Heavy Oil Conversion Chemistry: Part 1-The PNA Barrier

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1 HEAVY OIL CONVERSION CHEMISTRY: PART 1-THE PNA BARRIER

1.1 Introduction

It is well known that petroleum vacuum resids are difficult to convert into transportation fuels with delayed coking and ebullating-bed hydroconversion being the most common processes used. As a result, the impression is often conveyed that current resid processes are close to their maximum conversion, only because refineries are using 30 – 50 year old technology. In contrast, the author has recently written a book[1] that shows that there is considerable room for improving the conversion of both coking and hydroconversion processes of vacuum resids over what is commercially practiced.

Conversion of vacuum resids has been much neglected for technology improvement because the petroleum industry has been focused on lighter crude oils and their distillable liquid fractions. However, there are still practical maximum limits to conversion yields of vacuum resids that are imposed by the petroleum macromolecules themselves and by economics. Since the polynuclear aromatic (PNA) portions of the petroleum macromolecules cannot be chemically cracked and since the PNA portions promote insolubility, they provide the chemical barrier to conversion. Although the PNA's can be hydrogenated and then cracked to overcome the conversion barrier, this is a chemically inefficient process, causing an economic barrier to hydroconversion processes. As a result, all vacuum resid conversion processes, in addition to the desirable lower aromatic product, must produce a byproduct that is more aromatic than the feed. Nevertheless, with the increase in the proportion of heavy crudes being run at refineries and with the large resources of extra heavy oil in Canada and Venezuela, it is clear that new technology to convert vacuum resids needs to be developed and put in practice as soon as possible.

1.2 Objectives of Heavy Oil Conversion

Of course, the principal objective of heavy oil conversion processes is to maximize the conversion of the heavy oil to transportation fuels at minimum cost. At times, the secondary objective is to lower the viscosity and the density of the heavy oil, such as tar sands bitumen, to meet pipeline specifications so that it can be transported to refineries for further conversion. Nevertheless, wherever the vacuum resid portion of the heavy oil is converted, the objective is to remove catalyst poisons in the primary upgrading step so that the higher quality liquid products of the primary step might be more selectively converted in secondary upgrading steps by catalytic processes as illustrated in **Figure 1**. The catalyst poisons in vacuum resids are nickel, vanadium, basic nitrogen and coke formed from the PNA parts of the macromolecules.

The most common primary upgrading process is coking but visbreaking is still practiced outside North America and the separation process, fuels deasphalting, is becoming more common. Vacuum resid hydroconversion is a catalytic process that can be used as the primary step, particularly if the catalyst can be continuously replaced, as in LC-Fining and H-Oil ebullating-bed processes or in emerging dispersed catalyst

processes. The low quality byproducts of these primary upgrading processes, such as coke, residual fuel oil, and asphalt, commonly become fuel for power plants but in remote locations they may be piled or buried. However, gasification, that forms hydrogen from steam while producing carbon dioxide, is probably the most environmentally acceptable process for utilizing the low quality byproducts. Meanwhile, the secondary catalytic upgrading processes are hydrotreating followed by either fluid catalytic cracking or hydrocracking. The feeds to these secondary catalytic processes need not be distillable liquids but need to be low in catalyst poisons: nickel, vanadium, basic nitrogen and large ring PNA's. For example, high quality atmospheric resids often make good feeds to fluid catalytic cracking.
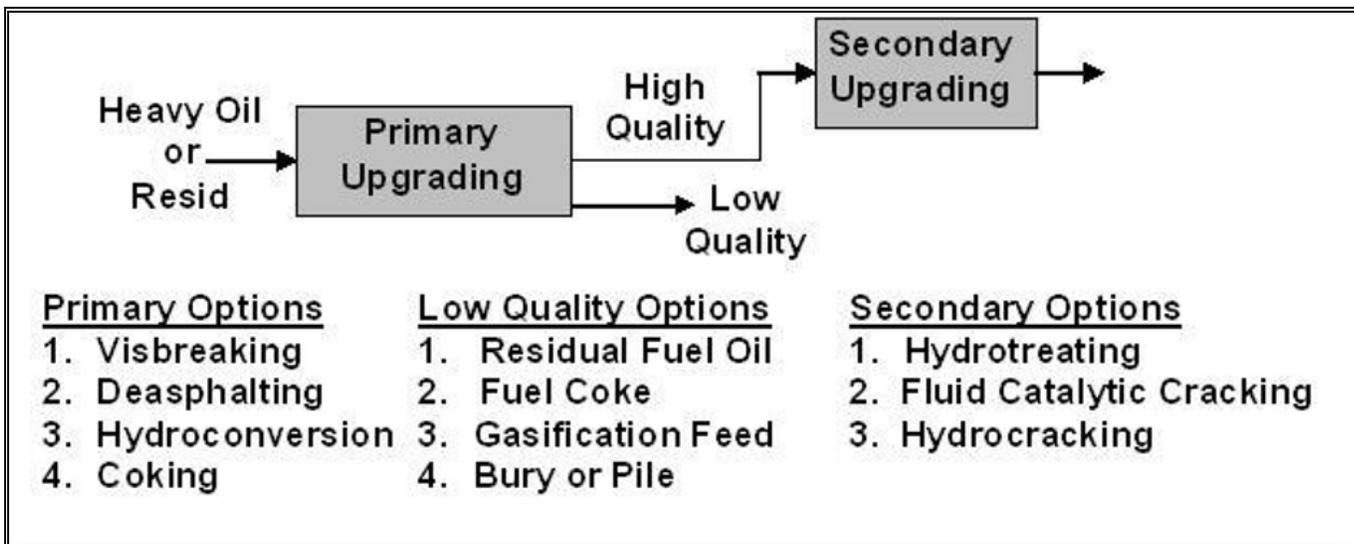

