

Solvent Deasphalting in Today's Deep Conversion Refinery

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R & D — Heavy Oil Upgrading

UOP, LLC

AIChE-Chicago Symposium

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**Refinery Processing and In-Plant Energy
Conservation and Optimization**



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Information Sharing is the objective of our presentation

- **UOP is investing:**
 - To develop better solutions in heavy oil conversion
 - To improve our analytical and modeling capability in heavy oil
- **The current market supports increased conversion of heavy residues**
 - Improved SDA coupled with HT/HC
 - Improved Primary residue conversion
 - Improved integration with downstream processes and H₂ production
- **We'd like your perspectives and feedback**



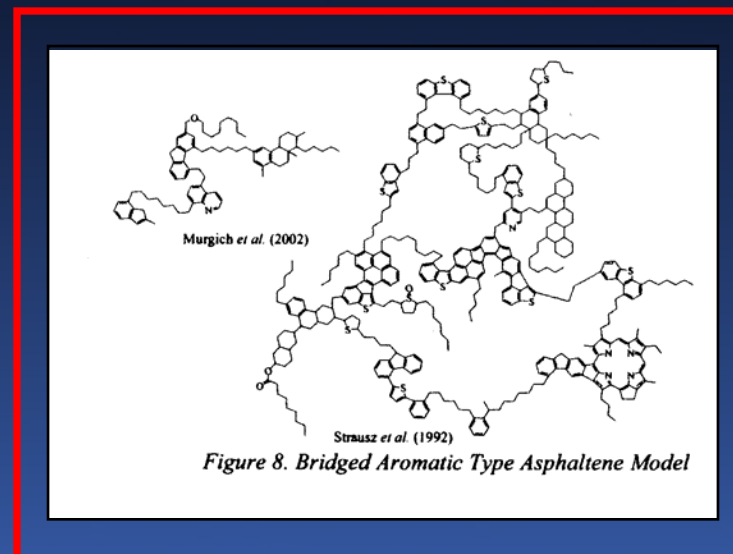
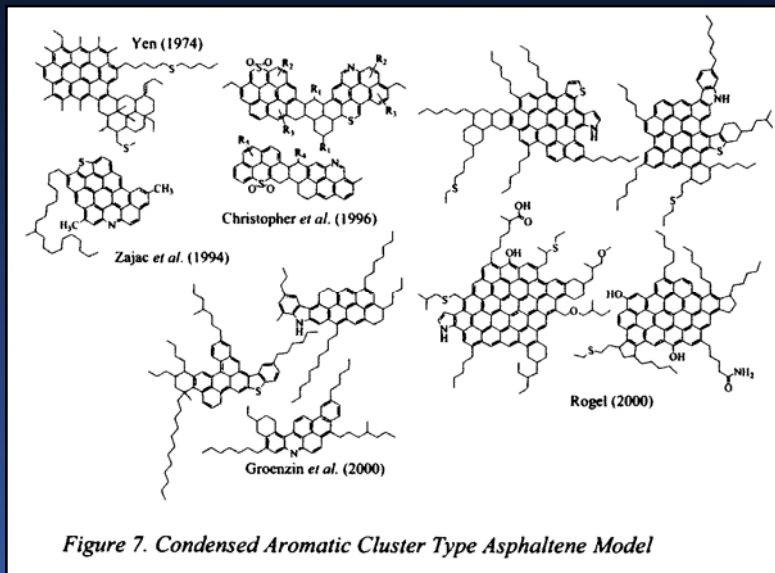
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- **Background—technologies for upgrading**
- **Solvent Deasphalting Technology**
- **Applications**
- **How we use solubility to evaluate heavy oil upgrading potential: the bench-scale “vacuum resid assay”**
- **Conclusions**

The \$10⁹ question

- Why would you coke vacuum residue?
- Why would you directly upgrade vacuum residue?

Which is the most realistic model of an “average” heptane - insoluble fraction?



Be very, very careful what you put into that head, because you will never, ever get it out¹.

--Thomas Cardinal Wolsey (1471-1530)

- The evidence from advanced NMR, RICO oxidation studies and analysis of flash pyrolysis products points to the bridged aromatic (“archipelago”²) model, rather than huge condensed multi-ring aromatics.
- It means that deeper cuts into vacuum residue are **contaminated** and **hydrogen-deficient**, but basically, **convertible** to fuels.
- Lab measurements of molecular weight are often over-estimated due to asphaltenes association

²Gray, Murray: “Recent Advances in Residue Upgrading Fundamentals” Resid Upgrading Tutorial, AIChE Spring Meeting, Atlanta GA, April 2005



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Major Existing Technologies For Heavy Fuel Oil Elimination

Primary upgrading	Downstream	Residue disposition
Coking	Hydrotreating, hydrocrack or FCC	Petcoke to fuel (power/steam) or gasify
Ebbulated Bed Hydrocracking	Hydrotreating, hydrocrack or FCC	Unconverted bottoms to fuel, gasify or to coker
Solvent Deasphalting	Deep hydrotreating, hydrocrack or FCC	Pitch to fuel or gasify or to coker

Major Existing Technologies For Heavy Fuel Oil Elimination

Primary upgrading	Downstream	Residue disposition
Coking	Hydrotreating, hydrocrack or FCC	Petcoke to fuel (power/steam) or gasify

- **Dominant for many years, especially in N. America**
- **A purely thermal conversion process, nearly all metals to coke**
- **Especially attractive with nearby coke off-take arrangement for power or gasification, less so with remote site.**
- **Lowest hydrogen requirement**

Major Existing Technologies For Heavy Fuel Oil Elimination

Primary upgrading	Downstream	Residue disposition
Ebbulated Bed Hydrocracking	Hydrotreating, hydrocrack or FCC	Unconverted bottoms to fuel, gasify or to coker

- **LC-finishing, H-Oil technologies allow deeper conversion up to a stability limit**
- **Have attributes of both thermal and catalytic conversion process**
- **Metals and some contaminants removed on catalyst, high makeup rates are a factor in economics**

Major Existing Technologies For Heavy Fuel Oil Elimination

Primary upgrading	Downstream	Residue disposition
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Solvent Deasphalting	Deep hydrotreating, hydrocrack or FCC	Pitch to fuel or gasify or to coker
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- Re-emerging in importance
- Deep-lift SDA can often prepare suitable feed for downstream fixed bed units at much lower cost
- SDA pitch is especially good feed for gasification

Technologies entering full commercialization

Primary upgrading	Downstream	Residue disposition
Slurry-phase hydrocracking	Hydrotreating, hydrocrack or FCC	Pitch to fuel, gasify or coker
Solvent Deasphalting	Hydrotreat and HC-integrated scheme	Pitch to gasification
Solvent Deasphalting	Thermal conversion	Gasify unconverted pitch

Recent example:
Synenco-Northern
Lights Upgrader

Recent example: Opti
Canada/Nexen Long
Lake Upgrader

- SDA and gasification-based hydrogen as a hedge against high natural gas prices.

SDA + gasification is an attractive combination

- **Gasification + full shift, hydrogen recovery (eg., UOP Selexol/PSA) on the order of 16,000 SCF/bbl of pitch feed³. Full hydrogen demand for low sulfur fuels can be provided**
- **Pitch gasification can be on the order of 20 % lower unit capital cost¹ than petcoke or coal considering elimination of the solids handling and slurry feed system**
- **Pitch gasification is a “dry” system, therefore 20-25 % lower oxygen consumption, higher cold gas efficiency compared to water-slurry feed.**

