# Multi-stage Processing of WY Coals to Liquid Fuels

Clean Coal Technology Fund Project #1217-20759

# EXECUTIVE SUMMARY

## Introduction

The government regulations worldwide impose more and more rigorous restrictions on the direct use of coal as a fuel, which is the main use of coal at the present time. With a significant part of its economy depending on the coal production and trading, the State of Wyoming has a strong interest in developing and commercializing the technologies for processing coal into value-added fuels and chemicals.

Liquid hydrocarbons – transportation fuels, motor oils, lubricants, solvents, and raw materials for chemical industry – constitute the principal group of products targeted by the coal conversion technologies. The major routes to produce liquid hydrocarbons from coal – pyrolysis, direct liquefaction, and indirect liquefaction – have been known for more than a century; each of them has a track record of extensive development efforts. With a relatively low price of crude petroleum, however, none of the existing methods of coal conversion is conclusively competitive on the modern market. New approaches are being trialed in the attempts to liquefy coal cheaper and more efficiently – the development of coal liquefaction technology is actively ongoing.

This project, targeting the development of novel process for direct liquefaction of Wyoming coals and mixed coal-biomass feeds, made a noteworthy contribution to the effort. Specifically, one of the conclusions is that appropriate design of the process and judicious choice of the process conditions might enable economically efficient direct conversion of Wyoming coals into added-value liquid hydrocarbons.

## Background

### *Liquid hydrocarbons from coal*

Among the strategies for converting coal into liquids, direct liquefaction (DCL) is considered as one of the most environmentally friendly, resource-conserving, and technically efficient. DCL breaks the coal species – a three-dimensional network of hydrocarbons with low hydrogen content, Figure 1 – into small molecules and increases their hydrogen-to-carbon ratio.

Technical challenges, associated primarily with the combination of high temperature (400-500ºC) and high pressure of hydrogen (up to 350 atm), impede a wide acceptance of DCL by the energy industry. Decreasing liquefaction temperature by even 50-100ºC or decreasing the pressure down to 20-50 atm would mark a significant progress in reducing capital costs and promoting economical competitiveness of DCL.

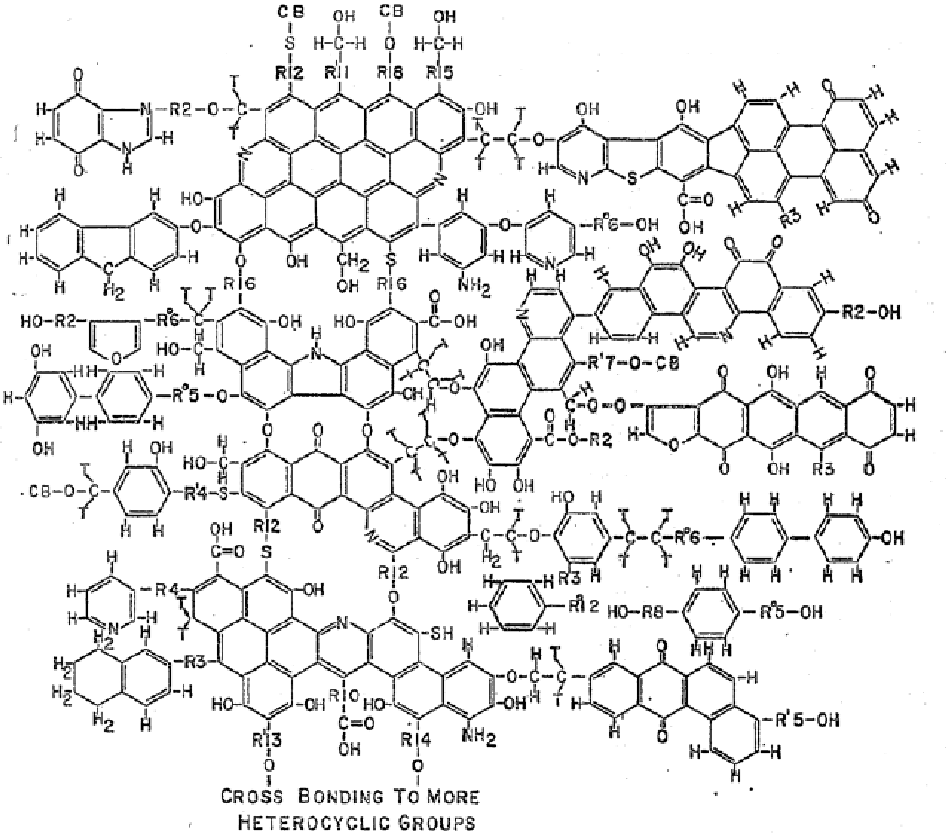


Figure 1. Structure of mid-rank coal.

