

ADVANCES AND NEW DIRECTIONS IN DIRECT LIQUEFACTION

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1.0 INTRODUCTION

With advances in single stage processes such as H-Coal, EDS and SRC, and refining and upgrading of coal liquids by Chevron and UOP, the direct liquefaction process has continuously evolved to the present two-stage catalytic configuration, which produces the highest liquid yield and product quality of any process worldwide.

The Two Stage Liquefaction (TSL) process has been successfully applied to bituminous and subbituminous coals, overcoming problems associated with earlier processes. But, potential for additional improvement is recognized in several areas:

- o Cleaning coal prior to liquefaction.
- o Low temperature and pressure preconditioning of feed coal.
- o Novel catalysts development to arrest regressive reactions and improve hydrotreatment and cracking reactions.
- o Improvement in hydrocarbon value recovery and reduced energy rejection by alternate bottoms processing techniques.

In this paper, after discussing briefly the history of liquefaction and development of the TSL process, present potential areas for research and development are presented.

2.0 BACKGROUND

During the 1970's, four single stage processes (SRC-I, SRC-II, H-Coal and EDS) received substantial interest. Two of these, SRC-I and SRC-II, primarily involved thermal liquefaction and hydrogenation reactions. Others utilized catalytic reactions as well. The liquids from these processes needed substantial upgrading to obtain marketable products (1). The common features and drawbacks of these processes are:

- o 90% or better coal conversion is obtained but, reaction severity is high (820-860°F temperature, 1500-3000 psi pressure and 20-60 minutes residence time).
- o Distillate yields are about 50% of MAF coal, which are low relative to recent developments.

- o Hydrogen utilization is good but, efficiency is low due to high yields of hydrocarbon gases.

Attempts to improve the distillate yields and reduce reaction severity resulted in the development of two stage liquefaction (TSL) processes.

3.0 INTEGRATED TWO STAGE LIQUEFACTION (ITSL)

A. Early Studies

In late 1970's several thermal coal dissolution investigations concluded that coal conversion is essentially complete in an extremely short residence time of 1-2 minutes. The investigations also observed that higher hydrotreatment temperature and residence times resulted in increased yield of hydrocarbon gases. About the same time, at Wilsonville (Runs 145-146), increased importance of liquid phase hydrogen transfer in liquefaction was observed. Combining these observations Lummus developed the ITSL process.

B. Lummus ITSL

The Lummus ITSL process, tested in a 500 lbs per day PDU, consists of a short contact time (SCT) coal dissolution first stage followed by a LC-Fining catalytic hydrotreater as a second stage. Based on petroleum background, Lummus introduced Antisolvent Deashing (ASDA) equipment between the two stages.

The SCT reactor operated at shorter residence times (2-3 min.) and low pressures (500-1000 psi), while maintaining coal conversions above 90% MAF. The hydrocarbon gas yields were low and hydrogen utilization efficiency was high. Distillate yields were significantly better than the single stage processes. The SCT resid was reactive not only for conversion to distillate but also for heteroatom removal. The ITSL process also showed that the ashy recycle is not detrimental to catalyst activity and that a lighter and more desirable product (-650°F) can be made with little loss in hydrogen efficiency.

C. Wilsonville ITSL

Scale-up of the ITSL process to 6 tons/day (24 times) was performed at Wilsonville. A H-Oil ebullated bed hydrotreater (in place of the LC-Fining unit) and a Kerr-McGee Critical Solvent Deashing (CSD) unit for ash removal (in place of ASDA) were utilized. In spite of the retrogressive reactions in the CSD that lowered the coal conversion from 92 to 88% and the high organic rejection with the ash concentrate stream, a distillate yield of about 54% was obtained.

Wilsonville increased the distillate yield to 62% by placing the de-asher after the second stage (after vacuum distillation) which had no detrimental effect on the catalytic activity in the second stage reactor. With this reconfigured ITSL (RITSL) operation, retrogressive

reactions were limited and good operability with on-stream time of more than 95% was demonstrated. This RITSL operation showed that deashing prior to second-stage hydrotreatment was not necessary.

To further reduce retrogressive reactions by minimizing holding time between the reactors (first and second stage) and to eliminate pressure let down and repressuring, the two reactors were operated in a close coupled ITSL (CCITSL) mode. In this operation, all the first stage gases (CO, H₂S, H₂O etc.) and light oil were removed prior to second stage. There was no significant impact on catalyst activity and there was no discernable loss in performance relative to ITSL (yields, allowable space velocities, etc.). However, more rigorous analysis at a consistent set of conditions is necessary to verify the improvement of CCITSL over RITSL.