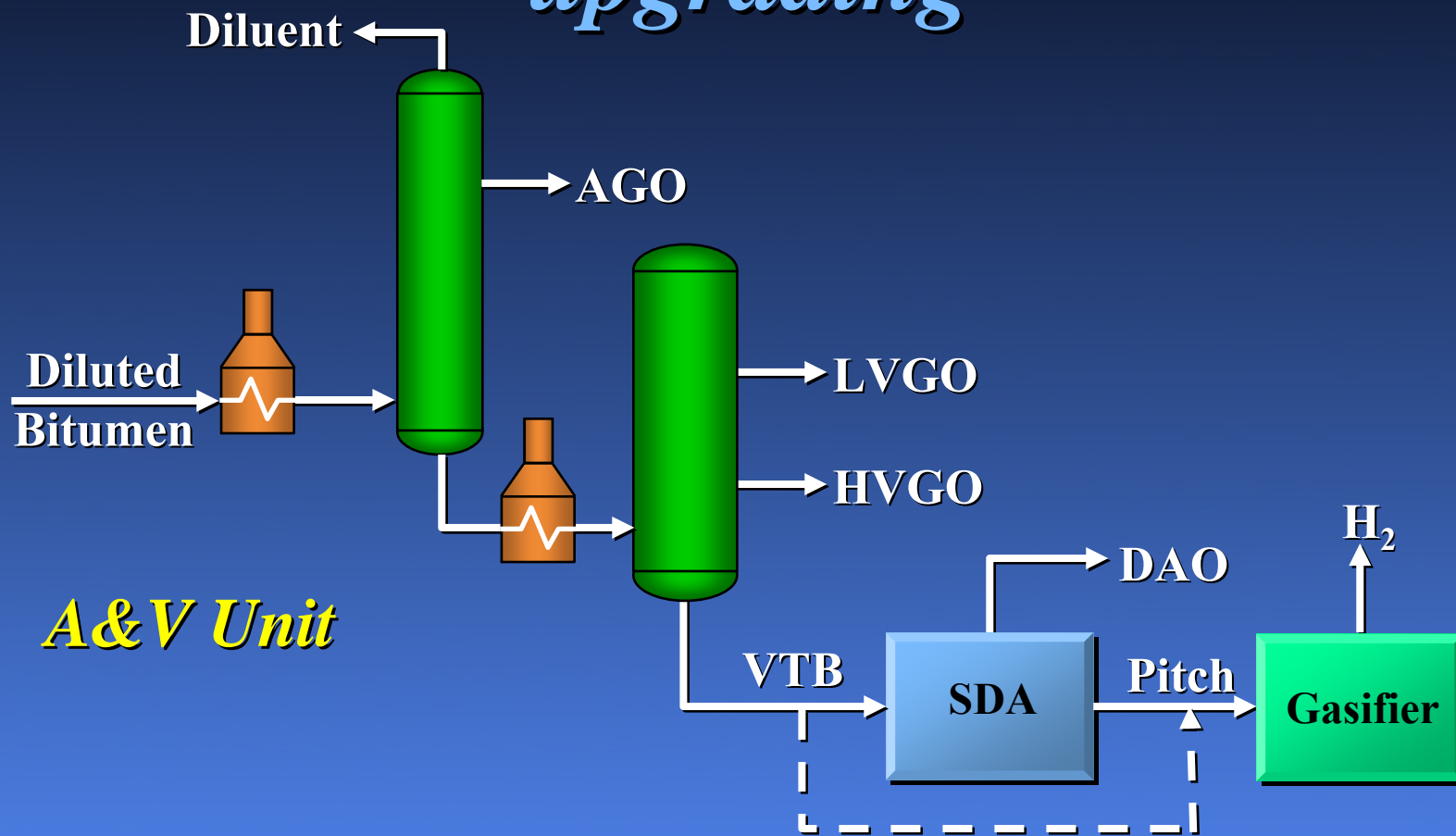
¹ Simbeck, “The Business Case For IGCC Development” SFA Pacific, Inc 2006

² Higman & Van Der Burgt, “Gasification”, Elsevier 2003 p. 113

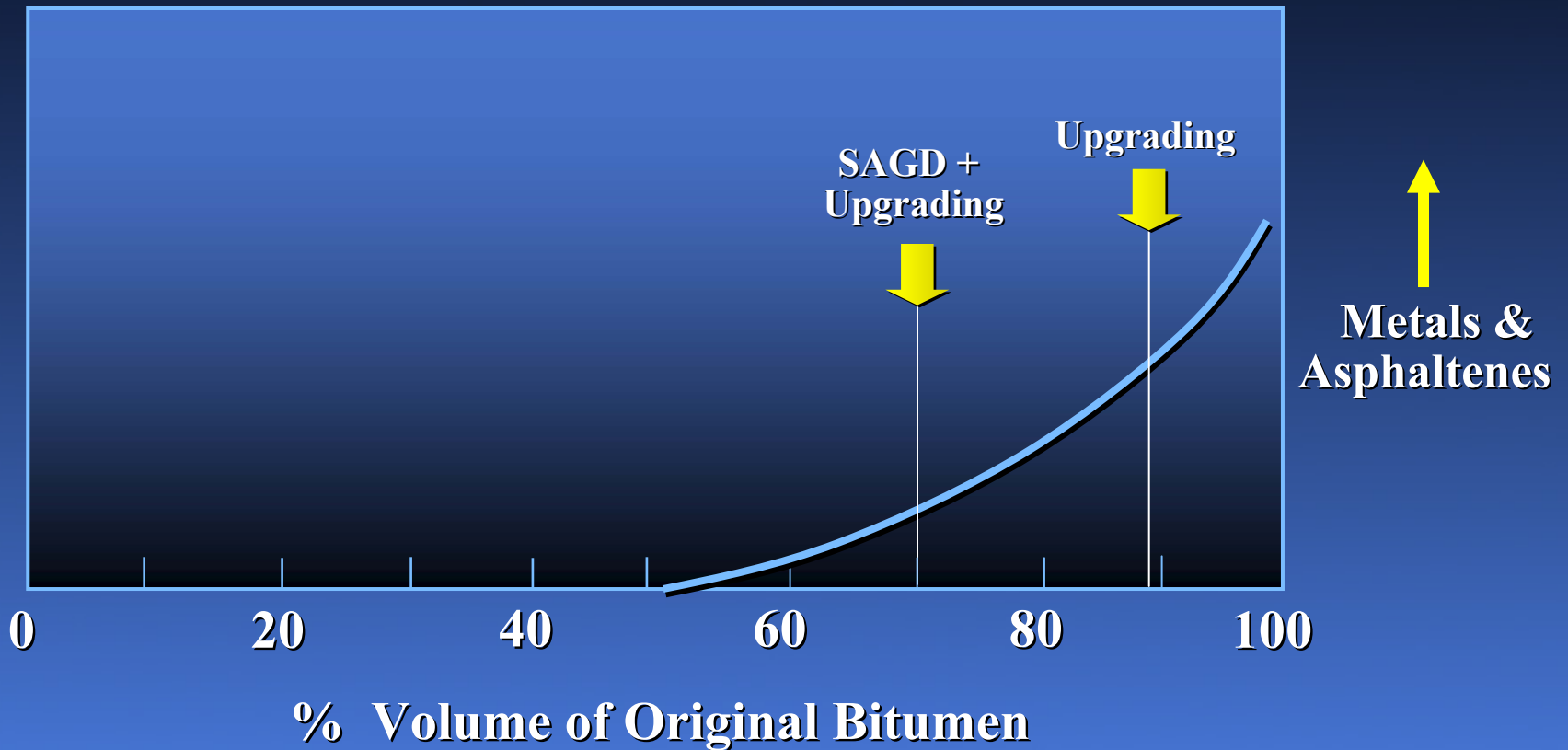
³ Wisdom, L. and Duddy, J. “First Commercial Residue Hydrocracker integrated with Gasification to be Self-Sufficient for its Hydrogen Consumption Requirements” 4th Upgrading and Refining of Heavy Oil, Bitumen and Synthetic Crude Conference, Edmonton September 25-27, 2006



Solvent deasphalting will produce pitch for gasifier feed in oilsands upgrading



How much residue needed for gasification to produce steam and hydrogen? Example: oilsands to synthetic crude



Kind acknowledgement to Len Flint, PhD; LENEFF Consulting

Gasification units feeding heavy residual liquids startup since 1998 + publicly announced

Plant name	Licensor	Startup year	Feed	Products
Synenco-Northern Lights Upgrader	GE	Engineering	Heavy residue	Hydrogen + Power
Northwest Upgrading, Ltd.	Lurgi	Engineering	hydrocracker bottoms	Hydrogen + Power
Fujian Petrochemical refinery expansion	Shell	Engineering	Heavy residue	Hydrogen + Power
Wilhelmshaven Raffineriegesellschaft deep conversion complex	Shell	Engineering	Asphalt	Hydrogen + Power
Lotos-Refinery Gdansk	Shell	Engineering	Asphalt	
Opti Canada, Ltd. Longlake upgrader	Shell	Startup 2007	Heavy "Orcrude" residue	Hydrogen + steam for oilsands extraction
Agip Raffinazione IGCC	Shell	2006	Visbreaker residue	Power
Nippon Petroleum Negishi IGCC	GE	2003	Vac. residue	Power
Nanjing Chemical Industry Ammonia Plant	GE	2002	Eureka pitch & Vacuum residue oil	Chemicals
api Energia S.p.A. IGCC Plant	GE	2001	Visbroken vacuum residue	Power
Jilin Chemicals Ammonia Plant	GE	2001	Visbreaker residue	Chemicals
Esso Singapore Chawan IGCC Plant	GE	2001	Residual oil	Power
Linde AG Singapore Syngas Plant	GE	2000	Residual oil	Chemicals
SARLUX srl IGCC Project	GE	2000	Visbreaker residue	Power
ExxonMobil Baytown Syngas Plant	GE	2000	Deasphalter pitch	Gaseous fuels
DEA, AG Wesseling Syngas Plant	GE	2000	Residual oil	Chemicals
ISAB Energy IGCC Project	GE	1999	Asphalt	Power



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Source: Gasification Technologies Council and press releases

