6	^{13}C2N2O	3	−0.0570	−14
	^{34}S	10	−0.1907	−12	^{34}S2S	0	−0.1904	−10
	S_2O	0	−0.1368	−2	^{34}S	6	−0.1371	−4
	O	5	−0.0765	−6	$^{13}CNOS$	0	−0.0768	−4
	O	10	−0.1435	−2	^{34}SSO	0	−0.1432	−14
	O	14	−0.1971	−10	$^{34}S_3$	0	−0.1968	−8

Table 11. continued

	compound type 1				compound type 2			
KMD difference	type 1	DBE 1	KMD 1	z* 1	type 2	DBE 2	KMD 2	z* 2
	N_2	6	−0.0787	−8	O_4	0	−0.0784	−6
	$^{13}CN_3$	12	−0.1627	−6	$^{34}S_2O$	1	−0.1631	−14
	$^{13}C_2HC$	12	−0.1429	−6	^{34}SSO	0	−0.1432	−14
	$^{13}C_2HC$	16	−0.1965	−14	$^{34}S_3$	0	−0.1968	−8
	$^{13}C_2N_2$	6	−0.0743	−6	$^{13}C_2O_4$	0	−0.0739	−2
	$^{13}C_2SN_2$	0	−0.0575	−4	^{13}CN	5	−0.0572	−6
	$^{13}C_2SO$	0	−0.0687	−4	$^{34}SN_2$	0	−0.0684	−4
0.3 mDa/odd	N_3	4	−0.0578	−3	$^{13}C_2N^{34}S$	0	−0.0581	−3
	^{13}CHC	5	−0.0514	−7	$^{13}C_2NS$	0	−0.0516	−5
	^{13}CS	5	−0.1150	−3	$^{13}C_2S_2N$	0	−0.1153	−1
	$^{13}CS_3$	0	−0.1753	−13	$^{13}C_2N$	14	−0.1756	−9
0.4 mDa/even	O_2	7	−0.1263	−8	$^{34}S_2$	0	−0.1267	−14
	O_3	1	−0.0688	−8	$^{34}SN_2$	0	−0.0684	−4
	O_3	4	−0.1090	−14	$^{13}C2S_2$	0	−0.1094	−2
	O_3	9	−0.1760	−10	$^{34}S_2O$	2	−0.1765	−2
	O_4	4	−0.1320	−14	$^{13}C_2S_2O$	0	−0.1323	−14
	SO_2	0	−0.0961	−4	$^{13}CN_3$	7	−0.0957	−10
	SO_2	7	−0.1899	−4	$^{34}S_2S$	0	−0.1904	−10
	SN_2	3	−0.1022	−12	$^{34}SO_2$	0	−0.1026	−2
	$^{34}SO_2$	7	−0.1963	−2	$^{34}S_3$	0	−0.1968	−8
	^{34}SO	7	−0.1734	−4	$^{13}C_2S_3$	0	−0.1730	−12
0.4 mDa/odd	NO_2	0	−0.0384	−9	^{13}CHC	4	−0.0380	−5
	$^{13}CSO_2$	0	−0.0939	−3	$^{13}C_2N_3$	7	−0.0935	−7
0.5 mDa/even	S	0	−0.0502	−8	O	3	−0.0497	−2
	S_2	0	−0.1139	−4	SO	3	−0.1134	−12
	S_2	1	−0.1273	−6	$^{34}S_2$	0	−0.1267	−14
	S_3	0	−0.1775	−14	S_2O	3	−0.1770	−8
	S_3	1	−0.1909	−2	$^{34}S_2S$	0	−0.1904	−10
	SO	0	−0.0732	−8	O_2	3	−0.0727	−14
	SO_2	0	−0.0961	−4	O_3	3	−0.0956	−12
	SO_2	3	−0.1363	−10	S_2O	0	−0.1368	−2
	S_2O	1	−0.1502	−4	$^{34}S_2O$	0	−0.1497	−12
	SN_2	0	−0.0620	−6	N_2O	3	−0.0615	−2
	N_2	7	−0.0921	−10	$^{13}C_2SO_2$	0	−0.0917	−2
	N_2	13	−0.1725	−8	$^{13}C_2S_3$	0	−0.1730	−12
	^{13}CS	0	−0.0480	−7	^{13}CO	3	−0.0475	−1
	^{13}CNS	0	−0.0539	−6	^{13}CNO	3	−0.0534	−14
	^{13}CSO	0	−0.0709	−5	$^{13}CO_2$	3	−0.0705	−13
	$^{13}CO_3$	5	−0.1202	−1	S_2N	0	−0.1197	−3
	$^{13}CS_2N$	0	−0.1175	−2	$^{13}CNOS$	3	−0.1170	−10
	$^{13}CS_2N$	0	−0.1175	−2	$^{13}C_2O_3$	5	−0.1180	−14
	$^{13}C_2O_3$	5	−0.1180	−14	$^{13}CS_2N$	0	−0.1175	−2
	$^{13}C_2S$	0	−0.0458	−6	$^{13}C_2O$	3	−0.0453	−14
	$^{13}C_2S_2$	0	−0.1094	−2	$^{13}C_2SO$	3	−0.1089	−10
	$^{13}C_2S_2O$	0	−0.1323	−14	$^{13}C_2SO_2$	3	−0.1318	−8
	$^{13}C_2S_3$	0	−0.1730	−12	$^{13}C_2S_2O$	3	−0.1725	−6
	$^{13}C_2SN_2$	0	−0.0575	−4	$^{13}C_2N_2O$	3	−0.0570	−14
	$^{13}C_2SO$	0	−0.0687	−4	$^{13}C_2O_2$	3	−0.0682	−12
	$^{13}C_2SO_2$	0	−0.0917	−2	$^{13}C_2O_3$	3	−0.0912	−10
	^{34}SS	0	−0.1203	−2	^{34}SO	3	−0.1198	−10
	$^{34}S_2S$	0	−0.1904	−10	$^{34}S_2O$	3	−0.1899	−4
	$^{34}SS_2$	0	−0.1839	−12	^{34}SSO	3	−0.1834	−6
	$^{34}SS_2$	1	−0.1973	−14	$^{34}S_3$	0	−0.1968	−8
	$^{34}SS_2$	18	−0.4251	−6	^{34}SSO	21	−0.4246	−14
	^{34}SSO	0	−0.1432	−14	$^{34}SO_2$	3	−0.1428	−8
0.5 mDa/odd	NS	0	−0.0561	−7	NO	3	−0.0556	−1

