Direct Coal Liquefaction: *Lessons Learned*

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Outline

- Why Liquefaction? Changing needs
- Overview of direct coal liquefaction process
  - Types of processes
  - Process evolution
  - Current status
- Chemical Lessons
  - Reaction pathways
  - Coal structure: what is needed to liquefy coal
- Conclusions
  - Opportunities for improvement

Why Coal Liquefaction?

- Alternate source for liquid fuels: national energy security
  - Germany, Japan, South Africa
- Production of a clean and reactive solid fuel: SRC
  - Liquids are a secondary product that may improve economics
- Oil embargos in the 1970's reinforced need for an alternate source of transportation fuel
- Low oil prices in the next two decades: declining interest
- Now? Energy security, efficiency, climate…

Liquefaction

- Increasing H/C ratio is a must; Two options
  - Reject carbon
    - Most pyrolysis processes
  - Add hydrogen
    - Dry pyrolysis with hydrogen not effective
    - Coal liquefaction; use a solvent to effect hydrogenation
- Products often solid at room temperature
- Liquefaction defined by solubility

Coal Liquefaction Approaches

- Pyrolysis or mild gasification
- Direct coal liquefaction
- Indirect coal liquefaction
- Co-processing
- Bioliquefaction

- *Substantial overlap in the chemistry of mild gasification, direct coal liquefaction, and co-processing*

Direct Coal Liquefaction Processes: 1970 to 1995

- Single-Stage Process: SRC-II, H-Coal, EDS
- Two-Stage Process: NTSL, ITSL, RITSL, DITSL, CTSL, CMSL…
  - Many variations depending on
    - Use of catalyst in the two stages (therm-cat, cat-cat)
    - Distillation between stages
    - Separation of solids between two stages or after second stage
    - Recycle of ashy bottom
    - Operation in H-balance

Single-Stage Processes

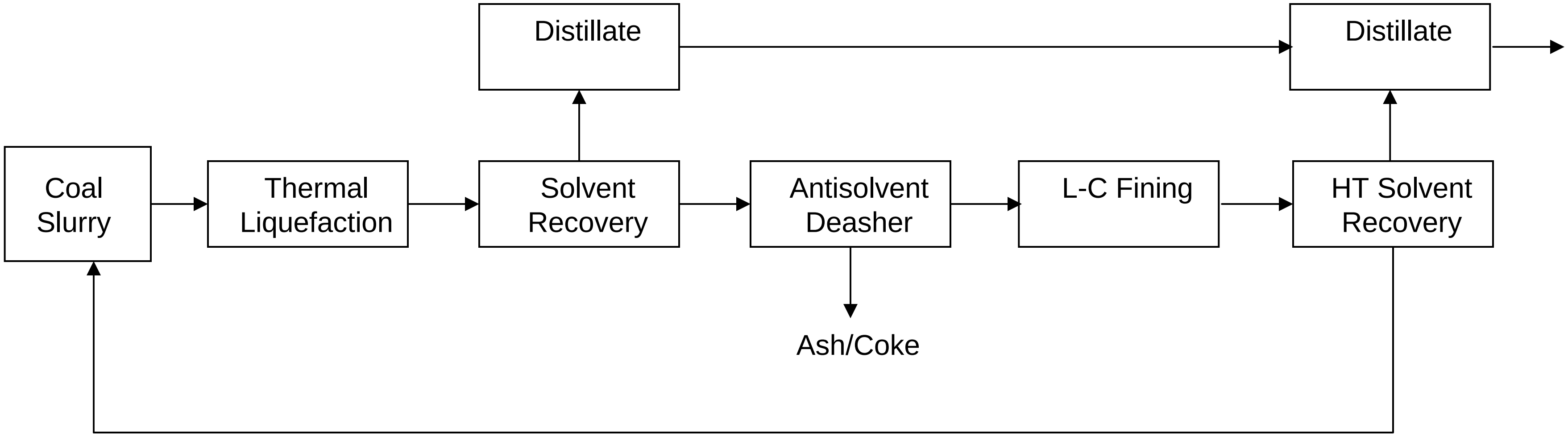
- Contact coal with a solvent (2:1) with hydrogen or with hydrogenated solvent at ca. 450°C
- Recycle light oil fraction
- Yield about 3 bbl oil/ton of coal with bituminous coals
- Not as effective for subbituminous coals
- Product difficult to refine (high aromaticity, N)
- High yield of light hydrocarbons; efficiency of hydrogen utilization is low
- Demonstrated the feasibility at ca. 200 tons/day

Lessons Learned

- Dissolution itself is fast!
- Coal liquefaction is better in heavier, more aromatic solvents
- Longer residence time is detrimental
- Process economics require maximizing liquids
- Higher temperatures lead to more gas
  - poorer hydrogen efficiency