Solvent Deasphalting: 70 year history

- **1930's: Lacey, Kay and other pioneers in fluid-phase equilibrium explain phase behavior**
- **1930's-40's: Propane deasphalting developed jointly by Kellogg, Standard of N. J, Standard of Indiana, Union Oil Co. for lube stocks**
- **1950's-60's: Increasingly, SDA units are commissioned to recover FCC feed; pitch to asphalt or heavy fuel oil**
- **1970's: UOP acquires DEMEX technology**
- **late 1970's: UOP commissions first SDA + hydrocracking scheme**
- **1997: UOP and Foster Wheeler USA merge technologies**



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UOP +Foster Wheeler USA SDA Process

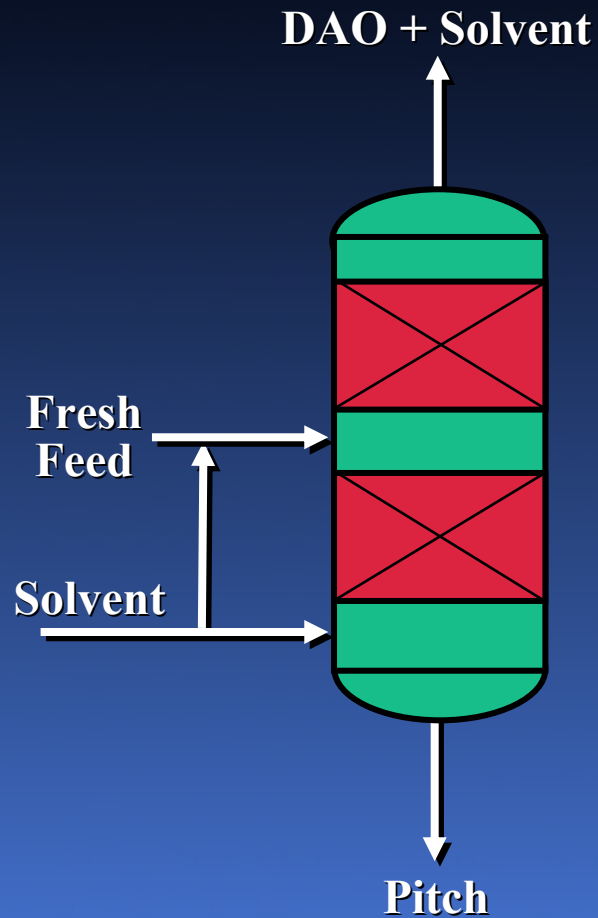
- **Combined experience covers all SDA applications**
 - **Lubes**
 - **Hydrocracking**
 - **FCC \ Resid FCC**
 - **Residue Hydrotreating**
- **50+ units licensed (~750,000 BPD total capacity)**



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Solvent Deasphalting

- **Physical separation of residues into**
 - Deasphalted oil (DAO)
 - Highly viscous, asphaltene-rich stream (Pitch)
- **Light paraffin solvent has high difference in solvent parameter, leading to 2 liquid phases**
 - L1: Light DAO
 - L2: Asphaltenes and resins (heavy DAO)
- **Supercritical separation of DAO and solvent**

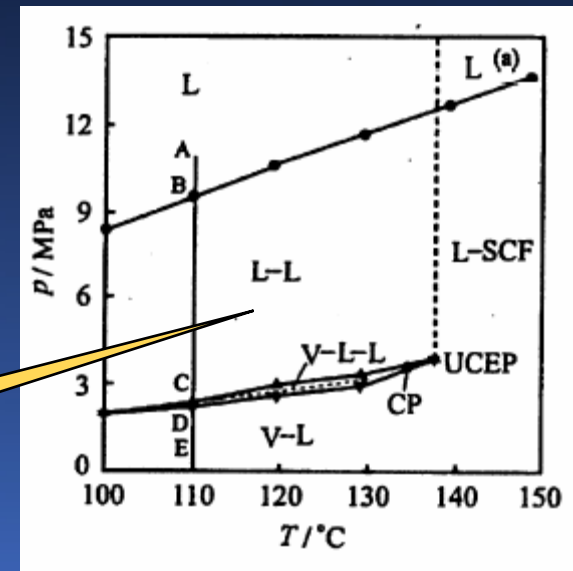


- Countercurrent column with high – efficiency packing establishes gradient for highest possible purity of DAO

Typical phase behavior of vacuum residue-solvent mixture

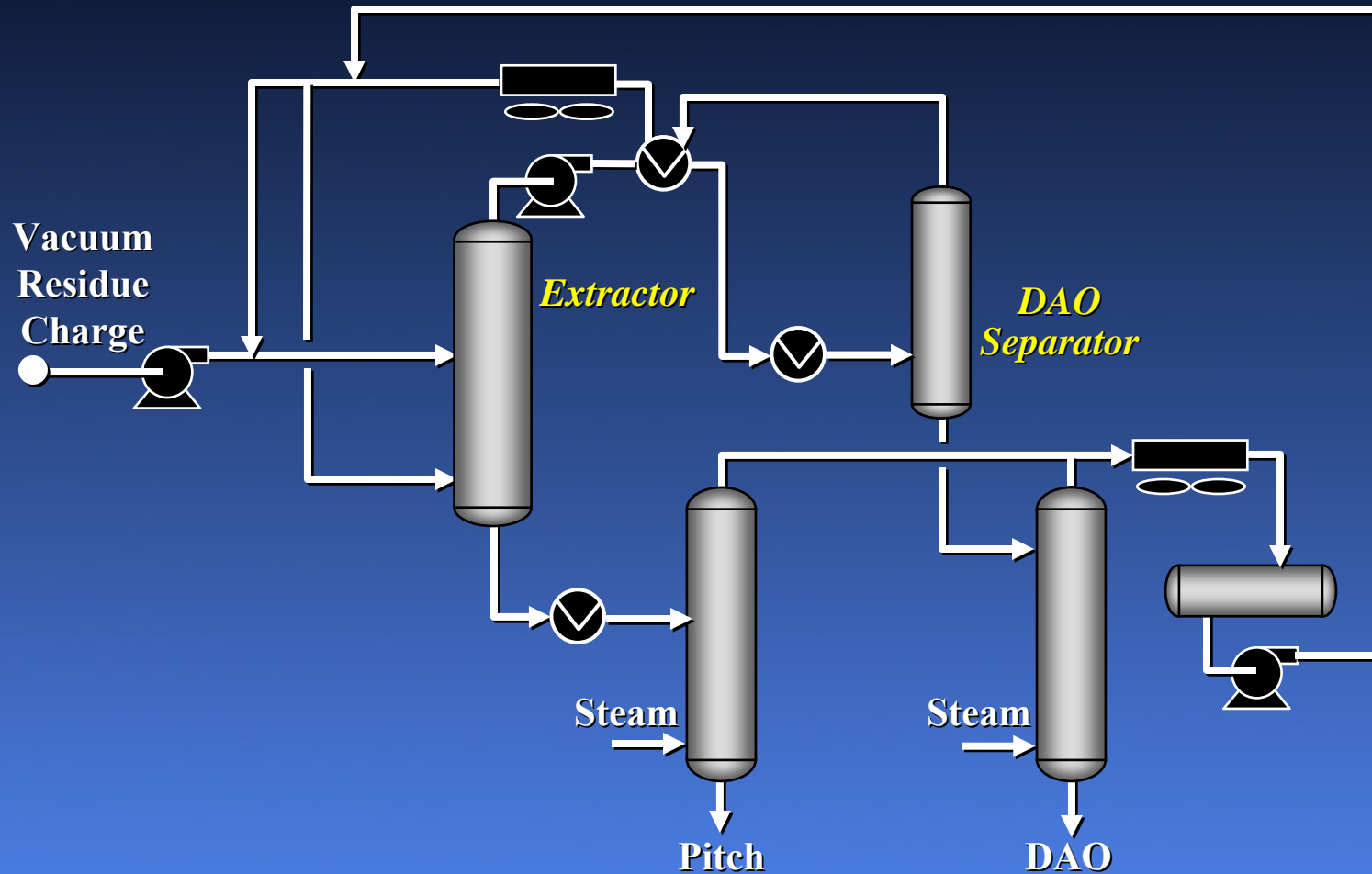
A fully-developed phase diagram for Dagang (paraffinic) residue in isobutane at constant solvent/oil ~2.0 wt ratio

