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THE SYNTHETIC NATURE OF GROUP III BASE OILS

by

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ABSTRACT

The use of the word “synthetic” in the lubricants industry has historically been synonymous with polymerized base oils such as PAOs, which are made from small molecules. Primarily this use evolved because these types of base oil were the only thing available for high performance lubricants. That changed a number of years ago when some lubricant manufacturers, primarily in Europe, began replacing PAOs with newly available Group III base oils, which are made from molecules substantially of the same size as the final product. This is currently causing a controversy in the lubricants industry as some producers see only polymerized base oils as the true and only synthetic.

This fairly narrow definition for a synthetic product is unique to the lubricants industry. For example, in an industry very closely related to lubricants, transportation fuels, synthetic fuels are generally considered to be liquid products manufactured from nontraditional hydrocarbon sources such as tar sands, coal, oil shale, or even ethanol from corn. What makes them synthetic is that they are not refined from crude oil, but manufactured by restructuring the original feed component into an entirely different useful fuel component. In contrast to crude oil refining, where the product molecules can substantially be traced back to the feed, these synthetic fuels’ molecular structure have little to no similarities to the original feed molecular structure, i.e., they are man-made species not typically found in nature.

With the expanding availability of Group III base oils and significant improvements in their performance, many lubricant suppliers are choosing to use a broader definition of synthetics more in line with that used in transportation fuels. Under this definition a key test of whether Group III base oils can be considered synthetic is to answer the question: Are their molecules largely altered from those appearing in the raw material or not? That is, are they man-made?

In this paper we take a look at the feed and product from Chevron's Richmond Lube Oil Plant during a Group III production block. Our analysis shows that as the feed molecules pass through the three catalytic steps of lube manufacture, virtually all are rearranged or altered in some way. The extensive chemical processing steps involved have resulted in a product that is essentially different chemically than the raw material. Therefore, they justifiably can be considered to be synthetic.

Beyond the issue of the definition of synthetic, base oil customers also typically look for high performance in these types of lubricant components. When properly designed, these Group III oils, particularly the newer Group III base oils made via all-hydroprocessing routes, can match or exceed the most critical performance characteristics of PAO. This includes viscosity index, Cold-Cranking Simulator viscosity, Noack volatility, and oxidation stability. We show data to demonstrate such performance.

INTRODUCTION

Modern base oil manufacturing has evolved to the point where a significant fraction of the final product is now synthetically derived from the non-lube portion of the “natural” vacuum gas oil feedstock. These non-lube components are reshaped and transformed by various catalytic processes into molecules with superior lubricating qualities. Base oils today can be designed and manufactured so that their performance closely matches PAOs in most commercially significant finished lube applications. Viscosity index (V.I.), pour point, and oxidation stability can now be independently controlled.

By contrast, traditional solvent refining has been essentially a subtraction process. Quality is improved by removing the worst non-lube molecules from the vacuum gas oil portion of the crude using chemical solvents. Solvents do not change the size or shape of the molecules in the product. They simply concentrate the good ones. Hydrofinishing is sometimes added to stabilize the most reactive molecules in the base oil by saturating reactive species with hydrogen. The impact of hydrofinishing depends on choice of processing severity, such as hydrogen pressure, type of catalyst, et cetera. Hydrofinishing associated with solvent processes are typically very mild, resulting in insignificant to no changes in the molecular structures of the vast majority of the solvent refined base oil. In contrast, an all-hydroprocessing manufacturing route combines three catalytic processes to significantly and selectively change the size, shape, and heteroatom content of the molecules to improve their lubricating properties. Hydrogen is added at high temperature and pressure in all three steps to make oil of exceptional stability. Impurities such as sulfur and nitrogen are essentially completely removed. In Group III manufacturing, feedstock is converted to saturates, which are enriched in isoparaffins. Reactive species, such as those containing aromatics, sulfur, and nitrogen are virtually gone and species that create problems with low temperature performance, such as normal-paraffins, are also eliminated.

ALL-HYDROPROCESSING ROUTE AT RICHMOND LUBE OIL PLANT

The three basic steps in the all-hydroprocessing route for lube base oil manufacturing are:

1. **HYDROCRACKING** – In this first step the majority of sulfur, nitrogen, and essentially all other non-hydrocarbon impurities are removed and most aromatics are saturated via hydrogen addition. Molecular reshaping of remaining saturated species occurs as rings are opened and paraffin isomers are redistributed, driven by thermodynamics with reaction rates facilitated by catalysts. Clean fuels are by-products of this and subsequent steps of the process.
2. **HYDROISOMERIZATION** – In this step n-paraffins and other molecules with waxy side chains are isomerized into branched molecules with much lower pour points. The majority of remaining aromatics are saturated and the majority of remaining sulfur and nitrogen species are removed.
3. **HYDROFINISHING** – In this final step any remaining non-isoparaffin impurities (sulfur species, nitrogen species, aromatics, and olefins) are removed to trace levels. Finishing at Richmond uses high pressure hydrogen and exceptionally reactive catalysts.

Earlier generations of Group III base oils¹ were not produced using the all hydroprocessing route, such as deployed at Richmond. Consequently, they do not have the stability and exceptional performance of these modern Group III oils. They also have measurable compositional differences that can be used to predict this shortfall in performance. Fortunately for North American consumers, those older generation stocks are made and sold in different markets. Many of these plants are being upgraded to technologies that will enable them to make the modern Group III oils.²

EXPERIMENTAL

We wanted to determine to what extent the three main catalytic steps in an all-hydroprocessing route “synthetically” alter the feed molecules. To do this we obtained feed and product samples from a recent Group III production run at our Richmond Lube Oil Plant (RLOP, Figure 1). We performed a series of physical separations and applied various analytical techniques to characterize the components in the oils.

These techniques were originally developed to help us understand how to build better base oils. Taking advantage of their availability we use them here to identify various classes of compounds that are catalytically transformed in the manufacturing process. By identifying these classes and adding the results, we will establish a quantitative but very conservative figure for the percent of original feedstock that has been transformed. Further qualitative data conclusively confirms that the quantitative percent transformed is conservative and most probably significantly higher.

Solvent Dewaxing

As a first step, we performed a conventional solvent dewaxing on the whole vacuum gas oil feedstock at -10°C . The wax yield was 34%. We can be sure this wax portion of the feedstock is catalytically altered during lube manufacturing. These molecules are selectively isomerized during the hydroisomerization step mentioned above. Chevron Group III base oils are catalytically hydroisomerized well below -10°C , so there is no -10°C wax remaining in the base oil.

Preparative HPLC

Next, we took the dewaxed oil and ran it through a preparative HPLC column to separate the aromatics, saturates, and polar fractions.

Approximately 250 mg of dewaxed oil dissolved in hexane was placed onto a preparative silica gel column. Using hexane as the eluent, the saturates fraction was collected from the beginning of the run until the aromatics elute, as indicated by UV absorption.

Results on Solvent Dewaxed VGO

- 59% Saturates
- 38% Aromatics

- 3% Polars

Almost none of the aromatics and polar molecules survive the hydrocracking and hydrofinishing steps. Our Group III base oils typically contain less than 0.1% aromatics and no polars. Therefore, at least 41% of the dewaxed oil (38% aromatics plus 3% polars) or 27% of the original VGO feedstock was transformed.

When you add the wax portion (34%) to the aromatics and polars, the subtotal now is 61% of the original VGO feedstock transformed (Figure 2).

GC Mass Spectroscopy

Next, we performed a GC-Mass Spec analysis of the saturates fraction of the dewaxed oil. Approximately 10 mg of the oil sample was dissolved in 100 μ L of dichloromethane, 1 μ L of which was injected onto a 15-meter non-polar capillary column. The mass spectrometer was scanned from 40 to 800 AMU in about 1 second.

The analysis showed that about 10% of the saturates fraction of the dewaxed oil was light n-paraffins. Normal paraffins are generally thought of as undesirable in lube oil because they tend to wax out at lower temperatures. In the hydroisomerization process, n-paraffins fit easily into the zeolitic pores in the catalyst and are converted to isoparaffins with a much lower pour point. The n-paraffin content in our Group III base oils typically is below the detection limit by standard methods. Therefore, at least 10% of the saturates fraction, or another 4% of the original VGO feedstock, has been transformed. This brings the total from 61% up to 65%.

Field Ionization Mass Spectroscopy

Next, we took a closer look at the saturates fraction of the dewaxed oil using Field Ionization Mass Spectroscopy.

