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SIMILAR COMPOSITIONS OF ALKANES FROM COAL, PETROLEUM, NATURAL GAS AND FISCHER-TROPSCH PRODUCT

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UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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by

R. A. Friedel[1] and A. G. Sharkey, Jr.[2]

ABSTRACT

Data on compositions of natural substances are important in the study of possible interrelationships. The similarity of the low molecular weight alkane isomers from crude oil and Fischer-Tropsch catalytic synthesis product has been reported (8).[3] A similar composition for the alkane isomers from high-temperature coal carbonization has been found. The composition of the C_4 to C_7 alkane isomers from these three sources can be calculated quantitatively with the equations previously developed to calculate alkane isomers in Fischer-Tropsch product. An interesting reversal of the concentrations of the monomethyl isomers from C_6(2 Me > 3 Me) to C_7 (3 Me > 2 Me) occurs in all three products; fragmentary comparisons at higher carbon numbers indicate some dissimilarities.

Naphthene isomers in the C_6 to C_7 range for crude oil and high-temperature coal carbonization also have similar compositions. Aliphatic hydrocarbons from low-temperature coal carbonization processes are considerably different, consisting mainly of normal alkanes.

INTRODUCTION

As part of a program at the Bureau of Mines to make comparisons of carbonaceous materials in nature, detailed analyses of hydrocarbon isomers from various sources have been investigated for similarities.

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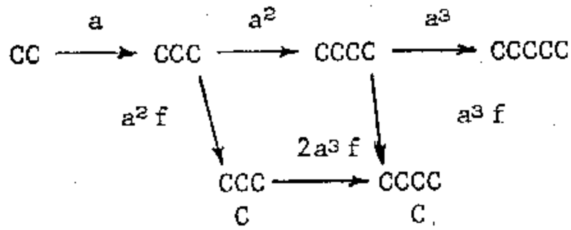
[1]Project coordinator, Spectrometry.
[2]Supervisory research physicist.
Both authors with the Bureau of Mines, Pittsburgh Coal Research Center, Pittsburgh, Pa.
[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

ISOMERIC COMPOSITION

Crude Oil

A similarity exists between the low molecular weight alkane isomers in crude oil and Fischer-Tropsch catalytic synthesis product (8); there is a possible significance for the origin of petroleum. The composition of the C_4 through C_7 alkane isomers in crude oils (13) can be calculated quantitatively with equations previously reported for calculating the alkane isomers in Fischer-Tropsch products (1, 6, 18). The equation for calculation of isomer distribution is $\phi_n = kF_n a^{n-2}$, where ϕ_n is the number of moles containing n carbon atoms, k is a constant and F_n is a function of f, a constant representing the ratio of chain branching, b, over chain lengthening, a. If $b = af$, the lengthening and branching of chains is illustrated as follows:



Part a of table 1 gives the comparison between Fischer-Tropsch and a representative crude oil. Part b presents a prediction of Fischer-Tropsch product, along with the relative concentrations of isomers in terms of a and f, and part c gives a prediction for crude oil compositions. In this last portion of the table, comparisons are given for branched isomers for $f = 0.176$; the relative amounts of branched isomers do not change greatly with different values of f. The comparison of observed and predicted normal C_6 and C_7 is not very similar with $f = 0.176$; however a change of f value to 0.1 produces a very close comparison for the normal compounds.

One of the interesting points concerning the prediction of crude oil and Fischer-Tropsch compositions is the quantitative success in predicting reversal of methyl isomers: In the C_6's the concentration of 2-methylpentane is found to be greater than that of 3-methylpentane, whereas in the C_7's the situation is reversed as 3-methylhexane becomes greater than 2-methylhexane.

The growth scheme used in this work is a modification of growth scheme B from reference 1: Addition of the carbon atom is permitted on the first two carbon atoms on one end of the growing chain and on substituents on the first three carbon atoms. The chain-branching factor is f, as usual, except in the formation of quarternary carbons in which case 0.1 f is used because of the low probability of substitution on tertiary carbon atoms.