FIGURE 1: HEAVY OIL CONVERSION INVOLVES PRIMARY AND SECONDARY STEPS (FROM IA WIEHE. *PROCESS CHEMISTRY OF PETROLEUM MACROMOLECULES.* **REPRINTED WITH PERMISSION. COPYRIGHT 2008. CRC PRESS, TAYLOR AND FRANCIS GROUP.)**

1.2.1 Ring Size of PNA's

How large does a PNA have to be to be considered unacceptable feed to secondary catalytic processing? As shown in **Figure 2**, this author considers the answer to be 5 aromatic rings although the jury is still out whether 4 ring aromatics are that valuable. Since the PNA's represent only a fraction of the total macromolecule in petroleum, the boiling points are much higher than the PNA's in **Figure 2**. Thus, distillable liquid products of resid conversion with boiling points less than 1000°F contain few, if any, PNA's of 5 rings or larger. However, vacuum resids may contain high fractions of macromolecules without PNA's of 5 rings or larger, essentially the fraction of saturates and aromatics in a SARA (saturates, aromatics, resins, and asphaltenes) separation of a vacuum resid. As a result, fuels deasphalting is a viable upgrading process for vacuum resids, such as Arabian Heavy, that contain 30% or more saturates plus aromatics but not for Athabasca vacuum resid that contains very little saturates plus aromatics.
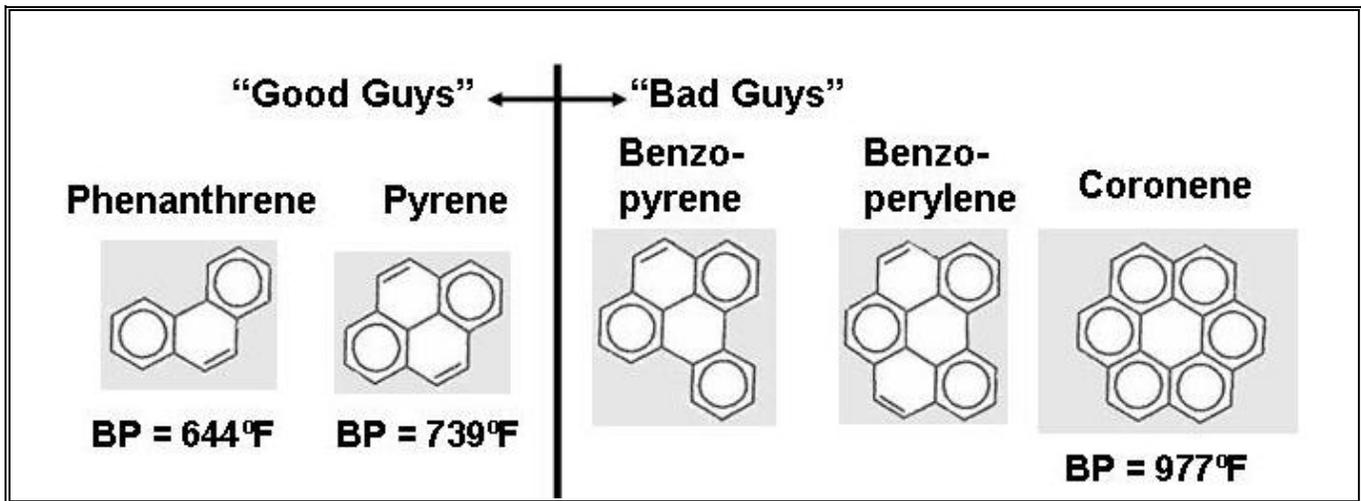
FIGURE 2: TARGET FOR PRIMARY UPGRADING IS TO LIMIT PNA'S TO 4 AROMATICS RINGS IN HIGH QUALITY PRODUCT (COPYRIGHT 2009 BY SOLUBLE SOLUTIONS.)