Field Ionization Mass Spectrometry is an analytical technique that produces predominantly molecular ions. This is especially important for saturates because their conventional mass spectra are very similar for the same compound type while giving limited, if any, information on a compound's molecular weight. Having the distributions of molecules within a compound type facilitates comparisons to unravel changes. A common basis (waxy feed) was used to permit valid comparisons between saturates in the feed and those in the product.

The FIMS work showed that the molecular weight distribution and ring content of the Group III base oil was significantly different from the "natural lube" portion of the VGO (Figure 3). Spectral subtraction showed that the Group III base oil was more concentrated in isoparaffins and 1-ring naphthenes than the "natural" portion of the feed (Figures 4 and 5). Many of these appear via hydroisomerization. These are the most desirable compounds in the base oil. They have the highest oxidation and thermal stability and they boost the viscosity index of the oil. Oxidation stability and V.I. are perhaps the two most important attributes of PAO-based synthetic oils.

Spectral subtraction also showed that most of the big multi-ring naphthenes in the feedstock are converted (Figures 6, 7, and 8). These are the least stable and least desirable components in Group III base oil. During the hydrocracking process, naphthenic rings are opened which transforms them into more desirable compounds or cracks them out of the lube boiling range.

Overall, we calculated that during processing at least 43% of the molecules in the dewaxed saturates fraction were altered by molecular weight or ring number. Excluding the 10% n-paraffins that have already been accounted for earlier, that contributes at least another 15% (=90% x 59% x 67%) of the VGO feedstock to the converted fraction, bringing the new total to 80%. With this piece included, we have shown conservatively that catalytic processing has synthetically altered at least 80% of the original VGO feedstock.

But we suspected that the molecules in the Group III base oil that happen to have the same molecular weight and ring number as those in the dewaxed feed saturates fraction still are not identical twins. NMR analysis, described below, gives a measure of the relative abundance of different molecular structures in the saturates fraction of the Group III base oil. Similar analyses were made in the past.^{3,4}

NMR

Both ¹H and ¹³C DEPT NMR spectroscopy were applied to these analyses, with the latter providing the most detailed structural characterization. The DEPT technique provides three semi-quantitative subspectra of methyl, methylene, and methyne carbons separately.^{5,6}

The spectrometer used was a Bruker MSL 500 (¹³C frequency 125.8 MHz). $\pi/2$ pulses for ¹H and ¹³C were 10.2 and 8 μ sec, respectively, for a 5 mm ¹³C probe. The DEPT spectra were acquired in about 1.5 hours. Separate spin-echo ¹³C spectra⁷ were acquired for another 3.5 hours in an effort to measure quaternary carbons, but none were seen in either sample.

Separate subspectra of the samples (Figures 9-11) could be assigned using the paper of Lindeman and Adams.⁸ These subspectra showed that the product had more interior methyl branches as expected. Isolated interior ethyl branches were also apparent in the product, as might arise from the opening of naphthenic rings. These structures are characteristic of the hydroisomerization process.

We identified 7 substructures via NMR and determined their relative abundance. But we cannot apply them directly to the numerical analysis of the feed because they reflect the relative abundance of these structures within the average molecule and do not tell us the exact structure of individual molecules.

This analysis shows that a significant amount of molecular rearrangement and transformation takes place within the saturates fraction itself. Some of the rearrangement is redistribution of isomers. Some is due to the appearance of high-quality lube molecules that were transformed from other species. This analysis shows that 80% conversion, as identified by the partial analyses in the earlier sections, is low. The actual amount is much higher. Virtually all molecules are synthetically converted to their saturated counterparts, created by hydrogen

saturation of sulfur, nitrogen, and aromatic species; opening of rings in cycloparaffins; isomerization of normal-paraffins; and isomerization of native isoparaffins to different isomers.

Analytical Summary

The closer the product and the feed were analyzed, the more was revealed about the synthetic nature of the product. The combined quantitative analysis conservatively showed that at least 80% of the original VGO feedstock in this Group III production run was confirmed to have been catalytically transformed during lube manufacture. Semi-quantitative NMR analysis and thermodynamic arguments indicate that a substantial fraction of the remaining 20% also was converted. A full compositional breakdown of all individual isomers would show just how close the transformation is to 100%. Future analytical techniques can be deployed to define the full extent of conversion more precisely.

SYNTHETIC PERFORMANCE

In addition to the synthetic moniker, customers are also concerned with performance. Modern Group III base oils perform at a level that is significantly higher than “conventional” base oils, both Group I and Group II, and substantially match existing levels of performance in finished lube applications already established by their traditional synthetic counterparts. In fact, many, like Chevron's UCBO, were specifically designed to perform like PAOs in the vast majority of finished lube applications. The most notable exception, arctic oils, have very small market presence.

Pour Point – Pour point is the one place where Group III oils allegedly fall short of PAO. While it is certainly true that the pour point of the neat VHVI base oil is substantially higher than that of a PAO of comparable viscosity, it is important to understand that what matters is the pour point of formulated lubricants, which are comprised of both base oils and additives. Fully formulated Group III-based lubricants are very responsive to pour point depressant additives, and can demonstrate pour points of -50°C or below when the Group III base oil are manufactured with modern isomerization catalysts such as Chevron's ISODEWAXING® catalyst. Products such as motor oils made with the lighter-grade PAOs, on the other hand, typically have *higher* pour points than the base fluid, so the gap in final product pour point between PAO-based and UCBO-based lubricants is much smaller than in the base fluids themselves. Moreover, it is entirely possible with modern Group III manufacturing technology to produce base oils of even lower pour point, although this is not currently common in the industry precisely because there is very little need for pour performance below -50°C .

Cold Crank Simulator – Viscosity in engine journal bearings during cold temperature startup is a key factor in determining the lowest temperature at which an engine will start. Cold Cranking Simulator (CCS) viscosity, as measured by ASTM Method D 5293, is determined under conditions similar to those experienced in engine bearings during starting. For base oils, this viscosity is determined almost entirely by viscosity and viscosity index. Since VHVI stocks such as Chevron's UCBO 4R have a V.I. comparable to that of 4 cSt PAO, one would expect comparable CCS performance. This is demonstrated in Figure 12, where it can be seen that 4R, with a kinematic viscosity of 4.2 cSt @ 100°C and a V.I. of 129, and PAO 4, with a viscosity of

3.9 cSt and V.I. of 123, have very similar CCS values, both about half that of a 4 cSt Group II base stock of about 100 V.I. This performance makes the UCBO very effective for formulating fuel-efficient multi-viscosity engine oils in the 0W-20 to 0W-50 range, one that has historically been achieved only with PAO-based products.

Noack Volatility – Noack volatility of an engine oil, as measured by ASTM D 5800 and similar methods, has been found to correlate with oil consumption in passenger car engines. Strict requirements for low volatility are important aspects of several recent and upcoming engine oil specifications, such as ACEA A-3 and B-3 in Europe and ILSAC GF-3 in North America. Figure 13 shows that from a blender’s perspective, Chevron Group III base oils are similarly effective as PAOs for achieving these low volatility requirements in engine oil applications. The viscosity index of modern Group III oils typically match or exceed PAO so they can match the volatility of PAOs at a reasonable distillation cut width.

Oxidation Stability – Oxidation and thermal stability are among the most important advantages that “synthetics” bring to the table. Better base oil stability means better additive stability and longer life. High stability is the key to making the premium-quality finished oils of the future with longer drain intervals. Here Group III oils routinely challenge PAO performance.

The benefit of all-hydroprocessed Group III base oils in oxidation stability is illustrated in Figure 14, for hydraulic oils formulated by using the same additive system in four different base oils. Here, the time required to reach an acid number of 2.0 (defined by neutralization of 2.0 mg of KOH/g of oil) in the Universal Oxidation Test (ASTM D 4871), a common measure of oil oxidation, was substantially longer for the Group III formulation than for either the Group I or II products. Moreover, the performance of the Group III product was essentially the same as that for the oil formulated with PAO.

The stability of modern Group III stocks depends mostly on their viscosity index, because V.I. is an indication of the fraction of highly-stable isoparaffinic structures in the base oil.⁹ However, because modern Group III stocks also undergo additional severe hydrofinishing after hydrocracking and hydroisomerization, they achieve an additional boost in stability because only trace amounts of aromatics and other impurities remain in the finished stocks. On the other hand, PAO performance seems to depend largely on residual olefin content. Olefins are an intermediate in PAO production that probably contribute to instability.

Table 1 lists a variety of North American lubricants of which the authors are aware which are based upon all-hydroprocessed Group III base stocks. These products include engine oils, industrial oils, and driveline fluids like automatic transmission fluid, and are targeted at the same performance levels achieved by traditional synthetic formulations.