4.0 CATALYTIC TWO-STAGE LIQUEFACTION (CTSL)

A. HRI CTSL (1984 - Present)

In CTSL, the first stage temperature was lowered to 750°F to more closely balance hydrogenation and cracking rates, and to allow the recycle solvent to be hydrogenated *in situ* to facilitate hydrogen transfer during coal dissolution. The second stage was operated at higher temperature (820-830°F) to promote resid hydrocracking and generation of an aromatic solvent, which is then hydrogenated in the first stage (see Figure 1). The lower first stage temperature provides better overall management of hydrogen consumption, with hydrocarbon gas yields reduced by about 50 percent. Higher distillate yields were attained by the reduction of resid in the rejected ash-concentrated stream and the subsequent conversion of that recovered resid to distillates.

A pressure filter reduces resid concentration in the reject stream (filter cake) below 45-50 percent. This change signalled the end of the "hydrogen balanced" process and showed that overall liquefaction economics improve if the process maximizes distillate yield and produces hydrogen by natural gas reforming or by coal gasification.

A third change by HRI was in the use of NiMo catalyst. The H-Coal process had used a cobalt-molybdenum (CoMo)-on-alumina catalyst (American Cyanamid 1442B), which is used in petroleum applications. In coal liquefaction, hydrogenation of solvent must occur first, before the aromatic molecules can thermally crack. The catalyst must hydrogenate large molecules which determine the rate at which resid is converted. The (NiMo) catalyst has a bimodal pore distribution with larger micropores, 115-125 Å, which allows easier diffusion, as opposed to 60-70 Å for H-Coal catalyst, and the nickel promoter is also more active for hydrogenation than cobalt.

The latest reported results with Illinois No. 6 coal show a 78 percent distillate yield (Table 1). Hydrogen efficiency is over 10 pounds of distillate per pound of hydrogen reacted. In addition, the two catalytic reaction stages produce a liquid with low heteroatom concentrations and a high H/C ratio.

B. Wilsonville CTSL (1986-Present)

The most significant differences at Wilsonville are the reactor temperatures. As in ITSL, most of the thermal cracking takes place in the first reactor and solvent hydrogenation is in the second reactor. Therefore, the first reactor is at the higher temperature (800-820^oF), while the second reactor is kept slightly lower at 795^oF. Other reaction conditions are similar to HRI CTSL, including the catalyst type. The distillate yields are about the same, i.e. 78% MAF Coal. Wilsonville deashes by CSD, and steady improvement has reduced organic rejection to 8-15 percent, about the same as achieved by HRI.

C. Evolution of Liquefaction Technology

Substantial improvements in liquefaction processes and catalysts associated with these processes have taken place. The yields and quality of liquids have improved substantially. History of process development improvements are shown in Table 1. Yields of distillates have increased from 41% to 78% (5 barrels/ton of MAF bituminous coal). Quality is comparable to or better than No. 2 Fuel Oil with good hydrogen content and very low heteroatom content.

5.0 FUTURE RESEARCH AND DEVELOPMENT

The overall goal of coal liquefaction R&D is to develop technology to produce marketable liquids economically (\$25/Bbl by 1995). This requires scientific and engineering knowledge based on:

- o Improved processes to provide product selectivity and quality, increased liquid yields per ton of coal and improved thermal efficiency--involves current as well as novel catalysts and processes.
- o Improved plant operability and onstream factors by process and component development.
- o Reduction of Capital and Operating costs by optimization and integration of R&D improvement.

Brief descriptions of significant areas follow:

A. Preconversion and Regressive Reactions

The preceding discussion placed emphasis on process improvements, principally on the coal dissolution and resid upgrading reactions. This requires a better understanding of coal conversion chemistry.

The term "first reactor" is a misnomer, because there is strong evidence that the coal has undergone considerable reaction before entering that vessel (2). Coals have been found to undergo changes at temperatures as low as 200°C. Suuberg (3) has measured the evolution of carbon dioxide from low rank coals at low temperatures and Solomon (4) has related this gas evolution to cross-linking, which reduces coal reactivity thereafter. The onset of swelling has been measured at 200°C, with completion at about 500°C (4), again an indication of cross-linking. Derbyshire has shown that soaking coal at temperatures below 400°C increases yield of toluene solubles, presumably as the result of increased hydrogen transfer from the solvent (5). Recently, with liquid-phase transfer, 85 percent conversion of sub-bituminous coal and 91 percent conversion of bituminous coal (to quinoline-solubles) in about 30 seconds at 425°C (6) was reported. These findings show that coal has already reacted in the preheater, and in all likelihood, the coal (or coal liquid), in the reactor may be less reactive and must have necessitated high severity reaction conditions to undo the damage that took place during heat-up.

