

**Heavy Oil Conversion Chemistry:
Part 2:
How to Improve Upgrading
Processes**

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1 HEAVY OIL CONVERSION CHEMISTRY: PART 2-HOW TO IMPROVE UPGRADING PROCESSES

1.1 Coking Processes

A coking process can be devised to improve liquid yield and to reduce coke and hydrocarbon gas yields for an example feed of Arabian Heavy vacuum resid. First, let us determine an upper bound on the liquid yield. Arabian Heavy vacuum resid was determined to have a hydrogen content of 10.18 wt% and a Conradson carbon residue of 22.3%. A Fluid Coking model predicts the yield of liquid product with this feed will be 61.4 wt% with a hydrogen content of 11.28 wt%. The upper limit of the conversion by coking to the same quality liquids, L, is obtained when no hydrocarbon gas is formed so that coke and liquids are the only products. Using a hydrogen balance and assuming a hydrogen content of coke equal to that of PNA cores (3.8 wt%):

$$100 (10.18) = 11.28 L + 3.8 (100 - L)$$

$$L = 85.3 \text{ wt\%}$$

$$\text{Coke Yield} = 100 - L = 14.7 \text{ wt\%}$$

Thus, considerable improvement in liquid yield of the same quality (hydrogen content) is theoretically possible from coking while obtaining much lower coke yield than Conradson carbon residue. While one will certainly not be able to obtain higher liquid yield of the same quality in converting Arabian Heavy vacuum resid without adding hydrogen, there may be other molecular barriers that prevent approaching this upper bound. As a result, ideal laboratory cokers were used to determine how much improvement can be achieved with this feed.

1.1.1 Two Directions to Improve the Liquid Yield

Minimizing the formation of (1) hydrocarbon gases and (2) PNA's of 5 aromatic rings or larger from smaller aromatics can raise liquid yield. Most of the hydrocarbon gases formed during coking are by the re cracking of volatile liquid products. Therefore, the ideal coker has a very short residence time for the vapor products before they are cooled below thermal cracking temperatures. In addition, the ideal coker needs to have a long residence time for the nonvolatile products so that the thermal reactions go to completion.

As shown in **Figure 1**, four different laboratory cokers were devised that have these ideal coker properties, to give a linear band of data of hydrogen content of the liquid product as a function of liquid yield. At the hydrogen content of the liquids from the Fluid Coking model (11.28 wt%) the line determines the yield of liquid product to be 69.3 wt% or 7.9 wt% higher than Fluid Coking with the same Arabian Heavy vacuum resid feed (10 wt% higher than delayed coking). Since coking degrades the high quality (saturates plus aromatics) portion of the vacuum resid feed by forming PNA's of 5 aromatic rings and larger from smaller aromatics, one method to avoid this degradation is to separate the high quality portion from the vacuum resid prior to coking.

This portion is added to the volatile liquid product of coking, while the lower quality portion of the vacuum resid is sent to a coker that has a short vapor phase residence time but a long resid/coke residence time. While fuels deasphalting might be the best commercial process for achieving this separation of the vacuum resid into higher and lower quality portions, in the laboratory a high cut-point distillation at very high vacuum was used to separate the 45 wt% portion with atmospheric boiling points below 1300°F as the high quality portion. As shown in **Figure 1**, the total yield of ideal coking plus prior separation was 76.2 wt% or 14.8 wt% higher than Fluid Coking at slightly lower quality (11.20 wt% hydrogen) while obtaining lower coke yield (19.6 wt%) than Conradson carbon residue of the feed (22.3 wt%).