<u>Table 1.</u>	
<u>Synthetic Quality Products Utilizing All-Hydroprocessed Group III Base Stocks</u>	
Available Now	Upcoming
Semi and Full Synthetic PCMO Semi-Synthetic HDMO DaimlerChrysler ATF+4® Ford Mercon® V ATF Compressor Oil	GF-3 PCMO (Semi and Full Synthetic) Extended Drain Gear Oil High Performance Automotive (Racing) Oils: Motor Oils Gear and Transmission Oils

CONCLUSIONS

Analysis of the feed and product from a commercial Group III production run show that a vast majority of feed molecules are synthetically altered by the three catalytic processes used to make modern all-hydroprocessed Group III base oils. These results support the claim that modern Group III base oils made utilizing an all-hydroprocessing route are essentially man-made or synthetic. In addition, their high performance in lubricant applications allows them to be used in high performance products often formulated with traditional synthetics such as PAO.

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Figure 1

Richmond Lube Oil Plant



Figure 2

Molecules in Natural VGO Feed

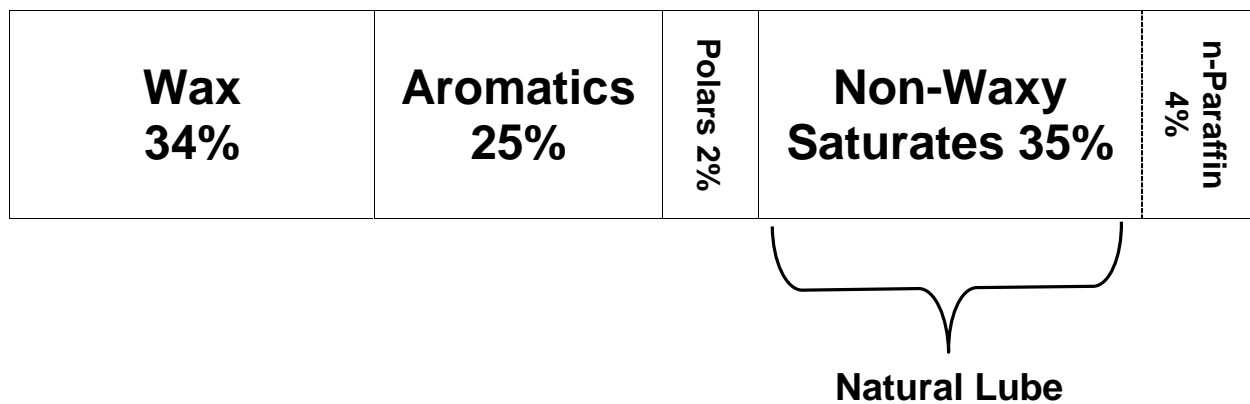
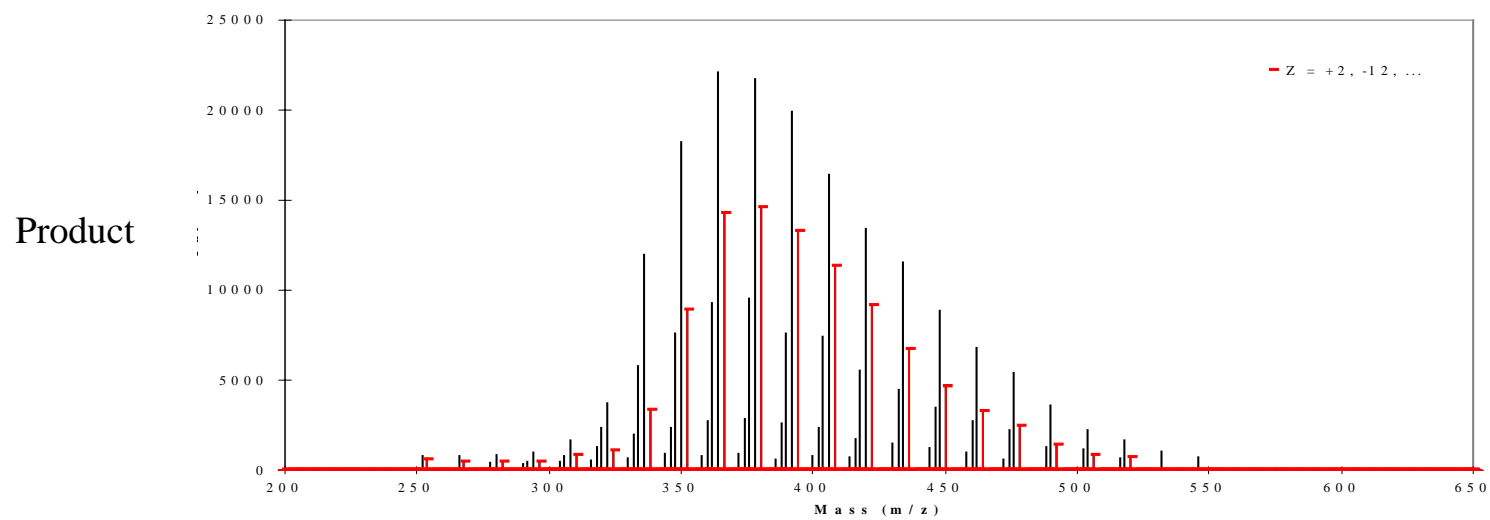
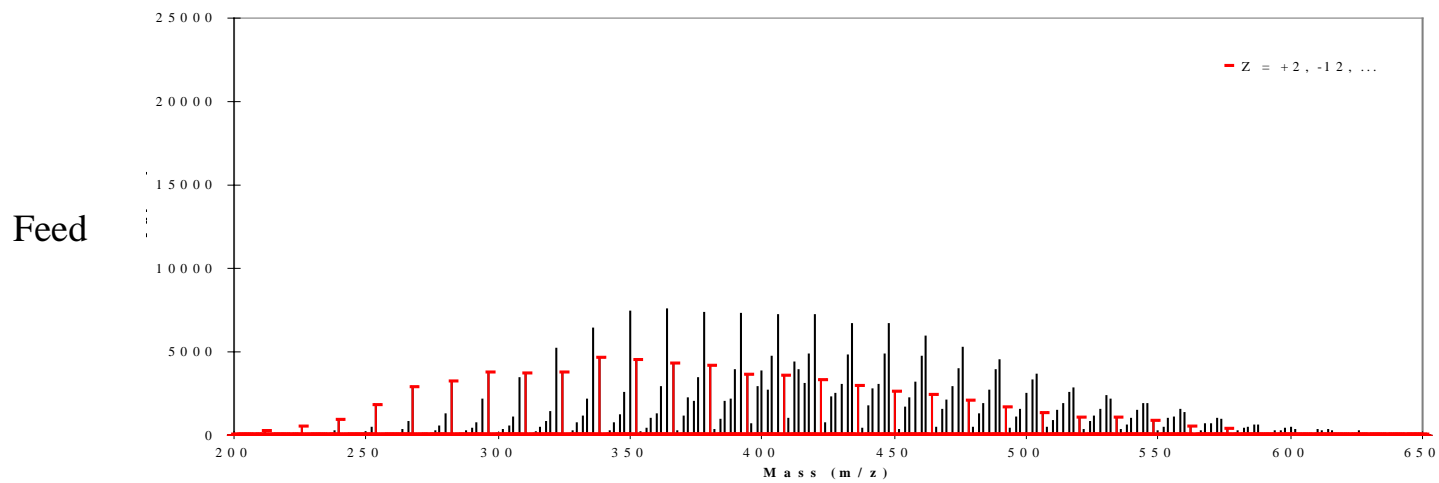