TABLE 1. - Alkane compositions; crude oil and Fischer-Tropsch product (F.T.), mole percent (data from reference 8)

	a. C_6-C_7 branched alkanes observed in crude oil and F.T.		b. Predicted and observed isomer distribution in F.T.			c. Predicted and observed isomer distribution in crude oil using modified F.T. equations			
	Crude oil No. 1	F.T.	Observed	Predicted, f = 0.0727		Observed No. 1		Predicted, f = 0.176	
n-Butane..................			89.4	93.2	a^2	87.4		84.8	
2-Methylpropane...........			10.6	6.8	$a^2 f$	12.6		15.2	
			100.0	100.0		100.0		100.0	
n-Pentane.................			81.2	82.1	a^3	65.8		65.3	
2-Methylbutane............			18.8	17.9	$3a^3 f$	33.8		34.5	
2,2-Dimethylpropane.......			100.0	100.0		0.4		0.2	
						100.0		100.0	
n-Hexane..................			78.9	73.2	a^4	56.6		49.6	
2-Methylpentane...........	53.9	53.1	11.2	15.9	$3a^4 f$		53.9		52.0
3-Methylpentane...........	38.8	45.0	9.5	10.5	$2a^4 f$		38.8		40.7
2,3-Dimethylbutane........	6.7	1.9	.4	.4	$2a^4 f^2$		6.7		6.1
2,2-Dimethylbutane........	0.6	-	100.0	100.0			0.6		1.2
	100.0	100.0				43.3[1] / 100	100	50.4[1] / 100	100
n-Heptane.................			65.9	64.6	a^5	56.4		37.7[2]	
2-Methylhexane............	35.6	38.4	13.1	14.0	$3a^5 f$		35.6		31.9
3-Methylhexane............	45.6	56.0	19.1	18.7	$4a^5 f$		45.6		46.3
2,3-Dimethylpentane.......	11.7	4.7	1.6	2.0	$6a^5 f^2$		11.7		11.9
2,4-Dimethylpentane.......	3.2	0.9	.3	.7	$2a^5 f^2$		3.2		3.8
3-Ethylpentane............	2.5	3.1[3]	100.0	100.0			2.5		4.4
2,2-Dimethylpentane.......	0.7	-					0.7		0.7
3,3-Dimethylpentane.......	0.5	-					0.5		0.8
2,2,3-Trimethylbutane.....	0.2	-					0.2		0.2
	100.0	103.1				43.6[1] / 100	100	62.3[1] / 100	100
n-Octane..................			61.0	57.1	a^6				
Methylheptanes............			36.4	37.4	$9a^6 f$				
Dimethylhexanes...........			2.6	5.4	$18a^6 f^2$				
			100.0	99.9					

[1] Total branched isomers.

[2] For f = 0.10, calculated and observed values are as follows: nC_7 56.1 (calculated), 56.4 (observed).
$isoC_7$'s 43.9 do 43.6 do.

[3] Calculated from reference 3.

There are very few data available on alkane isomers above C_7 for comparison of petroleum or for any other natural product. Some analyses, however, are available for the C_8 isomers from alkanes from crude oils. Predicted results from the Fischer-Tropsch equation with f = 0.1 are given in table 2, along with analyses of C_8 alkanes from two crude oils (2, 4). A very definite exception to the predicted values appears in the table, namely, the predominance of 2-methylheptane over 3-methylheptane. This observation is contrary to the prediction of the equation. According to scheme B (1) other C_8 analyses from crude oils show the same predominance of the 2-methylisomers.[4] A total of four C_8 analyses available for comparison represent crude oils from western and southwestern United States. As mentioned in reference 8, 11 out of 14 analyses through the C_7's showed the reversal; the three that did not have the predicted reversal also came from the southwest. It would be of interest to have analyses of C_8's in crudes from other parts of the world in order to study this reversal. Only partial analyses are available for C_9 alkanes, Ponca City (Oklahoma) crude oil (4) and a commercial reformate (5). Both of these partial analyses indicate that the reversal recurs and the 3-methylisomer again predominates. It will be of interest to see what happens in the case of future analyses of C_9 alkanes. Perhaps there is an alteration of predominance of the 2-methylisomer; perhaps it occurs only for the even carbon numbers. (See the following discussion on tobacco waxes.)