## *Liquid hydrocarbons from lignocellulosic biomass*

Biomass is one of the most abundant renewable and carbon-neutral feedstocks for the production of fuels and chemicals. The three major components of biomass are cellulose, hemicelluloses and lignin.

Lignin is only second to cellulose as the most plentiful renewable carbon source on Earth. It is an amorphous three-dimensional energy-rich biopolymer which is deposited in all vascular plants and provides rigidity and strength to their cell walls. Lignin consists of more than 60% wt. carbon and 25 to 28% wt. oxygen (Figure 2); it constitutes the part of biomass with the highest energy content, i.e., 9,000–11,000 Btu/lb versus 7,300–7,500 Btu/lb for cellulose. The lignin polymeric structure is composed primarily of three building units and can be converted directly to a variety of liquid hydrocarbon fuels and chemicals.

Currently, a limited supply of lignin is available as a by-product of the pulp and paper industry. It is expected that large quantities of lignin residue material will be available in the near future from cellulose-to-ethanol processes, biomass flash pyrolysis, and other biorefinery and associated processes. Other sources of lignin include agricultural and municipal wastes. In a typical biorefinery process, lignin appears as a residual material, which is combusted to generate process power. Upgrading the lignin residue by a catalytic conversion process to high-value fuels and fuel additives is an attractive proposition to enhance the competitiveness of biorefineries.

Decomposition of carbonaceous feedstocks (biomass, coals, and their mixtures) in aqueous media at elevated temperature – *solvothermal depolymerization (STD)* – has been considered as a potentially efficient route to produce synthetic liquid fuels.

Both STD and DCL are high-temperature (300-500°C) and high-pressure (100-500 atm) processes; the only principal difference between them is the use of hydrogen, Figure 3. Bergius-type DCL – Friedrich Bergius was awarded a Nobel Prize in 1931 for the development of the process – relies on participating of gaseous hydrogen in breaking down the coal polymers and in increasing hydrogen-to-carbon ratio of the liquid products. In STD, depending on the composition of the dissolving/dispersing medium, the chemically aggressive solvent molecules cause the cracking and end up as the constituents of the products. Numerous published studies prompted further research in the conditions of interest to practical implementation of STD on a large scale.