Two-Stage Liquefaction at Wilsonville

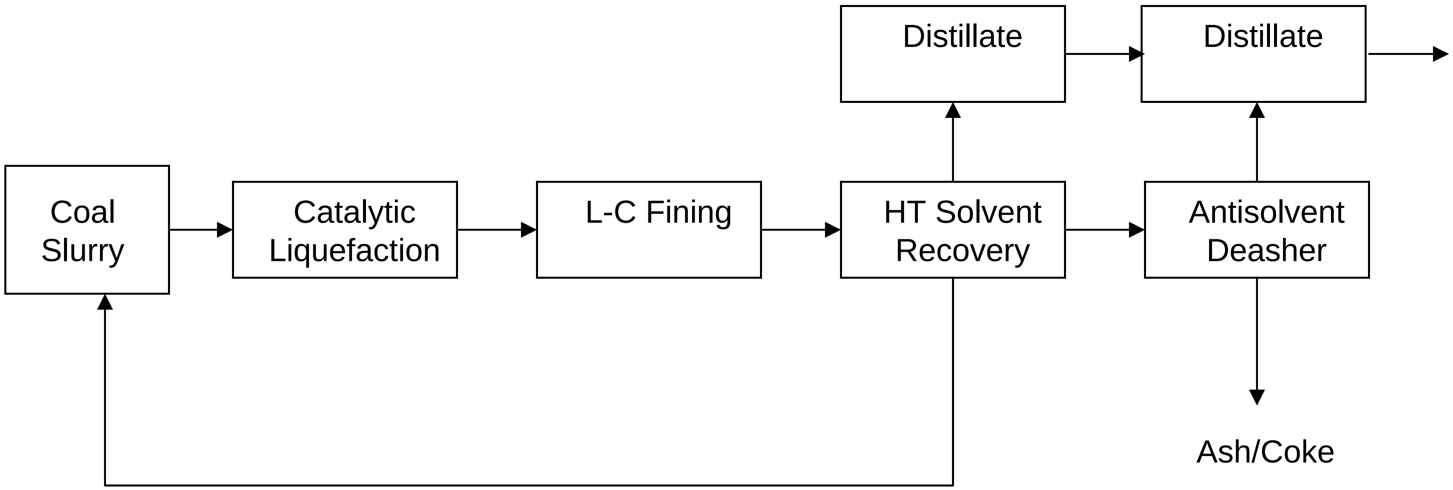
ITSL Initial Run



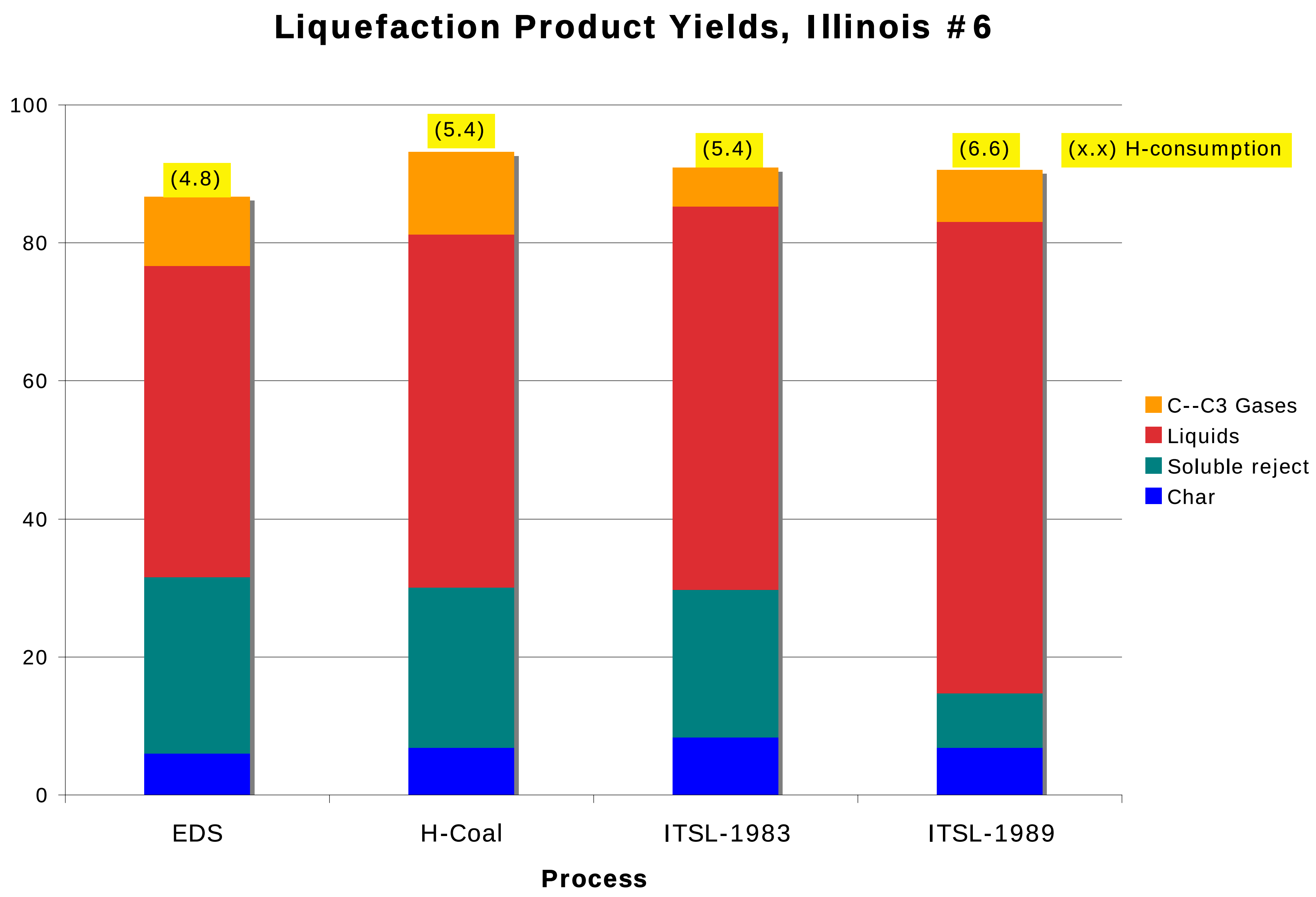
- Short contact thermal liquefaction
- Inter-stage separation
- Catalytic hydrotreating of de-ashed liquid
- Recycle of heavy hydrotreated solvent
- Hydrogen balance from coke gasification