Table 11. continued

KMD difference	compound type 1				compound type 2			
	type 1	DBE 1	KMD 1	z* 1	type 2	DBE 2	KMD 2	z* 2
	$^{13}CO_2$	3	−0.0705	−13	^{13}CSO	0	−0.0709	−5
	^{13}CS	0	−0.0480	−7	^{13}CO	3	−0.0475	−1
	$^{13}CS_2$	0	−0.1116	−3	^{13}CSO	3	−0.1111	−11
	$^{13}CSO_2$	0	−0.0939	−3	$^{13}CO_3$	3	−0.0934	−11
	$^{13}C_2NS$	0	−0.0516	−5	$^{13}C_2NO$	3	−0.0511	−13
	$^{13}C_2N^{34}S$	1	−0.0715	−5	^{13}CSO	0	−0.0709	−5

Except for low DBE and cyano compounds, nitrogen compounds are generally pyrrolic (containing a 5-membered ring with nitrogen) and pyridinic (containing a 6-membered ring with nitrogen). The KMDs of heterocompounds containing one nitrogen atom are listed in Table 8.

The KMD of heterocompounds can be calculated from DBE and the numbers of heteroatoms, by eq 5.

$$\begin{aligned} \text{KMD} &= 0.0134 - (0.0134 \times \text{DBE}) \\ &\quad - 0.06363 \times \text{S\#} - 0.022945 \times \text{O\#} \\ &\quad - 0.005862 \times \text{N\#} \end{aligned} \tag{5}$$

A partial list of KMDs for monoisotopic heterocompounds containing 2 and 3 heteroatoms is shown in Table 9.

Note the small differences in KMDs between SO series and S_2 series of 3 DBEs less and between SO series and O_2 series of 3 DBEs more, as that between S and O series. For example, the KMD of SO series of DBE = 3 is less than 0.5 mDa from that of S_2 series of DBE = 0 and O_2 series of DBE = 6. However, the z* values of these three series, SO (DBE = 3), S_2 (DBE = 0), and O_2 (DBE = 6) are −12, −4, and −6, respectively. The mass overlaps of less than 0.5 mDa between S_2 and SO series start at DBE = 0 for S_2 series and 3 for SO series and continue throughout the entire DBEs of the corresponding pairs. Similarly, the overlaps of less than 0.5 mDa between SO and O_2 series start at DBE = 0 for SO series and 3 for O_2 series.

The DBE, C#, and H# for hydrocarbons can be calculated from measured accurate mass, thus KMD, by eqs 2−4. However, for heterocompounds, a database of KMDs of various combinations of heteroatoms needs to be established for being used in elemental composition determination of measured accurate mass through KMD matching. Ambiguities or errors occur when matching the measured KMD that could have measurement errors with the KMDs in the database, especially for those having small differences in KMDs among the possible choices. Complete lists of the KMDs for even-mass and odd-mass series, including monoisotopic, ^{13}C, $^{13}C_2$, and ^{34}S series are provided as Supplementary Tables S1 and S2, respectively, in the Supporting Information. To assist in the correct elemental composition determination of the component, z* can be used in addition to the use of isotopic patterns of ^{13}C and ^{34}S species.

2.3. Mass Defect Overlaps. We investigated all of the possible overlaps of KMDs between compound series, including ^{13}C, $^{13}C_2$, ^{34}S, and $^{34}S_2$ isotopic species that can be present in significant amounts along with monoisotopic species. Through the sorting of mass defects from the highest to the lowest values in sequence for molecules of DBE ≤ 30 and the number of heteroatoms ≤3, we have found over 80% in the 1333 even mass series and ~55% in the 837 odd mass series of KMD overlaps having mass difference less than an electron mass of 0.548 mDa (548 μDa).[4] Only the differences in KMDs of adjacent series are counted. For example, among the 7 series shown in Table 10, the differences in KMDs of adjacent series after sorting are all less than an electron mass. The difference between SO_2 (DBE = 1) and O_3 (DBE = 4) and between $^{13}C_2SO$ (DBE = 3) and $^{13}C_2S_2$ (DBE = 0) are also less than 0.5 mDa, but not counted in the above statistics.

