# DIRECT COAL LIQUEFACTION: BRIDGING THE GAP BETWEEN R&D AND COMMERCIAL FEASIBILITY

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## INTRODUCTION

The more recent development of direct coal liquefaction processes for rapid commercial readiness started in 1975 and culminated in 1982. Four processes, SRC I and II, H-Coal and Exxon Donor Solvent (EDS) were at the point where they were considered serious contenders for commercialization (1,2,3).

Based principally on the experience gained in large pilot plants for each of the above processes, it could be stated that commercial-scale direct coal liquefaction facilities could be designed and constructed using available technology to give predictable yields and acceptable mechanical performance.

All the processes which were considered technologically ready for commercialization as well as those recently developed in process development units (PDU), i.e., Two-stage Liquefaction, were based on research done at laboratories of companies involved in petroleum processing. Their experience in petroleum residues processing, which turned out to be somewhat similar to direct coal liquefaction processing, gave them a leading hedge over other DOE supported laboratories involved in fundamental and applied research in direct coal liquefaction.

In this period of major effort for ERDA/DOE (1975-82) we learned that the development of this industrial technology requires meaningful cooperation among many scientific disciplines, including several branches of chemistry, physics, engineering, economics and others. It requires superior management to achieve a proper balance among the several branches involved, as priority shifts from one discipline to the other according to the progression of problems encountered. This is particularly true for direct coal liquefaction technology that involves complex operations, and deals with, what is now believed, a mixture of mostly reactive and partly refractory materials.

During the last three years, with the drastic curtailment of the DOE budget, and the shift towards novel research approaches, most of the recent applied research efforts were focused on a single aspect of coal liquefaction, namely obtaining high coal conversion, and neglecting other important coal processing components, i.e., the upgradability of the converted coal extracts produced from high conversion. An upgradability test would reveal whether the conditions used in converting the coal were too drastic, producing "refractory" compounds which would be difficult and expensive to downstream processing. This example and other neglected requirements for useful coal processing revealed a widening gap between fundamental and applied research direction on one hand, and process technological advances directed toward possible scaleup, on the other. This technological gap needs to be bridged and more meaningful coordination between R and D ought to be augmented. It is for this purpose that this paper is addressed to those researchers who are interested in pursuing the scaleup of research discoveries by pointing out the technological needs for their development into feasible process scaleup configurations and the production of marketable fuels. Also the paper summarizes some recent trends in direct coal liquefaction technology, which either have achieved or have the potential to achieve developmental stages, to serve as possible guideline for future research.

## BACKGROUND AND RECENT DEVELOPMENT

Earlier approaches to direct coal liquefaction have employed high severity operating conditions of pressure, temperature and coal/solvent slurry contact time, to achieve in one reactor the highest coal conversion and distillate yield possible. Several disadvantages are associated with this processing mode, namely: 1) the high hydrocarbon gas yield which causes high hydrogen consumption, 2) the production of lower quality solvent containing low boiling distillates, 3) the "regressive" formation of high boiling distillates and non-distillables which are "refractory to hydrogenation" and are the major cause of hydrotreating catalyst deactivation, 4) the extreme difficulty in controlling the highly exothermic reaction of molecular hydrogen with aromatics, particularly in large scale units, and 5) the production of lower quality distillate fuel products which require more severe hydrotreatments to meet transportation fuel specifications.

The accepted main mechanism for high severity conversion of coal is the homolitic thermal cleavage of bonds to yield free radicals, which are capped by hydrogen from the donor solvent or hydroaromatic structures in coals.

A more recent approach uses low severity operation in separated stages in order to optimize the coal dissolution step and coal extract upgrading step. The result is to substantially reduce, and in some cases eliminate, the disadvantages created by high severity processing.

Integrated staged operations in continuous units at Lummus, Wilsonville, Kerr-McGee and HRI have produced enhanced yields of high quality distillate product and recycle donor solvent, both with much reduced heteroatom content and lower hydrogen consumption compared to high severity single-stage processing (4).