Practical commercial operation

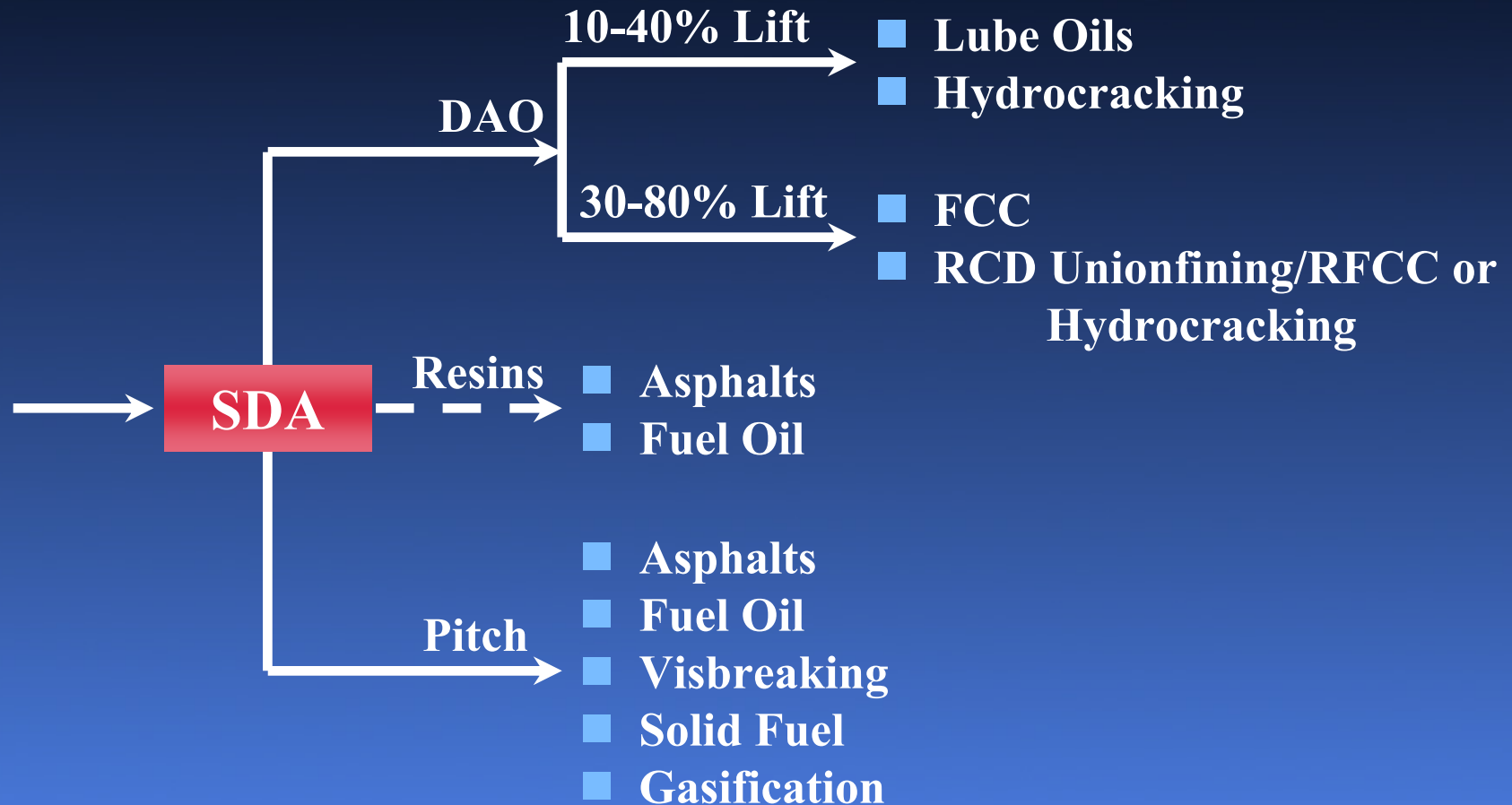


Zhao, S. Q. et. al. Acta Petrolei Sinica (Petroleum Processing Section) 17 (1) 2001 47-55

