



May 2009



*Carmagen. All the right people in all the right places.™*

## Research Reality (Part 2): Limitations of Model Compound Research

*By Winston K. Robbins, Ph.D.*

### Research Reality

In Part I of this series on "research reality," we summarized the factors that limited the application of laboratory research to engineering models (the Chemical Research Space - Figure 1). To probe process phenomena, research experiments are based on model compounds in a constant matrix. In this part of the series, we elaborate on the factors that affect the choice of model compounds for both upstream and downstream petroleum research.

### Model Compounds

Petroleum research is often frustrated by the wide variability in molecular composition among nominally similar streams. Crude oils vary in composition due to differences in source rock, maturation conditions, and reservoir environments. Process oils are a function of not only the source oil but also process design, catalyst, and operating conditions. Because refineries blend products from process streams to meet physical properties (octane, vapor pressure, density, etc), the differences in composition among finished products can be as large as those between crude oils themselves. Because it is not practical to study every possible compound in a stream, model compounds are used as surrogates for a class of molecules. Typically, tests are run in a benign matrix oil to facilitate analysis of the compound's behavior (More on the matrix oils in Part 3).

In reality, the research objectives define the type of model compound selected for experiments. Compounds with different functional groups may be used for fundamental physical phenomena or reaction mechanisms studies. In process studies, the stream of interest dictates the boiling range and hence a molecular weight range of model compounds to be studied. In sophisticated molecular modeling, molecular structures (isomers) must be considered.

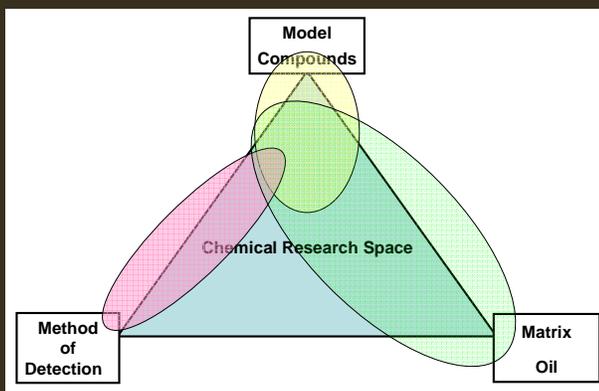


Figure 1 - Factors Influencing Coverage of a Chemical Process

### Reliability & Maintenance



*Reviewed a major European refinery's overall inspection, mechanical*

*integrity, and RBI programs with respect to those that are used at "World Class" facilities. As part of this effort, issued a manual that describes how such programs should be structured, what should be included in them, and specific procedures and checklists that typically are a part of such programs. Significant "gaps" were identified between what the refinery currently has in place vs. what "World Class" performers have. Follow-up activity to help the refinery close these gaps is planned.*

### Energy Management



*Completed initial scoping of overseas refinery to identify areas for further plant energy optimization and*

*heat recovery, plus the next phase of refinery-wide heat recovery study in greater detail with budgetary estimating. This resulted in identifying significant opportunities to recover energy by tuning operations and installing modest piping modifications at minimal capital cost.*

## Petroleum Functional Groups

For petroleum research, model compounds should be selected to be representative of functional group classes found in petroleum:

- Saturates (paraffins, naphthenes, cycloparaffins)
- Olefins and diolefins (only in cracked or coker liquids)
- Aromatics (alkylated benzenes, naphthalenes, and larger ring systems)
- S-Compounds (Elemental S, H<sub>2</sub>S, mercaptans, sulfides, thiophenes) and (disulfides or sulfoxides in oxidized samples)
- N-Heterocycles (pyrroles, pyridines, especially 3+ ring heterocyclics) and (aromatic amines in hydrotreated products)
- Oxygen compounds (ethers, carboxylic acids, and phenols) and (alkylated phenols in cracked stocks)
- Metals: Fe (corrosion products as suspended scale or ferrous carboxylate) and (Ni & V as porphyrins)
- In addition, some fractions with unique behavior (in particular, waxes and asphaltenes) are considered as classes.

