PROCESS NMR ASSOCIATES, LLC

TECHNICAL WHITE PAPER

Orthogonal ^{1}H and ^{13}C NMR Spectroscopy for Molecular-Structural Characterization of Petroleum Hydrocarbons

Resolution and quantification of naphthenic, normal-paraffinic, iso-paraffinic, aromatic, and olefinic carbons and protons in lubricant base oils and Fischer-Tropsch / GTL synthetic base stocks, with emphasis on carbon branching chemistry

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Abstract

The molecular-structural characterization of petroleum hydrocarbons is most defensible when quantitative ^{1}H and ^{13}C NMR data are treated as orthogonal measurements. Quantitative ^{13}C NMR supplies direct carbon-type information for normal paraffins, iso-paraffins, naphthenes, olefins, and aromatics. Quantitative ^{1}H NMR supplies a more sensitive hydrogen-type distribution that constrains aromatic substitution, olefin class, alkyl-chain length, terminal-group abundance, and branch density. This white paper extends, rather than duplicates, the April 2026 Process NMR Associates ^{13}C NMR Branching Research Brief. Its verified n-paraffin α/β/γ/δ/ε assignments, S_2-S_8 iso-paraffin assignments, Grant-Paul additivity rules, BI/FCI calculations, Chevron branches-per-100-carbon methodology, ACL and IP/NP parameters, Zhang viscosity-index ridge regression, and ExxonMobil/Chevron/Shell patent landscape are used as the controlling saturated-hydrocarbon foundation [1-6, 13, 49-60].

The differentiating work is placed on the proton-side framework and sp^2-carbon chemistry. Williams-type ^{1}H regions are organized as aromatic H at 6.0-9.0 ppm, olefinic H at 4.5-6.0 ppm, α-H at 2.0-4.0 ppm, β-H at 1.0-2.0 ppm, and γ-H at 0.5-1.0 ppm. Terminal vinyl $=CH_2$ near 4.9-5.0 ppm, terminal vinylic =CH- near 5.7-5.8 ppm, internal =CH- near 5.3-5.4 ppm, and vinylidene $=CH_2$ near 4.7 ppm are paired with ^{13}C assignments. This paired treatment is required for raw Fischer-Tropsch liquids, GTL intermediates, cracked products, PAO intermediates, and hydrofinished base oils [21-24, 28-33, 47, 48, 52, 57].

Aromatic analysis is expanded from a single aromatic-carbon percentage to ring type and substitution. Total aromatic H and C are reconciled with monoaromatic, diaromatic, and polyaromatic distributions; protonated, substituted, and bridgehead carbons are distinguished; and the Edwards DEPT-45 correction is used where bridgehead and nonprotonated carbon would otherwise be underestimated. Brown-Ladner and Sarpal ^{1}H-only routes are retained as model-derived estimates and are cross-checked against direct ^{13}C aromaticity and ASTM D5292-style aromatic H/C measurements [7-20, 25, 27, 34-36, 42-45].

All industrial review issues are integrated into the method architecture. Direct hydrogen and carbon fractions are kept separate from mass fractions, average-molecule outputs, chemometric predictions, and patent-defined parameters. Process stage, additives, matrix-specific T_1, $Cr(acac)_3$ response, temperature, viscosity, solvent, baseline, DEPT/APT/GASPE transfer efficiency, trace-level detection capability, molecular-weight distribution, and average-structure nonuniqueness are treated as controlled variables. The deliverable is framed as a reconciled molecular ledger with explicit residual and uncertainty terms.

Central conclusion

No single NMR scalar defines a petroleum base stock. BI, FCI, branches per 100 carbons, IP/NP, ACL, aromatic H/C, olefinic H/C, naphthenic carbon, carbon-number distribution, and average molecular weight are different projections of the same molecular ensemble. A defensible industrial result is obtained only when those projections are reconciled under a stated sample definition and acquisition protocol.

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1. Strategic Scope, Foundational Inheritance, and Measurement Architecture

1.1 Purpose and source inheritance

The April 2026 Process NMR Associates research brief established the saturated-hydrocarbon foundation needed for detailed ^{13}C NMR branching analysis. Its verified tables for n-paraffinic α, β, γ, δ, and ε carbons; iso-paraffinic S_2 through S_8 structures; naphthenic-carbon windows; Grant-Paul chemical-shift additivity; and industry branching equations are not re-derived at length. They are incorporated by reference and used as the internal calibration grid for the extended orthogonal workflow [1-6, 11-13, 49-60].

The new effort addresses the information lost when petroleum products are described only by saturated-carbon branching. Olefinic functionality can be the primary process indicator in a raw FT liquid, oligomerization intermediate, or hydrofinishing feed. Aromatic substitution and condensation can control solvency and oxidation behavior in Group I material, extracts, or aromatic base stocks. Naphthenic carbons can dominate density and solvency while remaining poorly separated from branch-proximal methylenes in one-dimensional ^{13}C spectra. Each class must therefore be resolved to the degree justified by the data and reconciled with the other classes [13, 21-45].

The intended output is not a molecule-by-molecule inventory. Petroleum base stocks are distributions. The proper output is a set of average, class-level, and topology-sensitive descriptors with documented assumptions. Two products with the same average carbon number may differ materially in branch position, uninterrupted methylene length, ring content, unsaturation type, aromatic substitution, and molecular-weight breadth. Those differences become visible only when the NMR observables and calculation basis remain explicit.

1.2 The molecular ledger and measurand hierarchy

The recommended interpretive structure is a molecular ledger. Hydrogen-side entries are aromatic H, olefinic H, α-H, β-H, γ-H, terminal methyl H, and branch-associated methyl H. Carbon-side entries are aromatic C, olefinic C, normal-paraffinic C, iso-paraffinic C, naphthenic C, carbon multiplicity, terminal-group C, recurring free-methylene C, branch-center C, quaternary C, and unassigned C. Average molecular weight, elemental H/C, density, refractive index, carbon-number distribution, and physical properties are balancing variables. A ledger is closed only when the calculated classes and average-molecule constraints are mutually credible and the residual is reported.

A recurrent industrial dispute is resolved by this hierarchy: the same spectral feature can have several legitimate meanings depending on the denominator. A 29.8 ppm integral may be expressed as percent total carbon, percent aliphatic carbon, average free carbon per molecule, or an input to a patent-defined window. A methyl integral may be a fraction of total hydrogen, non-benzylic aliphatic hydrogen, total carbon, or branch count. Numerical similarity does not establish analytical equivalence.

Table 1. Measurand hierarchy for orthogonal petroleum NMR.

Level	Representative output	Denominator / basis	Industrial interpretation	Primary risk
Direct spectral integral	Olefinic H, aromatic C, 29.8 ppm area	Total detected H or C, or a defined subregion	Closest to the measurement; comparable only under matched acquisition and processing	Baseline, overlap, relaxation, integration-boundary bias
Converted composition	Olefin wt%, aromatic wt%, PONA/PIONA fraction	Average molecular formula or class response model	Composition or conversion estimate	Model dependence and nonunique average structure
Topology parameter	BI, FCI, branches per 100 C, IP/NP, ACL	Patent- or literature-specific denominator	Branch amount, branch location, or unperturbed chain length	False equivalence among calculation recipes
Average-molecule parameter	Average rings, side-chain length, substitution	Elemental analysis and MW constrained by NMR	Structural comparison of complex mixtures	Distribution collapsed into a nonunique average molecule
Property prediction	Predicted VI, pour point, cetane, oxidation response	Empirical or chemometric model	Screening, process control, product development	Applicability-domain failure and confounding variables

1.3 Scope boundaries and product classification

The framework applies to petroleum lubricant base oils, highly paraffinic wax isomerates, FT waxes, GTL diesel and jet-range streams, synthetic paraffinic kerosene components, PAO intermediates and finished PAO, and selected aromatic or naphthenic base stocks. It can be extended to formulated lubricants only when additive contributions are separated or modeled. Antioxidants, detergents, dispersants, viscosity modifiers, esters, alkylated aromatics, polyisobutylene, and pour-point depressants can contribute in every region of interest. A formulated oil cannot be treated as a neat base oil merely because base oil dominates the mass.

API Groups I through V are product-classification categories, not NMR spectra. Groups I through III are defined through saturates, sulfur, and viscosity-index criteria; Group IV is PAO; Group V is a heterogeneous residual category. NMR can establish molecular architecture consistent with a claimed class, but it cannot independently certify the API group. GTL and hydroisomerized wax base stocks can exhibit Group III performance while retaining a structural history different from hydrocracked mineral base oil. PAO and FT-derived isoparaffins are not structurally interchangeable simply because both are synthetic and highly saturated.

2. Complete ^{1}H Proton-Type Framework

2.1 Williams-type integration regions

The Williams proton classification remains a practical starting point because it partitions the petroleum ^{1}H spectrum into chemically interpretable hydrogen classes without requiring molecule-specific assignment [7-9]. Aromatic hydrogen is integrated from approximately 6.0 to 9.0 ppm. Olefinic hydrogen is integrated from approximately 4.5 to 6.0 ppm. The α-H region from 2.0 to 4.0 ppm contains benzylic hydrogens, allylic hydrogens, and selected naphthenic or heteroatom-adjacent environments. The β-H region from 1.0 to 2.0 ppm contains much of the methylene and methine population in alkyl chains and naphthenic rings. The γ-H region from 0.5 to 1.0 ppm contains terminal and branched methyl hydrogens.

These boundaries are operational rather than fundamental. Allylic hydrogen encroaches on the lower α-H region. Highly substituted or conjugated olefins can approach the aromatic edge. Naphthenic methines and bridge-adjacent methylenes cross the β-H/α-H boundary. A reproducible method therefore requires locked integration limits, documented solvent and impurity exclusions, and a line-shape check on representative materials. Boundaries validated for light naphtha should not be transferred to viscous base oil without confirming that broadening and overlap have not changed the measurand.

Table 2. Operational ^{1}H regions and structural meaning.

