

C7 LIGHT HYDROCARBON STUDY

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A PROPOSAL

SUMMARY

A global collection of over 370 crude oil samples representing more than 80 petroleum systems of various ages and source rock types have been analyzed for light hydrocarbons using ultra high resolution gas chromatography. The results have been evaluated primarily with respect to the C7 interpretive schemes of Mango (1987, 1990, 1994) and BeMent *et al.* (1994). Light hydrocarbon parameters of Thompson (1983) have also been considered. The usefulness and limitations of light hydrocarbons in 1) performing oil/oil/condensate correlation studies; 2) determining post-generative alteration effects (e.g., fractionation during migration, water washing, mild biodegradation); 3) estimating thermal maturities of oils; and 4) predicting source rock depositional environments have been assessed. In addition, the effects of sample handling and light-end evaporation during storage have been addressed.

The above goals were accomplished by comparing the C7 light hydrocarbon interpretive schemes within the framework of traditional C15+ biomarker and stable carbon isotope data (already obtained) used to define the various petroleum systems represented by the oils in this study. It is suspected that C7 data may especially be useful in interpreting the origin and thermal history of light oils or condensates in which biomarkers are often absent or in very low abundance.

The analytical program is complete (data volumes are being issued in both hard copy and digital format) an interpretive report are completed and available for immediate delivery. Cost of participating is US \$30,000.

INTRODUCTION

The evaluation of light hydrocarbons in a crude oil or condensate sample may provide insights into the source of the oil or condensate, the environment under which the source was deposited, the maturity of the oil, the temperature at expulsion from the source rock, the effects of evaporative fractionation, and mixing. These interpretive schemes are inferred in the work of Mango (1987, 1990, 1992a-b, 1994), or cited by Thompson (1983), BeMent *et al.* (1994), and ten Haven (1995).

Mango (1987, 1990, 1992a-b, 1994) hypothesizes the formation of the light hydrocarbons by steady state catalysis within the source rock. This hypothesis is supported by invariant ratios of certain light hydrocarbons. However, while Mango focuses primarily on the reaction mechanisms that could lead to these invariant ratios, his work also infers that these light hydrocarbons carry valuable information regarding source, depositional environment, and temperature.

BeMent *et al.* (1994) presents data describing the absolute temperature of oil generation from certain light hydrocarbons based on geological calibration of source rock samples from four distinct basins. They state that 95% of the oils analyzed have been generated between 95° C and 135° C. In addition, general agreement with biomarker maturity assessments is cited by these authors.

On the other hand, Thompson (1983) proposed other scenarios where the light hydrocarbons may reflect secondary alteration effects as a result of oil becoming vaporized in gas and transported to other traps. The oil left behind was fractionated and Thompson described chemical characteristics for this effect.

The fact that reservoired petroleum may be from more than one source complicates the analysis of light hydrocarbons. However, ten Haven (1995) has utilized light hydrocarbons data in assessing mixing of crude oils and condensates in West Africa and Southeast Asia, and found C7 data useful in sorting out mixed oils, especially condensates.

This proposal is directed at evaluating the efficacy of light hydrocarbon interpretive schemes in determining sources, depositional environment, maturity, and temperature of expulsion on oils and condensates. Since condensates are particularly difficult to correlate to sources due to the absence of heavier components where the biological marker compounds are typically found, light hydrocarbon analysis is viewed as a potentially invaluable tool in their evaluation.

No data has been presented or published reconciling interpretive schemes for light hydrocarbons with other interpretive schemes such as carbon isotopes, biological markers, and bulk properties. Generalized interpretive schemes for the light hydrocarbons have been tested and compared to these well established interpretations.

OBJECTIVES

This proposal is directed at determining the effectiveness of light hydrocarbon interpretive schemes in determining source, maturity, depositional environment, and temperature of expulsion. A global oil/light oil/condensate collection of 370 samples representing 80 petroleum systems will be analyzed by whole oil gas chromatography to quantitatively determine the light hydrocarbons up to octane (n-C8). These oils have already been analyzed for biomarkers, carbon isotopes, and bulk properties such as sulfur content so a comprehensive interpretive scheme can readily be evaluated within a traditional framework.