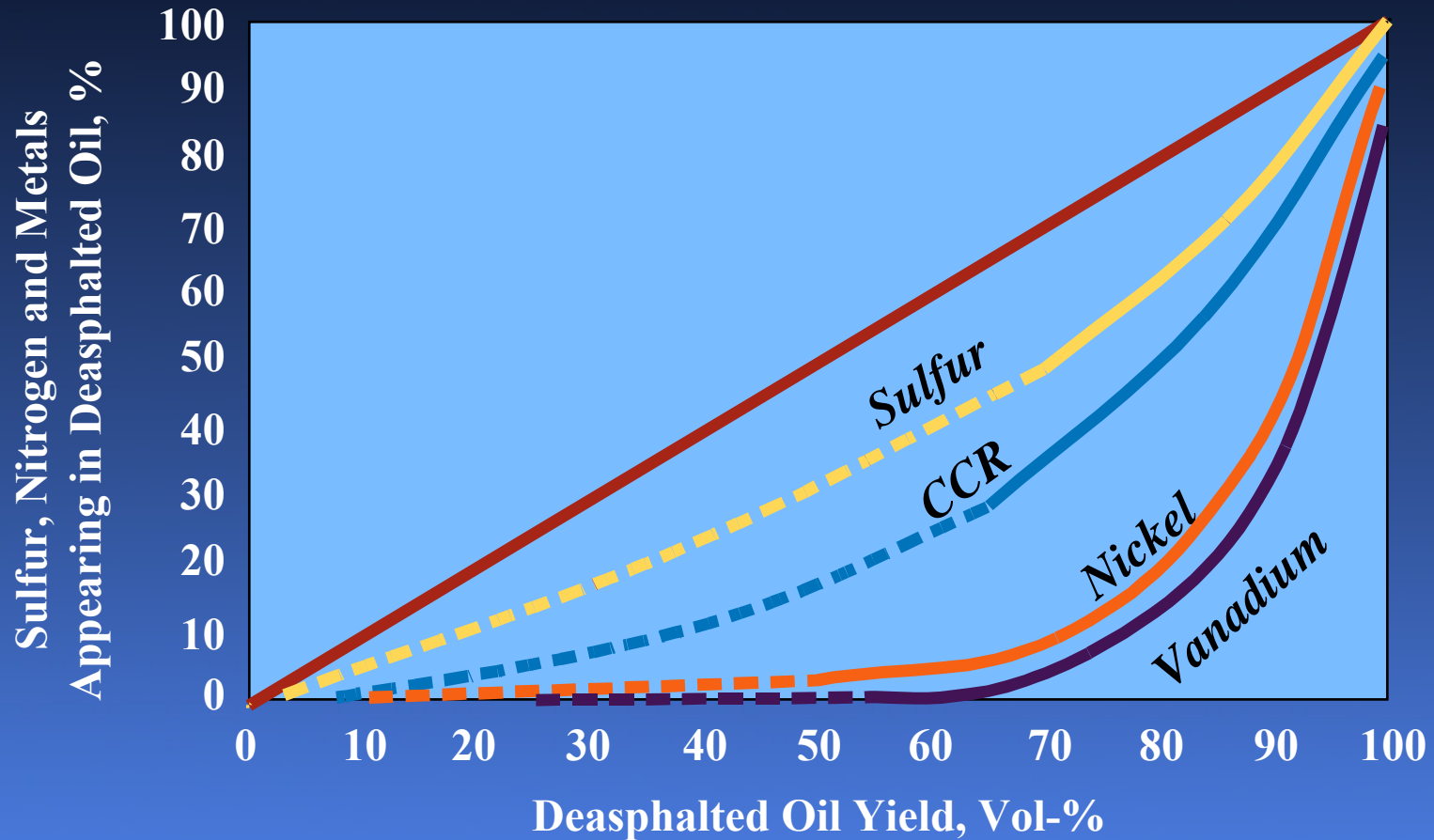
UOP/FW SDA Process Supercritical Design



UOP/FW SDA Typical Product Utilization



“Generic” SDA DAO Quality vs. Yield

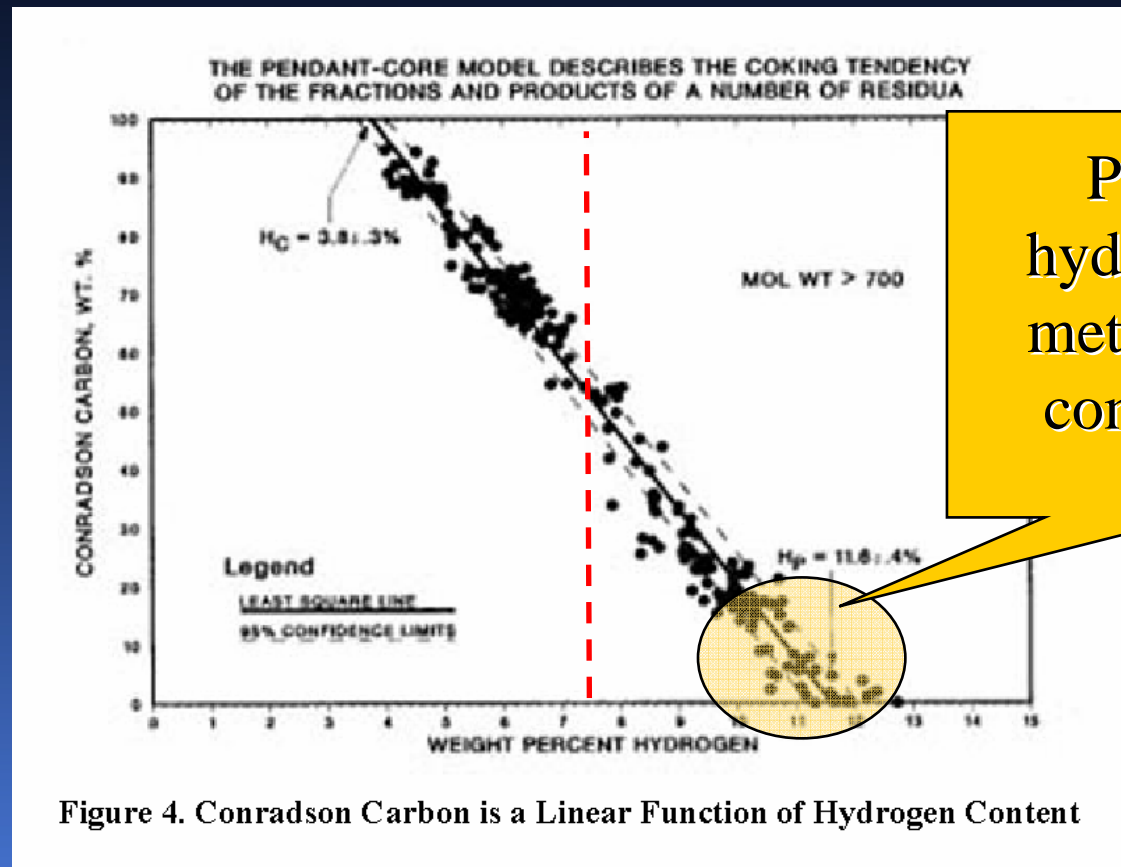


SDA has relatively good rejection of fixed-bed catalyst poisons

- **Metallo-porphyrins**
- **Some nitrogen and polars**
- **Almost all C7 insolubles**

Does not directly reject high concarbon species

For $mw > 700$, Conradson Carbon Residue is simply related to H content

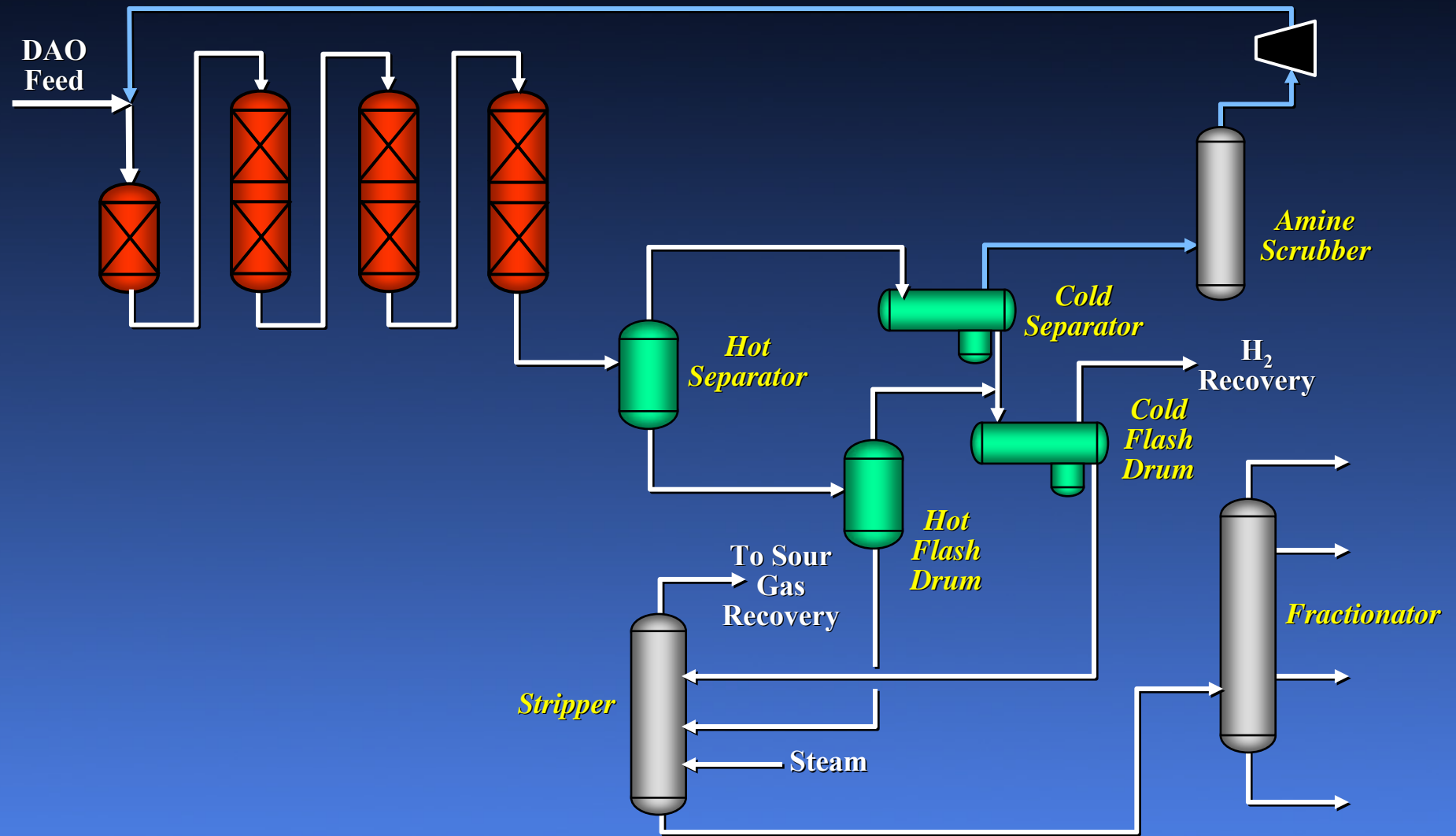


Source: Irv Wiehe, Soluble Solutions (www.solublesolutions.com)

Hydrocracking of Clean DAO Streams is Commercially Proven

	<i>Saudi Aramco Riyadh</i>	<i>New Zealand Refining</i>	<i>Hydrotreated Cold Lake DAO</i>
API Gravity	14.4	16.7	18.4
Sulfur, wt%	3.5		0.25
Nitrogen, wppm	2200	1500	2000
CCR, wt%	9.0	5.25	3.6
Ni + V, wppm	14	8.2	< 1

RCD Unionfining Process Used to Upgrade heavy DAO



Quantifying the Upgrading Potential of Vacuum Residue For Opportunity Crude

A modern approach



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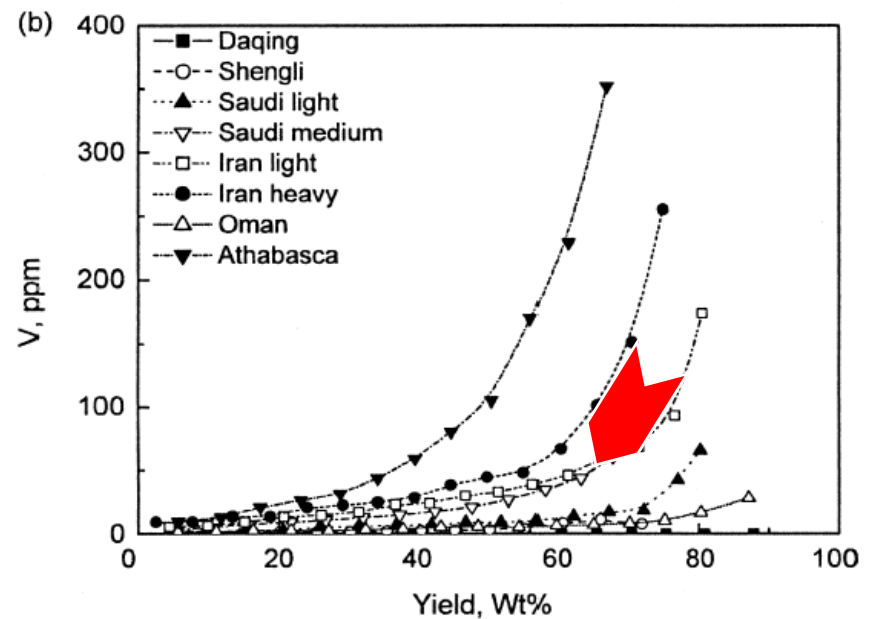
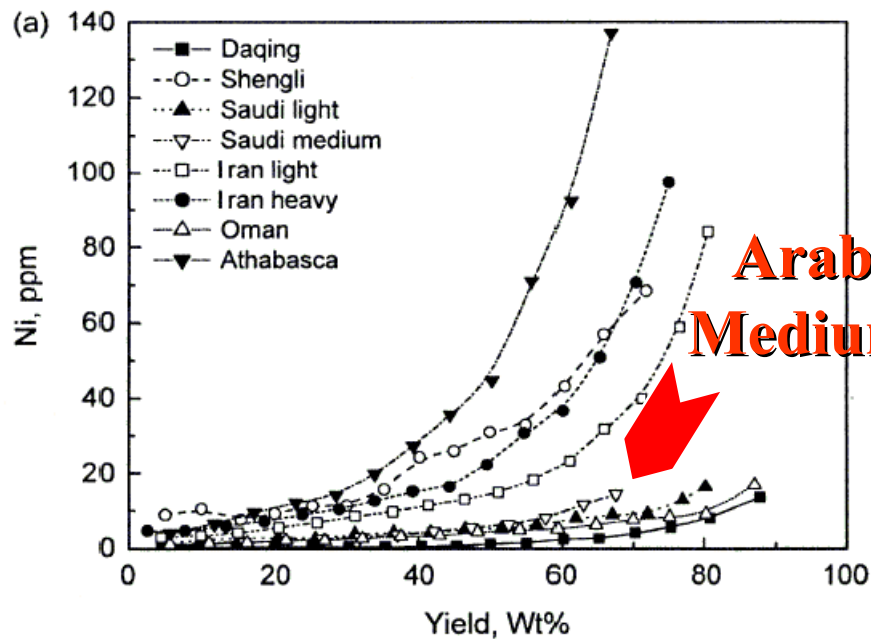
The Bottom of Barrel Varies Greatly By Crude Source