Region	Approximate δ (ppm)	Dominant proton types	Primary structural use	Principal confounders
Aromatic H	6.0-9.0	Ring protons on mono-, di-, and polyaromatics	Aromatic H fraction, H/C, substitution and condensation	Conjugated olefin edge; additive aromatics; trace baseline
Olefinic H	4.5-6.0	Terminal vinyl, vinylidene, internal alkene H	Olefin class, residual unsaturation, FT/GTL process state	Aromatic-edge overlap; model-dependent conversion to wt%
α-H	2.0-4.0	Benzylic, allylic, ring-junction, heteroatom-adjacent H	Aromatic substitution, allylic content, side-chain attachment	Several chemical classes share the interval
β-H	1.0-2.0	Chain CH_2/CH and naphthenic H	Alkyl-chain and ring contribution; Hβ/Hγ constraint	Severe overlap; viscosity- and temperature-dependent line shape
γ-H	0.5-1.0	Terminal and branch CH_3	BI, terminal-group abundance, branch density	Terminal/branch methyl overlap; low-field resolution

2.2 Olefinic substructure in the ^{1}H spectrum

The olefinic envelope must be subdivided whenever FT, GTL, cracked, oligomerization, or partially hydrofinished streams are examined. A terminal α-olefin R-CH=CH_2 generally exhibits terminal vinyl protons near 4.9-5.0 ppm and

the substituted vinylic proton near 5.7-5.8 ppm. A vinylidene group $R_2C=CH_2$ exhibits its two protons near approximately 4.65-4.75 ppm and lacks the terminal =CH- proton of a simple α-olefin. Internal cis/trans olefins generally contribute around 5.25-5.45 ppm. In complex mixtures, cis and trans forms may be distinguishable only as line-shape or centroid differences and should not be over-quantified without standards or separation.

The allylic envelope near roughly 1.7-2.2 ppm supplies support but is less selective because benzylic and naphthenic hydrogens overlap. Assignment of a terminal α-olefin should be supported by both the 4.9-5.0 ppm $=CH_2$ contribution and the 5.7-5.8 ppm =CH- contribution, with a plausible integral ratio after relaxation and baseline controls. A feature near 4.7 ppm without the terminal vinylic proton supports vinylidene functionality, but solvent, additive, and impurity signals must be excluded.

2.3 ^{1}H-only structural-parameter routes

Brown and Ladner used hydrogen-type distributions and elemental H/C to estimate carbon aromaticity in coal-like and petroleum-derived materials [7]. The calculation converts aliphatic-hydrogen fraction into an estimated aliphatic-carbon fraction through an assumed average aliphatic H/C ratio; aromaticity is obtained by difference. The method remains useful when ^{13}C sensitivity is inadequate, but branching, naphthenic rings, olefins, and heteroatom-adjacent carbon alter the effective aliphatic H/C ratio. The result must be labeled a model-derived estimate and reconciled with quantitative ^{13}C data whenever possible.

Sarpal and co-workers developed direct estimation of aromatic carbon content of base oils from ^{1}H NMR [25]. The route is attractive for routine work because ^{1}H NMR is sensitive and fast. It remains dependent on aromatic H, benzylic/α-H, total H/C, and assumed aromatic substitution. In highly hydroprocessed base oils, aromatic H approaches the practical LOQ; in heavily substituted or condensed systems, aromatic H can be small while aromatic C is appreciable. The ^{1}H-only C_a result should be checked against quantitative ^{13}C aromatic carbon, DEPT-derived protonated aromatic carbon, and elemental H/C.

Hβ/Hγ constrains average alkyl-chain length because terminal methyl hydrogen grows more slowly than interior-chain hydrogen as chain length increases. The α-H/aromatic-H ratio constrains aromatic substitution because each alkyl substituent introduces benzylic hydrogen while replacing an aromatic proton. These ratios are useful only after allylic and naphthenic contributions have been addressed. A high α-H/aromatic-H ratio can indicate extensive alkyl substitution, but it can also reflect an olefin-rich FT stream or naphthenic ring-junction hydrogen.

2.4 Quantitative ^{1}H integration

Quantitative ^{1}H NMR is often treated as automatic because proton T_1 values are shorter than carbon T_1 values. That assumption should not be accepted without verification. Relaxation delay must be sufficient for the longest relevant proton class, the pulse angle must be calibrated, receiver gain must be linear, and the baseline must remain stable across the intense aliphatic envelope and trace olefinic/aromatic regions. Highly viscous or waxy samples can show broadened signals and temperature-dependent integration. Dissolution, equilibration, and sample temperature therefore belong in the SOP.

For trace olefin and aromatic measurements, signal-to-noise and baseline uncertainty must be converted into class-specific detection and quantitation limits. A visually detectable feature is not automatically quantitative. Conversion of olefinic-H fraction to olefin wt% requires the number of olefinic hydrogens per average olefin molecule and average molecular weight. Terminal α-olefin, internal olefin, and vinylidene structures do not contribute the same proton pattern per unit mass. Direct olefinic-H fraction should be reported separately from modeled olefin wt%.

3. Olefinic Carbon and Proton Identification

3.1 Paired ^{1}H/^{13}C assignments

Olefin analysis is weighted heavily because raw and partially upgraded FT/GTL streams can be rich in α-olefins while final hydrofinished base oils are expected to contain very little reactive unsaturation. A saturated-carbon

branching analysis can therefore be technically detailed but process-incomplete. Presence, absence, and class of olefinic functionality must be treated as direct process-history indicators [21-24, 28-33, 47, 48, 52, 57].

The $=CH_2$ carbon of R-CH=CH_2 is commonly observed at approximately 108-115 ppm, while the substituted =CH- carbon appears near 138-140 ppm. The corresponding ^1H signals occur near 4.9-5.0 and 5.7-5.8 ppm. Internal olefinic carbons cluster near approximately 129-131 ppm, with cis/trans geometry, chain length, branching, and conjugation producing dispersion. Vinylidene $R_2C=CH_2$ retains a lower-range $=CH_2$ carbon and a more substituted quaternary sp^2 carbon at higher shift; the ^1H feature near 4.7 ppm lacks a corresponding terminal =CH- proton.

Table 3. Coupled olefinic assignments for petroleum hydrocarbon mixtures.

Olefin class	Diagnostic ^1H signals	Diagnostic ^{13}C signals	Process interpretation	Qualification
Terminal vinyl, R-CH=CH_2	$=CH_2$ about 4.9-5.0; =CH- about 5.7-5.8 ppm	$=CH_2$ about 108-115; =CH- about 138-140 ppm	Primary FT α-olefin marker; loss indicates hydrogenation, isomerization, oligomerization, or conversion	Integral ratio and paired carbon signals should be plausible
Vinylidene, $R_2C=CH_2$	$=CH_2$ about 4.65-4.75 ppm; no terminal =CH- H	$=CH_2$ in lower olefinic range; substituted quaternary sp^2 C higher	Oligomerization, skeletal rearrangement, or PAO/intermediate history	Quaternary carbon is absent from DEPT and may have long T_1
Internal cis/trans olefin	=CH- about 5.25-5.45 ppm	Olefinic CH commonly about 129-131 ppm	Double-bond migration or incomplete hydrogenation	Cis/trans quantitation usually requires standards or separation
Conjugated or styrenic olefin	May extend toward 5.8-6.5 ppm	Overlaps the broader aromatic sp^2 region	Cracked/aromatic stream or additive contribution	Separate from aromatic H/C by paired and orthogonal evidence

3.2 Cookson-Smith FT abundance determinations

Cookson and Smith demonstrated that ^{13}C NMR can determine structures and abundances of alkanes and olefins in Fischer-Tropsch products rather than merely report bulk unsaturation [21-24]. Their work connected terminal and branch carbon assignments to hydrocarbon abundance, average chain length, and boiling range. The methodological significance is that an olefin-rich FT stream can be described in terms of terminal versus internal unsaturation and normal versus branched chains, while the same carbon grammar can be carried into hydroisomerized and hydrofinished products.

The abundance calculation must be matched to the actual distribution. A raw FT condensate can contain a homologous series of α-olefins and n-alkanes. An upgraded stream may contain isomerized internal olefins, branched paraffins, cracked products, and residual oxygenates. A base-oil precursor may contain wax-range material that is only partly soluble at ambient temperature. The Cookson-Smith precedent supports abundance analysis, but it does not remove the need for carbon-number distribution, average molecular weight, and process-stage definition.

For an FT α-olefin series, ^1H NMR supplies a sensitive terminal-vinyl count while ^{13}C NMR confirms carbon class. When one terminal double bond per molecule is assumed, the terminal-vinyl hydrogen count can be related to molar abundance. Conversion to mass fraction requires an average olefin molecular weight constrained by simulated distillation, GC, FIMS, or another carbon-number method rather than inferred from a single NMR integral.

3.3 PONA and PIONA by NMR

NMR-based PONA and PIONA methods estimate paraffins, iso-paraffins, olefins, naphthenes, and aromatics from ^1H and, where used, ^{13}C distributions [28-33, 47, 48]. Straight-run gasoline methods established paraffin/naphthene/aromatic partitions; cracked-gasoline methods introduced explicit olefin treatment. Later dynamic approaches combined proton-region integrals with average chain length, molecular weight, bromine number, detailed hydrocarbon analysis, reformulyzer data, or simulated distillation.

These methods are useful models for FT/GTL analysis because they demonstrate how rapid ^1H measurements can be converted into hydrocarbon-class composition when response models and molecular assumptions are declared. They should not be transferred unchanged from naphtha to waxy base-oil fractions. Heavy materials have broader lines, higher viscosity, different average carbon number and olefin distributions, and potential solubility problems. The transferable

principle is a calibrated hydrogen balance constrained by carbon-side evidence and independent boiling-range or molecular-weight data.

3.4 Hydrofinishing control and sample history

Residual olefins can accelerate oxidation, color development, gum formation, and deposit-precursor chemistry. Chevron US7578926B2 uses ^{1}H NMR-defined olefin content as a control point for hydrofinishing and oxidation stability of base oils [57]. The relevant measurand must still be stated: total olefinic-H fraction is direct, olefin wt% is model-derived, and a patent-defined control value is recipe-specific. The raw regional integral, structural assignment, converted metric, LOQ, average molecular assumption, and matrix blank should all be retained.

Sample handling can change the result. FT α-olefins can isomerize or oxidize; volatile light olefins can be lost; wax crystallization can create a nonrepresentative aliquot; and oxygen exposure can alter trace unsaturation. Heated homogenization, sealed transfer, documented holding time, and replicate preparation are part of the analytical method, not housekeeping details.

3.5 Orthogonal confirmation and discrepant evidence

NMR should be paired with bromine number or iodine value for bulk unsaturation, GC or GC×GC for carbon-number and isomer distributions, simulated distillation for boiling range, and mass spectrometry for molecular classes when the decision is consequential. Those methods do not replace NMR; they constrain different failure modes.

Olefinic ^{1}H without observable olefinic ^{13}C does not automatically mean the proton signal is false. Trace ^{13}C may lie below the signal-to-noise of a branch-focused acquisition. More scans, greater concentration, a cryoprobe, or 2D ^{1}H-^{13}C correlation may be required. Conversely, broad sp^2 carbon without matching olefinic H may represent quaternary olefinic carbon, aromatic carbon, or a long-T_1/baseline artifact. The discrepancy is diagnostic and should be resolved rather than averaged away.