TABLE 2. - Octane isomers. Predicted composition compared with values observed in two crude oils, mole percent

C_8 alkanes	Crude oils		Predicted f = 0.1
	East Texas[1]	Ponca City[2]	
n-Octane	44.7	51.35	45.5
2-Methylheptane	23.3	19.21	13.7
3-Methylheptane	12.9	[3] 11.16	19.1
4-Methylheptane	5.1	5.58	9.1
2,3-Dimethylhexane	3.5	3.12	2.7
2,4-Dimethylhexane	2.3	2.23	2.8
2,5-Dimethylhexane	2.2	1.56	.9
3,4-Dimethylhexane	2.0	2.23	2.0
2,3,4-Trimethylpentane	1.1	.04	.18
3-Ethylhexane	1.7	([3])	2.90
2-Methyl-3-ethylpentane	.9	2.46	.48
2,2-Dimethylhexane	.5	.22	.18
3,3-Dimethylhexane	.6	.67	.30
2,2,3-Trimethylpentane	-	.04	.04
2,2,4-Trimethylpentane	-	.09	.03
3-Methyl-3-ethylpentane	-	-	.03
2,3,3-Trimethylpentane	.6	.04	.05
2,2,3,3-Tetramethylbutane	-	-	.0001

[1] See reference 2.
[2] See reference 4.
[3] 3-Methylheptane + 3-Ethylhexane.

[4] Made available to the authors by M. J. O'Neal, Shell Oil Co., Inc., Houston, Texas.

With regard to the origin of petroleum, these data appear to have some significance whether or not an inorganic origin of petroleum is indicated. The evidence for an organic origin, or principally organic origin, of petroleum is very strong. The fact is that a quantitative prediction results from the Fischer-Tropsch equations and it is the only one available at the present time. If the prediction is not indicative of organic synthesis, it may indicate the branching that occurs in organic syntheses by living species to form the precursors of petroleum alkanes.

Other Similarities, Fischer-Tropsch and Crude Oil

Other similarities between crude oil and Fischer-Tropsch products should be mentioned. First, polynuclear condensed aromatics are produced in syntheses involving catalytic hydrogenation of carbon monoxide, as shown in the Fischer-Tropsch work of Weitkamp (19). R. B. Anderson and L. J. E. Hofer, in our laboratory, attempted catalytic hydrogenations at elevated temperatures and found production of considerable amounts of aromatics as large as pyrene. This evidence is cited to indicate that the aromatics in petroleum could possibly be derived from catalytic syntheses of the Fischer-Tropsch type. Another similarity has been shown by the product obtained from catalysts used for many months in the Sasol commercial Fischer-Tropsch plant in South Africa. The spectral characteristics of this product were similar to those obtained for petroleum asphaltenes, according to our spectra of the product.

Coal Derivatives

In attempting to extend this investigation to coal products, it was evident that not many isomeric analyses have been carried out. In the case of low-temperature tar the species most reported have been normal olefins and normal alkanes (12). Branched alkane isomers are probably very low in concentration. However, limited data for high-temperature coal-tar (10) and for coal-hydrogenation products (7) indicate a close comparison of C_7 alkanes with those from crude oil and the values predicted by the Fischer-Tropsch equation (table 3, top part). A close comparison is notable also in the bottom part of table 3, which gives data for the C_6 and C_7 naphthenes from high-temperature coal carbonization, coal hydrogenation, and a crude oil.

The data recently published by Ouchi and Imuta (15) on a chloroform extract of Yubari coal also indicates similarities to petroleum. Branching is greater at the low carbon numbers and drops off at higher carbon numbers, as in crude oils (11) and Fischer-Tropsch product (17). The other similarity to crude oil is noted in the odd-even alternation of normal alkanes from C_{19} to C_{25} with the odd carbon number alkanes predominating.

Other data on analyses of coal products have been given by Girling (9). A list of alkanes, found but not quantitatively determined, from C_3 through C_7, indicates that the normals and monomethyl isomers predominate. This again is similar to crude oil and Fischer-Tropsch product.