- “Easy” (light sweet or medium crudes)
- Medium-Sour crudes (Middle Eastern)
- Heavy conventional crudes
- Bitumen/Superheavy
 - Vary in **amount** of 535 C+
 - Vary in **total contaminants**
 - Vary in **“depth” of contaminants**

“Depth of contaminants”

- **Lighter crude: Front end of non-distillables may be paraffinic/low metals, straightforward direct catalytic conversion**
- **Bitumen/ superheavy : contaminants distributed throughout, a more aggressive RCD+ hydrocracking approach.**
- **Analysis is crucial to understanding the conversion options**
- **Not simply a matter of bulk properties!**

Metals versus lift in 535 °C+ residue varies widely between crude types¹



¹ Zhao et. al. Fuel 84 (2005) 635-645

UOP Vacuum Residue Assay

- **Relatively new technique, not part of traditional industry crude assay**
- **Narrow fractions are extracted successively deeper into the residue to asphaltenes by changing the solubility parameter**
- **Teaches more about the processability of the heavy “non-distillable” fraction**
- **Can be used in study of technoeconomic potentials, what-if, LP modeling, etc.**



Sequential extraction of 535 ° C+ Resid

VAC SLOP ← LIGHT DAO → ← HEAVY DAO → ← END CUT →
RESID WAX



Lab breakup of a vacuum bottoms from heavy-
sour Middle Eastern crude



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$$\delta \cong \left(\frac{\Delta H^V - RT}{V_m} \right)^{1/2}$$

One-dimensional Hildebrand solvent parameter, for subcritical (liquid)

$$\delta = 1.25 P_c^{1/2} \left(\frac{\rho_r}{\rho_{r(liq)}} \right)$$

In supercritical region, Giddings¹ approximation

Where

ρ_r = reduced density

$\rho_{r(liq)}$ = reduced density at normal bp

P_c = critical pressure

ΔH_v = enthalpy of vaporization

R = gas constant

V_m = molar volume

Adjust solubility parameter ↑

Extract increasingly polar and higher mw portion of residue



Estimating solubility: the Scatchard-Hildebrand equation

$$\ln x_a = \frac{-M_a}{RT\rho_a \cdot [\delta_a - \delta_s]^2}$$

Where:

x_a = mole fraction solubility

M = molecular weight

R = gas constant

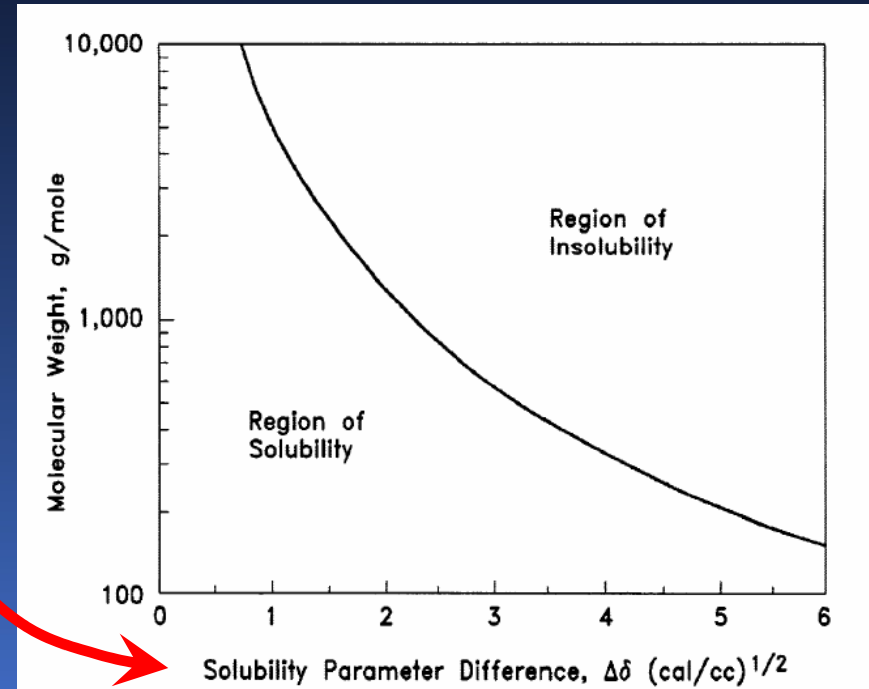
T = temperature

ρ = density

δ = solubility parameter

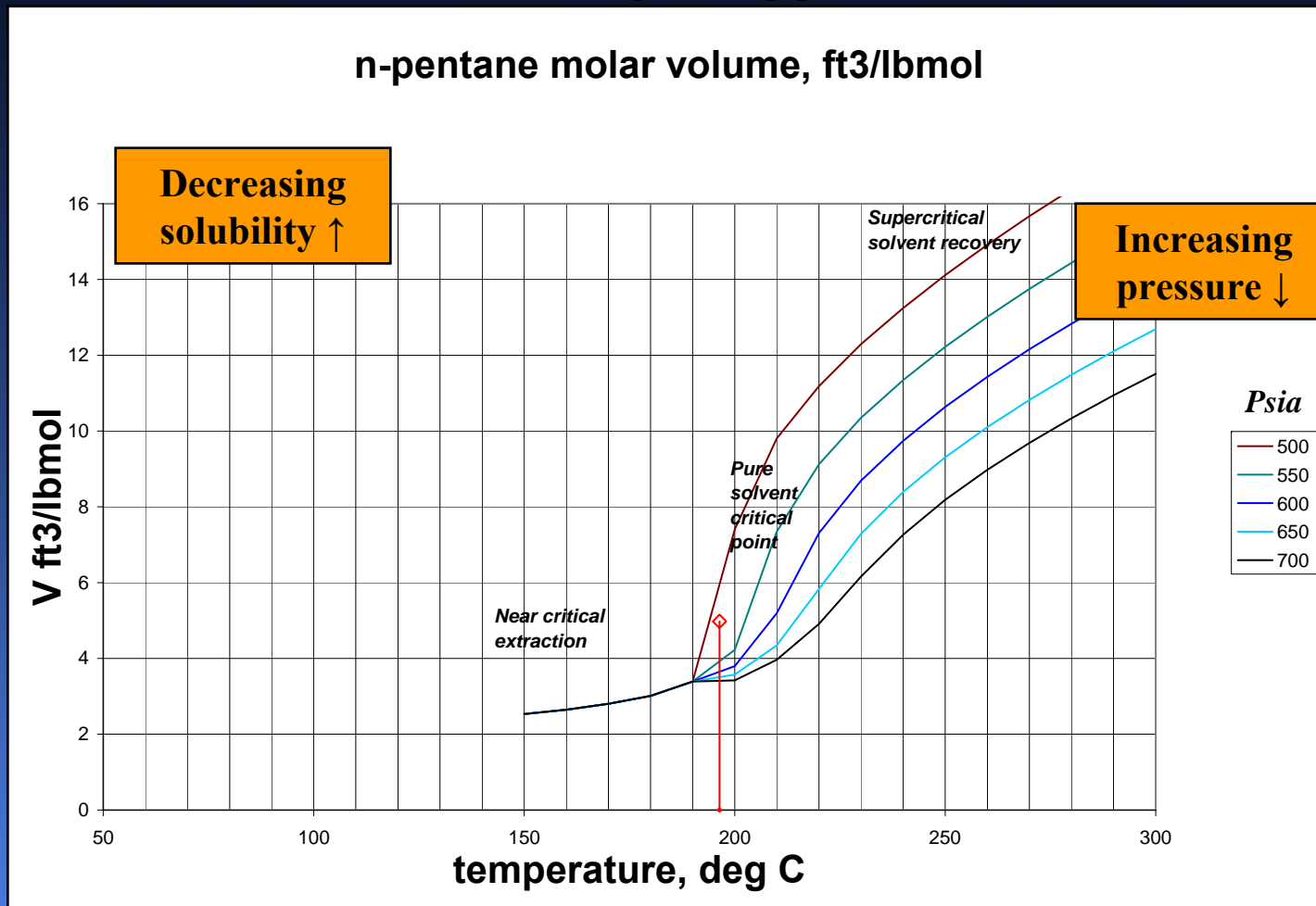
(a = incremental asphaltene or DAO,

s = solvent or light phase)