1.3 Pendant – PNA Core Building Block Model[2]

   The simplest model of the macromolecules in vacuum resids approximates the macromolecules to be composed of various combinations of two different building blocks: pendants and PNA cores. During coking, the pendants thermally crack off the macromolecules to become the distillable liquid product while the PNA cores remain nonvolatile and combine to form the coke as shown in **Figure 3** for the microcarbon test for measuring Conradson carbon residue. If one does a hydrogen balance around this reaction and solves for the Conradson carbon residue (coke yield), one predicts that the Conradson carbon residue is a linear function of the hydrogen content of the resid. Of course, this relationship cannot be expected to hold for macromolecules that are small enough in molecular weight (< 700) to be able to evaporate out of the Microcarbon tester without thermally cracking. As a result, the Conradson carbon residue is plotted against hydrogen content in Figure 4 for various vacuum resids, their SARA fractions, and fractions of their thermal products, including coke, with the requirement that the molecular weight be greater than 700. The data indeed falls in a linear band with the hydrogen content of the pendants to be 11.6±0.4% (zero Conradson carbon residue) and the hydrogen content of the PNA cores to be 3.8±0.3% (100% Conradson carbon residue). This simple model explains what is known about how Conradson carbon residue changes with processing: balances for physical separations (because hydrogen content balances), decreases for hydrogenation processes (because the hydrogen content increases), and slightly increases for thermal conversion (because hydrogen content slightly decreases in the liquid products since hydrocarbon gases are also formed).