More information on the mechanism of these preconversion reactions and their impact on process yields and product quality are required. The effects of time, temperature, solvent quality, and catalyst-dispersed or soluble-on the kinetics of coal dissolution below 400°C and on the structure of the liquid product must be quantified. Process developers will utilize this information to modify preheat conditions to supply a more reactive feed to the first reactor. The anticipated benefits are increased coal conversion, increased reactivity of coal liquids, smaller reactors, moderating reaction conditions and better hydrogen efficiency. A more reactive feed should also improve catalyst activity in both stages.

B. Hydrotreatment and Cracking Reactions

Process development has emphasized resid conversion and liquid yield, but how is conversion achieved? Unlike petroleum resid, which cracks thermally to smaller molecules, which are then hydrogenated, coal resid must first be hydrogenated before cracking can occur. Hydrogenation is catalytic, while the cracking reactions may be either thermal or catalytic. Little is known about the kinetics of these reactions, and this work has the potential to improve on current TSL performance.

Catalyst activity for conversion falls to about 20 percent of its initial value in a few days. Sandia has related most of the catalyst deactivation to carbon laydown on the catalyst and the inhibiting effects of certain nitrogen compounds in the coal liquids (7). Others point to phenols as a source of deactivation (8). The mechanism of deactivation is not understood. With additional information, improved catalysts and regeneration may be possible.

A better understanding of the kinetics of these reactions could greatly improve process economics or even cause a major modification of the process. Lummus Crest, Inc. (LCI) found that resid hydrogenation is rapid at 450°C (9) therefore, most of the second stage reactor volume is required for conversion, which might be by thermal cracking. Increasing the cracking functionality of the catalyst could significantly reduce reactor volume.

In addition to investigating the kinetics of resid hydrogenation/cracking, additional information is needed on kinetics of hydrogenating heavy distillate (650°F+), and hydrogen transfer rates from solvent to coal and from distillate to resid. This latter point is of great importance in the preheater reactions just discussed. The benefits of soaking at low temperature may be related to relative rates of thermal cracking and hydrogen transfer at 200-400°C. Therefore, this temperature range must be included in the kinetic study of hydrogenation and cracking.

C. Integration of Coal Beneficiation and Cleaning

The quality and quantity of resid (or organic) rejected is a function of ash composition in the coal. Removal of ash by coal beneficiation has been a fairly standard practice and interest in deep cleaning to remove pyritic sulfur has increased substantially in the last decade. This has resulted in significant advances, such as:

- o Heavy media cyclone cleaning
- o Oil agglomeration
- o Microbubble flotation
- o Molten caustic cleaning

Intuitively, reduced ash content reduces organic rejection and facilitates liquefaction and hydrotreating by reduced corrosion and erosion. However, reduced pyrites and sulfur may decrease the catalytic activity. As a result, benefits of beneficiation and cleaning were uncertain and liquefaction units operated with standard coal beneficiation used for power plants (10% ash).

Recent coal agglomeration work by Consol, Alberta Research Council and PETC, and liquefaction data from PETC, HRI and Wilsonville operations have shown the advantages of deep coal cleaning (about 5% ash). Liquid yields increased by 5% and energy rejection was reduced. Corresponding economic benefits were noted by Mitre.

There are many unanswered questions:

- o What are the liquefaction characteristics of cleaned coal?
- o Can selective coal cleaning improve the process substantially.

- o Should the coal be cleaned to an ash content of 1%, 2% ash or 5%? What limits this ash content - coal cleaning process or liquefaction process?
- o How do we integrate? With bottoms? With heavy distillates?
- o What are the implications of integration on liquefaction reactions, hydrotreating reactions and coal cleaning?
- o Which coal cleaning process is more attractive economically and under what conditions?

Future R&D should provide answers to some of the above.

D. Alternate Liquid/Solid Separation System

The Wilsonville PDU employs the CSD developed for the SRC-1 process and HRI uses pressure filtration because the feed is lighter and less viscous than deasher feeds of just a few years ago. Both CSD and filtration achieve high recovery of resid, but are expensive to install and operate. As a result, comparative economics of alternate systems and alternate processes are required to achieve even better results at lower cost.