4. Saturated and Naphthenic Carbon Architecture

4.1 Inherited normal-paraffin and iso-paraffin assignments

The foundational brief remains the controlling source for detailed saturated-carbon calculations. Normal paraffins are tracked by terminal CH_3 carbon at approximately 14.1 ppm, β-CH_2 at approximately 22.7 ppm, γ-CH_2 at approximately 31.9-32.0 ppm, and recurring δ/ε interior methylene carbon near approximately 29.4-29.9 ppm [1-6]. As chain length increases, the interior-methylene response becomes dominant and supplies the free-methylene information used in several industrial branch metrics.

Iso-paraffinic assignments are described by the S_2-S_8 system established in the base-oil literature and inherited from the April 2026 brief. The labels encode branch type and branch position through branch methyl, methine, and branch-proximal carbon resonances. Their value is not molecule-by-molecule reconstruction; it is the comparison of compatible branch-environment populations across hydrocracked, hydroisomerized, CTL, FT, and PAO-related materials [4-6, 26].

Table 4. Inherited saturated-carbon assignment anchors.

Structural class	Label	Approximate δ ^{13}C (ppm)	Detected atom / meaning	Use
n-Paraffin terminus	Cα	14.1	Terminal CH_3	Chain-end count and ACL
n-Paraffin second carbon	Cβ	22.7	β-CH_2	Normal-chain confirmation
n-Paraffin third carbon	Cγ	31.9-32.0	γ-CH_2	Normal-chain confirmation
n-Paraffin interior	Cδ/Cε	29.4-29.9	Recurring interior CH_2	Free-methylene, FCI, branch proximity
2-Methyl / isopropyl end	S_2	about 28.2	Branch-point CH	Near-end methyl branching
3-Methyl branch	S_3	about 11.4	Branch CH_3	Near-end branch type

Structural class	Label	Approximate δ ^{13}C (ppm)	Detected atom / meaning	Use
Ethyl branch	S_3'	about 10.7	Terminal CH_3 of ethyl branch	Ethyl-branch population
4-Methyl branch	S_4	about 14.2	Branch CH_3	Branch-position distribution
5-Methyl branch	S_5	about 14.3	Branch CH_3	Branch-position distribution
Mid-chain methyl branch	S_{67}	about 27.0	Branch-point CH	VI-sensitive central branching
Geminal dimethyl	S_8	24.0-25.6	CH_3 near a densely substituted center	Dense branching / unfavorable VI indicator

4.2 Naphthenic carbon and proton contributions

Naphthenic carbons form a broad, overlapping ^{13}C envelope from approximately 24 to 60 ppm. Unsubstituted cyclopentyl CH_2 environments often occur around 24.5-26.5 ppm, while cyclohexyl CH_2 environments are commonly observed around 26.5-28.5 ppm. Substituted ring methines, ring-junction carbons, and side-chain attachment carbons extend to higher chemical shift. These regions overlap normal-chain and branch-proximal methylenes, making naphthenic carbon the least direct of the major hydrocarbon-class measurements [11-13, 21, 22, 44-46].

Proton evidence is also overlapped. Naphthenic methylene and methine hydrogen contributes substantially to 1.0-2.2 ppm, with bridgehead or substituted positions extending toward the α-H region. A broad high-field envelope can support a naphthenic interpretation but cannot determine ring size or ring count by itself. Ring analysis is improved by DEPT/APT, average H/C, density, molecular weight, and mass-spectral Z-number distribution.

A common subtraction approach estimates naphthenic carbon after assigned normal- and iso-paraffinic contributions have been removed. That procedure is sensitive to every upstream assignment. A missed branch-proximal methylene becomes apparent naphthenic carbon; a baseline error under the 29.8 ppm peak changes both paraffinic and naphthenic balances. Reports must identify whether naphthenic carbon was measured by a direct region, a fitted spectral model, or residual subtraction.

4.3 Grant-Paul additivity and assignment discipline

Grant and Paul established the additive relationship used to predict ^{13}C chemical shifts in alkanes [1, 2]. The shift of a carbon is represented as a base value plus contributions from neighboring carbons at α through ε positions and steric corrections. The negative γ contribution expresses gamma-gauche shielding and explains why branch, conformation, and neighboring substitution are visible in petroleum ^{13}C spectra.

$$\delta C = B + \Sigma(n_i A_i) + S \quad (1)$$

For the inherited parameterization, B is approximately -2.3 ppm; α, β, γ, δ, and ε contributions are approximately +9.1, +9.4, -2.5, +0.3, and 0.0 ppm, respectively. Representative steric terms are about -1.1 ppm for tertiary substitution, -3.4 ppm for quaternary substitution, -3.7 ppm for adjacent 3°-3° centers, -8.4 ppm for 3°-4°, and -12.5 ppm for 4°-4°. These values explain why nominally similar methyl and methylene carbons occupy different branch regions.

Table 5. Grant-Paul parameters inherited from the foundational brief.

Term	Value (ppm)	Structural meaning
Base value, B	-2.3	Reference contribution in the additivity model
α effect	+9.1	Directly bonded carbon contribution
β effect	+9.4	Second-neighbor contribution
γ effect	-2.5	Gamma-gauche shielding
δ effect	+0.3	Fourth-neighbor contribution
ε effect	0.0	Longer-range contribution in the simplified model
Steric corrections	Tertiary -1.1; quaternary -3.4; 3°-3° -3.7; 3°-4° -8.4; 4°-4° -12.5	Crowding and adjacent high substitution

The additivity model should test assignments, not create false molecular specificity. Many petroleum structures contribute within a narrow shift band, and temperature, solvent, concentration, and unresolved conformations broaden the response. A peak name should represent a population of compatible environments unless a model compound, 2D correlation, or fractionation experiment establishes greater specificity.

4.4 Parallel branch nomenclature: S_2-S_8 and α′/β′/γ′ with P/T labels

US6210559B1 introduced a complementary branch vocabulary for FT diesel fuels and blend stocks [52]. Free-end methylene carbons are described as α, β, and γ relative to a normal chain end, while branch-perturbed carbons are α′, β′, and γ′. The patent also distinguishes pendant branches, P, from terminal branch-related groups, T, for methyl, ethyl, propyl, and butyl environments. This vocabulary is especially useful when branch placement is connected to cetane and cold-flow behavior.

The P/T system should be reported alongside, not substituted for, S_2-S_8. S_2-S_8 is more directly connected to lubricant-base-oil branch correlations and the Zhang VI model. α′/β′/γ′ and P/T are more directly connected to the FT diesel optimization logic of US6210559. Both describe topology, but their bins and denominators differ. Recalculation from the underlying spectrum is required before values are compared.

Table 6. Crosswalk between branch-description systems.

System	Representative signals / labels	Primary object	Best use	Non-equivalence warning
S_2-S_8	S_2, S_3, S_3', S_4, S_5, S_{67}, S_8	Specific branch structures and positions in base-oil ^{13}C spectra	VI, pour point, and base-oil branch interpretation	Signal populations do not map one-to-one to P/T counts
US6210559 branch-perturbed	α′ about 19.8; β′ about 37.4; γ′ about 27.4 ppm	Carbons perturbed by a nearby branch	FT diesel/blend-stock cetane and cold-flow optimization	Perturbed carbon count is not branch-center count
Pendant / terminal labels	P methyl about 19.6 vs T methyl about 22.5; P ethyl CH_3 about 10.8 vs T ethyl about 11.3 ppm	Branch group position relative to main chain	Pendant-versus-terminal topology	Chemical shifts are matrix- and temperature-dependent
Free end / interior	α about 22.8; β about 32.0; γ about 29.5; free interior about 29.9 ppm	Unperturbed end and interior chain carbons	Free-chain length and branch proximity	Overlaps conventional n-paraffin and FCI regions

5. Aromatic Ring-Type Analysis

5.1 Total aromatic hydrogen and carbon

Aromatic content must be described by more than a single aromatic-carbon percentage when structural interpretation is required. Monoaromatic, diaromatic, and polyaromatic systems differ in H/C, substitution density, bridgehead carbon, solvency, polarity, oxidation behavior, and environmental significance. In highly hydroprocessed base oils, aromatic signals can be near the practical LOQ. In Group I base oils, extracts, cycle oils, clarified oils, and heavy fractions, the aromatic envelope can dominate the structural description [13-15, 19, 25, 27, 34-36, 42-45].

Total aromatic H is measured from 6.0-9.0 ppm under validated quantitative conditions. Total aromatic C is commonly measured from approximately 110-160 ppm in quantitative inverse-gated ^{13}C spectra. Protonated aromatic carbons are concentrated approximately at 118-130 ppm, while substituted and bridgehead carbons occupy overlapping regions extending through about 130-150 ppm. Exact boundaries depend on ring type, substitution, heteroatoms, and conjugation.

Low aromatic H with measurable aromatic C indicates high substitution, high condensation, or both. Measurable aromatic H with unexpectedly low aromatic C can indicate inadequate carbon sensitivity, incomplete relaxation, or incorrect proton assignment. The orthogonal comparison is therefore a diagnostic control, not merely a duplicate result.

5.2 Monoaromatic, diaromatic, and polyaromatic distribution

Bansal and co-workers estimated total aromatics and their distribution as monoaromatic and global di-plus aromatic classes in diesel-range products by NMR [27]. The method uses the different H/C balances associated with ring condensation and substitution. A monoaromatic ring normally carries a higher aromatic H/C ratio than a condensed diaromatic or polyaromatic system at comparable substitution. When protonated and nonprotonated aromatic carbon are separated, ring-class distribution is constrained more effectively than by total aromatic carbon alone.

"Di-plus" is operational. It does not imply that each molecule has been assigned as exactly diaromatic or polyaromatic. It is a global condensed-aromatic contribution derived from average spectral balances. The output is suitable for class comparison and process monitoring, not as a substitute for molecular speciation by chromatography or high-resolution mass spectrometry.

5.3 Protonated, substituted, and bridgehead aromatic carbon

Protonated aromatic carbon is directly related to aromatic H, whereas substituted and bridgehead carbon has no attached proton. A quantitative ^{13}C spectrum integrates all aromatic carbon but does not separate these classes. DEPT-45 supplies positive response from protonated aromatic CH and can be used with the quantitative spectrum to estimate the nonprotonated balance. APT and selected spin-echo methods provide additional multiplicity discrimination.

The Edwards DEPT-45 correction addresses bridgehead and other nonprotonated aromatic carbon that can be underestimated when structural parameters are calculated from uncorrected protonated-carbon response or assumptions that do not account for the nonprotonated balance. In aromatic-rich petroleum materials, the correction can increase inferred condensed-ring contribution and materially change average ring-size estimates [13, 14]. The correction must be calibrated against actual DEPT transfer behavior and the quantitative total aromatic integral. DEPT response is not inherently quantitative.