TABLE 3. - Alkane and naphthene compositions: Crude oil and coal derivatives, mole percent

	Predicted, F.-T. equation f = 0.1	Crude oil No. 1[1]	Coal, high temp. carb.[2]	Coal, hydro-genation[3]
	ALKANES			
n-Heptane....................	54.6	56.5	64.1	60
2-Methylhexane................	16.4	15.5	12.4	
3-Methylhexane................	22.9	19.9	12.9	
2,3-Dimethylpentane...........	3.4	5.1	7.7	
2,4-Dimethylpentane...........	1.1	1.4	-	40
3-Ethylpentane................	1.2	1.1	2.5	
2,2-Dimethylpentane...........	.2	.2	-	
3,3-Dimethylpentane...........	.2	.2	0.4	
2,2,3-Trimethylbutane.........	.03	.1	-	
	100.03	100.0	100.0	100
	NAPHTHENES			
Cyclohexane...................		41.4	90.5	28.6
Methylcyclopentane............		58.6	9.5	71.4
		100.0	100.0	100.0
Methylcyclohexane.............		58.5	64.4	35.6
1,1-Dimethylcyclopentane......		1.8	2.0	
1,trans-2-Dimethylcyclopentane		16.0	14.5	
1,trans-3-Dimethylcyclopentane		7.9	13.6	47.8
1,cis-2-Dimethylcyclopentane..		-	5.5	
1,cis-3-Dimethylcyclopentane..		7.9	-	
Ethylcyclopentane.............		7.9	-	16.6
		100.0	100.0	100.0

[1]See reference 13.
[2]See reference 10.
[3]See references 7 and 12.

At this stage the comparisons of the analyses are considered interesting but too sparse to draw any conclusions concerning relationships between petroleum and coal.

Natural Gas

A search has also been made for data on alkane isomers from natural gas. So far the search has been unsuccessful. Only one isomeric analysis has been found, provided by the Institute of Gas Technology and shown in table 4. Comparison of natural gas data with those found in crude oil and in predictions of the Fischer-Tropsch equation is not very good, particularly in the C_7's. It is hoped that better data will be forthcoming both from natural gas and from coal. In the search for natural gas data, at least one company contacted has decided that its research department should obtain isomeric data on many natural gases.

TABLE 4. - Isomeric analysis of a natural gas condensate

	Natural gas[1]	Crude oil No. 1
n-Pentane	64.8	65.8
i-Pentane	35.2	33.8
2,2-Dimethylpropane	-	0.4
	100.0	100.0
n-Hexane	37.5	56.7
2-Methylpentane	45.5	23.3
3-Methylpentane	15.8	16.8
2,3-Dimethylbutane	1.2	2.9
2,2-Dimethylbutane	-	0.3
	100.0	100.0
n-Heptane	12.6	56.5
2-Methylhexane } 2,3-Dimethylpentane }	17.8	20.6
3-Methylhexane } 2,4-Dimethylpentane }	12.6	19.9
2,2-Dimethylpentane } 2,2,3-Trimethylbutane }	23.6	1.7
3-Ethylpentane	19.3	1.1
3,3-Dimethylpentane	14.1	0.2
	100.0	100.0
C_8 isomers	Present	Present
Cyclohexane	do.	Do.
Benzene	do.	Do.
Toluene	do.	Do.

[1]Analysis supplied by Duane V. Kniebes of the Institute of Gas Technology, Chicago, Illinois.

Pyrolysis

Good analytical data are being turned out by tobacco company research laboratories for cigarette smoke and for constituents of tobacco leaves. A recent article on analyses of cigarette smoke by Philippe and coworkers (16) demonstrated that the normal and monomethyl isomers in C_5 and C_6 alkanes were very similar to those obtained from thermal cracking of petroleum. These are data on only a few compounds and no dimethylisomers were found. It is perhaps not surprising that a slight similarity exists since petroleum compounds in high molecular weight ranges are primarily straight chained, apparently branched only on one end. In fact, some researchers have found that the waxes from tobacco have similar structures (14). Also, the 2-methyl- and 3-methylisomers predominate alternately as the carbon number increases.

Thermal cracking of higher components of crude oils can produce low molecular weight alkanes having isomeric compositions similar to the alkanes found in crude oils.

SUMMARY

The similarity shown in the distribution of alkane and naphthene isomers from a variety of natural substances is an important discovery. The mechanism of growth of carbon skeletons in these various substances must have been quite similar.

The calculation of isomeric alkane distributions in natural substances, even including a specific reversal of concentrations of methyl isomers, indicates that growth schemes of the Fischer-Tropsch type or similar types cannot be disregarded in considerations of origin.

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