## Stream Characterization

Selection of model compounds begins with stream characterization. An evaluation of available analytical data for a suite of process feeds/products by advanced characterization techniques will reveal the pertinent functional groups, range of molecules within a class, and prevalent isomers (where possible). All compounds identified should be considered, however, because the most prevalent feed species may not be the one critical to the research. Functional groups can be accurately determined in such characterization. The identification of molecules and especially isomers may be less valid depending on the sophistication of the characterization techniques.

## Ideal Model Compounds

The knowledge of the stream composition allows model compounds to be chosen that best suit the research objective, functional group, molecular weight, and structure (Figure 2). As suggested by this figure, these factors are not entirely independent, but rather are linked. Consideration of each of these factors helps define the ideal composition of a model compound for a research study.

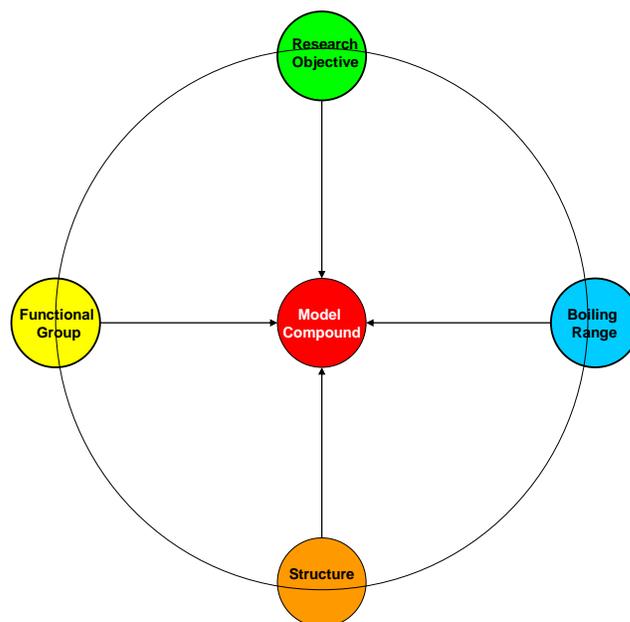


Figure 2. Factors Influencing Model Compound Selection

**Research Objective:** Research is often undertaken to understand the contribution of molecules to specific "activity," such as a physical property or reaction. In fundamental studies, it may be sufficient to select model compounds solely by functional group. In process research, however, it becomes imperative that the model compound reflects the functional group, molecular weight, and structures found in the process. In difficult problem solving studies, it may be necessary to differentiate among specific structures of a compound. Thus, the research objective sets boundaries on the range of compounds that should be considered.

**Functional Group:** The initial analytical evaluation identifies the functional groups that are present. Research objectives may narrow the options to "active" functional groups. Alternatively, the target "activity" may suggest that a variety of functional groups need to be researched. Ideally, the functional group in the compound should be consistent with types found in petroleum, i.e., the rest of the molecule being hydrocarbon in nature. [High resolution techniques have demonstrated the existence of molecules with more than one heteroatom (S,N, or O), especially in gas oils and higher boiling streams.] The use of model compounds with single functionalities is recommended to avoid difficulties in interpretation of conflicting activities.

**Boiling Range:** Most classes of compounds in petroleum exist as homologous series, i.e., compounds that differ by the number of -CH<sub>2</sub>- groups attached to a core structure. For example, toluene and p-xylene are the first two homologs in the series starting with a core benzene ring. Because the boiling



point increases as molecular weight (MW) increases, compounds with the same functional group core may be found in many different distillate cuts. In crude oils, homologous series can include compounds >C40. Because the hydrocarbon portion of the molecules affects physical properties other than boiling point, process research should be carried out with model compounds that fall within the boiling range of the stream under study.

**Molecular Structure:** The location of a functional group within a molecule affects its properties and reaction pathways. The location and number of "hydrocarbon" attachments to a core structure have similar effects. Consequently, the research objective influences the choice of molecular structures. If the objective is to follow the functional group specifically in a fundamental, then the most basic structure should be chosen. On the other hand, if the objective is to study core reactivity in molecules representative of a petroleum stream, then more complex structures may be necessary.