Figure 3

Natural Lube Molecules Are Rearranged



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Figure 4

By Comparing Feed With Product Many Isoparaffins Appear

Paraffins

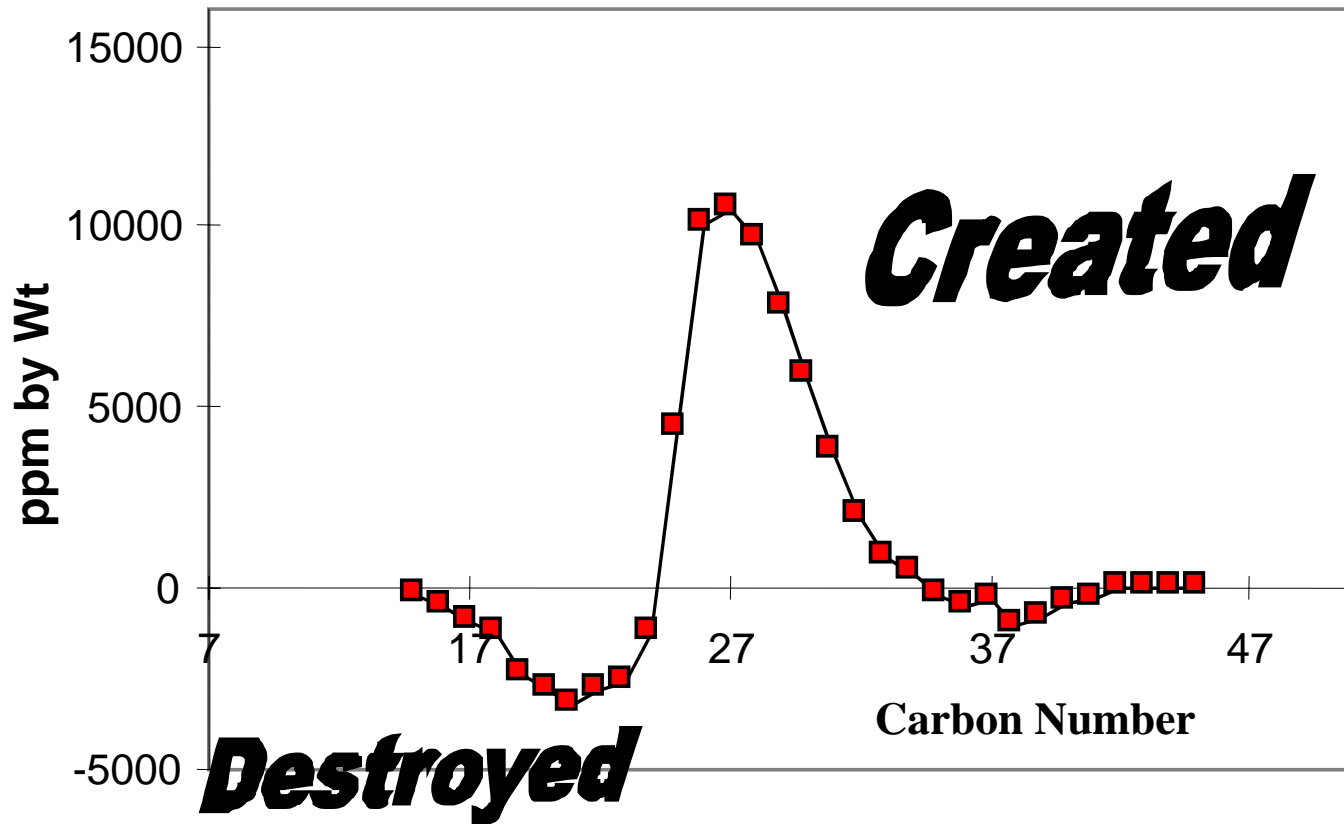