Table 7. Aromatic descriptors and their evidentiary meaning.

Descriptor	Primary NMR evidence	Interpretation	Main confounder
Total aromatic H	^{1}H 6.0-9.0 ppm	Direct ring-proton fraction; sensitive trace screen	Conjugated olefin overlap and additive aromatics
Total aromatic C	Quantitative ^{13}C about 110-160 ppm	Direct carbon aromaticity, f_a	Long T_1, low sensitivity, sp^2 boundary overlap
Protonated aromatic C	DEPT-45 aromatic CH or HSQC support	Aromatic CH fraction and H/C constraint	Transfer efficiency and response nonuniformity
Substituted aromatic C	Total aromatic C minus protonated and bridgehead estimates	Alkyl or heteroatom substitution density	Residual calculation compounds upstream errors
Bridgehead / ring-junction C	Corrected nonprotonated aromatic balance	Condensation and average ring-size constraint	Overlap with substituted carbon; model dependence
Mono / di-plus distribution	Combined aromatic H/C and carbon-type balance	Operational ring-class distribution	Average-class result, not molecular identification

5.4 ASTM D5292 as a historical analytical anchor

ASTM D5292 historically provided procedures for aromatic hydrogen and aromatic carbon contents of hydrocarbon oils by high-resolution NMR [42]. The standard has been withdrawn, but its measurement logic remains a useful anchor. Proton procedures determine aromatic H, while the carbon procedure uses inverse-gated decoupled ^{13}C NMR, a relaxation agent such as $Cr(acac)_3$, and aromatic-versus-aliphatic integration. It defines the total aromatic H/C problem; it does not resolve mono versus di-plus aromatics or substituted versus bridgehead carbon.

A current laboratory should not claim conformance to a withdrawn standard without qualification. It can state that an ASTM D5292-style or historically aligned procedure was used and provide modern validation. Method status, instrument field, matrix, relaxation study, calibration, LOD/LOQ, and deviations should be stated. The historical method is best used as a bridge to legacy datasets.

5.5 Aromatic confounders

Additive aromaticity can dominate trace base-oil aromatic measurements. Phenolic and aminic antioxidants, alkylated aromatic carriers, detergent components, friction modifiers, and viscosity-modifier fragments can contribute aromatic H and C. An additive-containing finished lubricant must be analyzed after base-oil separation, with an additive blank, or through a validated deconvolution model. The uncertainty is fundamentally different from that of a neat base oil.

Conjugated olefins and styrenic structures can overlap the lower aromatic-proton and aromatic-carbon regions. Heteroatom-substituted aromatics can lie outside conventional hydrocarbon subregions. In heavy fractions, paramagnetic species and viscosity can broaden and attenuate signals. Reports should distinguish total sp^2 carbon, assigned aromatic carbon, and assigned olefinic carbon when the boundary cannot be closed confidently.

6. Multiplicity Editing and Quantitative Acquisition

6.1 Quantitative ^{13}C acquisition requirements

Quantitative ^{13}C NMR requires more discipline than a visually clean spectrum. Inverse-gated ^{1}H decoupling suppresses differential nuclear Overhauser enhancement. $Cr(acac)_3$ is commonly used to shorten T_1. Delays of at least five times the longest relevant T_1 are preferred for absolute carbon quantitation. Concentrations around 15-25 wt% in $CDCl_3$ are often practical for liquid base oils, while waxes and heavy fractions may require higher temperature, alternate solvents, or modified concentration [16-18, 21, 24, 37, 38, 42].

Those conditions are starting points, not universal guarantees. $Cr(acac)_3$ does not necessarily shorten aromatic, olefinic, quaternary, and aliphatic carbon equally. Oxygen, viscosity, concentration, temperature, and solvent change relaxation and line shape. A representative T_1 study should include the slowest expected classes, especially quaternary sp^2 carbon and low-level aromatic carbon. A branch-analysis acquisition optimized for intense aliphatic peaks may be inadequate for trace olefin or aromatic quantitation.

The method must state pulse angle, calibrated pulse width, acquisition time, relaxation delay, decoupling mode, relaxation-agent concentration, temperature, scans, spectral width, digital resolution, apodization, phasing, baseline correction, integration boundaries, and line fitting. In a patent comparison, a small delay or boundary difference can determine whether a sample falls inside or outside a claimed range.

Table 8. Quantitative ^{13}C controls and failure modes.

Control	Preferred practice	Failure if uncontrolled	Verification
Decoupling	Inverse-gated ^{1}H decoupling	Differential NOE biases $CH_3/CH_2/CH$/quaternary integrals	Compare gated and continuously decoupled representative spectra
Relaxation	Measure representative T_1; use at least 5× the longest relevant T_1	Long-T_1 aromatic, olefinic, or quaternary carbon is undercounted	Inversion- or saturation-recovery study
Relaxation agent	Matrix-specific $Cr(acac)_3$ concentration and mixing control	Nonuniform relaxation, precipitation, line broadening	Concentration series and recovery study
Temperature	Controlled, equilibrated, above wax clouding when needed	Phase separation, viscosity broadening, shift drift	Temperature challenge and replicate aliquots
Concentration / solvent	Documented wt% and complete dissolution	Shift changes, line broadening, selective insolubility	Mass balance and homogeneity check
Signal-to-noise	Set for the weakest class to be quantified	False precision at trace olefin/aromatic levels	Blank, spike, and replicate LOQ study
Processing	Locked phase, baseline, apodization, and integration SOP	Analyst-dependent results and FCI drift	Reprocessing reproducibility and blind analyst check

6.2 DEPT-45/90/135 and APT

DEPT-45 generally displays protonated CH, CH_2, and CH_3 with the same phase; DEPT-90 emphasizes CH; DEPT-135 displays CH and CH_3 in one phase and CH_2 in the opposite phase. Quaternary carbon is absent. In saturated base

oils, DEPT-90 is useful for branch methines, while DEPT-135 separates methyl/methine contributions from methylene-rich chain carbon. APT includes quaternary carbon and is useful as a check in PAO or highly branched material.

Neither DEPT nor APT should be treated as quantitatively uniform without validation. Transfer depends on one-bond ^{1}JCH, pulse calibration, relaxation during the sequence, and line broadening. Petroleum mixtures contain distributions of couplings and T_1/T_2. Branch counts should be normalized to a quantitative single-pulse carbon denominator and supported by response-factor studies using representative model compounds or characterized reference materials.

6.3 Shell GASPE and spin-echo alternatives

Shell patent practice uses GASPE, a gated spin-echo editing strategy, with vapor-pressure osmometry and field-ionization mass spectrometry to characterize FT-derived base oils and greases [58-60]. The method supplies multiplicity information supporting average branch number, side-chain distribution, ring content, and carbon-number/Z-number distributions. Shell's descriptor space is deliberately different from ExxonMobil BI/FCI and Chevron branches-per-100-carbon language.

GASPE can be advantageous for selected waxy materials and multiplicity classes, but it is not automatically a universal quantitative replacement for DEPT or APT. Echo timing, coupling evolution, relaxation, temperature, and viscosity must be matched to the matrix. Patent comparisons should reproduce the relevant protocol as closely as practical and document every deviation.

6.4 Temperature, viscosity, phase behavior, and 2D support

Temperature control is essential for FT waxes, heavy GTL intermediates, and high-viscosity base oils. A sample homogeneous at 50 °C can partially crystallize at room temperature and leave a liquid phase depleted in high-carbon-number normal paraffins. The tube should be equilibrated at the acquisition temperature, inspected for phase separation, and mixed under a controlled protocol before each replicate. Chemical shifts and line widths change with temperature, concentration, and solvent, especially in the 29.6-29.9 ppm free-methylene region and closely spaced branch peaks.

HSQC, HMBC, COSY, TOCSY, J-resolved, and diffusion-edited experiments can resolve disputed assignments and distinguish additive, olefinic, and aromatic contributions. HSQC is useful for pairing terminal-vinyl ^{1}H and ^{13}C; HMBC can connect branch methyls to branch centers; DOSY can sometimes separate lower-MW additives from base-oil envelopes. These experiments are generally not primary quantitative measurements because transfer efficiencies and relaxation vary.

7. Branching Metrics and Combined-NMR Average Molecular Parameters

7.1 Equations and denominators

The principal branching equations are inherited from the April 2026 brief and summarized here only to complete the orthogonal framework. They are not interchangeable because they use different nuclei, regions, and denominators. Every result should carry the calculation name, equation, integration limits, and basis.

$$BI = 100 \times I_h(0.50\text{-}1.05\ ppm) / I_h(0.50\text{-}2.10\ ppm) \quad (2)$$

BI is a ^{1}H NMR ratio of non-benzylic methyl hydrogen to total non-benzylic aliphatic hydrogen under patent-defined limits [49-51]. It increases with methyl abundance but does not directly count branch centers. Normal chain-end methyl and branch methyl must be handled according to the applicable recipe.

$$FCI = xfree,C \times \bar{N}C / 100 \quad (3)$$

FCI converts the percentage of qualifying recurring free-methylene carbon into the average number of such carbons per molecule by multiplying by average carbon number [49-51]. The qualifying carbon definition, typically carbon sufficiently remote from chain ends and branches, must be taken from the applicable patent. FCI is not simply the percent area at 29.8 ppm.

$$Branches\ per\ 100\ C = 100 \times \bar{B} / \bar{N}C \quad (4)$$

Chevron's approach divides average branches per molecule by average carbon number and multiplies by 100 [53-56]. Branch count is obtained from edited ^{13}C populations and patent-specific assignment rules. Average carbon number may be approximated from MW for paraffinic material or obtained from a direct distribution.

$$ACL = 2 \times NP / NP\alpha \quad (5)$$

Average chain length is obtained from normal-paraffin carbon relative to terminal normal-paraffin CH_3, recognizing two chain ends per linear segment [4, 5]. NP and NPα must be defined consistently, and terminal groups from branches or cyclic substituents must not be misassigned.

$$IP/NP = IIP / INP \quad (6)$$

IP/NP is a class ratio under the inherited region map, not a branch count. A high IP/NP can arise from many branch-position distributions and does not substitute for S_2-S_8 analysis.

The Zhang ridge-regression relationship predicts viscosity index from an S_2-S_8 branch-variable vector [6]. It can be written as $VI = \beta_0 + \Sigma\beta_i x_i$, with the verified coefficient vector and preprocessing inherited from the foundational brief. The coefficients are specific to the CTL base-oil training set and should not be transplanted without external validation. The transferable finding is that mid-chain S_{67} branching was positively associated with VI, while selected ethyl and dense/geminal branch environments were unfavorable.