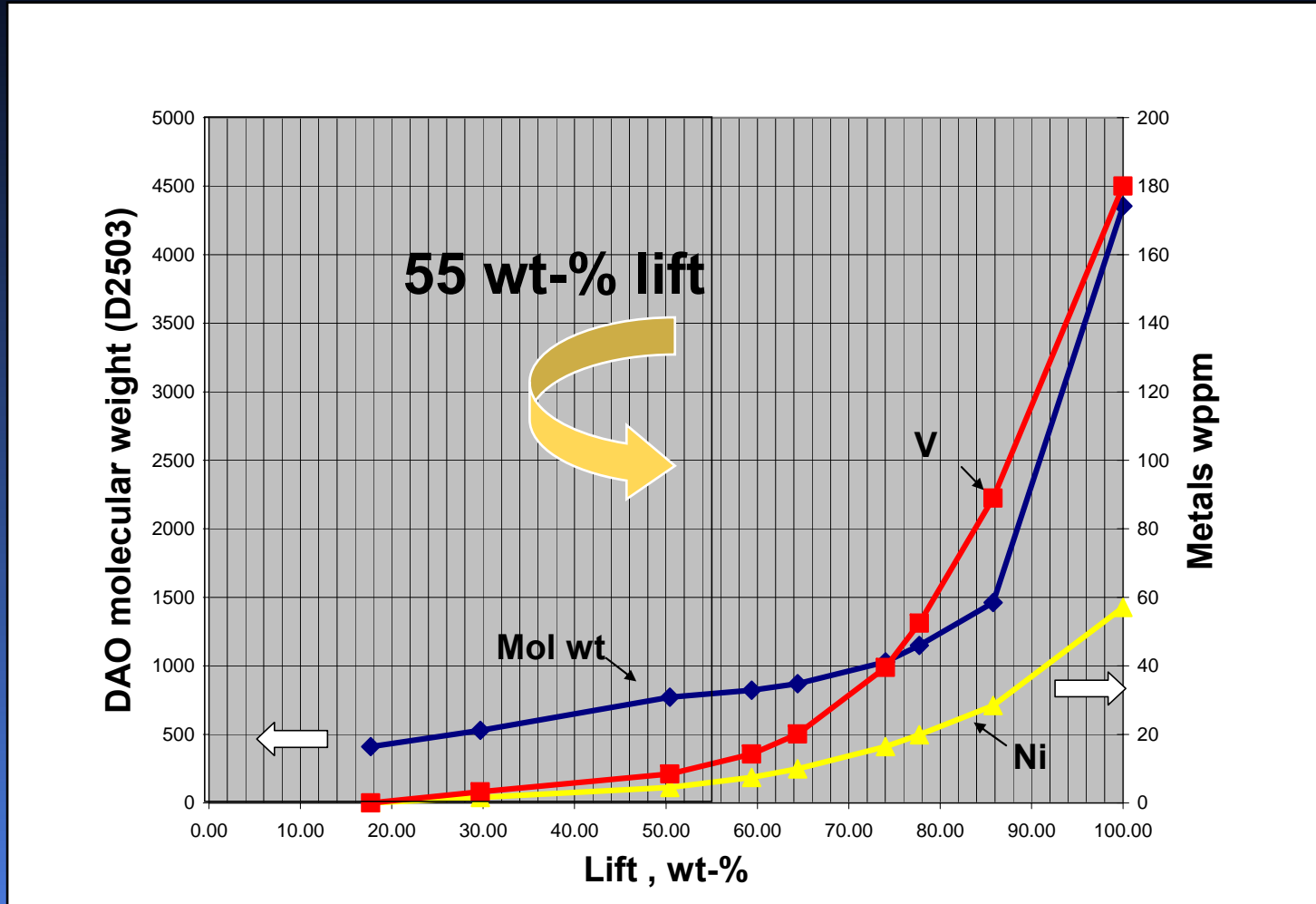


Source: Schabron, US 6,773,921 (2004)