Figure 5

1-Ring Naphthenes Appear

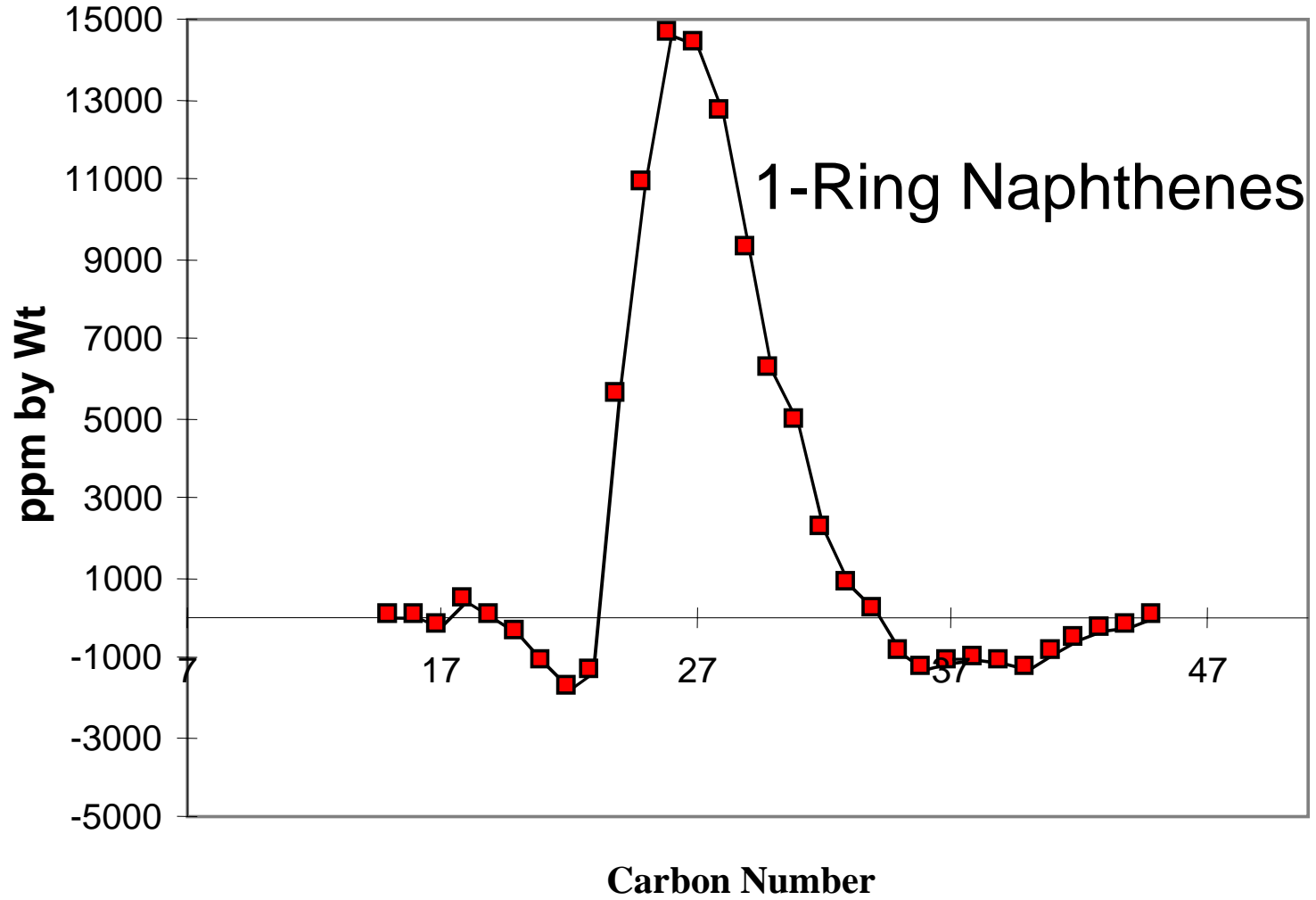


Figure 6

Fewer 2-Ring Naphthenes Appear

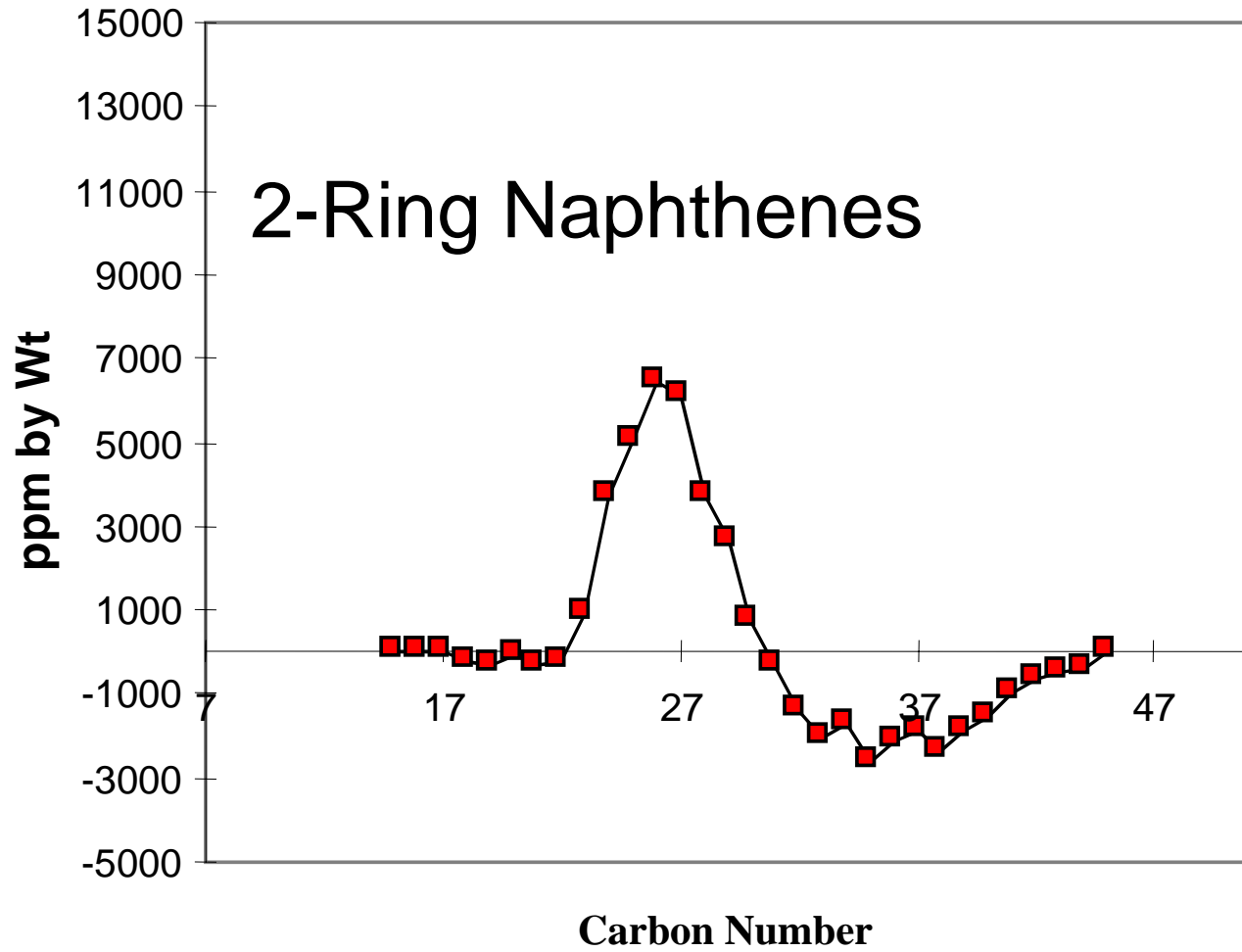


Figure 7

More 3-Ring Naphthenes Are Destroyed