The following will be completed:

- quantitative analysis of light hydrocarbons up to octane (n-C8);
- compilation of interpretive results in the framework of Mango's (1990) C7 isomer interpretive schemes;
- comparison of light hydrocarbon interpretive schemes to traditional source/family interpretations based on biological marker/carbon isotope results on the same oils;
- comparison of calculated light hydrocarbon expulsion temperatures (BeMent, 1994) to maturation interpretations based on biological marker results on the same oils;
- evaluation of the effects of sample handling, storage (evaporation), and mild biodegradation on light hydrocarbon interpretations.

BACKGROUND

The light hydrocarbons present in a crude oil or condensate provide detailed clues to the geological and thermal history of the derivation of those products. These compounds are present in most nondegraded oil and represent the bulk of the petroleum in condensates. The light hydrocarbons provide information regarding the source of these hydrocarbons and its depositional environment, maturity, and temperature of expulsion (Mango, 1990; BeMent *et al.*, 1994). Also, the light hydrocarbons may be used to correlate oils and condensates but it is not known how reliable these correlations might be.

The light hydrocarbons are thought to be derived from two potential sources: the cracking of organic matter in a source rock or from oil already formed. However, a more recent hypothesis suggests that the light hydrocarbons are formed strictly from steady state catalysis of organic matter present in source rocks and are not the result of themolytic cracking of oil already formed (Mango, 1987, 1990).

The hypothesis of Mango suggests the steady state catalysis of normal alkanes into other products. He has proposed reaction mechanisms and product generation schemes for certain C7 hydrocarbons from heptane which are detailed in Appendix I. Steady state catalysis would mean that certain compounds are formed from precursor compounds at a constant rate. Based on hypothesized reaction pathways and evaluation of a large oil database, Mango was able to determine a variety of compound ratios which are constant but source, temperature, and pressure dependent (Mango, 1987, 1990).

While Mango focused on the mechanisms and reaction pathways for the formation of the C7 hydrocarbons, his work also revealed numerous relationships of the C7 hydrocarbons which may be utilized for assessing source facies, depositional environment, maturity, temperature of expulsion (Mango, 1987, 1990; BeMent *et al.*, 1994), extent of mixing (ten Haven, 1995), and potentially oil/condensate to oil/condensate correlations.

LIGHT HYDROCARBON ANALYSIS

Separation of all the C7 hydrocarbon isomers requires ultra high resolution gas chromatography (UHRGC) in order to obtain baseline resolution of the compounds of interest. Mango (1990; 1994) utilized seventeen C7 compounds in his work. These compounds are listed in Table 1 with the peaks identified in an example gas chromatographic fingerprint of a North Sea crude oil (Figure 1).

Note that compound 14, *cis*-1,2-dimethylcyclopentane (*c*-1,2 DMP), is not resolved in the above chromatogram as it coelutes with methylcyclohexane under these gas chromatographic conditions. However, it is present in relatively constant proportion to the *trans* configuration of 1,2 DMP (Mango, personal communication). This compound can be resolved under different GC conditions which will be utilized on certain oils to confirm the relative constancy of this proportion.

As can be seen in the oil fingerprint most other light hydrocarbons are resolved by this technique. These compounds will also be included in the quantitative analysis package.

Since the light hydrocarbons are very volatile having low boiling points, the effects of sample alteration, i.e., partial evaporation of light compounds, will be evaluated separately. This will clarify the extent that light hydrocarbon ratios and data may be utilized on any given sample.

IDENTIFICATION AND QUANTITATION

A standard oil, the Norwegian Petroleum Directorate North Sea Oil, will be used as a routine standard for evaluation of chromatographic conditions and, in part, for peak identification. Each light hydrocarbon peak in this oil has been verified by gas chromatography mass spectrometry. Subsequent identification will be by retention time under ultra high resolution gas chromatographic conditions.

All GC analyses have been performed with internal standard(s) to determine quantitative amounts of each of the light hydrocarbons. All compounds less than heptane (n-C7) have been resolved and quantitated. Methylcyclohexane, ethylcyclopentane, and octane (n-C8) have also be resolved and the peaks quantitated.

GAS CHROMATOGRAPHY RESULTS

All GC fingerprint and quantitative peak areas as well as digitized analog traces are provided on computer media. Data is available in ASCII format as well as in spreadsheet or database format. These data are available on computer media (diskettes) or by electronic transfer. The digitized analog GC fingerprints are also available at this time.