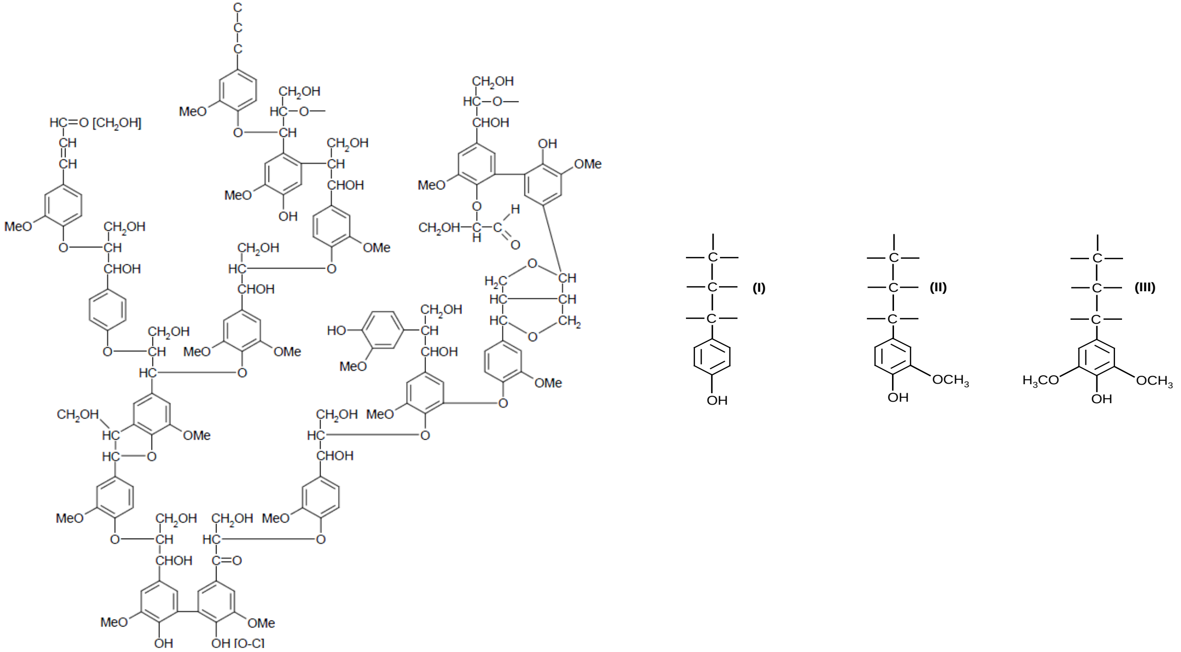


**Figure 2. Polymeric model of softwood lignin and lignin building units: p-hydroxyphenylpropane (I), guaiacylpropane (II), and syringylpropane (III).**

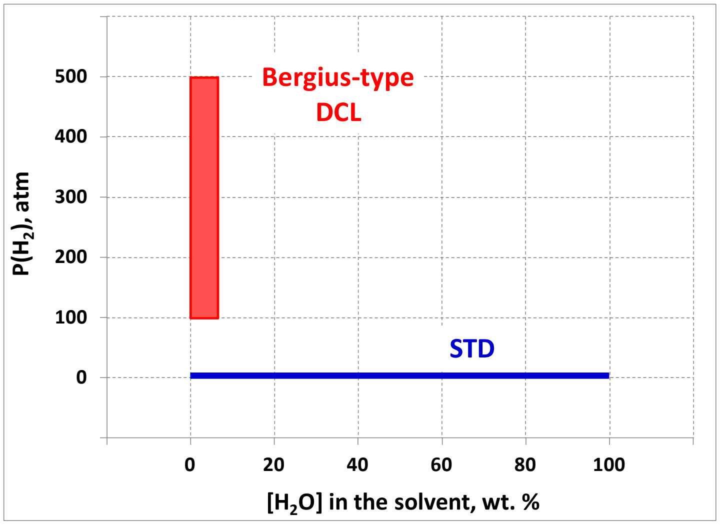


**Figure 3. DCL and STD: processes for direct conversion of carbonaceous feedstock into liquids.**

## Scope of work and the main results

The project “Conversion of Low-Rank Wyoming Coals into Gasoline by Direct Liquefaction” funded by Clean Coal Technology Fund of Wyoming and by the Department of Energy (NETL), studied direct conversion of Wyoming coals and coal-lignin mixed feeds into liquid hydrocarbons in conditions highly relevant to practice and targeted the following objectives:

- explore new approaches for converting coal and biomass into liquid hydrocarbons,
- identify technically/economically viable methods,
- determine further steps necessary to develop, scale up, and commercialize the technology.

The originally proposed approach – Thermosolv process that includes solvothermal depolymerization (STD) of coal-lignin feed as the first stage – has been reconsidered during the project after obtaining the results on inadequate performance of STD, including low conversion and formation of considerable amount of undesirable side products. Overall, the revealed drawbacks do not render aqueous media as the most appropriate choice for commercial implementation of STD for processing coals and lignins.

Focus of the work was shifted to studying better-performing Bergius-type process – direct liquefaction of carbonaceous feedstocks involving organic solvents and pressure of hydrogen (DCL).

The present understanding of the process mechanism leads to expectations of the positive effects that a combination of certain additives and the process conditions might deliver. These innovations in the process design became the focus of systematic studies.