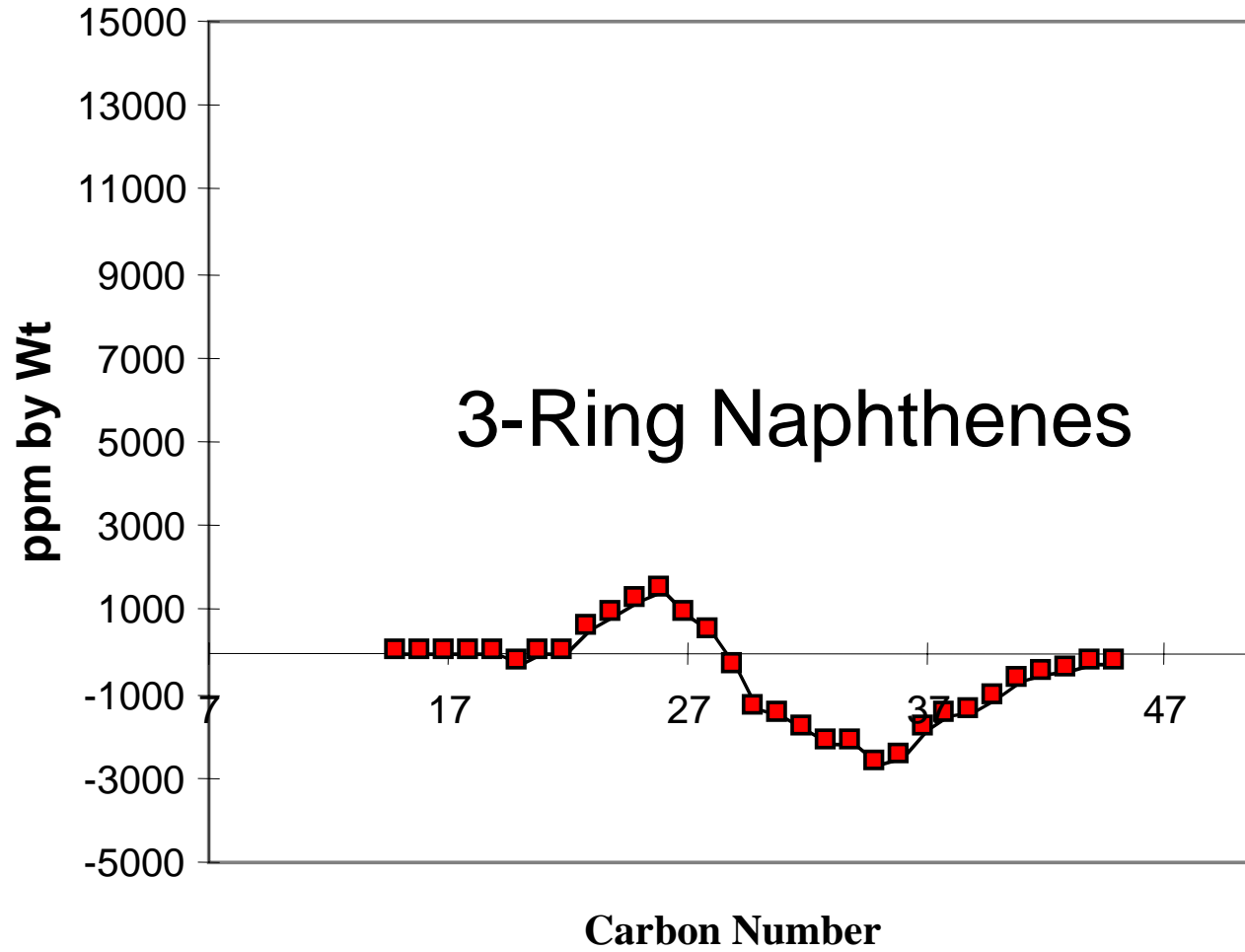


Figure 8

Larger Naphthenes Are Destroyed

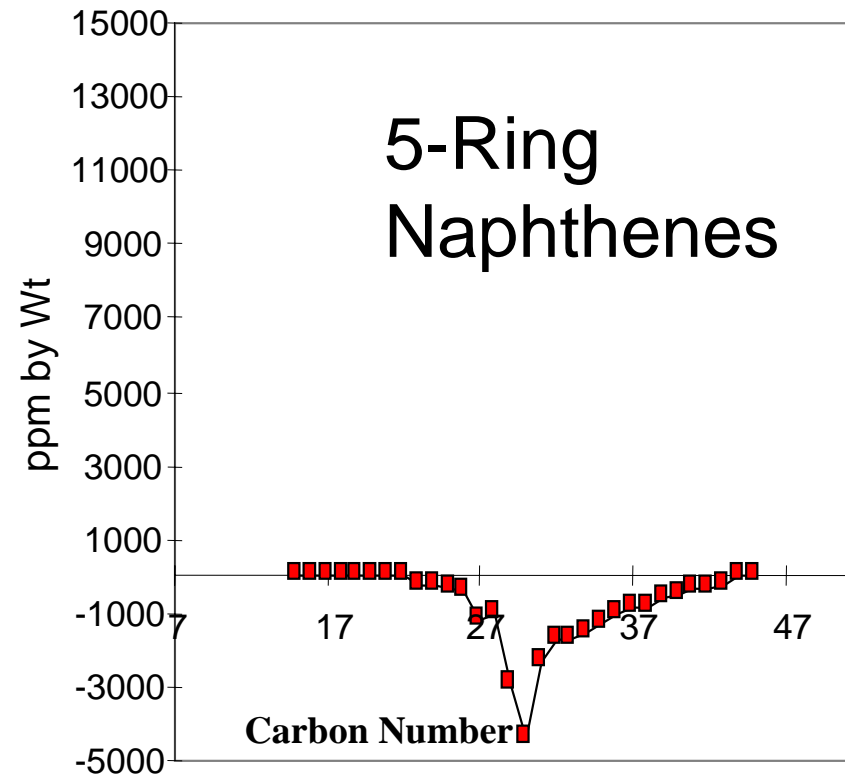
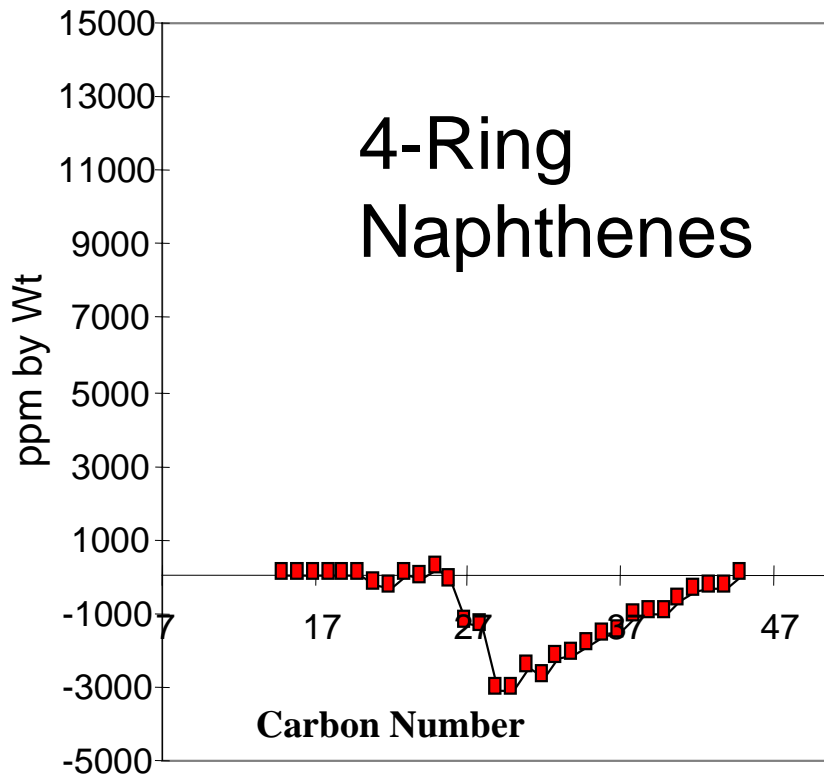
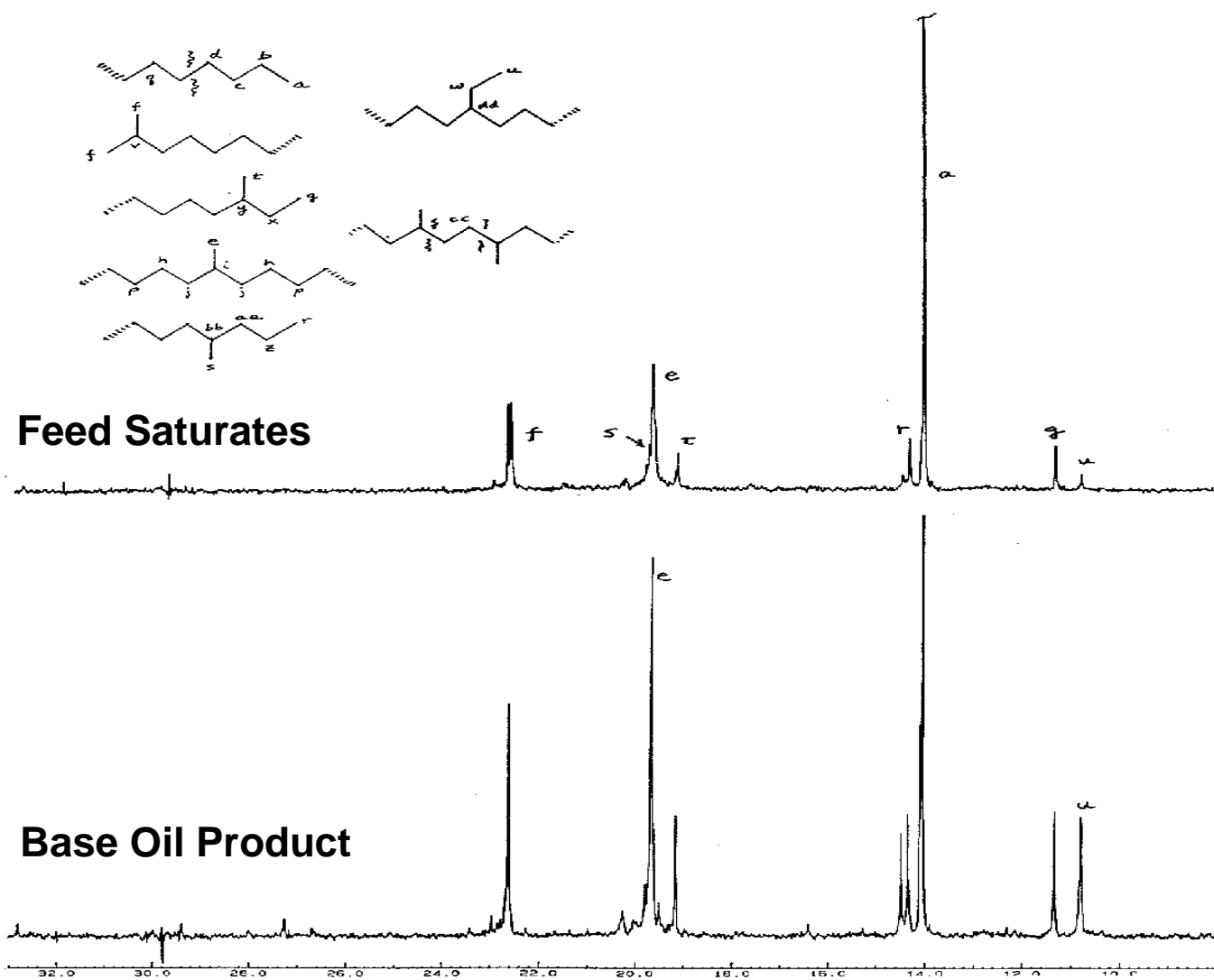