Recent work on integrated staged coal liquefaction processing and other DOE supported projects, as well as development of new analytical techniques, have provided substantial amounts of new information. The result has been to change substantially our approach to coal liquefaction techniques and to inspire new thoughts in unraveling the complex mechanism of direct coal liquefaction at low severity operations. Important new information includes:

> Low severity processing forms mostly reactive low molecular-weight fragments. Conversely, single stage thermal and thermal/catalytic processing produce high-molecular weight products thought to be actually condensation products of such smaller fragments and consequently, less reactive (5).
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> Thermally produced coal extracts contain a high level of heteroatom compounds and are "refractory" to catalytic hydrogenation (6). Conversely, low severity produced extracts are low in heteroatoms and more easily hydrogenatable, consistently yielding excellent equilibrium donor solvent, as proved in all Integrated Two Stage Liquefaction (ITSL) operation (7).

No high viscosity gel region is apparent over the 280-350°C temperature range for a slurry of bituminous coal and ITSL solvent, as was the case for slurries prepared with the same coal and other types of solvent (8).

Proton NMR analysis, modified to provide data on ITSL distillate and non-distillate fractions, serves to create a kinetic model for coal extract hydroprocessing, thus enabling us to distinguish catalytic hydrogenation and cracking reactions, and to predict the solvent donor capability as well as the yield structure of the upgraded products (9).

A mixture of condensed aromatics, hydroaromatics, paraffins and their respective heteroatom derivatives is produced during coal liquefaction. This mixture tends to be unstable because of the incompatibility between polar heteroatom compounds and hydrocarbons, as well as between condensed aromatics and paraffins. Condensed hydroaromatics, having closer affinity for both aromatics and paraffins, tends to keep them in solution, thus contributing to the stability of the coal extract. Low severity coal extraction yields larger quantity of hydroaromatics and smaller amount of high heteroatom, condensed aromatics and paraffins (9)

Best catalysts tested are those modified to suppress the hydrocracking activity and enhance hydrogenation functionality (7).

Coal derived transportation fuels possess inherent high premium quality which due mostly to their hydroaromatic (naphthenic) nature. Coal-derived naphthas contain large quantities of highly alkylated cyclohexanes which, by reforming, convert to the corresponding benzenes and in the process, recover a large portion of the hydrogen to make the overall coal liquefaction approach economically more attractive. Alkylated benzenes are the major contributors to the high octane gasoline thus formed. Coal derived middle distillate is constituted mostly of di-and tri-hydroaromatics and corresponding aromatics. Refining must convert the aromatics to less than ten percent level to meet marketable jet and diesel fuel specifications of smoke point and cetane number, respectively (10).

Phenols inhibit catalytic denitrogenation of coal derived liquids (11). Nitrogen compounds inhibit catalytic hydrogenation of aromatics (12).

Recycle solvent produced at high severity (SRC-I) and modified by removing part of the heteroatom compounds, produces significantly higher oil yield and coal conversion compared to the data obtained with the unmodified solvent (13).

## SIGNIGICANCE OF RECENT DEVELOPMENT

Processing coals at low-severity operations has the potential for simplifying the process scheme, drastically reducing reaction severity and instability of the reaction intermediate products, and yielding superior quality fuel products.

Novel research approaches will have to compete against the superior achievements obtained at low-severity processing, rather than citing small improvements over high-severity processing results.

Other significant conclusions derived from low-severity liquefaction are:

A mechanism of the initial coal extraction different than that for the high severity operation must be invoked for the low severity conversion in which coal and donor solvent first form an "adduct," possibly by interaction of both hydrogen and covalent bonds. Bond cleavage of the adduct is accomplished by weakening the coal aromatic structure through hydrogen transfer from the donor solvent to the coal. This overall hydroaromatic structure is more easily cracked thermally.