Resid Reactant

P-P

P-P-P

P-●-P

P-P-●-P-●

P-●-●-P-●-P-P

P-●-P-●-P-●-P-●

Distillable Liquids   **Conradson Carbon Residue**

→   nP   +   -●-●-●-●-

Hydrogen Content: H H_P H_C

H Balance: $100\ H = (100 - CCR)\ H_P + CCR\ H_C$
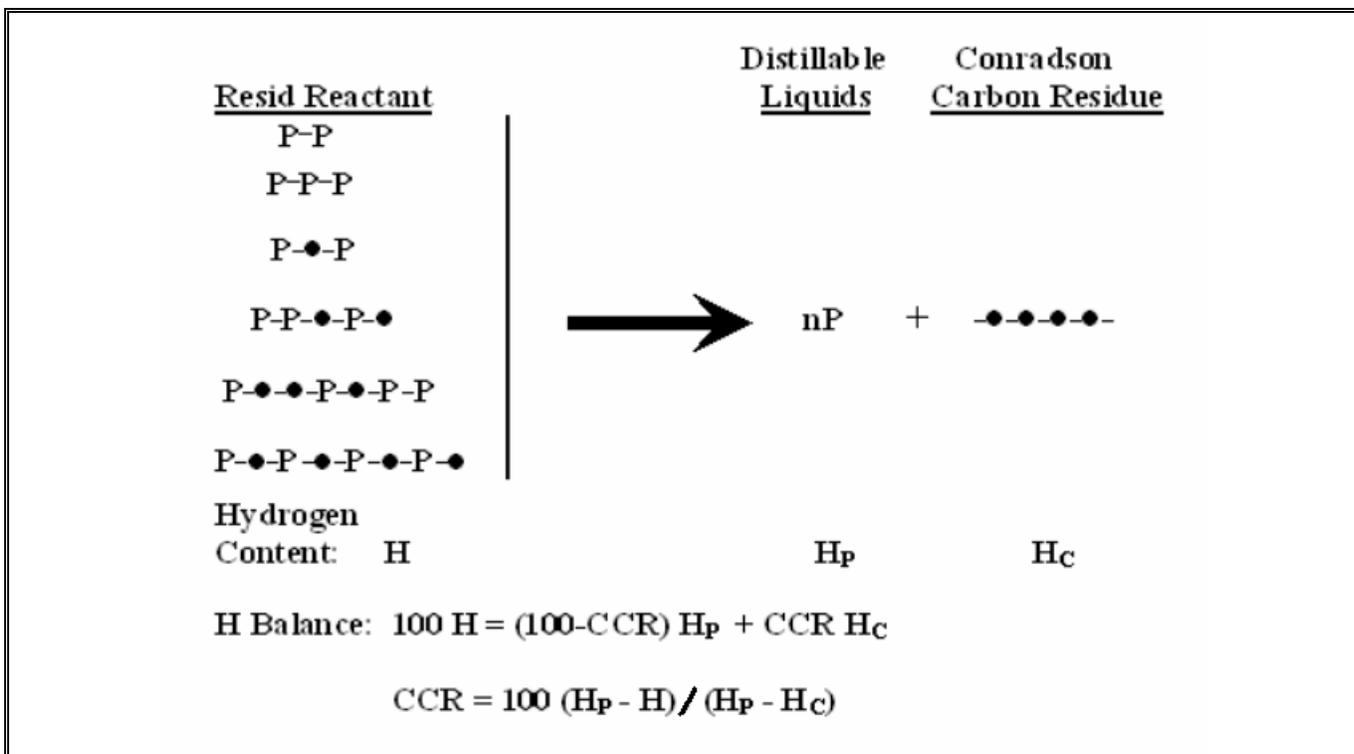
$$CCR = 100\ (H_P - H) / (H_P - H_C)$$

FIGURE 3: MODEL SHOWS CONRADSON CARBON RESIDUE (CCR) IS A LINEAR FUNCTION OF THE HYDROGEN CONTENT (FROM IA WIEHE. *ENERGY & FUELS* 8: 536-544, 1994. REPRINTED WITH PERMISSION. COPYRIGHT 1994. AMERICAN CHEMICAL SOCIETY.)