Recently, a fluid coking study (10) showed that over 60 percent of the toluene solubles in the deasher feed is recoverable as coker distillate. This is also expensive, but Mitre has estimated that it has economic advantages over CSD (11). Additionally, the coker distillate is highly aromatic and analyses by Consol have shown that, after hydrogenation, it is capable of effecting higher coal conversion than recycle solvents currently being used (12). Therefore, coking is being investigated, not only as a viable alternative approach to liquid/solid separation, but as a possible source of improved coal reactivity.

Should deep cleaning of coal become an integral step of direct liquefaction, the solids rejected will be only about 9 percent of MAF coal, and solids removal by vacuum distillation may become attractive. Total organics rejected in the vacuum tower bottoms would be only about 11 percent (less than 15 percent by CSD). Most of the bottoms will be recycled to the solvent tank and a small purge stream will remove ash, possibly by coal beneficiation. This alternate liquid/solid separation scheme is dependent on improvements elsewhere in the process and corresponding follow-up R&D, process integration and economic evaluation are required.

E. Systems Integration Schemes

Research to improve direct liquefaction technology must take into account the integrated nature of the process. A change made in any component in the process will impact others. Therefore, the entire

system, its technical viability and overall economics, must be considered as process improvements occur. For example, the alternative liquid/solid separation discussed earlier (Figure 2) uses a vacuum tower as the means of liquid/solid separation and may result in many process changes:

- o The composition of the recycle solvent will be changed (ratio of solvent/resid/solids);
- o The vacuum tower bottom may be fed to coal beneficiation to recover more organics;
- o The vacuum tower overhead may be the agglomerating oil for beneficiation;
- o The vacuum tower bottoms may be fed to a coker to recover coker distillate, and the coker distillate may be hydrogenated in the second stage.
- o The hydrogenated coker distillate may leave as product or may be recycled as solvent. Its effect on solvent quality is, as yet, unknown.

Similarly, the investigation of preconversion reactions may well result in changes that may effect the entire process and a similar systems approach will be necessary. Even changes in catalyst or reaction conditions must be viewed in terms of its impact on overall operability and economics of the process. Coordinated R&D with systems integration schemes are required.

F. Integration and Optimization

The direct liquefaction section is part of a larger plant. Some of the other areas that must be considered include:

- o Hydrogen production and purification
- o Coal preparation and handling
- o Waste processing and disposal
- o Refining and upgrading of coal liquids to marketable products

The first three areas constitute a large fraction of the cost of a liquefaction plant and R&D to improve these operations could greatly improve the overall economics of liquefaction.

Hydrogen production is always a potentially fruitful topic for research because of the cost of the hydrogen plant. Should hydrogen be made by gasification of CSD or vacuum tower bottoms, or by gasification of coal, or by reforming of natural gas? Whichever is selected will effect the entire plant. The effect of carbon monoxide on cata-

lyst activity is still not clear. Research is needed in that area. If CO has no inhibiting effect on catalyst activity, the hydrogen plant can be simplified. Conversely, the economic incentive of a less expensive hydrogen plant may be the impetus to develop such a CO-resistant hydrotreating catalyst. What are the requirements for recycle gas purification? How can they be integrated and optimized?

Similarly, it is to be expected that the use of coals different than those tested to date may require process modifications to achieve optimum yields. These coals may require different liquefaction processing or coal preparation. Weathering and oxidation effects on reactivity may have to be investigated.

The refining of coal liquids has received relatively little attention, even though this is the step that makes the marketable products that are the ultimate goal of the plant. Chevron (1) has already shown that a heavy distillable coal liquid is difficult to refine. This finding directed efforts to the production of a lighter (-650°F) coal liquid, which has been achieved successfully. However, further integration with the utilities and refiners may lead to other process modifications in order to make coal liquids more valuable, either as a refinery feed or as marketable products.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The current CTSL process is the best direct liquefaction process in the world. It produces the highest yield of liquid product, having the highest quality-- and it does this at a lower cost per barrel than previous processes. Significant improvements, however, are attainable and are needed to be competitive with crude oil prices (\$25/bbl). These will come from research on the fundamentals of coal liquefaction and on process modifications. All research must be performed with an understanding of the effect it will have on the entire process. The most promising areas for future research are in preconversion chemistry and retrograde reactions, hydrogenation and cracking reactions, coal preparation, and solids rejection. Many of these programs are already in progress. The results are expected to provide a better understanding of liquefaction and foster a new generation of more economic and efficient direct liquefaction technology.