Two-Stage Liquefaction at Wilsonville

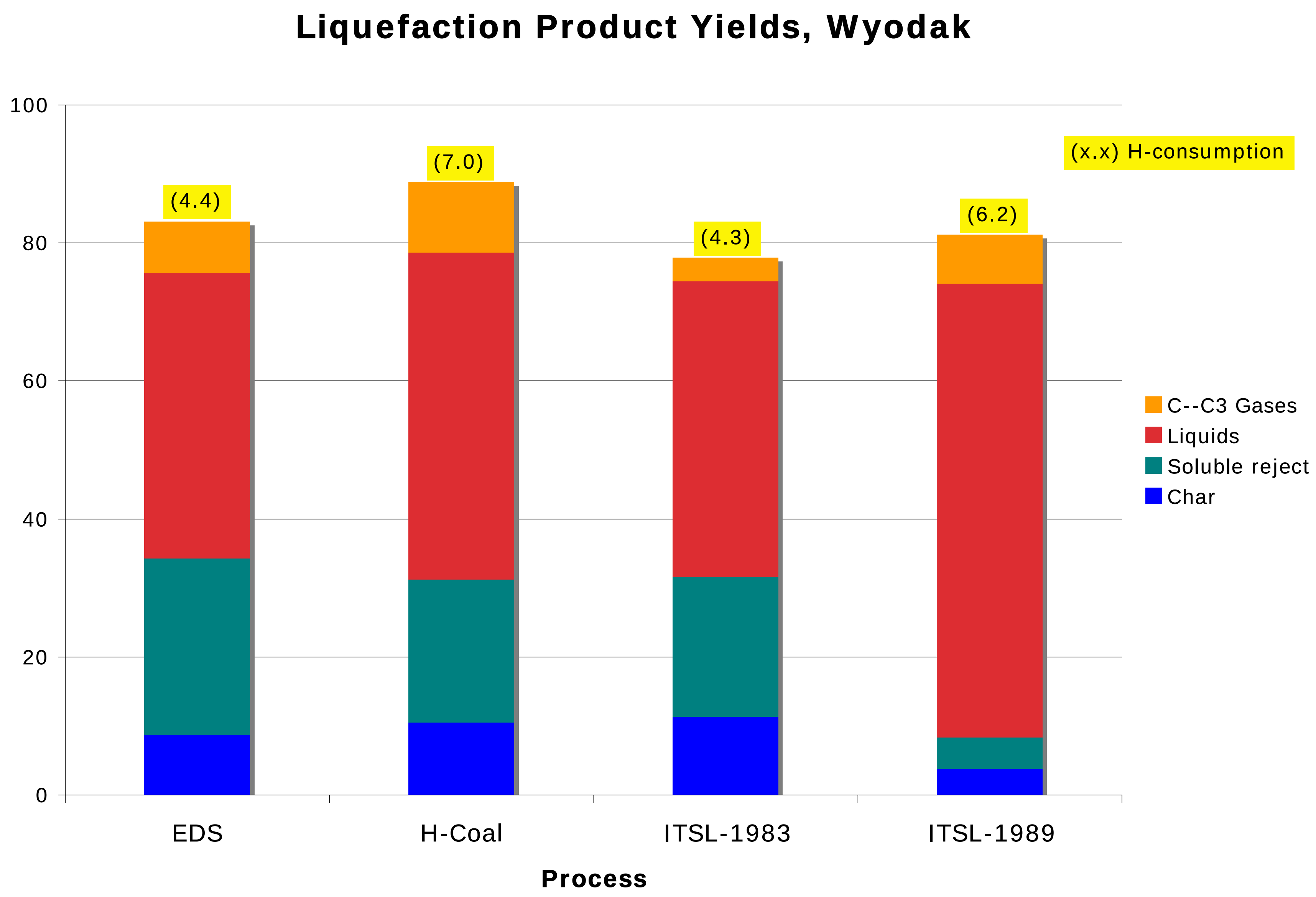
ITSL Final Run



- Low severity catalytic liquefaction
- No Inter-stage separation
- Moderate severity hydrotreating and hydrocracking
- Match rate of solvent hydrogenation with that of coal decomposition
- Ashy bottoms recycle
- Make hydrogen from steam reforming of methane