The compound series of KMD overlaps less than an electron mass are summarized in Table 11. The DBEs, KMDs and z*'s of the lowest series of each pair of overlapping compound types are listed. For a mass spectrometer capable of resolving doublets less than 1 mDa with negligible measurement errors, such as using "walking" calibration,[3] almost all of the overlapping types can be resolved.

Most of the overlapping series of mass difference less than 0.1 mDa involve $^{34}S_2$ and $^{34}S_3$ species that are generally present in insignificant amounts in fossil oils. Almost all of the overlapping series are differentiable by the difference in z* values. They can also be differentiated from the associated isotopic patterns in mass spectra. Only the z* values of the lowest series of overlapping compound types are listed in Table 11. The entire tables of KMD and z* values for the compound types of interest, i.e., other series in the same type with increasing z* values, can be easily expanded based on the values given in Table 11 and Supplementary Tables in the Supporting Information.

3. CONCLUSION

With continuous improvement in mass resolving power, particularly in FT-ICR MS that currently can resolve species with mass difference of a single electron, misidentification of molecular formula can still occur due to insufficient resolving power for all overlapping species present in petroleum and other fossil oils. We have investigated the ultimate resolving power required for all possible overlapping series in mass.

For the investigation we use Kendrick mass defects as a convenient means for looking into mass overlaps between hydrocarbon and heterocompound series because a single value of mass defect is obtained for entire homologous series when using the Kendrick mass scale, i.e., $^{12}CH_2$ = 14.000000. For the monoisotopic, ^{13}C, $^{13}C_2$, ^{34}S, and $^{34}S_2$ species with the total number of heteroatoms ≤3 (except O_4) and with DBE ≤ 30, we have found over 80% of even-mass series and 55% of odd-mass series having overlapping series with mass difference less than an electron. Previously introduced nominal mass series are recommended for resolving these overlapping series. The identification and quantitation of ^{13}C and ^{34}S isotopic species by mass spectrometry, if applicable (without interference of other species), would further assist in the differentiation of overlapping series. However, the ultimate goal of resolving power is 0.1 mDa (100 μDa), less than the mass of an electron. With a mass spectrometer of resolving power of 0.1 mDa, i.e., 5 million at 500 Da or 10 million at 1000 Da, almost all of the overlapping series in fossil resources can be resolved for accurate determination of elemental composition of molecules. This should be one of the goals for developing future mass spectrometers with higher resolving power, such as 21-T FT-ICR.[4]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supplementary tables of data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hsu, C. S. Definition of hydrogen deficiency for hydrocarbons with functional groups. *Energy Fuels* **2010**, *24* (7), 4097−4098.

(2) Lobodin, V. V.; Hsu, C. S.; Marshall, A. G. Compositional space boundaries for organic compounds. *Prep. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **2011**, *56* (2), 427−428.

(3) Savory, J. J.; Kaiser, N. K.; McKenna, A. M.; Xian, F.; Blakney, G. T.; Rodgers, R. P.; Hendrickson, C. L.; Marshall, A. G. Parts-per-billion Fourier transform ion cyclotron resonance mass measurement accuracy with a "walking" calibration equation. *Anal. Chem.* **2011**, *83* (5), 1732−1736.

(4) Hsu, C. S.; Hendrickson, C. L.; Rodgers, R. P.; McKenna, A. M.; Marshall, A. G. Petroleomics: advanced molecular probe for petroleum heavy ends. *J. Mass Spectrom.* **2011**, *46* (4), 337−343.

(5) Kendrick, E. A mass scale based on CH_2 = 14.0000 for high resolution mass spectrometry of organic compounds. *Anal. Chem.* **1963**, *35*, 2146−2154.

(6) Hsu, C. S.; Qian, K.; Chen, Y. C. An innovative approach to data analysis in hydrocarbon characterization by online liquid chromatography mass spectrometry. *Anal. Chim. Acta* **1992**, *264*, 79−89.

(7) Hsu, C. S. Diophantine approach to isotopic abundance calculations. *Anal. Chem.* **1984**, *56*, 1356−1361.

(8) Tissot, B. P.; Welte, D. H. *Petroleum Formation and Occurrence*, 2nd ed.; Springer-Verlag: Berlin, Heidelberg, New York, Tokyo, 1984.

(9) Hsu, C. S.; Lobodin, V. V.; Rodgers, R. P.; McKenna, A. M.; Marshall, A. G. Compositional boundaries for fossil hydrocarbons. *Energy Fuels* **2011**, *25* (5), 2174−2178.

(10) Hsu, C. S.; Robinson, P. R. *Practical Advances in Hydrocarbon Processing*; Springer: New York, 2006.