1.3.1 Solvent-Resid Phase Diagram

A species in the pendant – PNA core building block model can be characterized by two properties: the molecular weight that determines the size and the hydrogen content that determines the ratio of the number of pendant blocks to the number of PNA core blocks. Thus, the solvent **Figure 5** shows that when the molecular weight is plotted versus hydrogen content for fractions of vacuum resids and their thermal reaction products, each fraction (saturates, aromatics, resins, asphaltenes, and coke) falls in an unique area of the diagram. Not only is Conradson carbon residue related to hydrogen content, forming an additional x-axis in **Figure 5,** but so is solubility parameter. Thus, as the fraction of PNA cores increases for a macromolecule, the solubility of that macromolecule decreases in common solvents and in oils. Therefore, the thermal stability, low volatility, and low solubility of the large PNA's in vacuum resids are responsible for the tendency of vacuum resids to form coke and other carbonaceous deposits during conversion.
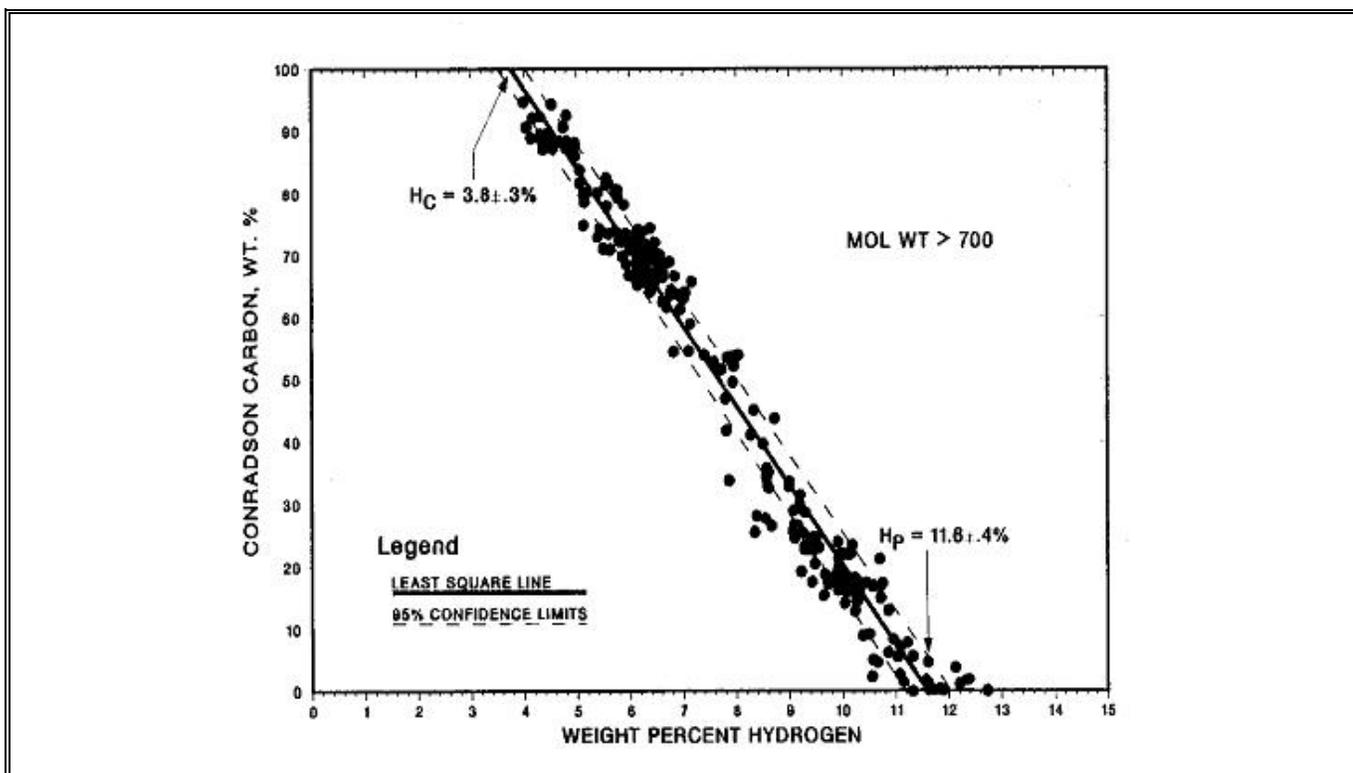
FIGURE 4: CONRADSON CARBON RESIDUE IS A LINEAR FUNCTION OF HYDROGEN CONTENT (FROM IA WIEHE. *ENERGY & FUELS* 8: 536-544, 1994. REPRINTED WITH PERMISSION. COPYRIGHT 1994. AMERICAN CHEMICAL SOCIETY.)
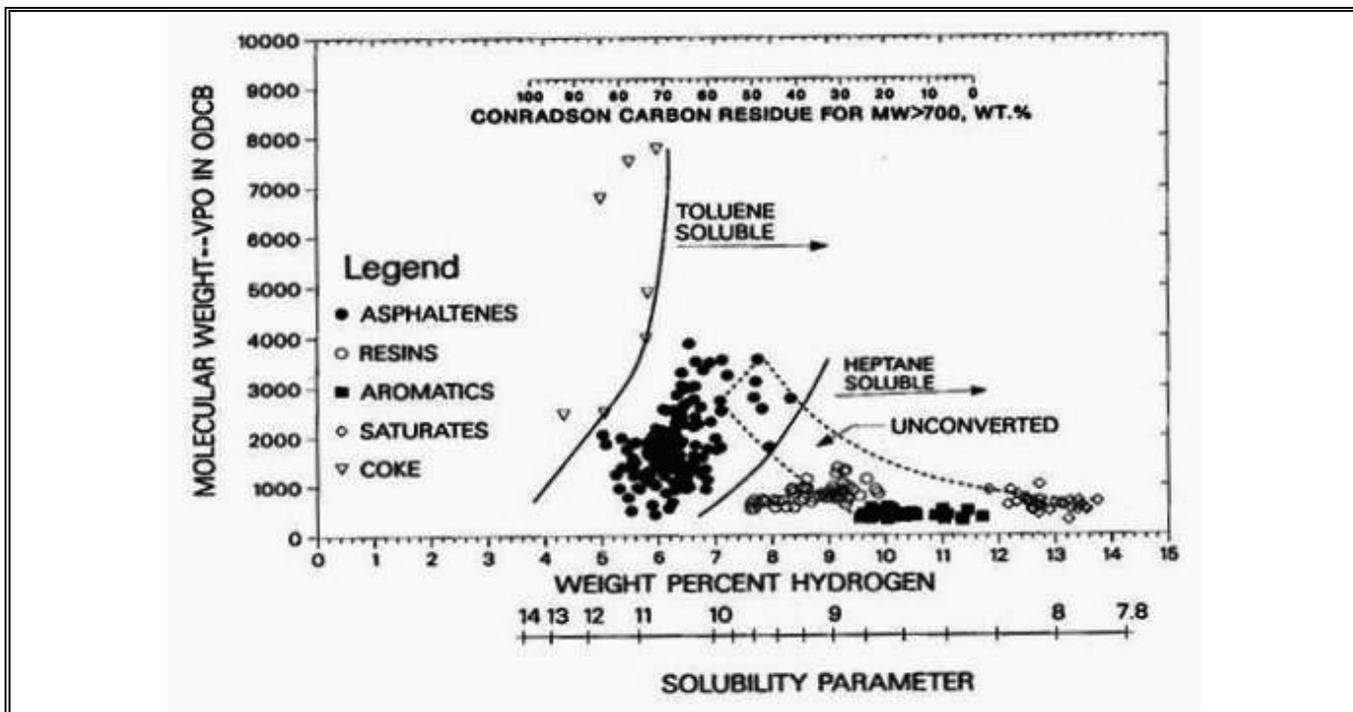