- Schindler, 1989



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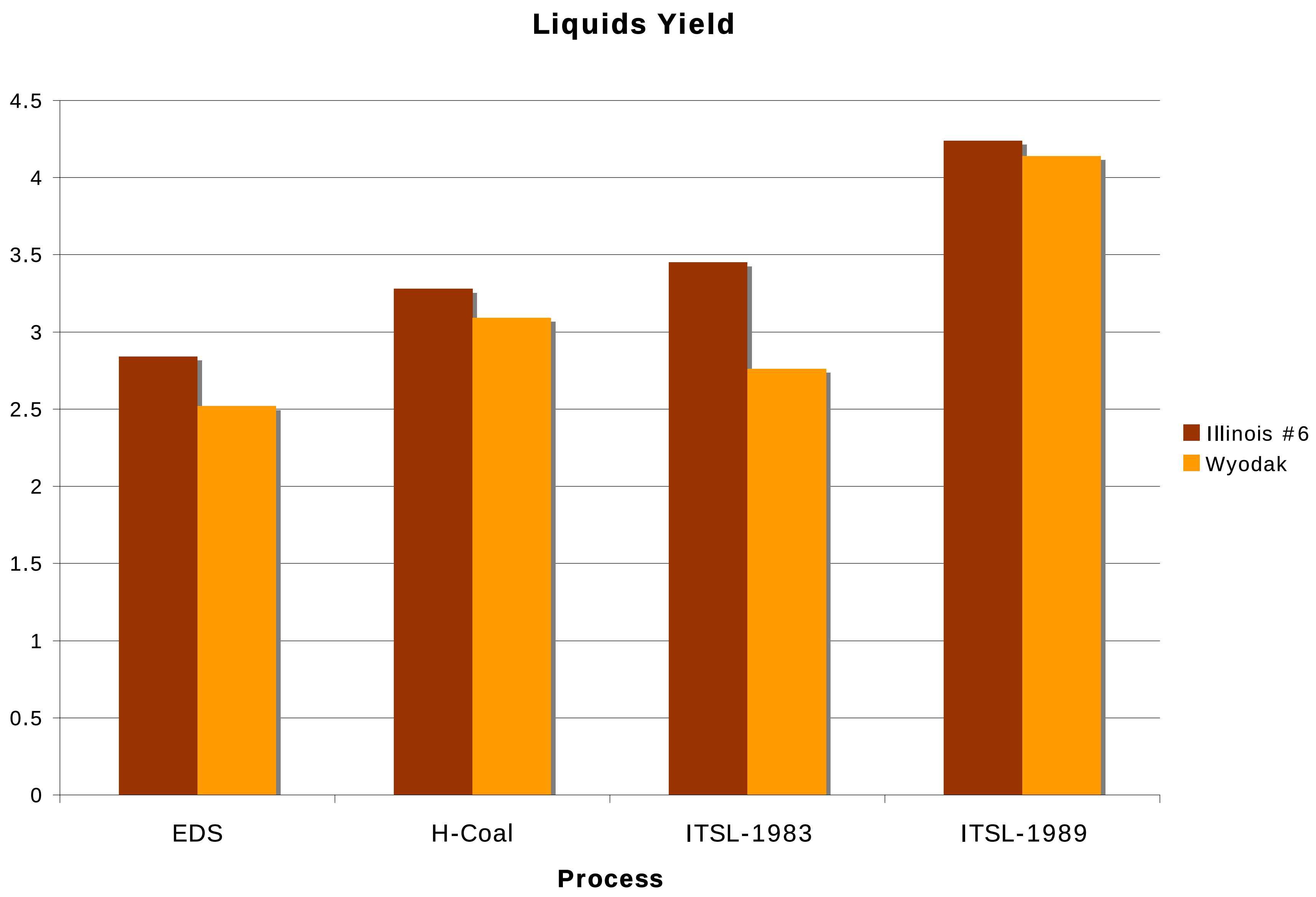
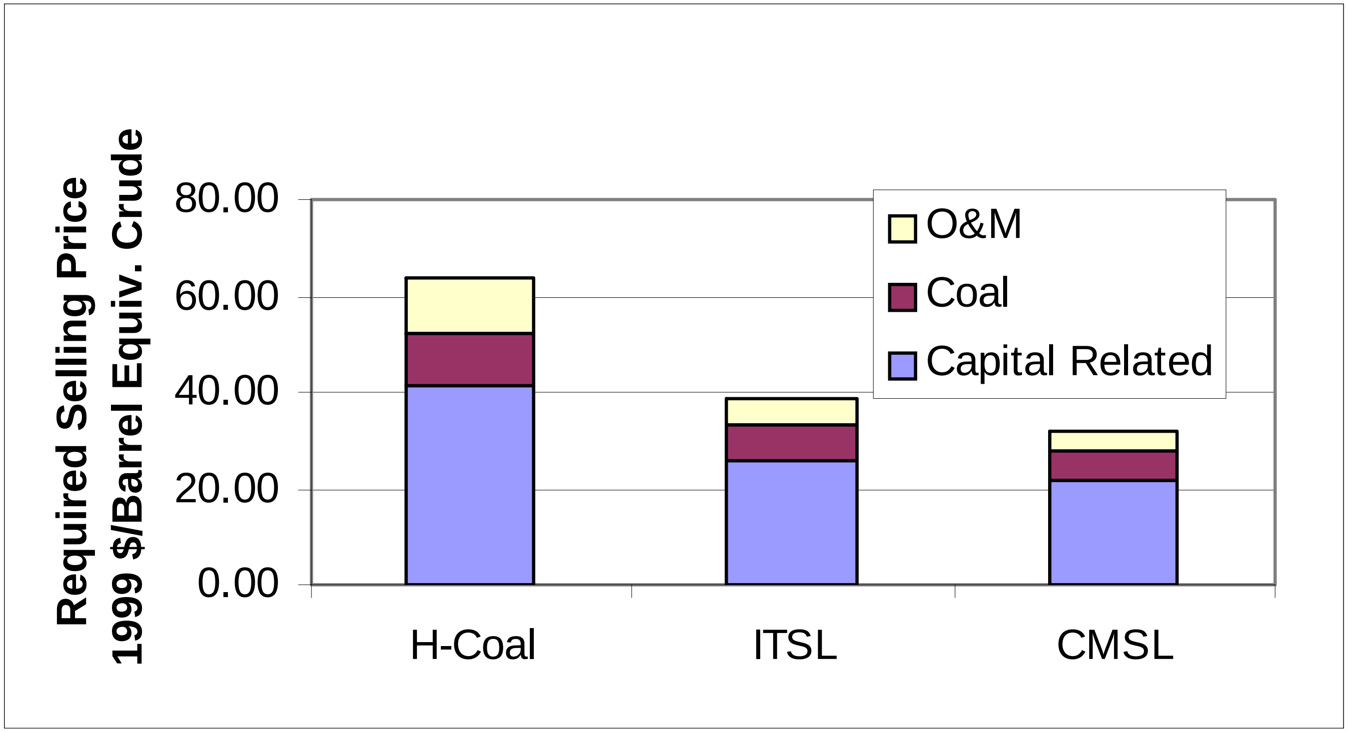