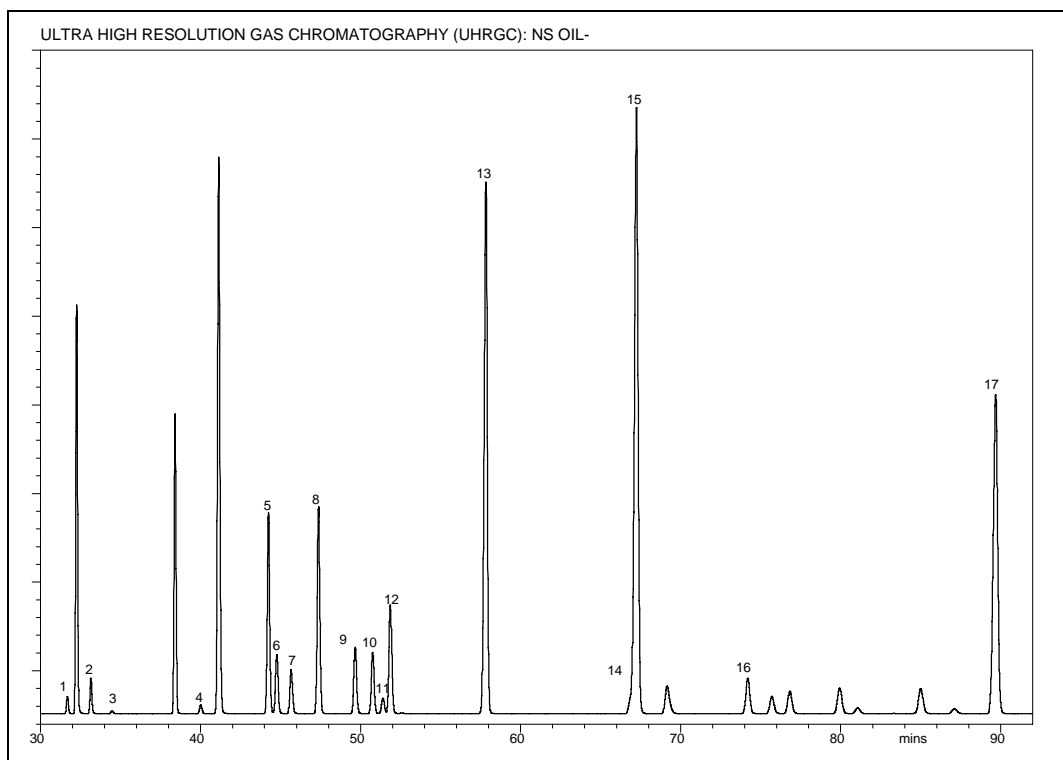


Figure 1. C7 Isomer Gas Chromatogram.

Table 1. C7 Hydrocarbons utilized by Mango (1990) (in relative elution order).

1. 2,2-dimethylpentane	10. <i>trans</i> -1,3-dimethylcyclopentane
2. 2,4-dimethylpentane	11. 3-ethylpentane
3. 2,2,3-trimethylbutane (2,3,3)	12. <i>trans</i> -1,2-dimethylcyclopentane
4. 3,3-dimethylpentane	13. <i>n</i> -heptane
5. 2-methylhexane	14. <i>cis</i> -1,2-dimethylcyclopentane
6. 2,3-dimethylpentane	15. methylcyclohexane
7. 1,1-dimethylcyclopentane	16. ethylcyclopentane
8. 3-methylhexane	17. toluene
9. <i>cis</i> -1,3-dimethylcyclopentane	

PETROLEUM SYSTEMS

Over 370 crude oil samples have been selected from GeoMark's world-wide collection encompassing a complete range of source ages (Precambrian to Miocene), source rock types (marine shale, carbonate, marl, hypersaline, lacustrine, coal/resin, paralic/deltaic) and basins. The oils in the study have already been classified into more than 80 separate petroleum systems based on the stable carbon isotope composition of the saturate and aromatic hydrocarbon fractions and the terpane/sterane biomarker distributions (as well as independent geological considerations). Whole crude GC data (e.g., Pr/Ph) and %S, Ni/V data are also available for comparison. In addition, oil samples are included which were generated from different levels of thermal maturity (based upon various biomarker maturity ratios) within many of the petroleum systems. The various petroleum systems to be tested are listed and briefly classified below.