For example, in vacuum gas oils (VGO), mono-aromatics have an average of 3.5 attachments to the core benzene ring and some of the attachments exist as saturated rings. Thus, although it fits the functional group and boiling range of a VGO and functionality, nonadecylbenzene (benzene with a single linear 19 carbon side chain) may not be a suitable choice as a model compound. In the extreme, where a few compounds in a class appear to be contributing the majority of the "activity," model compounds with specific structure may need to be found.

### Availability

There is an additional factor that contributes to the actual model compounds used: availability. Once the ideal properties of a model compound have been identified, sources must be found. While many isomers of petroleum-related compounds are available for compounds with <10 carbon atoms, only a few higher molecular weight compounds are available for each class. Thus, with rare exceptions, studies for fractions boiling above gasoline are based on a number of limited model compounds. Compounds can be purchased from chemical supply companies, specialty production companies, or commercial synthesis labs. Supplies (or the lack thereof) can be identified without searching for specific compounds. Supplies of some compounds with representative functional groups can be screened using class searches within the supply house on-line tools. (Many of the compounds found, however, fail to relate to petroleum.) The cost of custom synthesized compounds often limits their use to small scale experiments. Purchased compounds should be checked for purity (and purified, if necessary) because impurities can introduce experimental artifacts. In reality, the choice of model

compounds is usually a compromise between the ideal and the available. The following paragraphs describe some examples of the use of model compounds and compromises involved.

## Fundamental Studies

### A. H<sub>2</sub>S Evolution

In support of engineering studies on hydrogen sulfide release during steam stimulation of buried bitumen, a fundamental study was undertaken to determine mechanistic details of the thermal reactions of sulfur functional groups with and without water. In this study, model compound decomposition of nine pure sulfur compounds was studied in water or cyclohexane in sealed vials heated to 250°C and 300°C (Katritzky and Siskin, 1991) (Table 1).

Table 1. Sulfur Compounds Studied for H<sub>2</sub>S Evolution

Functional Group	Compound	MW
Aliphatic Mercaptan (R-SH)	1-Decanethiol	174
Aromatic Mercaptan (Ar-SH)	1-Naphthyl thiol	160
Aliphatic Sulfide (R-S-R)	Dioctyl sulfide	258
Aliphatic Disulfide (R-S-S-R)	Didecyl disulfide	314
Alicyclic Sulfide	Tetrahydrothiophene	88
Aromatic Sulfide (Ar-S-Ar)	1,1'Dinaphthyl sulfide	286
Aromatic Disulfide (Ar-S-R)	1,1'Dinaphthyl disulfide	318
Aromatic Sulfide	Thiophene	84
Aliphatic Aromatic Sulfide	1-naphthyl1-octyl sulfide	272

The model compounds included some sulfur functional groups found in petroleum as well as some that might be formed in situ. In such a fundamental study, the functional group was the essential factor in selecting available model compounds (structure and boiling range were not considered important under the reaction conditions).

### B. Corrosion Inhibition

Model compounds have been used to screen functional groups for effect on inhibition of CO<sub>2</sub> induced corrosion and phase wetting in crude oil pipelines (Ayello, et al, 2008). An evaluation of adsorption literature suggested that several of the functional groups found in petroleum could participate in interactions at oil/water/steel interfaces. A suite of surface active compounds with different functional groups were selected to represent functional groups that are commonly found in crude oil (Table 2). The study confirmed that accumulation of surface active compounds at the metal surface alters the wettability of steel and reduces its corrosion.



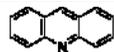
Furthermore, accumulation of the surface active compounds at the oil/water interface modifies the flow behavior of oil-water mixtures. The most surface active functional groups were carboxylic acids (myristic acid), mercaptans (tetradecanethiol), and basic N-compounds (acridine).