- Schindler, 1989

Process Economics



Major Lesson: Liquefaction is extremely capital intensive

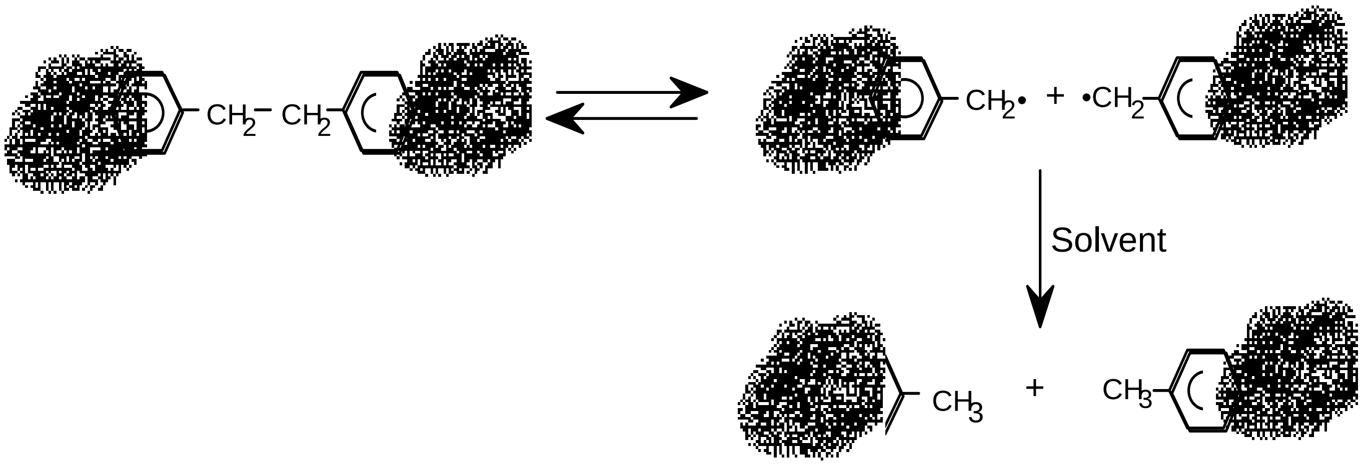
- Burke, Winschel, Gray, 2001

Summary

- Coal liquefaction is technically feasible
- Process demonstrated at large scale (~200 tpd) for a variety of coals
  - US: H-Coal, EDS
  - Canada: Canmet Co-processing
  - Japan: Victoria Brown Coal Liquefaction, NEDOL
  - UK, Germany
  - China: Shenhua project (2007)
- Economics not competitive, but not prohibitive either (~$20B for 50,000 bpd)