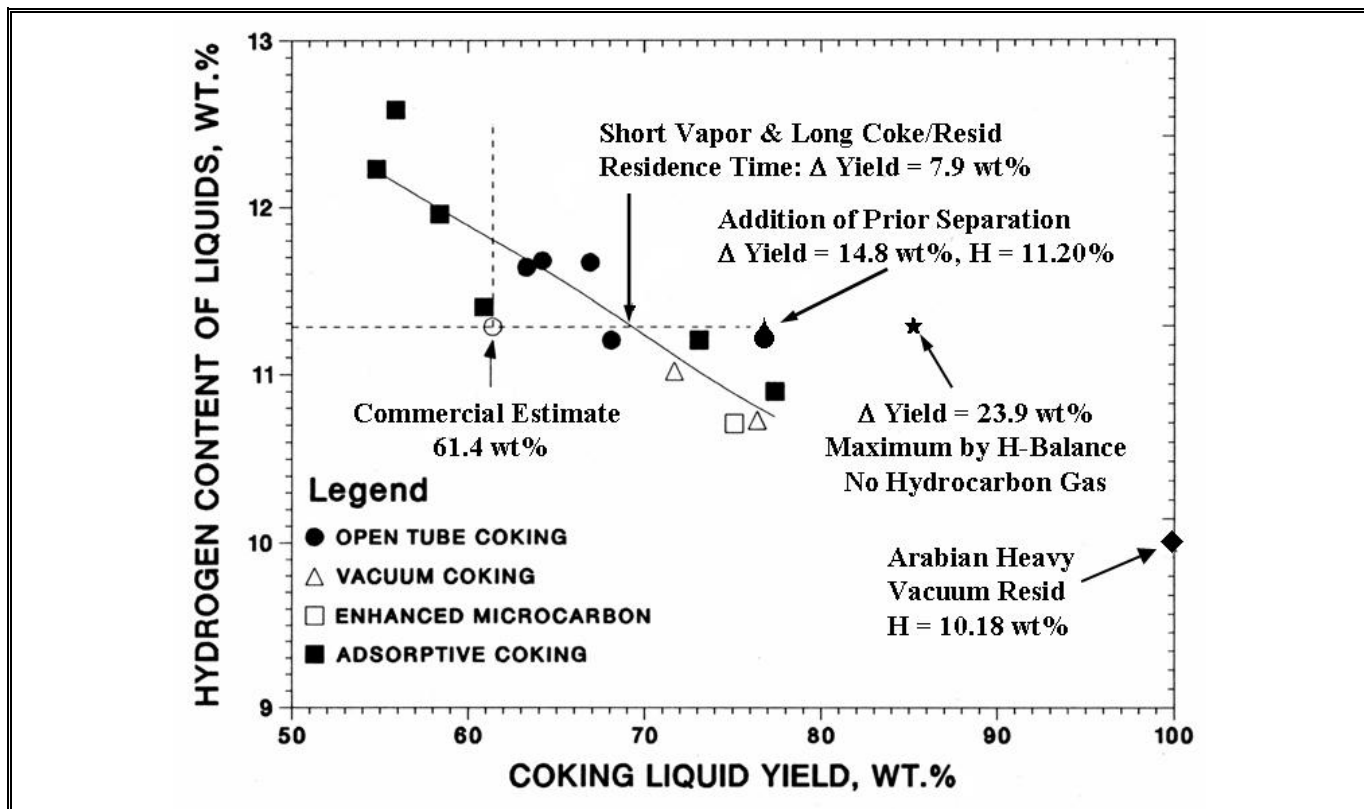


FIGURE 1: BOTH SHORT VAPOR RESIDENCE TIME AND PRIOR SEPARATION IMPROVE COKING YIELD (FROM IA WIEHE. *PROCESS CHEMISTRY OF PETROLEUM MACROMOLECULES*. REPRINTED WITH PERMISSION. COPYRIGHT 2008. CRC PRESS, TAYLOR AND FRANCIS GROUP.)

1.1.2 Room for Improvement

Contrary to the common opinion that coking of vacuum resid is a mature technology, this section demonstrates that substantial improvements in coking are possible. Actually, deasphalting the vacuum resid, coking the asphalt, and sending both this volatile coker product and the deasphalted oil to secondary catalytic upgrading is already practiced in a few refineries and would be a large improvement for many others. While the degree of improvement depends on the fraction of saturates plus aromatics in the vacuum resid feed, most

vacuum resids contain greater than 30 wt% saturates plus aromatics. Although Athabasca vacuum resid is an exception, a vacuum resid from a different Canadian bitumen, Cold Lake, contains 35 wt% saturates plus aromatics¹. The development of a commercial coker that achieves short vapor phase residence time and long resid/coke residence time is more difficult but this section demonstrates that the reward is significant. Actually, one such coker based on cross-flow fluid bed technology is under development by ETX Systems Inc.^{2,3}

1.2 Visbreaking Processes

In visbreaking, the resid is thermally cracked in either a coil in a furnace or heated in a furnace coil and soaked in an up-flow, insulated reactor. The degree of conversion is low (about 28 wt% for Arabian Heavy vacuum resid) but the heavy product can be blended into residual fuel oil. The degree of conversion is limited by coke formation in the reactor (insolubility at reaction temperatures), asphaltene sediments in the heavy product (insolubility on cooling), or incompatibility of the heavy product with other residual fuel oils. All of these limitations are a result of asphaltenes becoming less soluble by the cracking of pendants off PNA cores¹ and can be extended by increasing the solvency of the rest of the oil for these partially converted asphaltenes.