<i>REGION</i>	<i>Petroleum System</i>	<i>No. of Oils</i>
<i>Middle East</i>		
Saudi Arabia, Kuwait, Bahrain, Iraq	1) U. Jurassic Carbonates (3 sub-families)	9
	2) Silurian Shales	1
Iran	3) L. Cretaceous Carbonates	5
	4) Tertiary Shales	2
	5) U. Cretaceous Carbonates	2
	6) Mixed origin	2
Oman	7) InfraCambrian Marls	2
Syria, Turkey	8) Cretaceous Carbonates I	6
	9) Cretaceous Carbonates II 2 sub-families	10
	10) Triassic Marls	3
	11) Triassic Lacustrine	1
	12) Silurian Shales	7
	13) Mixed origin	3
	<i>North Africa</i>	
Egypt, Gulf of Suez	14) Cretaceous Carbonates I	3
	15) Cretaceous/Eocene Carbonate/Marls II	4
Western Desert	16) U. Cretaceous Marine Shales	3
	17) L. Cretaceous Marine Shales/Marls	2
	18) Jurassic Paralic/Deltaic Shales	2
Libya	19) U. Cretaceous Marine Shales 3 sub-families	7
	20) Paleocene Marine Shales 2 sub-families	5
	21) Pre-Cretaceous Lacustrine	2
Algeria	22) Silurian Shales I 2 sub-families	13
	23) Silurian Shales II	3
	24) Devonian Shales 2 sub-families	10

REGION	Petroleum System	No. of Oils	
Europe			
Spain	25) Miocene Shales	8	
	26) Tertiary Carbonates	2	
North Sea	27) U. Jurassic Shales 3 sub-families	9	
	28) Devonian Lacustrine	1	
South America			
West Venezuela	29) U. Cretaceous Carbonate/Phosph.	5	
	30) U. Cretaceous Carbonate/Marls 2 sub-families	15	
	31) U. Cretaceous Shales	4	
Eastern Venezuela	32) Cretaceous Marls	3	
	33) Mesozoic Marl/Evaporites	2	
	34) Cretaceous Marine/Tertiary Terr. Mix	4	
Ecuador	35) U. Cretaceous Carbonates 2 sub-families	7	
	36) U. Cretaceous Marls/Shales 2 sub-families	4	
Peru	37) Cretaceous Shales	2	
	Coastal Basins	38) Miocene Shales	2
Brazil	39) Campos Cretaceous Lacustrine	3	
	40) Recon. Cretaceous Lacustrine	4	
	41) Espirito Santos Marine Shales	2	
	42) Sergipe Restricted Transitional Marls	3	
	43) Ceara Hypersaline Marine	4	
	West Africa	44) Tertiary Paralic/Deltaic Shales	2
		45) U. Cretaceous Marine Shales	3
	46) L. Cretaceous Lacustrine Shales	4	
Colombia, Llanos	47) U. Cretaceous Shales	10	
Colombia, M. Mag.	48) U. Cretaceous Marls	10	
Bolivia	49) Devonian Shales	4	
Argentina, Northwest Basin	50) Cretaceous Marls 2 sub-families	4	
	51) Paleozoic Shales	3	
Argentina, Austral	52) Cretaceous Paralic/Deltaic Shales	3	
North America			
Coastal California Basins	53) Miocene Silic./Carbonate/Phosph. 2 sub-families	7	
	54) Triassic Marl	1	
Anadarko Basin	55) U. Devonian Shales	5	
Uinta Basin	56) Eocene Lacustrine Marls	5	
Williston Basin	57) Carboniferous Carbonates	5	
	58) Ordovician Shales	3	
Big Horn/Powder River	59) Permian Carbonates/Phosph.	6	
Michigan Basin	60) Ordovician Carbonates	2	
Gulf Coast	61) Jurassic Carbonates	2	