Figure 9

NMR Results – CH₃ Structures



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Figure 10

NMR Results – CH₂ Structures

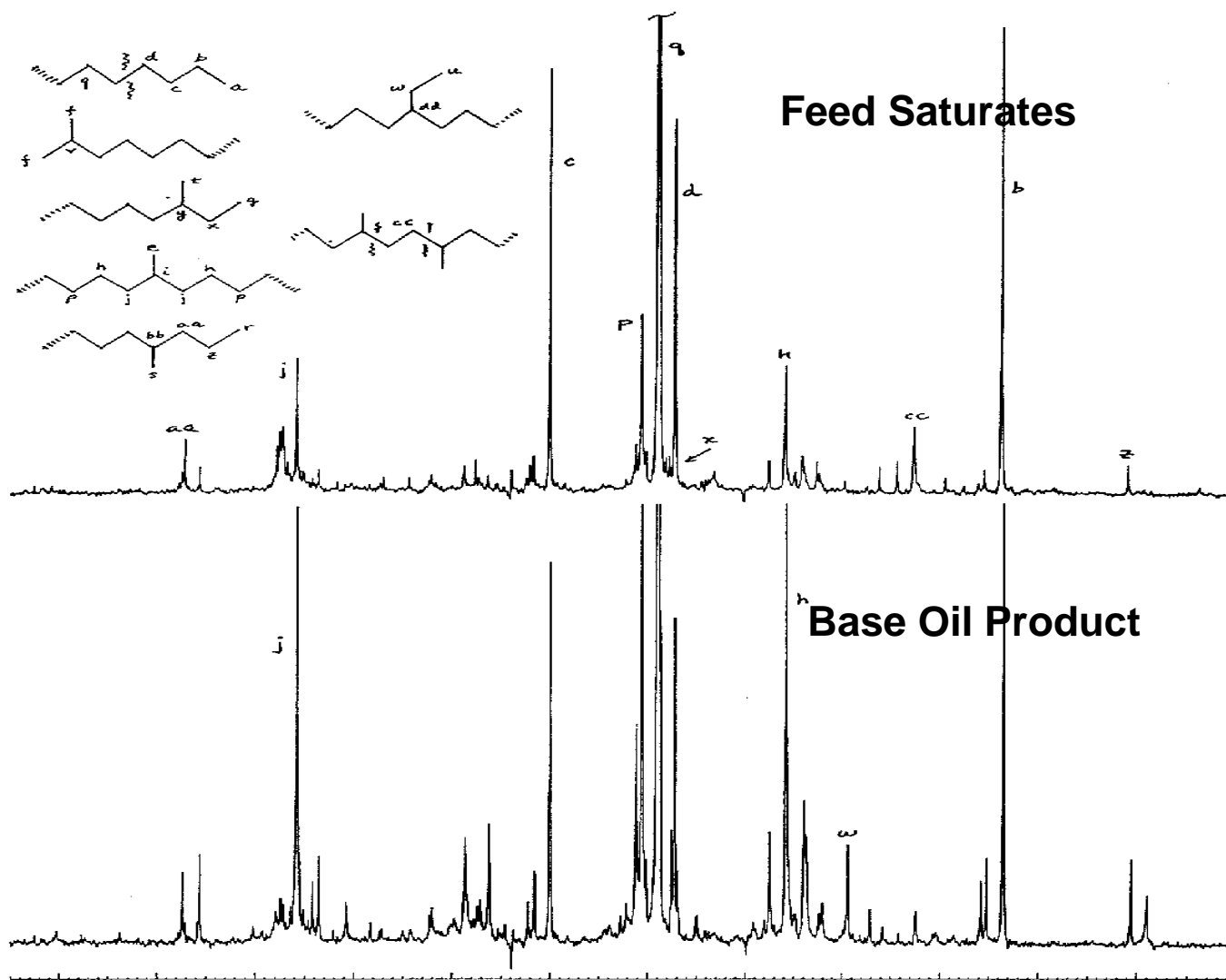
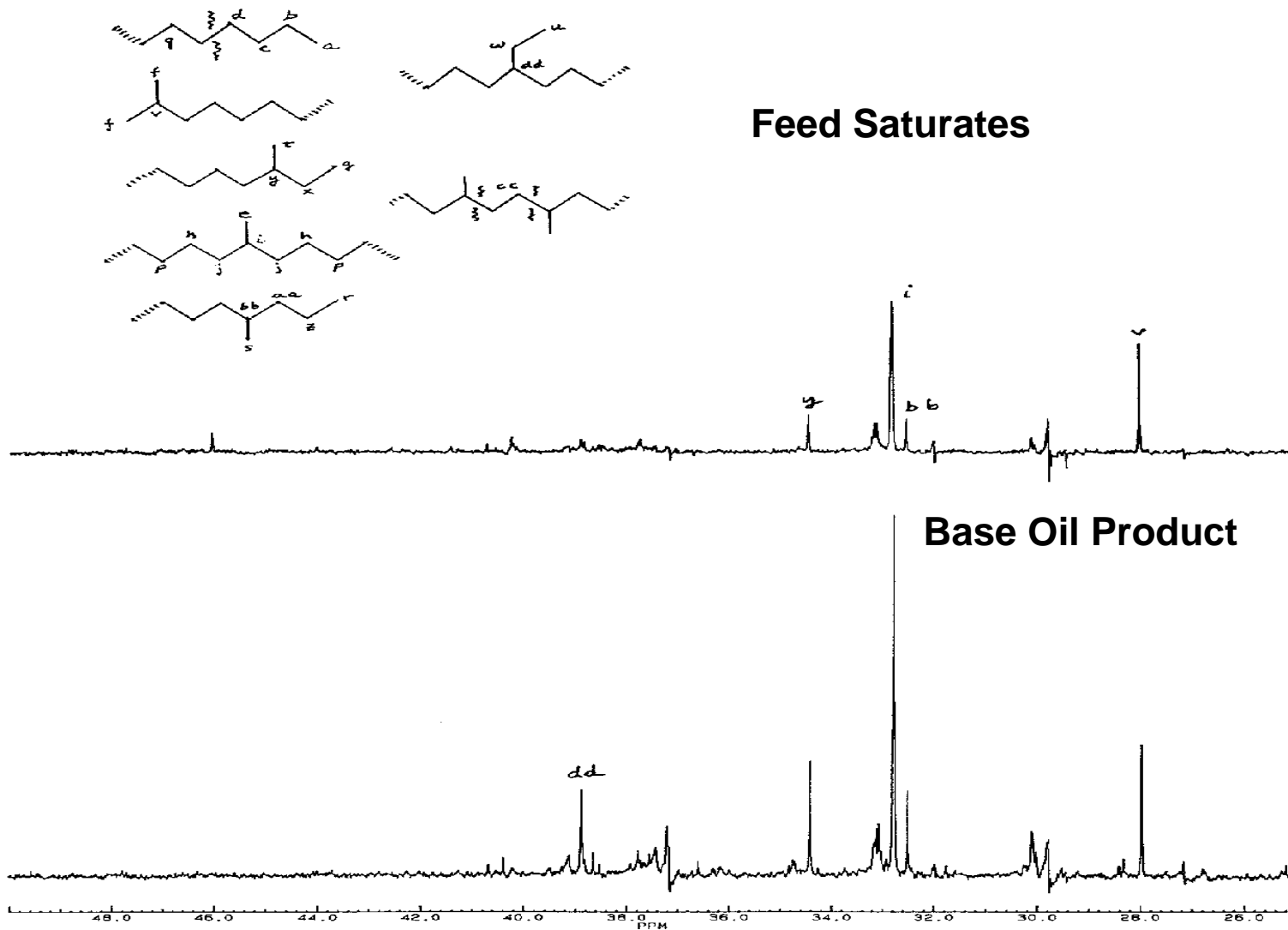