Since coke in resid thermal cracking was previously believed to be a direct reaction product, the discovery⁴ that coke is triggered by the phase separation of converted asphaltenes from a medium rich in natural hydrogen donors to form a phase lean in hydrogen donors opened the door to significant visbreaking conversion improvement. Although several methods are discussed elsewhere¹, two are mentioned here. Probably, the most practical method for improving the solvency of converted asphaltenes to increase visbreaker conversion is to remove the nonsolvent by stripping out the distillable liquid product by adding steam to the visbreaker. A second method is to deasphalt the heavy visbreaker product into deasphalted oil, resins, and asphalt fractions. The deasphalted oil is sent to secondary catalytic upgrading and the asphalt is sent to a coker or a gasifier. Meanwhile, the resins are recycled back to the inlet of the visbreaker both to improve the solvency of converted asphaltenes and to be further converted. Theoretically, this recycle process could get vacuum resid conversions similar to coking. Even more important is that these two methods also can be used to improve hydroconversion processes.

1.3 Hydroconversion Processes

These processes still rely on thermal cracking but the partial hydrogenation of aromatics, including PNA's, replenish hydrogen donors. By terminating free radicals, hydrogen donors greatly reduce aromatics combining to form larger PNA's. As a result, hydroconversion processes are able to achieve much higher vacuum resid conversions than visbreaking. Nevertheless, the limits of conversion are similar to visbreaking: coking in the reactor or precipitating asphaltene sediments in the heavy product. These limits just occur at much higher conversions than in visbreaking.

1.3.1 Dispersed TMS Catalyst

Ebullating-bed hydroconversion processes, H-Oil and LC-Fining, which allow for continuously replacing the catalyst are most conventionally used to deal with the catalyst poisons in vacuum resids. Since the heavy byproduct of conversion is typically blended into heavy fuel oil, the precipitation of converted asphaltenes to foul heat exchangers and form sediments in the heavy fuel oil usually limits the conversion (65-70 wt% for Arabian Heavy vacuum resid). However, if the conversion is raised further, coking in the reactor or hot separators would occur. Nevertheless, there are a number of processes under development that use about 100 ppm of dispersed catalyst (transition metal sulfides, TMS) added with the feed, such as Microcat-RC, Eni Slurry Technology, HDH-SHP, (HC)₃, and HCAT, that promise to achieve much higher conversions than ebullating-bed processes. The small, dispersed catalyst particles overcome the mass transfer disadvantage of conventional catalysts with pores that can plug up with nickel, vanadium, and coke during conversion. In addition, dispersed catalyst processes typically use slurry bubble column reactors that can use hydrogen to strip out the distillable liquid product, nonsolvents for converted asphaltenes, in order to maintain asphaltene solubility in the reactor, preventing coke formation. Although conversions in dispersed catalytic processes can be above 95 wt% and well over 100 vol%, it is questionable that such high conversions are economical. As is shown in **Figure 2**, these very high hydroconversions require hydrogenating and cracking the outside rings of PNA's to produce hydrocarbon gases and eventually 4-ring aromatics. This process is slow because hydrogen donation from the partially hydrogenated PNA reacts much faster than cracking of the saturated ring. In addition, the products, hydrocarbon gases and 4-ring aromatics, are not very valuable and consume considerable hydrogen. While the economics are very dependent on local situations, it is questionable that much conversion of PNA's of 5 rings or larger is wise. This would limit the hydroconversion of Arabian Heavy vacuum resid to the range of 85-90 wt%, still much higher than currently obtained by ebullating-bed hydroconversion processes. Otherwise, increasing the hydroconversion of Arabian Heavy vacuum resid from 85 to 95 wt% can double the reactor size and double the hydrogen consumption to obtain a marginal liquid product of the poorest quality.