Traditional View of Bond Cleavage During Liquefaction

WEAK BOND HOMOLYSIS



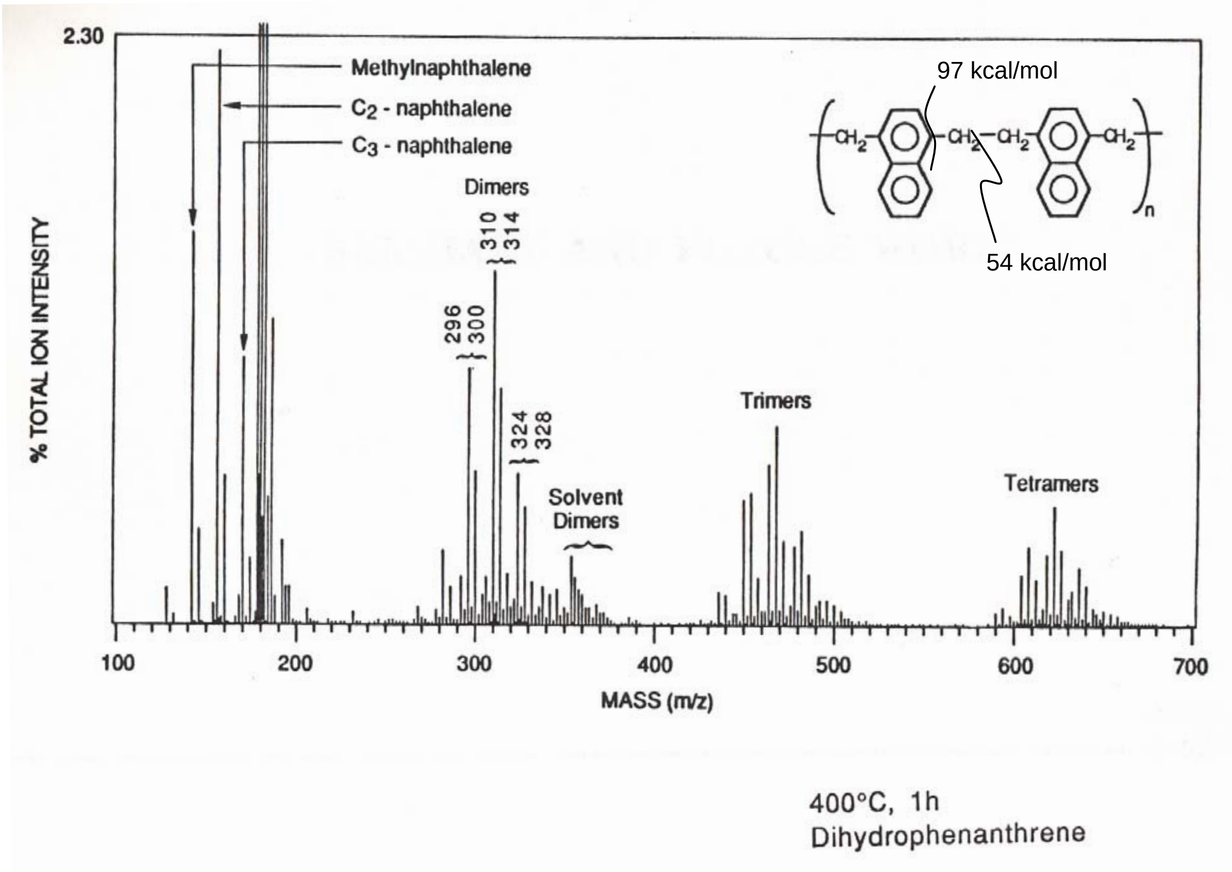
Solvent merely stabilizes thermally generated radicals; not involved in inducing bond cleavage.

Inadequacy of “Donor Solvent”

- Liquefaction yields do not correlate with weakness of C-H bond in the donor solvent
  - Dihydroanthracene with a much weaker C-H bond than dihydropyrene or dihydrophenanthrene consistently yields lower conversion to THF-solubles
  - Discrepancy even more glaring under “H-shuttling” conditions
- Bonds too strong to cleave by simple homolysis are nonetheless broken under liquefaction conditions