These model compounds were selected because they were readily available compounds with appropriate functionality. However, they are structurally quite different from those found in crude oils:

- Carboxylic acids (naphthenic acids) in crude oils have a -CH<sub>2</sub>-COOH functionality attached to multiple saturated rings
- Most N-compounds have multiple alkyl side chains that substantially increase solubility in the oil matrix (carbazole was only tested in a modified matrix at low concentrations)
- Basic N in petroleum generally occurs in the form of phenathridines (where the N is in a “bent” molecule in comparison with the linear structure of acridine).

Although the compounds used in these experiments were not typical of the structures in crude oil, they were sufficient to rank the effects of crude oil functional groups.

Table 2. Model Compounds Used for Testing Pipeline Wettability and Corrosion Inhibition

Hetero-atom	Name	Formula		Molecular weight g·mol <sup>-1</sup>
Oxygen	Myristic acid	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>12</sub> COOH		228.37
Sulfur	Dibenzothiophene	C <sub>12</sub> H <sub>8</sub> S		184.26
	Diocetyl sulfide	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> S(CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>		258.51
	1-Tetradecanethiol	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>13</sub> SH		230.45
Nitrogen	Carbazole	C <sub>12</sub> H <sub>9</sub> N		167.2
	Acridine	C <sub>13</sub> H <sub>9</sub> N		179.2

## Process Studies

### A. Desulfurization of Naphtha

Cat cracked naphtha is generally recognized as the source of >90% of sulfur in blended gasoline. In recent studies, sulfides, thiophenes, and thiols have been isolated and characterized in FCC and RCC gasolines (Xia 2003, 006). Although the majority of the thiols are below C<sub>4</sub>, more than 20 individual C[1]~C[9] thiols were identified. The higher concentrations of >C<sub>5</sub> thiols cause RCC gasoline to be more difficult to sweeten than FCC gasoline. To reach 2006 sulfur limits, the sulfides, thiophenes, and residual mercaptans must be removed. Model compounds have been used to optimize catalytic conditions that reduce the sulfur with minimal saturation of high-octane olefins. Post-process conditions are also optimized to minimize the formation of "new" mercaptans by the reaction of product H<sub>2</sub>S with feed olefins (mercaptan reversion) (Cook 2004).



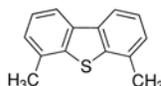
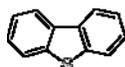
Compounds are available to model all the functionalities over the entire boiling range for this gasoline example.



## B. Desulfurization of Gas Oils

This availability is not true in the case of hydrotreating higher boiling fractions such as gas oils. An engineering "rule of thumb" is that two-thirds of the sulfur in gas oils is thiophenic and one third sulfidic. Because sulfides are much more readily reduced in hydrotreating than thiophenes, much of the pioneering studies on catalytic hydrotreating were carried out on dibenzothiophene (I).

However, as hydrotreating was pushed to its limits, some "hard sulfur" resisted removal under conditions where the dibenzothiophene (I) was readily removed. Initially, the resistant molecules were identified solely as alkylated dibenzothiophenes, i.e., higher MW homologs of the basic structure. However, advanced characterization demonstrated that the "hard" sulfur molecules had alkylation in both "beta" positions that sterically blocked access of the sulfur to the catalytic surface. Therefore more recent optimization studies have included 4,6 dimethyldibenzothiophene (II) as a model compound. Originally, this compound had to be custom synthesized specifically for testing. It is now commercial due to its significance in hydrotreating studies.



## Summary

Model compounds can be used to probe physical properties and reaction mechanisms. The characteristic of an "ideal" model compound are defined by research objective, functional group, boiling range, and structure as revealed by advanced characterization of a process stream. However, availability often limits research to less than ideal compounds. With these compounds, only a portion of the Chemical Research Space in Figure 1 is probed. This limitation must be recognized in building or evaluating engineering models.

*Dr. Robbins has extensive experience in applying advanced characterization techniques to petroleum composition and has applied this experience to the selection of model compounds in research programs. Through Carmagen, he is available for consultation on selection of appropriate model compounds or for evaluation of research based on them. Please contact Jerry Lacatena if you'd like more information on Carmagen's expertise in these areas.*