The apparent non-intervention of the hydrogen gas in the donor solvent/coal reaction, in spite of the imposed high hydrogen partial pressure, would indicate that the donatable hydrogen present in the solvent is transferred much faster to the coal than the hydrogen gas which has to transfer first to

the solvent and finally, to the coal. Also, donor solvent-coal reaction is seemingly faster than the occurrence of most repolymerization reactions known as "regressive" reactions. In the absence of a reacting gas phase the SCT reactor flowdynamics would be reduced to relatively simple liquid/solid two phase reaction, anticipating better correlation between data produced in bench- and scale-up units.

Removal of heteroatoms from freshly formed preasphalthenes might be sufficient to convert them to toluene solubles and ultimately to yield mostly hydroaromatics.

The low severity coal extraction is apparently thermally neutral in that the exothermic hydrogenation of condensed aromatics is equalized by the endothermic dehydrogenation of the hydroaromatics, the major constituents of the donor solvent. Thus, low severity extraction is inherently much more controllable than the exothermal hydrogen-gas/solvent/coal high severity reaction, an extremely important factor in scale-up operations.

## GENERAL THOUGHTS AND RECOMMENDATIONS

First of all we need to recognize that future coal liquefaction commercial efforts will be market-driven instead of technology-driven. In some industries like computers, a technical breakthrough creates a new market. For coal liquefaction, and for synfuels in general, the market will point the direction and technology will clear the path.

With these thoughts in mind, one needs to acknowledge that the cyclic nature of coal derived products, eventually containing some of the heteroatom impurities will require new standard specifications for their safe use. Consequently, to meet today's fuel specifications and avoid possible unknown problem in the future, one must first practically remove most of the heteroatoms and all of the mineral matter from coal liquids. Obviously it would be advantageous to remove a large portion of the mineral from the organic matters prior to introducing coal into the slurry vessel. Also advantageous would be to either remove the heteroatoms in the early stage of coal extraction and/or to weaken the carbon-heteroatom bonds for ease of heteroatom removal in subsequent stages. Experimental results at Suntech (11) advises to remove first the more abundant oxygen, which seems to tie up the nitrogen compounds via hydrogen bonding, and thus making easier the subsequent nitrogen removal.

Complementary fundamental studies on C-O and C-N bond scission should be emphasized over the current C-C bond cracking effort.

Most of the sulfur is converted to hydrogen sulfide during liquefaction and upgrading, and the $H_2S$ must be kept in the system as catalyst itself and as "activator" of transition metal catalysts.

Preservation of highly reactive, small fragments in the coal extract is of utmost importance in producing an excellent donor solvent and high quality distillate fuel products. For this purpose, the fragments should be withdrawn from the extraction reactor as soon as they are formed. The unconverted coal can be further converted by recycling it with the preasphalthenes as part of the recycle solvent. This approach appears to be especially successful in processing low reactivity coals such as Wyodak subbituminous coal (7) and supports the claim (14) that conversion is not coal limited but process limited.

Better preservation of the reactive small fragments can be achieved by increasing the donatable hydrogen level and decreasing the heteroatom content of the recycle solvent. It is important for the donatable hydrogen to match the hydrogen acceptability of the coal as both conditions become more reactive with increasing temperature. Consequently, it is advisable to allow for a thermal soaking treatment, i.e., at 250-350°C temperature range for 10-30 minutes, prior to a very short contact time (SCT) action of rapid heating (two minutes or less) to the 450°C exit temperature. It is evident that all the above activities are interdependent and the improvements maximized in an integrated recycle process.

It is extremely difficult to capture in research bench scale units the essence of the results produced in the integrated recycle process, because most of the key benefits, i.e., coal conversion and enhanced donor solvent quality, are obtained only after several cycles of the integrated staged operations. Bench scale researchers could avoid the long and tedious recycle operations by applying the aforementioned kinetic model for coal extract hydroprocessing (9) and using proto-NMR data of the coal extract to predict solvent donor capability and yield structure of the upgraded products.

The recommendations made will also preserve the highly valuable cyclic characteristics of the final fuel products, minimizing the formation of paraffins. Conversion of hydroaromatics to either paraffins or to aromatics, if desirable to meet fuel specifications, is achieved under easy and controlled operations.

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