Table 9. Non-equivalence of common branch metrics.

Metric	Nucleus / data	What it measures	What it does not measure	Required companion
BI	^1H regional integration	Relative methyl-H abundance	Branch position or branch-center count	^{13}C branch assignments and MW
FCI	Quantitative ^{13}C plus average carbon number	Average unperturbed interior carbon per molecule	Total branching by itself	$\bar{N}C$ and validated 29.8 ppm assignment
Branches per 100 C	Edited ^{13}C plus $\bar{N}C$	Normalized branch-center abundance	Hydrogen branching index or free-chain length	Editing-response validation and MW
ACL	Normal-paraffin C and terminal CH_3	Average linear-segment length	Whole-molecule carbon number when rings/branches are present	NP assignment and terminal-group audit
IP/NP	Quantitative ^{13}C class populations	Iso- versus normal-paraffin balance	Specific branch topology	S_2-S_8 or P/T distribution
Zhang VI model	Multiple ^{13}C branch variables	Empirical VI prediction in model domain	Causal mechanism or universal VI	External validation, viscosity grade, carbon-number distribution

7.2 Clutter-Petrakis combined-NMR framework

Clutter, Petrakis, Stenger, and Jensen established the combined $^1H/^{13}C$ framework for average molecular parameters in petroleum fractions [9]. Elemental analysis and average molecular weight define an average molecular formula. Quantitative ^1H partitions hydrogen into aromatic, olefinic, α, β, and γ classes. Quantitative ^{13}C partitions carbon into aromatic, olefinic, paraffinic, iso-paraffinic, and naphthenic classes. Multiplicity editing further separates CH_3, CH_2, CH, and quaternary carbon.

The framework is powerful because every parameter has a spectral origin and a mass-balance consequence. If molecular weight increases while terminal methyl abundance remains constant, chain length must increase. If aromatic C increases without proportional aromatic H, substitution or condensation must increase. If branch methyl H increases without matching branch methine or branch-proximal carbon, the integration boundary, response factor, or branch model must be challenged.

Average aromatic-ring number, naphthenic-ring number, side-chain length, substitution index, and surrogate formula can be calculated for appropriate heavy materials [9, 10, 19, 34-36]. In finished base oils, more reliable outputs are usually carbon-class fractions, branch descriptors, residual olefin/aromatic content, and naphthenic/paraffinic balance. A detailed surrogate molecule can create unwarranted specificity when the true material is a distribution.

7.3 Closure, residuals, and nonuniqueness

A molecular ledger must include an explicit residual. Carbon fractions and hydrogen fractions should close within uncertainty. NMR-implied H/C should be compared with elemental analysis. Carbon number implied by terminal groups and chain length should be compared with average MW or mass-spectral distribution. Failure to close identifies overlap, relaxation bias, additive interference, phase heterogeneity, or an inappropriate model.

Average structures are nonunique. A mixture of long normal paraffins and compact highly branched molecules can produce the same average methyl/methylene ratio as a uniform population of moderately branched molecules. A mixture of monoaromatics and condensed aromatics can produce the same average aromatic H/C as a different substitution distribution. FIMS, GC×GC, GPC, detailed hydrocarbon analysis, or other distribution-sensitive methods are required when breadth or multimodality matters.

7.4 n-d-M as a screening complement

ASTM D3238 n-d-M calculations estimate aromatic, naphthenic, and paraffinic carbon distributions from refractive index, density, and molecular weight [43]. The method is useful for historical comparison and screening but is not equivalent to direct NMR. It does not provide branch topology, olefin type, aromatic substitution, carbon multiplicity, or a direct residual. Disagreement between n-d-M and NMR can be informative because it exposes empirical-domain failure, sulfur correction, density effects, or NMR assignment bias.

8. Product-Class and Process-Stage Applications

8.1 API Group I, II, and III base oils

API base-oil groups are commercial and performance classifications defined by saturates, sulfur, and viscosity index; they are not uniquely defined by an NMR spectrum. NMR nevertheless supplies a molecular explanation for many group-level differences. Group I solvent-refined oils commonly retain greater aromatic and naphthenic content and broader structural heterogeneity. Group II hydroprocessed oils show reduced aromaticity and increased saturation. Group III severely hydrocracked or hydroisomerized oils are highly saturated and are differentiated principally by carbon-number distribution, branch placement, chain length, residual ring carbon, and trace aromatic or olefinic content [5, 13, 25, 28, 39-41].

Group assignment should therefore be stated from the applicable specification or supplier data, while NMR is used to characterize the molecular population within that group. A near-zero aromatic integral does not prove Group III status, and a high VI prediction from an NMR model does not replace measured viscosity index. Sulfur, saturates, volatility, pour point, and viscosity data remain independent release measurements.

Table 10. NMR interpretation by base-oil group and process state.

Material / stage	Dominant NMR questions	Preferred NMR set	Required orthogonal context	Principal confounder
Group I neat base oil	Aromatic H/C, mono versus di-plus aromatics, naphthenic/paraffinic balance, side-chain substitution	Quantitative ^{1}H and ^{13}C; DEPT-45/90/135 or APT	Elemental analysis, density, RI, MW, measured VI	Aromatic overlap and additive carryover
Group II neat base oil	Residual aromaticity, naphthenic carbon, branching and chain length	Quantitative $^{1}H/^{13}C$; DEPT/APT	Saturates, sulfur, MW, viscosity and pour point	Trace-level aromatic LOQ and naphthenic overlap
Group III / wax isomerate	BI/FCI, branches per 100 C, S_2-S_8 distribution, residual normal paraffin, trace olefin/aromatic content	Quantitative $^{1}H/^{13}C$; DEPT/APT; temperature control	MW or carbon-number distribution, measured VI, cloud/pour point	29.8 ppm integration, branch-response factors, wax phase behavior
Raw FT liquid or condensate	α-Olefin abundance, n-alkane/olefin homologs, oxygenates, branch perturbation	Quantitative $^{1}H/^{13}C$ with olefin subregions; 2D confirmation as needed	GC×GC/DHA, SIMDIS, bromine number, oxygenate analysis	Volatile loss, oxidation, broad carbon-number distribution
FT wax / hydroisomerization feed	Normal-chain length, wax homogeneity, terminal groups, trace unsaturation	Heated quantitative $^{1}H/^{13}C$; DEPT/APT	High-temperature SIMDIS, DSC/cloud point, MW distribution	Crystallization and incomplete dissolution

Material / stage	Dominant NMR questions	Preferred NMR set	Required orthogonal context	Principal confounder
Hydroisomerized intermediate	Branch-type evolution, residual normal paraffin, internal olefin formation	Quantitative $^{1}H/^{13}C$; DEPT; olefin classification	Process severity, MW distribution, bromine number	Concurrent cracking and isomerization
Hydrofinished GTL base stock	Trace olefin endpoint, final branch architecture, residual aromaticity	High-S/N quantitative ^{1}H; confirmatory ^{13}C; DEPT/APT	Oxidation stability, color, bromine number, viscosity	Trace integration and additive contamination
Formulated lubricant	Base-oil identity versus additive package contribution	Fractionation or validated multicomponent $^{1}H/^{13}C$ model	Additive formulation, elemental and chromatographic data	Additive aromatic, olefinic, and broad aliphatic signals

8.2 FT waxes, GTL diesel, jet, and synthetic base stocks

FT waxes and GTL products provide a clean demonstration of the value of orthogonal NMR. Long normal chains generate an intense recurring-methylene ^{13}C response near 29.8 ppm and comparatively simple aliphatic ^{1}H envelopes. Raw FT liquids can contain terminal α-olefins, whereas hydroisomerization increases iso-paraffinic branch environments and hydrofinishing suppresses residual unsaturation [21-24, 37, 38, 52, 57].

GTL diesel and synthetic jet components require a different balance from lubricant base oils. Cetane quality, density, cold flow, flash point, volatility, lubricity, seal swell, and material compatibility are influenced by carbon-number distribution, normal-paraffin content, branch location, naphthenic content, aromatics, and olefins. US6210559 is relevant because it uses branch-perturbed ^{13}C statistics and pendant/terminal branch nomenclature to guide FT diesel and blend-stock optimization [52]. NMR can define molecular building blocks, but finished-fuel certification requires the complete applicable specification and fit-for-purpose testing.

For aviation applications, a highly paraffinic spectrum should not be interpreted as proof of pathway approval, blend limit, or compliance with a synthetic aviation-fuel annex. Aromatic content, distillation behavior, freezing point, density, thermal stability, combustion properties, trace contaminants, and material-compatibility requirements must be established independently. NMR is a compositional and process diagnostic within that larger qualification system.

8.3 PAO and API Group IV

PAO is produced by oligomerization of α-olefins and subsequent hydrogenation. Its branch architecture reflects feed carbon number, catalyst, oligomerization pathway, oligomer distribution, skeletal rearrangement, and hydrogenation severity. Quantitative ^{1}H and ^{13}C NMR with DEPT/APT can identify residual vinyl, vinylidene, and internal olefin functionality, branch methines, branch methyls, quaternary centers, and average chain topology [26].

PAO should not be described as FT-like merely because both materials are synthetic, saturated, high-VI paraffinic fluids. PAO has an oligomeric architecture and may contain carbon environments that violate wax-isomerate assumptions used in BI/FCI or branches-per-100-carbon recipes. Patent or competitive comparisons must first establish that the same terminal-group, branch-center, average-carbon-number, and quaternary-carbon assumptions apply.

8.4 API Group V and mixed base-stock systems

Group V is a residual category rather than one molecular family. Esters, alkylated naphthalenes, polyalkylene glycols, phosphate esters, silicone fluids, and other specialty base stocks have distinct ^{1}H and ^{13}C chemistries. The hydrocarbon region map in this paper can be applied only to the hydrocarbon portion of a Group V material or blend. Carbonyl, ether, heteroatom-adjacent, and silicon-bearing resonances require compound-class-specific methods.

In mixed base-stock systems, an apparent change in aromatic H/C, olefinic H, or methyl/methylene balance can arise from blend ratio rather than degradation or process drift. Blend-component reference spectra, gravimetric blends, and multivariate resolution should be used before hydrocarbon branching metrics are interpreted. The report should state whether results are based on the neat base oil, separated hydrocarbon fraction, or complete formulation.

8.5 Additive-containing lubricants

Additive packages introduce first-order interference. Alkylated diphenylamines, hindered phenols, salicylates, sulfonates, dispersants, viscosity modifiers, antifoams, friction modifiers, and carriers can contribute aromatic, benzylic,

olefinic, carbonyl-adjacent, and broad aliphatic signals. Their concentrations may be small by mass but large relative to the trace aromatic or olefinic content of a modern Group III or GTL base oil.