REGION	Petroleum System	No. of Oils
Siberia		
West Siberia	62) U. Jurassic Shales 6 sub-families	19
East Siberia	63) Precambrian Marls	11
Far East		
Australia, Gippsland	64) U. Cretaceous Coals/Resins	5
New Zealand, Taranaki	65) U. Cretaceous Coals/Resins	6
China	66) Paleogene Lacustrine (fresh) 2 sub-families	3
	67) Paleogene Lacustrine (saline)	2
Thailand, Gulf	68) Paleogene Coals/Resins	3
	69) Paleogene Lacustrine	2
Thailand, Phits.	70) Paleogene Lacustrine	3
Thailand, Khorat	71) Permian Carbonates	2
Vietnam	72) Paleogene Lacustrine	2
Philippines	73) Miocene Carbonates	10
Indonesia, Sumatra	74) Paleogene Lacustrine 2 sub-families	6
	75) Paleogene Coals/Resins 2 sub-families	4
Indonesia, Mahakam	76) Paleogene Paralic/Deltaic 2 sub-families	8
Indonesia, W.Natuna	77) Paleogene Lacustrine	2
Indonesia, Arjuna	78) Paleogene Coals/Resins	1
Indonesia, Penyu	79) Paleogene Lacustrine	1
Indonesia, E.Java Sea	80) Paleogene Coals/Resins	4
Japan	81) Miocene Marine Shales	4
Taiwan	82) Tertiary Paralic/Deltaic Shales	4
	83) Tertiary Lacustrine Shales	2

A generalized location map of these petroleum systems is illustrated in Figure 2.

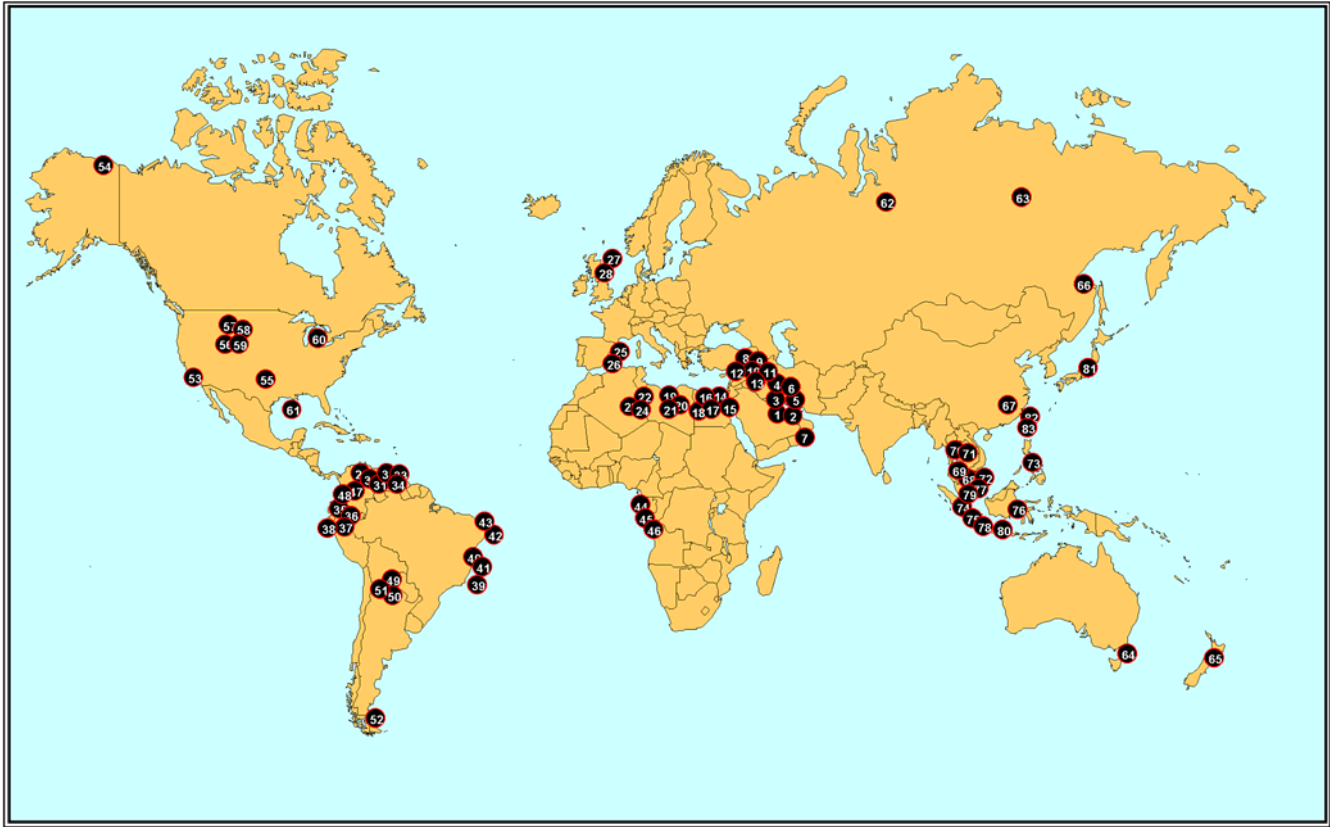


Figure 1. Samples analyzed for this study.