FIGURE 5: THE SOLVENT – RESID PHASE DIAGRAM (FROM IA WIEHE. *IND ENG CHEM RES.* 31: 530-536, 1992. REPRINTED WITH PERMISSION. COPYRIGHT 1992. AMERICAN CHEMICAL SOCIETY.)

1.3.2   Coke Yield Relative to CCR

Despite the surprising success of such a simple model, one of the most valuable learnings from the pendant – PNA core building block model is a result of a failure of the model. If this model were always correct, in a coking process one could not reduce the yield of coke below Conradson carbon residue. The fraction of PNA cores in a vacuum resid would specify the minimum coke yield. By forming a hydrocarbon gas byproduct, one could decrease the hydrogen content of the condensed products and increase the coke yield above Conradson carbon residue. Indeed, commercial cokers obtain coke yields 1.2 – 1.6 times Conradson carbon residue while producing significant yields of hydrocarbon gases and recycling a heavy product. Nevertheless, when model compound pendant – core molecules with small aromatic cores (even one aromatic ring) were reacted in the Microcarbon tester, significant yields of Conradson carbon residue were obtained as shown in **Figure 6** and **Table 1**. Thus, aromatic cores need not be five rings and larger to form coke. If the aromatic core is highly substituted, cracking off of one or two pendants does not reduce the molecular weight sufficiently to make the macromolecule volatile enough to escape the coker, allowing the remaining macromolecules to combine and form larger macromolecules with multiple cores. As a result, coke can be formed from small ring aromatics, even during the Microcarbon test for measuring Conradson carbon residue. This insight provided the hope and the direction to improve greatly the liquid yield while decreasing the coke yield from coking processes without lowering the liquid product quality.