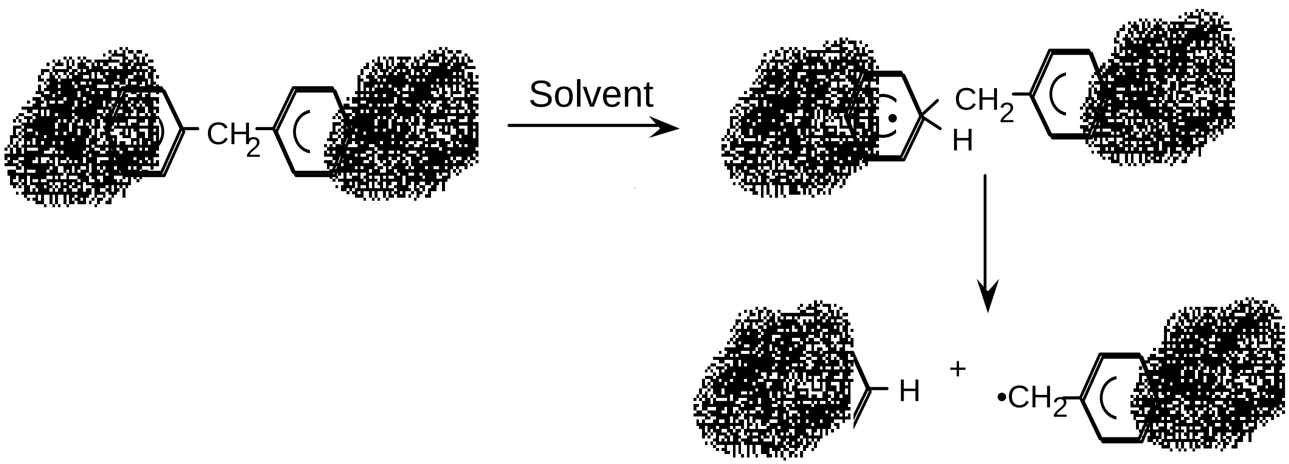
“Liquefaction” of a Bibenzyl Polymer FI-Mass Spectrum

Hydrogenolysis of strong C_{aryl}-C_{alkyl} bond comparable to thermolysis of weak C_{alkyl}-C_{alkyl} bond