COST AND TIMING

The analytical program and interpretive report are complete (data volumes are being issued in both hard copy and digital format) and is immediately available. Cost of participating is US \$30,000.

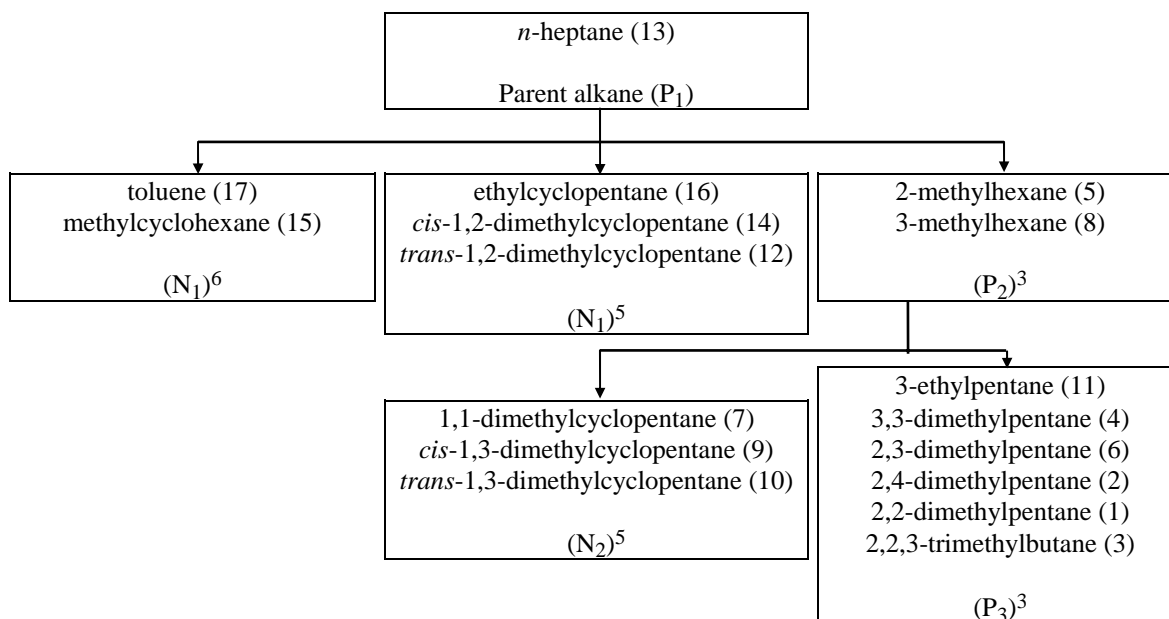
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APPENDIX I
(AFTER MANGO, 1987, 1990, 1994)



where P_1 = first parent, P_2 = second parent, P_3 = daughter products of second parent, N_1 = cyclopentane daughter products of P_1 , N_2 = cyclopentane daughter products of P_2 .

- Notes: 1) The subscripted numbers represent the hypothesized precursor compound either P_1 or P_2 .
- 2) The superscripted numbers represent the number of ring carbons in the hypothesized ring closure steps.
- 3) The kinetic expressions used by Mango (1994) may be inserted by substituting "k" for the "P" or "N" throughout the flow chart above while maintaining the subscripts and superscripts.

Invariant Ratios:

- 1) $(2MH + 2,3DMP) / (3MH + 2,4DMP)$
- 2) $P_3 / (P_2 + N_2)$

Ring Preference Ratios:

- 1) $(N_1)^5 / (N_1)^6 = (k_1)^5 / (k_1)^6$ (ratio of P_1 daughters)
- 2) $P_3 / N_2 = (k_2)^3 / k_2^5$ (ratio of P_2 daughters)

Ring Preference Plots:

- 1) P_1 / D_1 versus $(k_1)^3 / [(k_1)^5 + (k_1)^6]$, where D_1 = sum of all except n -C7;
- 2) n -heptane versus $\ln[(N_1)^5 / (N_1)^6]$;
- 3) P_2 versus $\ln(P_3 / N_2)$.