As a result, certain negative and positive effects and trends of high importance to practice have been discovered. The found effects point at the specific features of the liquefaction mechanism that are currently underutilized yet could be exploited to intensify the process or to simplify it. ***Overall, a proper design of the process and judicious choice of the process conditions might enable economically efficient direct conversion of Wyoming coals into added-value liquid hydrocarbons.***

## Future work

The existing technologies of direct coal conversion into synthetic oil for, primarily, production of motor fuels, assume high capital costs (~$1B), which in conjunction with other drawbacks – uncertainty of the economical situation, low long-term oil prices, strict environmental regulations, trends in the energy industry and automotive market – make the construction of a fully-fledged facility in Wyoming unjustified. The technological advances enabling milder liquefaction conditions would definitely help to reduce the costs and promote economical efficiency of DCL. These developments are actively ongoing worldwide; the work described in this report targeted them also. To overcome completely the market acceptance barrier and to make DCL economically attractive, however, further work consisting of closely interwoven efforts on the technology development as well as engineering, marketing and economical studies is needed.

The production of synthetic oil and liquid motor fuels for general use (gasoline, diesel) from coal faces strict competition with well-established processing of natural oils. At the same time, the chemical structure of low-rank Wyoming coals offers an opportunity to produce liquid hydrocarbons with high content of so-called polycyclic naphthenes that are relatively rare in natural oils. Focusing on producing and marketing naphthenes for niche applications – transformer and engine oils, coolants, cutting liquids, lubricants, plasticizing oils for adhesives, and high-value jet fuels – might render the DCL economically efficient. For example, the price of engine oils could be 3-10 times higher than the price of fuel.

Inspired by the promising results obtained in this project, we are considering, as the next step of developing DCL, a process specially designed for the small-to-medium scale (50-1000 bbl/day) production on naphthenes; tentative schematic is shown in Figure 4. The features to explore include:

- utilizing certain solvents and/or additives to maximize the yield of naphthenes,
- using syngas as the hydrogen source instead of pure hydrogen,
- using oxygen-rich biomass to produce syngas by steam conversion,
- using Ni nanopowder as the regenerable catalyst,
- keeping the conversion relatively low (at least, not targeting the maximization of conversion) to enhance the selectivity of producing the naphthenes and to yield, optionally, additional product – solid carbon-enriched residue with the properties similar to anthracitic coals.

The DCL experiments have shown that negative effect of the decrease of hydrogen pressure on conversion is moderate. Decreasing the pressure opens an opportunity to use synthesis gas instead of pure hydrogen. Hydrogen production by gasification or natural gas reforming is a satellite of DCL and bears a significant fraction of the overall process costs. Generating syngas through biomass gasification, and eliminating altogether hydrogen separation (Figure 4), will further simplify the process and decrease the costs. Furthermore, using oxygen-rich biomass instead of natural gas as the feed for gasification will enable the efficient use of steam conversion, eliminating the need for autothermal process requiring oxygen. The heat required for gasification can be provided from burning the CO-rich tail syngas, Figure 4.

Finely dispersed metallic Ni shown to be active catalyst, affecting the selectivity and conversion of direct liquefaction. Advantages of Ni is that it can be regenerated and reused: separated from the product slurry by magnetic separation and regenerated by the Mond process utilizing the unique property of nickel to form a volatile carbonyl. Carbon monoxide will be available as co-products of hydrogen (syngas) synthesis in biomass gasification. The heat required for purification of oxidized and sulfurized nickel as well as for the synthesis/decomposition of Ni carbonyl could be recuperated from the main DCL process and from burning the CO-rich tail syngas, Figure 4.

The liquid product of the targeted DCL process – a mixture of liquid hydrocarbons rich in polycyclic aromatics – will be further refined to separate aromatics followed by their hydrotreatment to produce naphthenes. Other fractions resulting from the coal-derived liquids, and containing the products of conversion of the additives, could be further processed at a refinery. The other product of potential value would be high-BTU carbon-rich coke.

The next phase of the development will optimize the conditions for DCL and scale up the process to ~1 kg coal/day. Afterwards, we will design, build, and test run a pilot-scale plant for the production of 10-50 gal/day of coal-derived liquids.