For a base-oil composition claim, the hydrocarbon base stock should be isolated or the additive contribution should be measured independently. Valid options include preparative separation, dialysis or precipitation of high-MW components, solid-phase extraction, additive-package blanks, or calibrated multicomponent modeling. A whole-formulation spectrum without additive control is usually unsuitable for patent-defined BI/FCI, trace aromaticity, or olefin endpoint claims.

9. Structure-Property Correlations and Their Limits

9.1 Viscosity index and kinematic viscosity

Viscosity index is affected by molecular size, shape, branch position, branch density, ring content, and carbon-number distribution. Long, relatively extended paraffinic structures often support high VI, while excessive or poorly placed branching can reduce effective chain extension. Mid-chain branch environments represented by S_{67} were positively associated with VI in the Zhang CTL base-oil ridge-regression dataset, while selected ethyl and dense branch environments were unfavorable [6].

That relationship is empirical and domain-specific. A VI model trained on one CTL or FT family can fail when viscosity grade, average molecular weight, hydrocracking severity, naphthenic content, PAO content, or analytical processing changes. KV_{40}, KV_{100}, VI, and molecular-weight distribution should be included as measured variables. A prediction should be reported with model version, preprocessing, calibration range, leverage or applicability-domain statistic, prediction interval, and external-validation performance.

9.2 Pour point, cloud point, and low-temperature rheology

Low-temperature behavior reflects crystallizable normal-paraffin sequences, carbon-number distribution, branch position, branch spacing, and molecular-weight breadth. Branching can disrupt crystal packing and lower pour point, but the result is not monotonic. Too little branching leaves long crystallizable sequences; excessive branching can reduce VI or create complex wax-network behavior. FCI, recurring methylene content, ACL, and branch position should therefore be evaluated together [39-41, 49-56].

Pour point and cloud point are bulk phase-transition measurements and should not be inferred from NMR alone. Two oils with similar BI can differ in low-temperature behavior because one has a narrow high-carbon-number distribution and the other has a broader distribution containing a small wax-rich tail. DSC, optical cloud-point analysis, low-temperature viscosity, and SIMDIS or mass-spectral distribution are appropriate companions.

9.3 Oxidation stability and hydrofinishing

Olefinic functionality is a direct oxidation liability and a process-control marker. Terminal, internal, vinylidene, and conjugated olefins differ in reactivity, and residual unsaturation should be interpreted together with sulfur, nitrogen, aromaticity, trace metals, antioxidant content, and processing history. US7578926 formalizes a ^{1}H NMR olefin endpoint in a hydrofinishing context [57].

A low olefinic-H result does not by itself guarantee high oxidation stability. Naphthenic and aromatic structures, heteroatoms, peroxides, catalyst residues, dissolved oxygen, and additive response can dominate. Conversely, a base stock with measurable residual olefin may perform adequately after formulation with antioxidants. NMR should be used to define the reactive structural inventory, while oxidation tests establish performance.

9.4 Solvency, seal behavior, air release, and foaming

Aromatic and naphthenic content affect solvency and additive response, while molecular weight, viscosity, surface activity, and branch topology can influence air release and foaming. ExxonMobil patent practice relates branch descriptors to lubricant performance, including air-release behavior [49-51]. These properties are multivariate and can

be affected by trace polar contaminants or antifoam additives at concentrations too low to dominate the hydrocarbon NMR spectrum.

The molecular interpretation should therefore be framed as mechanistic support rather than a single-variable prediction. A high FCI or a particular branch count may correlate with a property in a defined product family, but causality should not be claimed without controlled experiments. Measured air release, foaming, seal swell, solvency indices, and additive-response tests remain the decision criteria.

9.5 Chemometric and machine-learning models

Whole-spectrum PCA, PLS regression, ridge regression, elastic net, support-vector methods, random forests, and neural networks can capture information that is lost when spectra are reduced to a small set of integrals [6, 46, 47]. They are useful for process monitoring, product-family classification, VI or viscosity prediction, and detection of atypical lots. Their validity depends on sample design and transfer control, not algorithm sophistication.

A defensible model requires representative calibration samples, locked acquisition and preprocessing, separation of development and external validation, control of lot and process confounding, documented instrument transfer, and a prespecified applicability domain. Cross-validation alone is not an independent performance claim. Batch, refinery, catalyst, viscosity grade, and carbon-number range should not be allowed to encode the class label inadvertently.

Chemometric predictions should be chemically constrained. Negative class fractions, impossible C/H closure, or a VI prediction inconsistent with measured KV_{40} and KV_{100} should trigger rejection or review. The model output should be accompanied by spectral residuals and interpretable variables so that a statistically unusual sample can be investigated chemically.

10. Patent and Technical Landscape

10.1 Distinct industrial parameter spaces

The ExxonMobil, Chevron, and Shell patent families describe overlapping hydrocarbon chemistry through deliberately different analytical languages. ExxonMobil emphasizes BI, free methylene or $CH_2 \geq 4$ populations, FCI, and related average-molecule parameters. Chevron emphasizes branches per 100 carbons, limits on branch position, edited-carbon counting, and olefin endpoints. Shell combines GASPE carbon editing with VPO and FIMS to describe branch number, ring content, side-chain distribution, and carbon-number/Z-number distributions [49-60].

These parameters are not synonyms. BI is a proton methyl-hydrogen ratio. FCI is a carbon-side recurring-methylene quantity scaled by average carbon number. Branches per 100 carbons is a branch-center normalization. GASPE/FIMS/VPO descriptors combine multiplicity editing, molecular mass, and distribution information. A laboratory comparison must apply each claim recipe independently and must not convert one parameter to another by an undocumented empirical relation.

10.2 US6210559 and branch-perturbed carbon nomenclature

US6210559B1, assigned to Exxon Research and Engineering Company, uses ^{13}C NMR spectroscopy to optimize Fischer-Tropsch diesel fuels and blend stocks [52]. Its analytical contribution is the explicit treatment of branch-perturbed α′, β′, and γ′ carbon populations and pendant versus terminal branch nomenclature for methyl, ethyl, propyl, and butyl groups. Those descriptors were connected to cetane and cold-flow behavior in FT fuel and blend-stock contexts.

The P/T and α′/β′/γ′ language should be reported alongside, not substituted for, the S_2-S_8 system. S_2-S_8 is more directly connected to specific lubricant-base-oil branch structures and the Zhang VI model. P/T nomenclature is especially useful when terminal versus pendant branch length and FT diesel optimization are being evaluated. The same peak can contribute to different derived descriptors under the two systems, so the calculation map should be shown.

Table 11. Parallel branch languages used in lubricant and FT product analysis.

Descriptor family	Representative carbon evidence	Primary use	Key limitation
S_2-S_8	Specific branch methyl, methine, and branch-proximal resonances	Base-oil branch topology and structure-property modeling	Peak overlap and matrix-specific response
α′/β′/γ′	Carbons one, two, and three positions from branch perturbation	FT diesel branch perturbation and cold-flow/cetane analysis	Population definitions are patent-specific
P methyl / ethyl / propyl / butyl	Pendant branch terminal groups	Branch-length distribution	Requires separation from main-chain ends
T methyl / ethyl / propyl / butyl	Terminal branch/end-group environments	Terminal branch-length and chain-end description	Can overlap normal chain termini
BI/FCI	^{1}H methyl fraction plus recurring interior ^{13}C	Wax-isomerate/base-oil claim space	Does not uniquely identify branch position
Branches per 100 C	Edited branch centers normalized to carbon number	Chevron optimized-branching claim space	Requires validated branch-center response

10.3 US7578926 and olefin-defined hydrofinishing

US7578926B2, assigned to Chevron U.S.A. Inc., defines a process to enhance oxidation stability of base oils by analyzing olefins using ^{1}H NMR [57]. The patent is important because it places olefinic ^{1}H directly in an industrial base-oil control strategy rather than treating unsaturation as a peripheral fuel property. It supports routine use of the 4.5-6.0 ppm region as a hydrofinishing endpoint, provided the patent method, conversion basis, and sample matrix are reproduced.

An expert comparison should distinguish the direct spectral measurement from the claim metric. The direct result is an integrated olefinic-H fraction under stated boundaries. A converted olefin content may depend on assumed unsaturation class and molecular weight. A process endpoint may also include a property threshold. Each layer should be reported separately so that disagreement can be localized to spectrum, conversion, or claim construction.

10.4 Patent metadata and analytical implications

Table 12. Principal verified patents used in this white paper.

Patent	Title / assignee	Analytical center	Critical laboratory control
US7067049B1	Formulated Lubricant Oils Containing High-Performance Base Oils Derived from Highly Paraffinic Hydrocarbons; ExxonMobil	BI, FCI, free methylene, highly paraffinic base-oil claims	Patent-region boundaries, MW/carbon number, neat base-stock definition
US6846778B2	Synthetic Isoparaffinic Premium Heavy Lubricant Base Stock; ExxonMobil	Isoparaffinic heavy base-stock structure	Viscosity grade and average-molecule basis
US8389451B2	Lubricant Air Release Rates; ExxonMobil	Branch/free-carbon descriptors and performance	Property method and base-oil/formulation distinction
US6210559B1	Use of ^{13}C NMR Spectroscopy to Produce Optimum Fischer-Tropsch Diesel Fuels and Blend Stocks; Exxon	α′/β′/γ′ and pendant/terminal branch statistics	Peak map, FT process stage, cetane/cold-flow data
US20050077208A1 / US20050077209A1	Lubricant Base Oils with Optimized Branching / Processes for Producing Them; Chevron	Branches per 100 C and branch-position limits	DEPT/APT response, average carbon number, 2-position assignment
US7053254B2	Process for Improving Lubricating Properties of Base Oils Using FT-Derived Bottoms; Chevron	FT-bottoms upgrading and branch control	Feed/product distinction and boiling-range distribution
US7476645B2	PAO and FT-Derived Lubricant Base Oil Blends; Chevron	Blend composition and synthetic-base-stock structure	PAO versus FT spectral deconvolution
US7578926B2	Process to Enhance Oxidation Stability of Base Oils by Analysis of Olefins Using ^{1}H NMR; Chevron	Olefinic-H hydrofinishing endpoint	Trace LOQ, olefin model, additives and sample history
EP2075314A1 / US7531081B2 / WO2013189953A1	Grease Formulations; Base Oil Composition; Heavy FT-Derived and Alkylated Aromatic Base Oil Compositions; Shell	GASPE/VPO/FIMS descriptor space	Echo timing, temperature, MW and FIMS distribution

10.5 Patent-comparison evidence package

A patent-comparison report should preserve the original free-induction decays, pulse programs, pulse calibrations, relaxation studies, sample masses, solvent and $Cr(acac)_3$ preparation records, temperature logs, processing parameters, integration regions, peak-fit files, molecular-weight data, calculation spreadsheets, and software versions. Screenshots or final tables are not sufficient.