Solvent deasphalting operation based on solubility difference

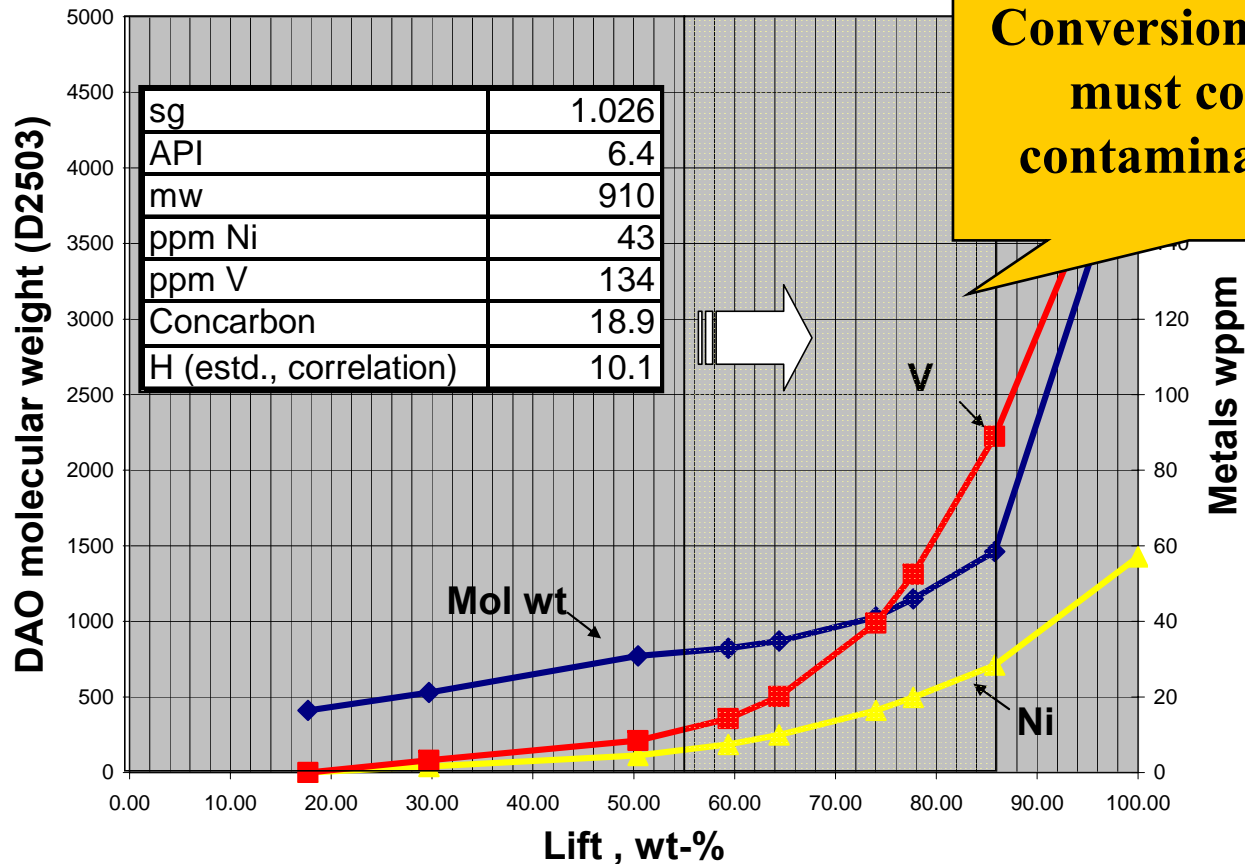


SDA example—Middle Eastern sour mol wt and metals on incremental cuts



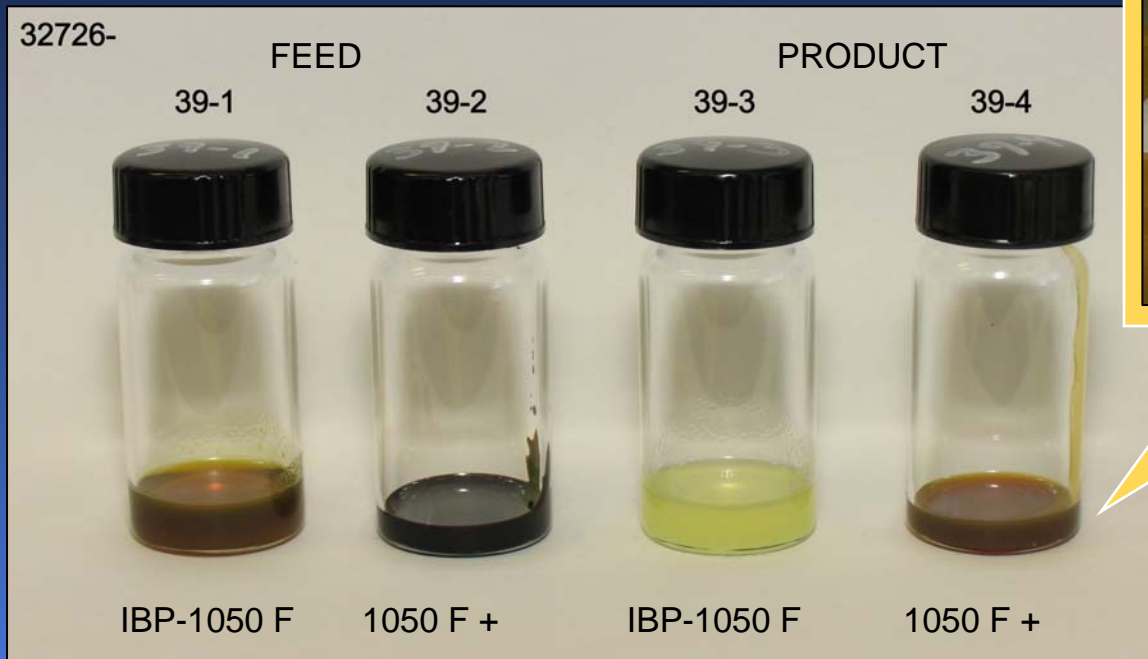
Moving into heavier cut

Composite properties



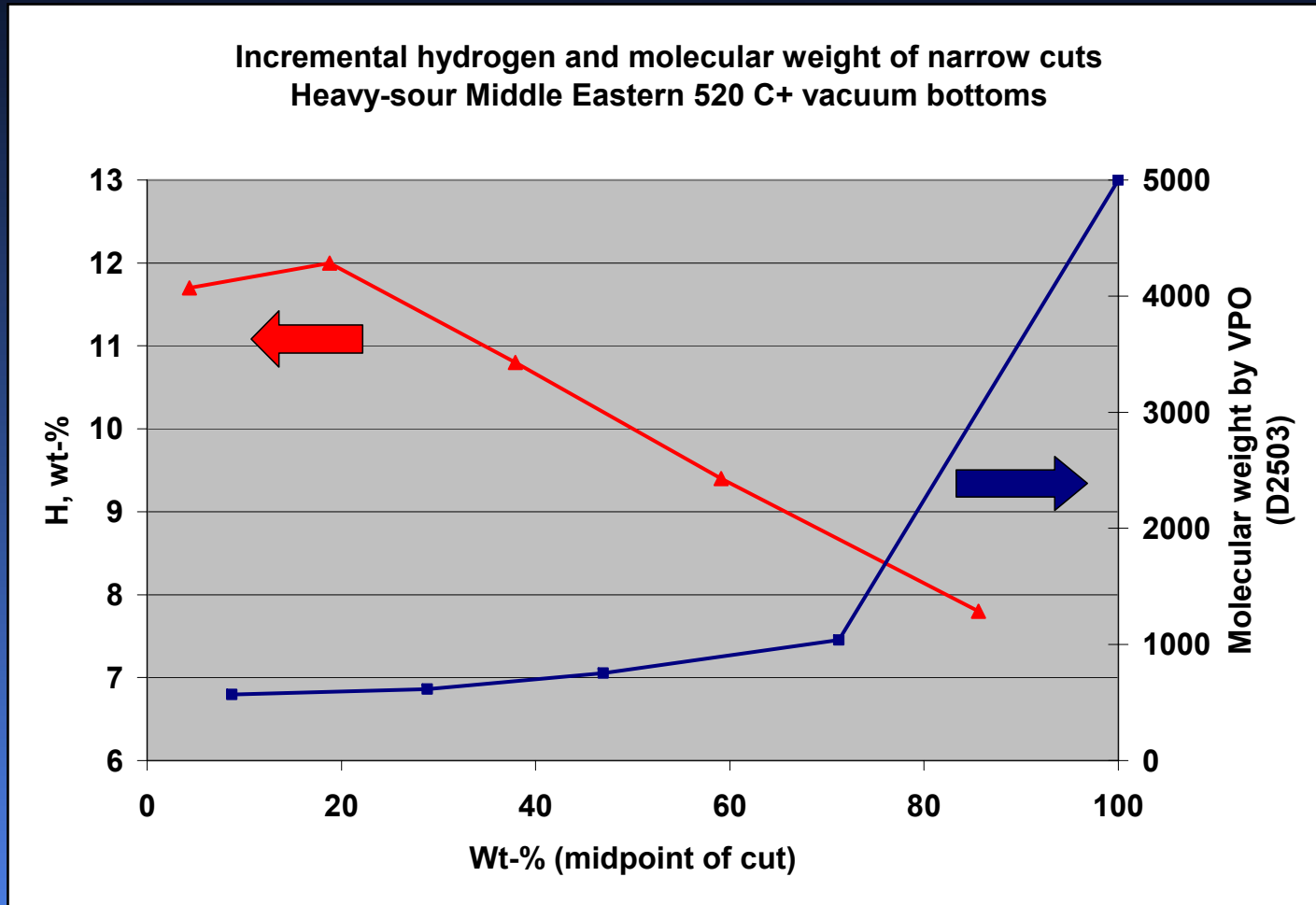
**Conversion potential
must consider
contaminants load**

Example of hydrotreating blend of heavy vacuum gas oil/deasphalted oil



Further
breakdown by
solubility in
extractive assay

Example: upgrading potential vs. depth of lift



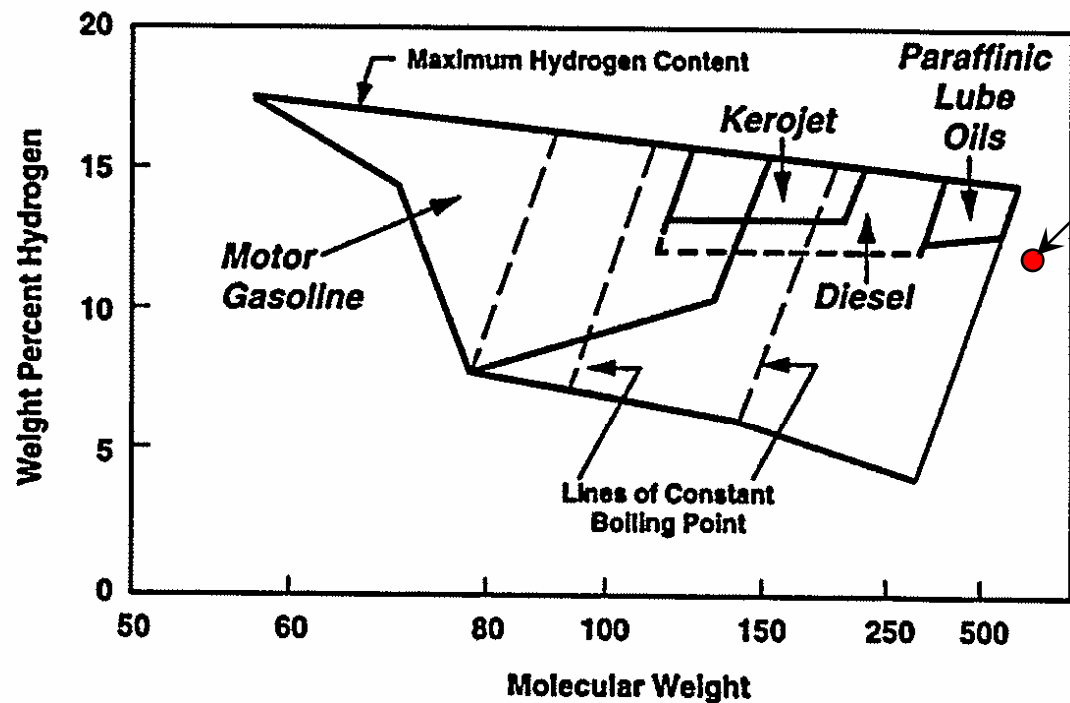


FIGURE 7.1.1 Stangeland diagram showing product hydrogen content. Regions that meet the specifications for jet/kerosene, diesel, and lube products all border the paraffin line. Aromatic compounds hurt the quality of these products.

Light DAO from vacuum resid of previous example

Bridge, A. G. and U. K. Mukherjee in R. A. Meyers, Handbook of Petroleum Refining Processes 3 ed. McGraw-Hill 2003 p. 7.5

Summary

- **SDA has a unique fit as an enabler of direct catalytic upgrading of residue to clean fuels**
- **SDA pitch is well-proven in feeding gasification based hydrogen, steam and power production**
- **The principles of solvency can be used in a modern technique for evaluating the potential upgrading value of a target residue**

Q & A