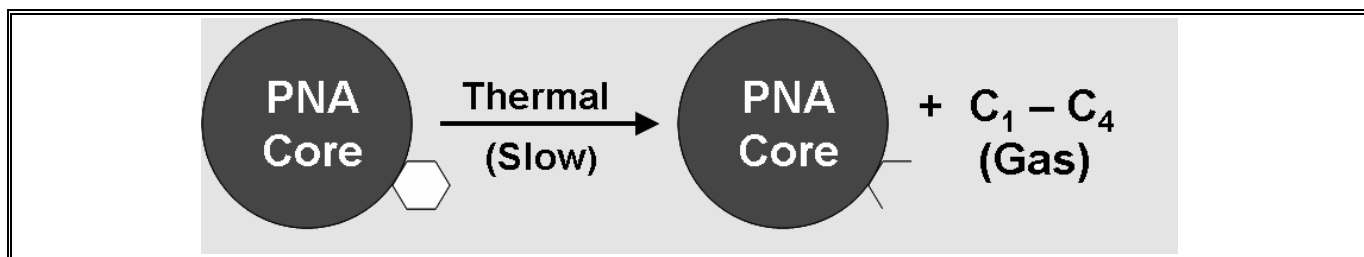


FIGURE 2: PROBLEM OF CONVERTING LARGE PNA'S BY HYDROCONVERSION (FROM KA GOULD; IA WIEHE. *ENERGY & FUELS* 21: 1199-1204, 2007. REPRINTED WITH PERMISSION. COPYRIGHT 2007. AMERICAN CHEMICAL SOCIETY.)

1.3.2 Managing PNA Cores by Deasphalting

As with the other primary upgrading processes, deasphalting can allow one to manage PNA cores and greatly improve hydroconversion. Eni Slurry Technology^{5,6}, which successfully passed the demonstration scale, uses deasphalting to separate the nonvolatile product. The deasphalted oil is sent to secondary upgrading along with the volatile liquids while most of the asphalt along with the slurry catalyst is recycled to the inlet of the reactor for additional conversion. This lowers hydrogen consumption without the need to crack large PNA's to obtain only volatile product while reducing the catalyst consumption. As a result, Eni Slurry Technology obtains 89 wt% conversion of Arabian Heavy vacuum resid. However, the author favors a deasphalting process that separates the heavy product of hydroconversion into three fractions: deasphalted oil, resins, and asphalt. In this way the quality of the deasphalted oil can be controlled to meet the requirements for secondary upgrading and the quality of the asphalt can be controlled separately to remove 5 ring PNA's and larger. Meanwhile, the resin fraction, that is too poor in quality to send to secondary upgrading but is not high enough in concentration of 5 ring PNA's or larger to dispose with the asphalt, is recycled for further conversion. This type of deasphalter could greatly increase the conversion of ebullating-bed hydroconversion but would require coking or gasification of the asphalt, rather than blending with residual fuel oil.

1.4 Deasphalting Processes

Surprisingly, the separation of vacuum resids cannot be improved by using different nonsolvents than the traditional use of light alkanes: propane, isobutane, n-butane, and n-pentane. The Conradson carbon residue separation is limited by the macromolecules themselves because the large PNA's (cores) in vacuum resids are chemically bonded to high quality parts of the macromolecules (pendants). As a result, no matter how the separation is performed, for a given limit in Conradson carbon residue of the higher quality fraction the best that any separation will do is to match the yield of the higher quality fractions of the other separations (about 50 wt% yield at a Conradson carbon residue of 4 wt% of the deasphalted oil for Arabian Heavy vacuum resid). There just are not any higher quality macromolecules present. While the separation of the metals, nickel and vanadium, do not have a molecular limitation, these metals are in porphyrin structures that cause them to associate with PNA's and act in deasphalting like they have a molecular limitation. Therefore, it makes sense to continue using the traditional light alkane nonsolvents in deasphalting of vacuum resids and take advantage of supercritical solvent recovery. However, these fuels deasphalters can be constructed and operated at much lower cost than deasphalters designed for lubes separation. Fuels deasphalters can be much shorter in height, can use packing rather than trays, can be without a temperature gradient, and can run at much lower nonsolvent-to-oil ratio.

The strength of deasphalting is that its combination with each conversion process—coking, visbreaking, and hydroconversion—is much better than either the conversion process or deasphalting alone. Conversion

reduces the molecular limited separation and separation on the basis of PNA's allows one to convert vacuum resid more effectively.

1.5 Conclusions

Vacuum resid conversion processes can greatly be improved over what is currently practiced but are still constrained by PNA cores and by economics. Particularly, the use of deasphalting to manage PNA cores can significantly increase the yields of existing vacuum resid conversion processes. However, two sets of processes under development, a new generation coking process and dispersed catalyst hydroconversion processes, offer even greater conversion yields. More detailed information on heavy oil conversion, on use of high performance liquid chromatography for measuring PNA size distribution, and on fouling mitigation of both opportunity crudes and vacuum resid conversion processes is available in the author's recent book¹.

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1.7 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.