Claim-specific results should be separated from general characterization. The report should first present direct ^{1}H and ^{13}C evidence, then the calculation under the patent recipe, then method deviations, uncertainty, and sensitivity analysis. Where a claim term is legally disputed, alternative calculations can be shown without selecting a legal construction. The analyst should not conceal the degree to which a conclusion depends on a boundary, response factor, or average-molecular-weight assumption.

11. Industrial Method Validation, Deployment, and Quality Control

11.1 Define the measurand before validating the method

Validation begins with a precise measurand. “Olefin content” can mean olefinic-H mol%, olefinic-C mol%, total monoolefin wt%, bromine-number-equivalent unsaturation, or a patent-defined process metric. “Branching” can mean methyl-H fraction, branch centers per 100 carbons, specific S_2-S_8 populations, or a model-derived index. A method cannot be validated against an undefined target.

The sample population must also be defined. A method validated on neat, hydrofinished Group III base oils is not automatically valid for raw FT condensate, wax, PAO, aromatic Group I oil, or additive-containing lubricant. Matrix, viscosity grade, carbon-number range, expected aromatic/olefin level, and temperature range define the analytical domain.

11.2 Validation characteristics

Precision should include repeat acquisition, repeat processing, repeat sample preparation, and between-day or between-instrument components. Bias should be evaluated with gravimetric model blends, characterized hydrocarbon standards, cross-method comparison, or mass balance. Selectivity should be challenged with aromatics, conjugated olefins, oxygenates, additives, and naphthenic/branch overlap. Linearity should be established over the decision range, not merely at major-component levels.

LOD and LOQ must be class- and matrix-specific. Trace olefinic ^{1}H in a finished base oil may be limited by baseline curvature and satellite or impurity signals, while trace olefinic ^{13}C is often limited by sensitivity and long relaxation. Aromatic carbon LOQ can be worse than aromatic-H LOQ. A single instrument-wide detection limit is not defensible.

Robustness should include solvent, concentration, $Cr(acac)_3$ level, temperature, equilibration time, pulse calibration, relaxation delay, apodization, baseline algorithm, and integration-boundary challenges. Intermediate precision should include different analysts and, when relevant, different field strengths. Decision uncertainty should include conversion-model uncertainty and MW uncertainty in addition to spectral repeatability.

Table 13. Validation design for orthogonal petroleum NMR.

Validation characteristic	Minimum study	Industrial acceptance question
Identity / selectivity	Model compounds, known base oils, additive and aromatic/olefin interference challenges	Can each reported class be distinguished under the intended matrix?
Precision	At least replicate preparation, acquisition, processing, day, and analyst components	Is total variance small relative to specification or claim distance?
Bias / trueness	Gravimetric blends, characterized standards, mass balance, and orthogonal method comparison	Does the result recover known composition without matrix-dependent bias?
Linearity / range	Multiple levels spanning blank through upper process or product range	Is the model valid across the actual decision interval?
LOD / LOQ	Matrix blanks, low-level spikes, baseline and S/N criteria	Can trace aromatic or olefin content be quantified rather than merely detected?

Validation characteristic	Minimum study	Industrial acceptance question
Robustness	Designed changes in T, concentration, $Cr(acac)_3$, delay, processing and boundaries	Which variables can change the decision?
Uncertainty	Bottom-up or top-down model including MW and conversion assumptions	What interval should accompany the reported measurand?
Transferability	Independent instrument/site or field-strength study	Can a method or chemometric model be transferred without recalibration?

11.3 System suitability and continuing QC

Each batch should include a chemical-shift and line-shape reference, a quantitative-integration control, a low-level olefin/aromatic control when those classes are reported, and a matrix-representative control sample. The system-suitability plan should specify frequency, target values, control limits, and corrective action. A reference material that tests only a sharp isolated proton peak does not control the baseline and overlap behavior of a petroleum matrix.

Control charts should be maintained for key ratios, line width, signal-to-noise, chemical-shift drift, pulse calibration, and control-sample recoveries. Reprocessing changes should be versioned. Integration regions and baseline parameters should not be adjusted to force agreement with a prior result. Out-of-control conditions should trigger root-cause investigation and, when necessary, reintegration or reacquisition of affected samples.

11.4 Orthogonal method matrix

Table 14. Orthogonal methods used to close NMR capability gaps.

Question	Primary NMR evidence	Orthogonal method	What the orthogonal method resolves
Olefin class and amount	^1H 4.5-6.0 ppm plus ^{13}C 108-140 ppm	Bromine number/iodine value; GC×GC or DHA; FTIR where validated	Bulk unsaturation and molecular isomer/carbon-number distribution
Carbon-number and MW distribution	Terminal-group and recurring-methylene balances	SIMDIS, FIMS, GC-MS, GPC, VPO	Distribution breadth, multimodality, average molecular mass
Aromatic class	Aromatic H/C, DEPT-45, mono/di-plus model	HPLC, SFC, GC×GC, UV/fluorescence, MS	Ring-number and molecular-class distribution
Naphthenic carbon	Broad ^{13}C aliphatic residual and edited CH/CH_2	GC×GC-MS, FIMS, n-d-M as legacy comparator	Ring-number and paraffin/naphthene discrimination
Elemental closure	NMR-implied H/C and heteroatom-adjacent signals	CHNS/O, sulfur, nitrogen, trace metals	Average formula and nonhydrocarbon contributors
Low-temperature performance	FCI, ACL, branch position, carbon distribution	Pour/cloud point, DSC, MRV/CCS or low-temperature viscosity	Actual phase behavior and rheology
Oxidation performance	Olefinic H/C, aromaticity, branch/ring inventory	Oxidation stability, peroxide, color, deposit tests	Net performance under controlled stress
Blend or formulation identity	Whole-spectrum $^1H/^{13}C$ and chemometrics	Chromatography, additive elemental markers, formulation records	Component identity and concentration

11.5 High-field-informed, low-field-deployed architecture

High-field NMR should be used to establish assignments, resolve overlap, quantify carbon classes, and build reference libraries. Benchtop ^1H NMR at approximately 60-80 MHz can then be deployed for rapid process or QC screening when the question is expressed as robust broad-region integrals or validated whole-spectrum chemometrics. The transfer should be empirical; high-field regions should be convolved to the lower field and tested against actual benchtop spectra.

Benchtop instruments are well suited to total aromatic-H, total olefinic-H at sufficiently high concentration, methyl/methylene balance, blend fingerprinting, and process classification. They are not expected to resolve S_2-S_8 carbon branch peaks or trace aromatic/olefin subclasses with the specificity of high-field ^{13}C NMR. A two-tier system is therefore recommended: low-field screening and control-charting, with high-field confirmation for exceptions, model maintenance, patent comparison, and structural disputes.

11.6 Data integrity, chain of custody, and reproducibility

For litigation, supplier disputes, and patent work, chain of custody should include sample receipt, seal condition, storage, subsampling, heating and mixing history, preparation records, tube identification, acquisition queue, and raw-data hash. Electronic records should preserve original FIDs, metadata, processed spectra, audit trails, scripts, and calculation files. Reprocessed spectra should not overwrite prior versions.

Software and algorithm versions matter. Baseline correction, peak fitting, denoising, bucketing, and chemometric preprocessing can change low-level results. Any manual intervention should be documented. A third party should be able to regenerate the reported tables from the retained raw data and declared workflow.

12. Expert-Review Confounders and Evidentiary Controls

12.1 Analytical challenges an opposing expert is likely to raise

An opposing expert will first ask whether the sample and measurand were defined correctly. A neat base-stock claim cannot be proved from an additive-containing finished lubricant without separation or deconvolution. A raw FT feed, isomerization intermediate, hydrofinished product, and blended finished oil cannot be compared as though they were the same population. The report must identify the process stage, lot, storage history, and physical homogeneity.

The second challenge will concern quantitative conditions. Excellent spectral appearance does not establish quantitative ^{13}C response. The longest relevant T_1, inverse-gated decoupling, $Cr(acac)_3$ concentration, temperature, complete dissolution, pulse calibration, and sufficient signal-to-noise must be demonstrated. DEPT, APT, and GASPE response must be calibrated before edited peak area is used as a count.

The third challenge will concern overlap and model dependence. Naphthenic carbon overlaps paraffinic and branch environments; olefinic and aromatic sp^2 regions overlap at their boundaries; bridgehead and substituted aromatic carbon overlap; normal-chain end groups can overlap branch terminal groups. A residual calculation can magnify all upstream errors. The report should show alternative boundary or response-factor calculations where the conclusion is sensitive.

The fourth challenge will concern average-molecule nonuniqueness. An average carbon number or surrogate structure does not prove that any actual molecule has that structure. Distribution-sensitive methods should be supplied when claim language or performance depends on a narrow range, a tail population, or branch placement along individual molecules.

The fifth challenge will concern model transport. Brown-Ladner, Sarpal direct C_a, Bansal mono/di-plus aromatics, the Zhang VI regression, PONA/PIONA calculations, and patent algorithms are valid only under their assumptions and calibration domains. The report should state whether each model was used as published, revalidated, or used only as a qualitative comparator.

12.2 Incorporated controls and decision rules

Table 15. Expert-review challenge, control, and reporting response.

Potential challenge	Control incorporated in this framework	Required report disclosure
Wrong sample basis	Process-stage and formulation classification before analysis	Neat/separated/formulated status, lot, storage, homogenization
Nonquantitative ^{13}C	Matrix T_1 study, inverse-gated decoupling, $Cr(acac)_3$ and delay validation	Pulse program, delay, T_1 data, relaxation-agent concentration and temperature
Edited-spectrum area treated as direct count	Model-compound/reference response factors and quantitative denominator	DEPT/APT/GASPE timing, response correction and uncertainty
Trace peak below LOQ	Matrix blank, spike recovery, baseline uncertainty and class-specific LOQ	Detected versus quantified status and upper confidence bound
Olefin/aromatic overlap	Paired $^1H/^{13}C$, 2D support, standards, orthogonal methods	Assigned, unresolved, and total-sp^2 fractions separately
Naphthenic/branch overlap	Edited spectra, subtraction audit, orthogonal distribution data	Operational region definition and residual uncertainty
Average structure overclaimed	Distribution data and explicit average-molecule language	No molecule-specific claim unless independently established
Patent metrics conflated	Independent claim-recipe calculations	Direct data, each equation, denominator, deviations and sensitivity

Potential challenge	Control incorporated in this framework	Required report disclosure
Chemometric overfit	External validation, applicability domain, drift monitoring	Calibration population, validation design, prediction interval
Additive interference	Separation, additive blank, or validated multicomponent model	Component basis and residual additive contribution

12.3 Reference and patent verification status

The scholarly references retained in this paper were restricted to works in which NMR is central to the petroleum, fuel, base-oil, wax, olefin, aromatic, or quantitative-method question. DOI-bearing records were matched to the verified metadata inherited from the April 2026 audit and the targeted olefin/aromatic search. Legacy works without DOI, books, technical reports, and ASTM methods were checked as bibliographic records rather than represented as Crossref records. Patent number, title, inventors, assignee, and filed, publication, or grant dates were checked against authoritative patent-family records.