Emerging View of Bond Cleavage

SOLVENT MEDIATED HYDROGENOLYSIS OF STRONG BONDS

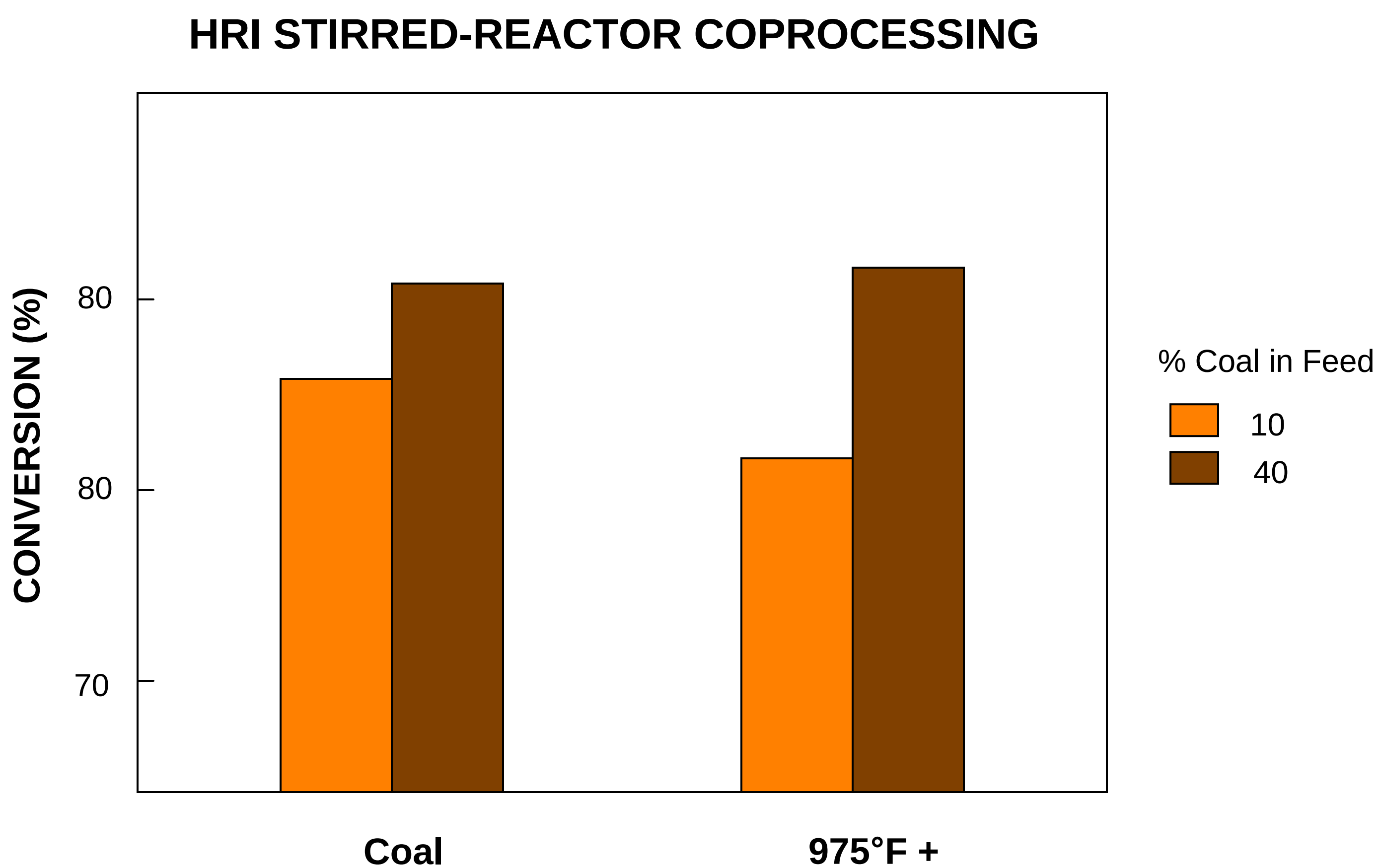


Solvent engenders bond scission

Implications of Solvent-Mediated Hydrogenolysis

- Draw attention to H-accepting and H-transfer properties of solvent components
- Rationalize otherwise inexplicable behavior
  - Increased liquids yields from partial replacement of donor hydroaromatic with nondonor aromatic
  - Efficacy of pyrene and related PAH
  - Role of C-supported catalysts
- Design processes that maximize H-utilization efficiency

Increased Coal Content Aids Conversion of Coal and of Non-Distillables



Aromatics in coal mobilize the H in the resid for conversion

-Duddy, Panvelker, 1991

Coal Conversion with Dispersed Catalysts

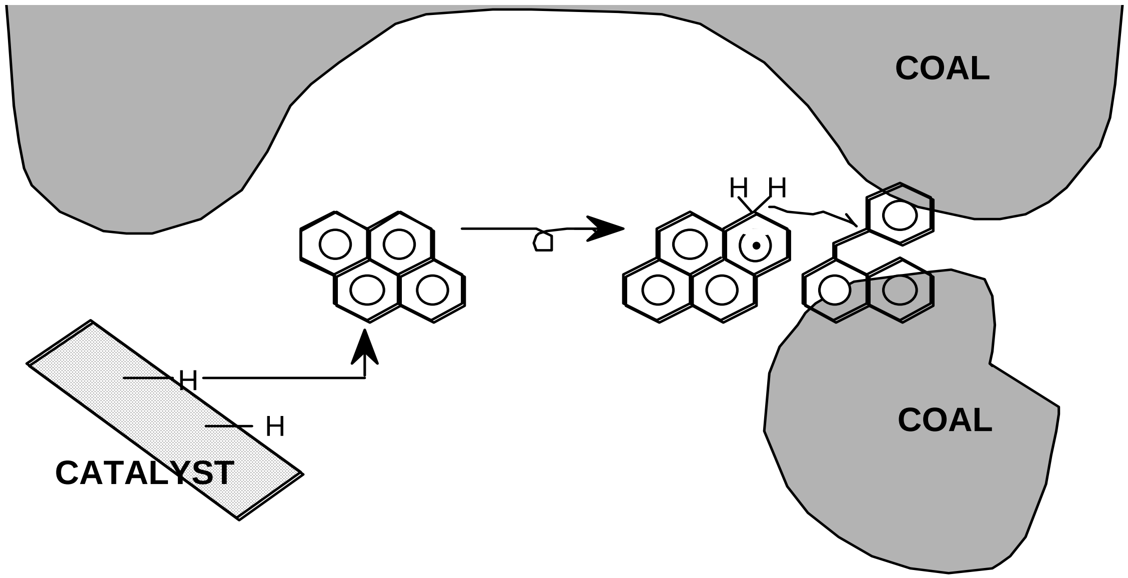
Recycled IOM is more effective than freshly activated catalyst

	Yield (%maf coal)	
	Fresh Catalyst	Recycled IOMs
THF-Solubles	86	95
Cyclohexane-Solubles	36	64

Conversion of Illinois No. 6, Burning Star coal in hydrotreated V-178 distillate
Programmed heating at 8°C/min to 425°C under H_2 pressure

- Bockrath, 1992

Potential Role of H-Transfer in Catalytic Systems



Coal Structure

- Application of polymer theory
  - Characterization of cluster size and mean molecular weight between clusters
  - Rank dependent trends
- ^{13}C-NMR: Relatively small clusters of 8 to 18 carbons only
- Distribution of oxygen, sulfur, and nitrogen functionalities
- Role of non-covalent linkages

Emerging Opportunities

- *Thermal efficiency of coal to oil by DCL: ~65%*
  - *About 7 times worse than crude oil refining (95%)*
- Facile dissolution of bituminous coals in certain solvents (Iino)
  - Possible application for hyper clean coal
- Augmented Pyrolysis (Miura)
  - Mild gasification of methanol soaked coals to co-produce liquids and high reactivity chars
- Direct carbon fuel cell: coal, biomass, petcoke…

Conclusions

- Coal liquefaction: technically feasible, but the process to synthetic crude is not economic
- Converting coal to transportation fuel for IC engines does not reduce CO_2 emissions
- If needed for energy security, milder processes with high coal to oil yields must be demonstrated at commercially relevant scales

Acknowledgments

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