Next, this insight about the macromolecules in vacuum resids being composed of pendants and cores will be exploited in suggesting significant improvements in the primary upgrading processes.
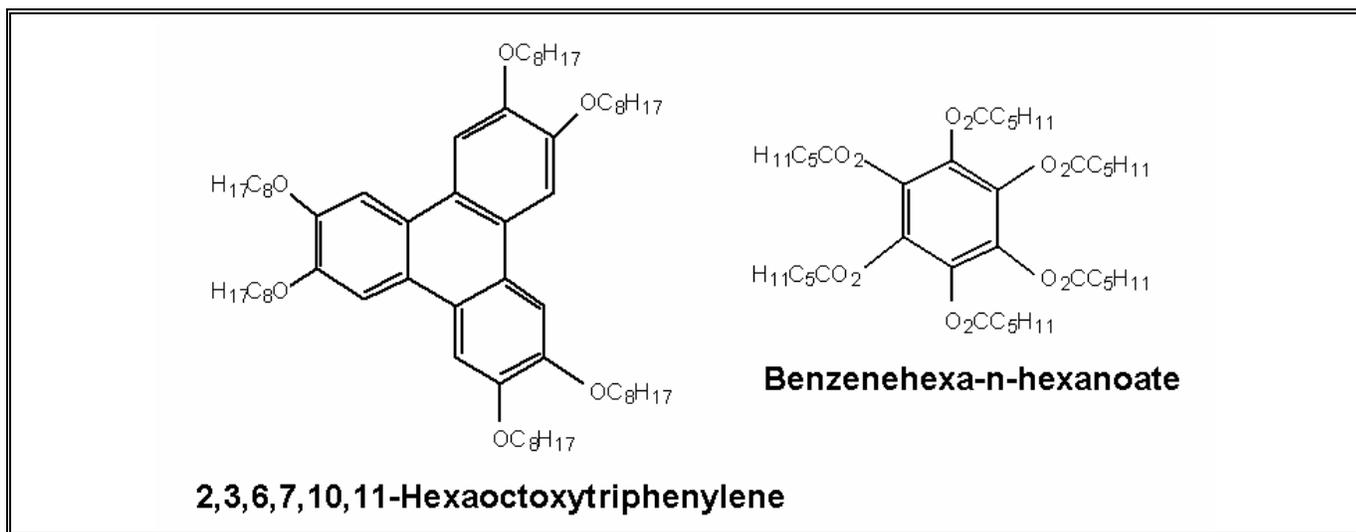

FIGURE 6: MODEL PENDANT-CORE COMPOUNDS (FROM IA WIEHE. *ENERGY & FUELS* 8: 536-544, 1994. REPRINTED WITH PERMISSION. COPYRIGHT 1994. AMERICAN CHEMICAL SOCIETY.)

Large PNA's not Required to Form Coke							
Compound	CCR (wt.%)	C (wt.%)	H (wt.%)	H/C (atomic)	O(wt.%)	Mol.Wt. (amu)	Molecular Formula
Hexaoctoxytriphenylene	24.1	79.46	10.91	1.64	9.62	998	$C_{66} H_{108} O_6$
Benzenehexa-n-hexanoate	14.0	65.66	9.35	1.57	24.99	768	$C_{42} H_{66} O_{12}$

TABLE 1: LARGE PNA'S NOT REQUIRED TO FORM COKE (SOURCE: IA WIEHE. *ENERGY & FUELS* 8: 536-544, 1994. REPRINTED WITH PERMISSION. COPYRIGHT 1994. AMERICAN CHEMICAL SOCIETY.)

1.4 References

[1]   IA Wiehe. Process Chemistry of Petroleum Macromolecules. Baton Raton: CRC Press, 2008.

[2]   IA Wiehe. The Pendant-Core Building Block Model of Petroleum Residua. Energy & Fuels 8: 536-544, 1994.

1.5 Biography of Author

For over 10 years Irwin (Irv) Wiehe has been president of Soluble Solutions, a consulting company specializing in improving the processing of petroleum resids and heavy oils and in the solving of refinery fouling problems, such as preventing the processing of incompatible crude oils. In addition to consulting, Irv has taught 23 short courses in these two fields, sponsored by 16 different organizations in 8 different countries. Irv has a PhD in chemical engineering from Washington University (St. Louis) and worked at Exxon Corporate Research for 22 years. He is internationally known for unique general concepts, such as the Oil Compatibility Model, the Phase-Separation Kinetic Model for Coke Formation, the Pendant-Core Building Block Model of Resids, and the Solvent-Resid Phase Diagram. In addition, Irv is the founder of two annual conferences that have been meeting for over ten years: the International Conference on Refinery Processing for the American Institute of Chemical Engineers (AIChE) and the International Conference on Petroleum Phase Behavior and Fouling. Irv, who has held most of the elected offices in the Fuels and Petrochemicals Division of AIChE, including chairman, received the Division's Distinguished Service Award and was elected a Fellow of AIChE, both in 2007. In 2008 Irv's book, *Process Chemistry of Petroleum Macromolecules*, that summarizes his 30+ years of research of heavy oils and devising innovative solutions to heavy oil conversion and refinery fouling problems, was published by CRC Press.