No DOI-bearing reference that failed title, author, journal, year, or DOI matching was retained. No failed record is therefore listed in the References. The non-DOI records retained by design are References [7, 8, 10-12, 42, 43] and the patent records [49-60], which are not Crossref journal records. ASTM D5292 is explicitly identified as withdrawn rather than presented as a current active method.

12.4 Remaining limitations that cannot be removed by drafting

Some limitations are intrinsic. NMR class analysis cannot always distinguish all structural isomers in a broad petroleum mixture. Trace ^{13}C quantitation may be impractical within routine turnaround time. Average-molecule solutions remain nonunique. Patent claim interpretation is a legal question. Product performance and certification require independent tests. These are not failures of the method; they define the boundary within which the NMR evidence is reliable.

The appropriate response is not to suppress the limitation but to state it quantitatively. Unresolved sp^2 carbon should be reported as unresolved. A modeled wt% should not be labeled as a direct integral. A result below LOQ should be reported as an upper bound or detected-not-quantified. A model prediction outside its calibration domain should be withheld. Those controls make the NMR result more defensible, not less useful.

13. Recommended Analytical and Reporting Framework

13.1 Tiered analytical workflow

The workflow should begin with a written decision statement: identity, process endpoint, product release, supplier comparison, patent claim comparison, property prediction, or research characterization. The sample basis and required measurands should then be defined. The minimum acquisition is selected from that decision rather than from a fixed instrument menu.

Tier 1 is quantitative ^{1}H NMR. Aromatic H, olefinic H, α-H, β-H, γ-H, terminal-vinyl, internal-olefin, and vinylidene regions are integrated under validated relaxation and baseline conditions. BI or other proton-defined parameters are calculated only when the applicable region definitions are satisfied.

Tier 2 is quantitative inverse-gated ^{13}C NMR with matrix-qualified $Cr(acac)_3$, temperature, and relaxation delay. Carbon is partitioned into normal-paraffinic, iso-paraffinic, naphthenic, olefinic, and aromatic classes. S_2-S_8, n-paraffin α/β/γ/δ/ε, and Grant-Paul assignments are applied from the foundational brief.

Tier 3 is multiplicity and connectivity support. DEPT-45/90/135, APT, GASPE when relevant, HSQC, HMBC, or other 2D experiments are used to resolve branch centers, quaternary carbon, olefin type, and aromatic CH/nonprotonated balance. Edited experiments are response-qualified before numerical counting.

Tier 4 closes the molecular balance with elemental analysis, average molecular weight or distribution, SIMDIS or detailed hydrocarbon analysis, bromine number, mass spectrometry, and physical-property data. Tier 5 applies chemometric or patent-specific calculations with versioned scripts and an applicability-domain statement.

13.2 Standardized reporting sequence

Table 16. Recommended report architecture and minimum disclosure.

Report block	Minimum content	Decision value
Sample definition	Material class, process stage, neat/separated/formulated status, lot, storage and homogenization	Prevents invalid cross-stage or additive-confounded comparison
Acquisition and processing	Instrument, field, probe, solvent, concentration, $Cr(acac)_3$, temperature, pulse, delay, scans, processing and regions	Establishes reproducibility and quantitative basis
Direct ^1H results	Aromatic, olefinic, α, β, γ fractions; terminal/internal/vinylidene evidence; BI if applicable	High-sensitivity hydrogen ledger
Direct ^{13}C results	Normal/iso/naphthenic/olefinic/aromatic C; α/β/γ/δ/ε and S_2-S_8 evidence	Carbon ledger and branch architecture
Edited/2D evidence	DEPT/APT/GASPE response, aromatic CH correction, quaternary and connectivity evidence	Resolves multiplicity and contested assignments
Derived parameters	ACL, IP/NP, FCI, branches per 100 C, P/T and α′/β′/γ′, aromatic ring-type outputs	Converts direct data under named equations
Closure and uncertainty	C/H closure, unassigned residual, precision, LOQ, model and MW uncertainty	Shows whether the molecular ledger is internally consistent
Orthogonal confirmation	MW/carbon distribution, GC, bromine, elemental and physical-property data	Closes distribution and performance gaps
Interpretation	Structure-property or patent comparison with explicit assumptions and domain	Supports decision without overclaiming
Data package	FID, metadata, processed spectra, scripts, worksheets, audit trail and hashes	Enables independent reproduction and expert review

13.3 Recommended result language

Results should distinguish direct measurements from derived estimates. Appropriate language is: “olefinic hydrogens represented X mol% of integrated hydrogen under the stated regions”; “the modeled monoolefin content was Y wt% using an average molecular weight of Z”; “aromatic carbon was below the validated LOQ”; or “the branch-center population was calculated under the US20050077208 recipe.” Inappropriate language is: “the sample contains Y% olefins” when only a low-S/N ^1H region was integrated without a structural or MW model.

A patent conclusion should state the method and uncertainty: “The calculated FCI under the stated interpretation was X with an expanded uncertainty of U; the nearest claim boundary was B.” A property conclusion should state model status: “The predicted VI was X within the validated calibration domain; measured VI was Y.” This discipline separates analytical evidence from legal or commercial conclusions.

13.4 Recommended industrial implementation roadmap

Implementation should proceed through a matrix-representative reference set, high-field assignment and quantitative validation, orthogonal characterization, SOP locking, control-chart establishment, and only then low-field or automated deployment. Historical samples should be reprocessed only under a documented bridging study. Supplier or process changes should trigger applicability-domain review.

For Process NMR Associates, the preferred operating model is high-field-informed and low-field-deployed. High-field $^1H/^{13}C$ NMR establishes the structural truth set and resolves disputes. Benchtop ^1H NMR supplies rapid process surveillance, lot comparison, and chemometric screening. Exceptions, model drift, and legally consequential results are escalated to the full high-field and orthogonal workflow.

Industrial implementation rule

No derived branch, olefin, aromatic, or property metric should be released unless the direct $^1H/^{13}C$ evidence, sample basis, calculation recipe, uncertainty class, and orthogonal constraints have been documented. When the molecular ledger does not close, the discrepancy is the result to be investigated.

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[58] European Patent Application EP2075314A1. "Grease Formulations." Inventors: Gilbert Robert Bernard Germaine; David John Wedlock; Alan Richard Wheatley. Applicant: Shell Internationale Research Maatschappij B.V. Filed December 11, 2007; published July 1, 2009.

[59] U.S. Patent US7531081B2. "Base Oil Composition." Inventors: Mervyn Frank Daniel; Gilbert Robert Bernard Germaine; David John Wedlock. Assignee: Shell Oil Company. Priority February 13, 2001; filed February 13, 2002; granted May 12, 2009.

[60] International Patent Application WO2013189953A1. "Lubricating Oil Compositions Comprising Heavy Fischer-Tropsch Derived and Alkylated Aromatic Base Oil." Inventor: David John Wedlock. Applicants: Shell Internationale Research Maatschappij B.V.; Shell Oil Company. Priority June 21, 2012; filed June 18, 2013; published December 27, 2013.

Summary

A defensible molecular description of lubricant base oils and FT/GTL synthetic stocks is obtained when quantitative ^{1}H and ^{13}C NMR are used as orthogonal measurements. The April 2026 Process NMR Associates brief supplies the saturated-carbon foundation: n-paraffin α/β/γ/δ/ε assignments, S_2-S_8 branch environments, Grant-Paul additivity, BI/FCI, branches per 100 carbons, ACL, IP/NP, the Zhang VI model, and the ExxonMobil/Chevron/Shell patent landscape. This paper extends that foundation without duplicating it.

The first extension is a complete ^{1}H proton-type framework. Aromatic H, olefinic H, α-H, β-H, and γ-H are integrated as separate measurands. Brown-Ladner and Sarpal direct-C_a routes are recognized as model-derived carbon estimates, while Hβ/Hγ and α-H/aromatic-H ratios constrain side-chain length and aromatic substitution. Direct hydrogen fractions are kept separate from wt% conversions and average-molecule outputs.

The second and most heavily weighted extension is olefin chemistry. Terminal α-olefin, vinylidene, and internal cis/trans olefin signatures are paired across ^{1}H and ^{13}C. Cookson-Smith abundance analysis, PONA/PIONA methods, US6210559 branch-perturbation nomenclature, and US7578926 hydrofinishing control demonstrate that olefin NMR is a process and product-definition tool. Raw FT streams, hydroisomerization intermediates, PAO intermediates, and hydrofinished base stocks should not be evaluated with a single undifferentiated unsaturation number.

The third extension is aromatic ring-type analysis. Total aromatic H and C are reconciled with protonated, substituted, and bridgehead carbon; the Edwards DEPT-45 correction controls underestimation of nonprotonated aromatic carbon; and Bansal mono/di-plus analysis provides an operational ring-class distribution. ASTM D5292 is treated as a withdrawn historical anchor rather than a current conformance claim.

The industrial controls are explicit. Process stage, additives, matrix-specific T_1, $Cr(acac)_3$ response, temperature, viscosity, dissolution, baseline, trace LOQ, DEPT/APT/GASPE response, molecular-weight distribution, and average-structure nonuniqueness are incorporated into the analytical design. BI, FCI, branches per 100 carbons, S_2-S_8, P/T branches, and α′/β′/γ′ populations are kept in their own calculation spaces. Structure-property and chemometric models are used only within validated domains.

The recommended output is a reconciled molecular ledger containing aromatic H/C, olefinic H/C and type, normal- and iso-paraffin populations, naphthenic carbon, branch type, ACL, IP/NP, patent-defined metrics, average molecular weight or carbon-number distribution, an unassigned residual, and an uncertainty statement. When that ledger closes, NMR provides a high-confidence molecular description. When it does not close, the discrepancy identifies the next analytical question.

Final technical position

Orthogonal $^{1}H/^{13}C$ NMR should be used as a controlled molecular-accounting system, not as a collection of isolated spectral ratios. Direct integrals, model-derived composition, patent-defined parameters, property predictions, and certification tests must remain distinguishable. That separation is the basis for reliable process control, defensible supplier comparison, and credible expert testimony.