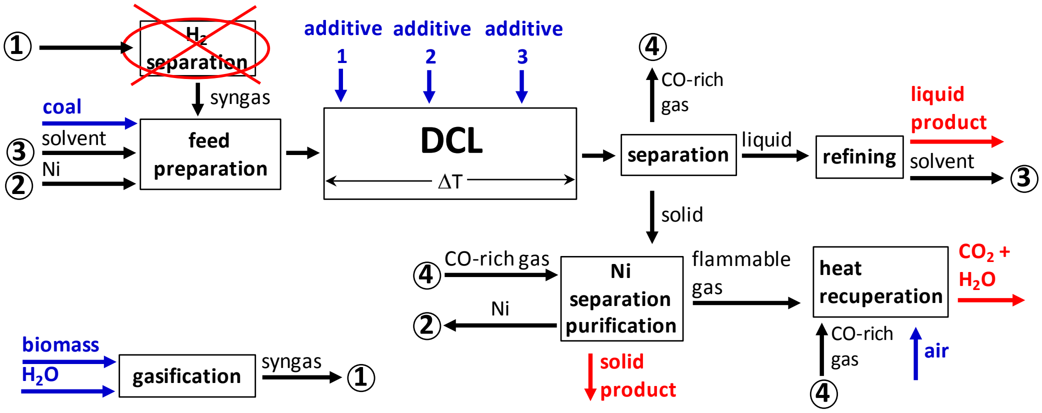
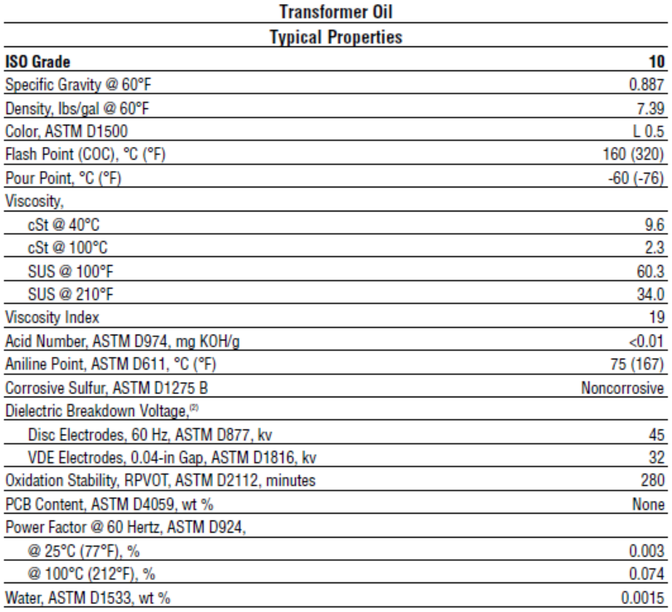


Figure 4. Coal liquefaction yielding added-value liquid (heavy naphthenic oil) and solid (high-BTU refined coal) products.



| Transformer Oil | |
|---|---|
| **Typical Properties** | |
| **ISO Grade** | **10** |
| Specific Gravity @ 60°F | 0.887 |
| Density, lbs/gal @ 60°F | 7.39 |
| Color, ASTM D1500 | L 0.5 |
| Flash Point (COC), °C (°F) | 160 (320) |
| Pour Point, °C (°F) | -60 (-76) |
| Viscosity, | |
| cSt @ 40°C | 9.6 |
| cSt @ 100°C | 2.3 |
| SUS @ 100°F | 60.3 |
| SUS @ 210°F | 34.0 |
| Viscosity Index | 19 |
| Acid Number, ASTM D974, mg KOH/g | <0.01 |
| Aniline Point, ASTM D611, °C (°F) | 75 (167) |
| Corrosive Sulfur, ASTM D1275 B | Noncorrosive |
| Dielectric Breakdown Voltage,[2] | |
| Disc Electrodes, 60 Hz, ASTM D877, kv | 45 |
| VDE Electrodes, 0.04-in Gap, ASTM D1816, kv | 32 |
| Oxidation Stability, RPVOT, ASTM D2112, minutes | 280 |
| PCB Content, ASTM D4059, wt % | None |
| Power Factor @ 60 Hertz, ASTM D924, | |
| @ 25°C (77°F), % | 0.003 |
| @ 100°C (212°F), % | 0.074 |
| Water, ASTM D1533, wt % | 0.0015 |

Figure 5. Specifications of 76 Transformer Oil (bulk price $10/gal) formulated with hydrotreated naphthenic base oils.