Conversion of Low-Rank Wyoming Coals into Gasoline by Direct Liquefaction

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History of DCL: Bergius process

- coal is not carbon
- unsaturated hydrocarbons
- should be capable of absorbing large quantities of H₂
- turns into heavy petroleum hydrocarbons

Summer 1913:

150 atm (2,200 psi) H₂
400-450°C
80% conversion

Agitated coal slurry in a tank at high P(H₂) and T

- gaseous
- liquid
- benzene-solubles
DCL: motivation

Global motivation
- there is more recoverable coal than oil on the planet
- strong economies - Europe, China, Australia - no oil but abundant coal reserves
- high-value naphthenic products (solvents, lubricants, fuels)

Wyoming’s interest
- abundant coal reserves
- coal is a significant part of Wyoming’s economy
- low-rank coals are well suitable for direct liquefaction
State of DCL and competition

State of the technology
- no operating plants exist in U.S.
- technical challenges ↔
  - high capital (~$1B) and operating costs

Competition
Other conversion technologies
- gasification of coal or natural gas followed by Fischer-Tropsch condensation
  - inherently inefficient (breaking all C-C, C-H bonds before putting some of them back)
  - losing high-value products
- pyrolysis
  - low yield

Compressed and liquid gases
- low energy density
- no infrastructure

Other carbonaceous feedstocks: biogas and biomass
- sparse resources, no economy of scale
- high H consumption
DCL projects at WRI

Phase I  1 year
Conversion of low-rank WY coals into gasoline by direct liquefaction

- $200,000 under Cooperative Agreement DE-FC26-08NT43293 with DOE
- June 2010 – June 2011

Scope of work: screening conditions for liquefaction of Wyodak and other WY coals

Phase II  2 years
Multi-stage processing of WY coals to liquid fuels

- $1M = $500K (CCTF) + $250K (Ambre Energy) + $250K (DOE-NETL)
- July 2011 – March 2014

Scope of work: more in-depth study of coal liquefaction
  - co-processing of coal and biomass
  - screening of perspective catalysts and additives
  - screening of liquefaction conditions to minimize temperature, pressure, reaction time
WRI’s work: revisiting DCL process

**Conventional coal liquefaction**
- 400-500°C
- 2,000-3,000 psi H₂
- H-cracking catalysts

**New approaches in cracking**
- solvolysis (Organosolv pulping)
- radical initiators (endothermic fuels; recycling waste plastic, WRC’s patent 6,861,568)

Liquefaction of mixed carbonaceous feeds
- solvothermal depolymerization: H₂O/ROH as reacting medium
- biomass- or waste-derived additives
- additional radical initiators
- radical stabilizers other than H₂

coal → 2 coal*
2 coal* + RCH – CHR → 2 coal – H + RC = CR
coal* + H₂ → coal – H + H*
H* + coal – coal → coal – H + coal*

→ stabilization of coal radicals
→ radical-induced coal cracking

\[ \text{Solvothermal depolymerization: } \text{H}_2\text{O/ROH as reacting medium} \]

\[ \text{Bergius-type DCL} \]

\[ \text{Solvothermal depolymerization} \]

\[ [\text{H}_2\text{O}] \text{ in the solvent, wt. %} \]
Solvothermal depolymerization: the idea

**depolymerization**
- water, phenolics
- 350-450°C

lignin + coal → phenolics

hydroprocessing

aromatic/naphthenic hydrocarbons
Solvothermal depolymerization: results

Coal:
• low conversion

Lignin:
• controlled depolymerization achieved
• unavoidable side reaction: char formation

Decrease of the molecular weight of depolymerization products with the increase of residence time.

Black flakes of char formed on the reactor walls.
Bergius-type DCL

**Reaction**
- batch process in a stirred autoclave
- volume 50 mL, $P_{\text{max}} = 5000$ psi, $T_{\text{max}} = 500°C$
- Decker coal
- typically, 12 g of tetralin, 1000 psi $H_2$

**Analysis**
- consecutive Soxlet extraction in
  - hexane
  - toluene (optional)
  - THF
- size-exclusion chromatography

products $\rightarrow$ hexane extraction $\rightarrow$ hexane fraction $\rightarrow$ hexane residue

hexane residue $\rightarrow$ THF extraction $\rightarrow$ THF fraction $\rightarrow$ THF residue
Effect of temperature on conversion

- Total conversion predictably increases with temperature.
- Yield of hexane fraction increases with temperature and the yield of THF fraction decreases.

- Average MW of the reaction products shifts to lower values with the increase of reaction temperature.
Solvent’s effect on conversion

- adding hexane to tetralin decreases conversion
- replacing tetralin with toluene results in practically the same yield of hexane fraction yet eliminates THF-solubles
Solvent’s effect on conversion

- presence of significant amounts of methanol or water does not affect negatively the liquefaction
- not necessary to dry up the coal
- presence of octane – as well as of hexane - decreases conversion
No noticeable effect from co-feeding lignin and coal: they are converted independently of one another.
Organic additives

Some additives increase coal conversion:

- ethyl phenyl ether Et-O-Ph

Et-O-Ph noticeably diminishes negative effect of hexane.
Radical initiators

Ammonium persulfate provides observable positive effect on conversion.

Increased yield of hexane-solubles upon addition of (NH₄)₂S₂O₈ confirmed by SEC.
Radical initiators: positive effect of (NH$_4$)$_2$S$_2$O$_8$

Positive effect of persulfate at 350°C

- increase of the total conversion by ~10%
- increased yield of low-molecular-weight products
- while possibly not practical, use of persulfate shows the promising concept

Persulfate diminishes the negative effect of hexane on conversion.
Catalysts: Raney Ni

Raney Ni favorably increases the yield of hexane-solubles and decreases the yield of THF-solubles, largely compensating the decrease of H₂ pressure.

1000 psi H₂

500 psi H₂

Raney Ni (3 g), tetralin (12 g)
1000 psi H₂, 350°C, 3 hours

Raney Ni (3 g), tetralin (12 g)
500 psi H₂, 350°C, 3 hours
Future work

• further investigating the process chemistry
• high-value naphthenic products: lubricants and specialty oils
• part of the complex technological and economic development
Summary

• direct liquefaction of Wyoming coals has been studied in conditions relevant to practice

• the effect of
  ➢ alternative reacting medium – solvothermal depolymerization, and
  ➢ additives (including lignin and biomass-derivable chemicals), solvents, and catalysts on DCL has been studied

• solvothermal depolymerization of coals and lignins in aqueous media carries notable drawbacks

• most additives do not appreciably affect the process or affect it negatively

• positive effect of some additives on DCL has been discovered; its origin remains to be clarified

• the full potential of DCL for economically competitive production of chemicals and fuels remains to be explored

• a judicious choice of catalysts, solvents, and additives might enable practical and economically efficient direct conversion of Wyoming coals into liquid hydrocarbons
Acknowledgements

Funding
State of Wyoming / University of Wyoming School of Energy Resources
Ambre Energy
The U.S. Department of Energy

Western Research Institute
Vijay Sethi
Sajo Naik
Joseph Rovani
Ryan Boysen

Ambre Energy
Nicholas Drinnan

Jantra Fuels and Chemicals
Wlodzimierz Zmierczak