Figure 11

NMR Results – CH Structures



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Figure 12

Cold Cranking Performance
Group III Comparable to PAO

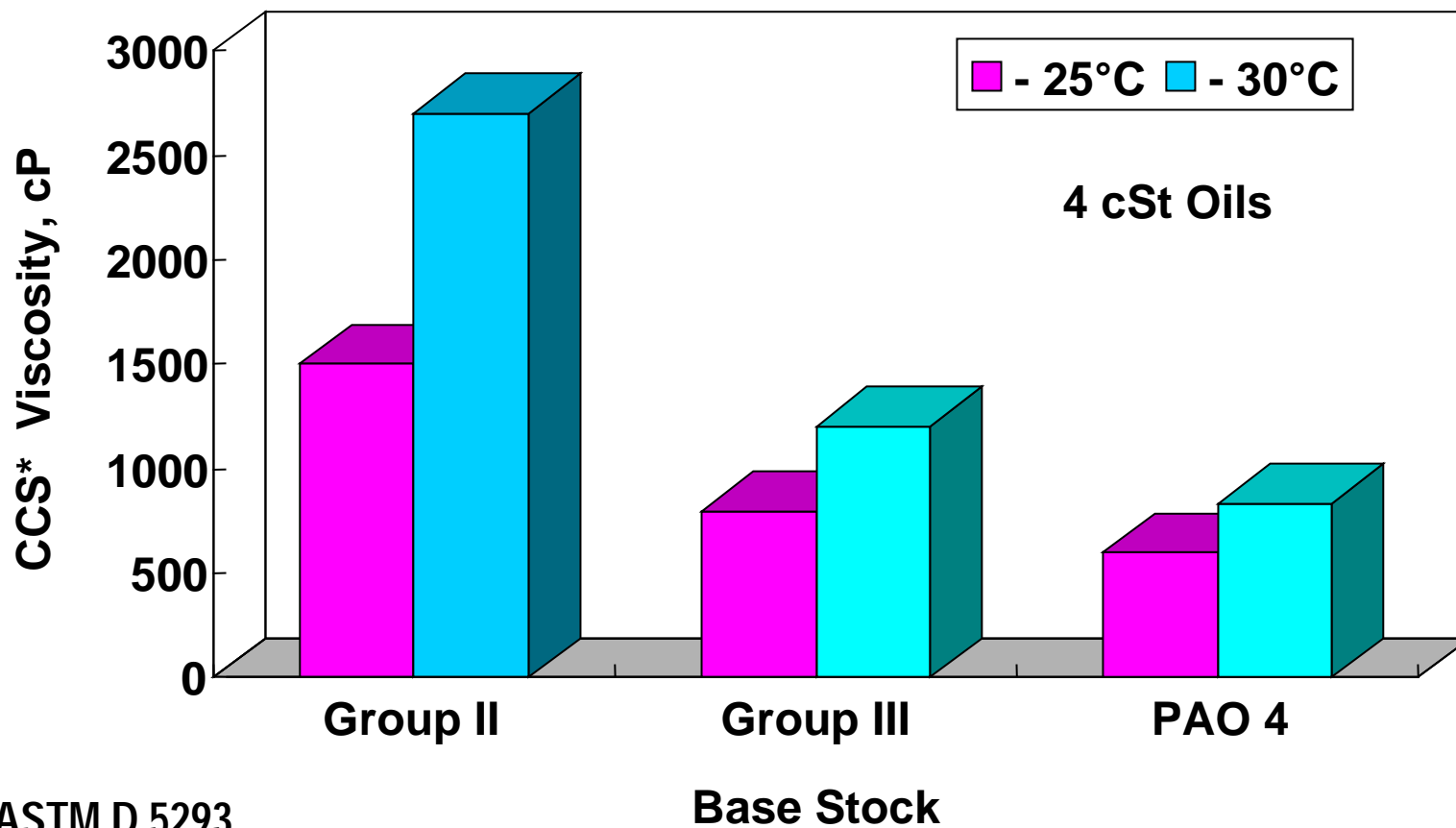
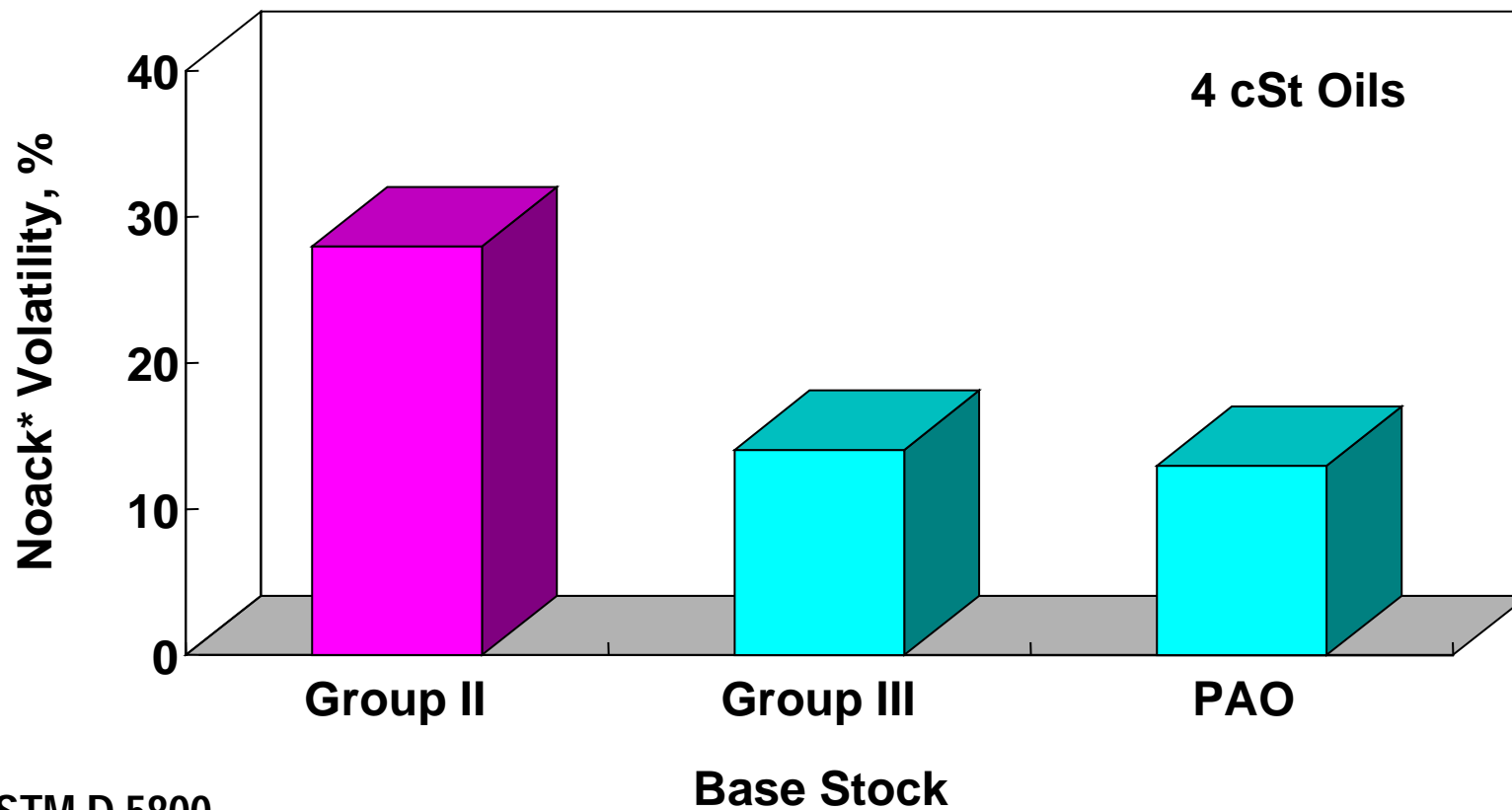


Figure 13

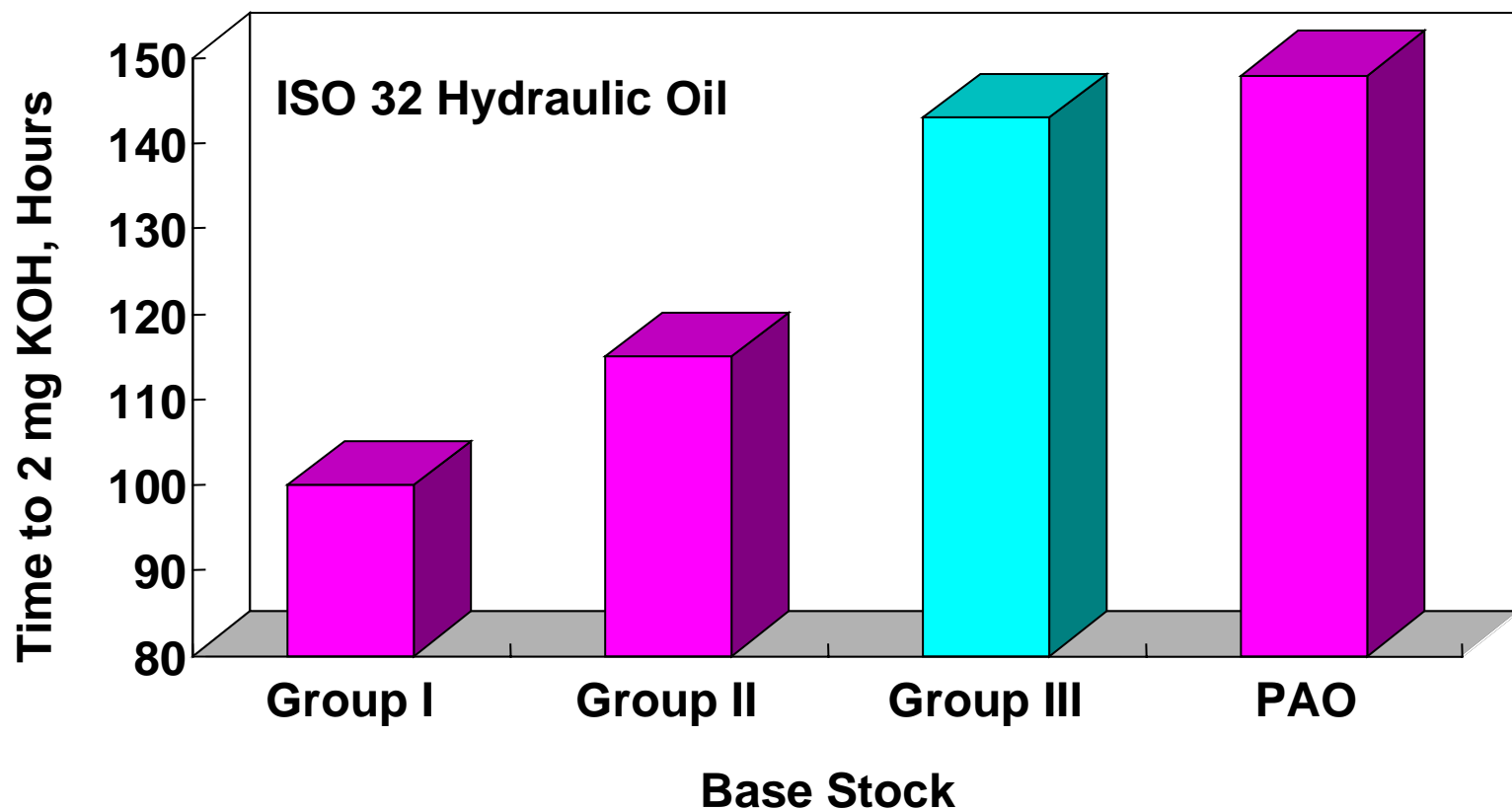
Group III Performance Versus PAO
Comparable Noack Volatility



*ASTM D 5800

Figure 14

Oxidation Stability
Acid Number in Hydraulic Oils



Universal Oxidation Test, ASTM D 4871, at 170°C

Figure 15

Products* Formulated With Group III Base Oils

Available Now

- Semi & Full Synthetic PCMO
- Semi-Synthetic HDMO
- Mercon V ATF
- Chrysler ATF+4
- Compressor Oil

Upcoming

- GF-3 PCMO (Semi & Full Synthetic)
- Long-Drain Gear Oils
- High Performance Automotive (Racing) Oils:
 - ◆ Motor Oils
 - ◆ Gear & Trans Oils

*North America