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**Table 1. CTSL DEMONSTRATION RUN COMPARISON WITH H-COAL
(ILLINOIS NO. 6 COAL)**

Process	H-Coal (PDU-5)	CTSL Run No.	
		(227-20)	(227-47)
YIELDS, Wt% MAF			
C ₁ -C ₄	11.3	6.6	8.6
C ₅ -390°F	22.3	18.2	19.7
390-650°F	20.5	32.6	36.0
650-975°F	8.2	16.4	22.2 ¹
975°F+ Oil	20.8	12.6	2.7 ¹
HYDROGEN CONSUMPTION	6.1	6.3	7.3
COAL CONVERSION, Wt% MAF	93.7	94.8	96.8
975°F+ CONVERSION, Wt% MAF	72.9	82.2	94.1 ¹
C₅-975°F, Wt% MAF	51.0	67.2	77.9 ^{1, 2}
HYDROGEN EFFICIENCY	8.4	10.7	10.7
C₅- DISTILLATE PRODUCT QUALITY			
EP, °F	975	975	750
°API	20.2	23.5	27.6
% Hydrogen	10.63	11.19	11.73
% Nitrogen	0.49	0.33	0.25
% Sulfur	0.2	0.05	0.01
BBL/TON	3.3	4.1	5.0

¹750°F Distillate end point.

²Coal contained 5.8% ash.

NOTE: All data at catalyst age representative of typical commercial replacement rates.

**Table 2 HISTORY OF PROCESS DEVELOPMENT AND PERFORMANCE
FOR BITUMINOUS COAL LIQUEFACTION**

Process	Configuration	Distillate (wt% MAF coal)	Yield (bbt/t MAF coal)	Distillate Quality (gravity °API)	Nonhydrocarbon (wt%)		
					S	O	N
SRC II (1982)	One-stage, noncatalytic	41	2.4	12.3	0.33	2.33	1.0
H-Coal (1982)	One-stage, catalytic	52	3.3	20.2*	0.20	1.0	0.50
Wilsonville (1985), RITSL	Integrated two-stage, thermal-catalytic	62	3.8	20.2**	0.23	1.9	0.25
Wilsonville (1986), CTSL	Integrated close- coupled two-stage catalytic-catalytic	70	4.5	26.8**	0.11	<1	0.16
Wilsonville (1987), CTSL	Integrated close- coupled two-stage low-ash coal	78	5.0	+	+	+	+
HRI, CTSL (1987)	Catalytic-catalytic	78	5.0	27.6	0.01	-	0.25

*Light product distribution, with over 30% of product in gasoline boiling range; less than heavy turbine fuel.

**Higher boiling point distribution, with 20% of product in gasoline fraction and over 40% turbine fuel range.

*API and elemental analysis data unavailable at this time.

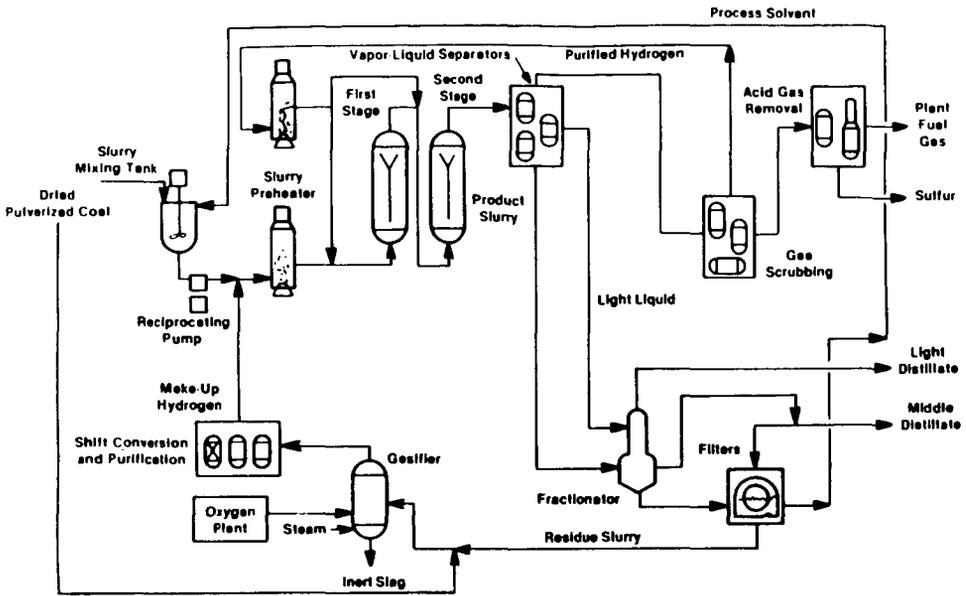


FIGURE 1. HRI CATALYTIC TWO-STAGE LIQUEFACTION

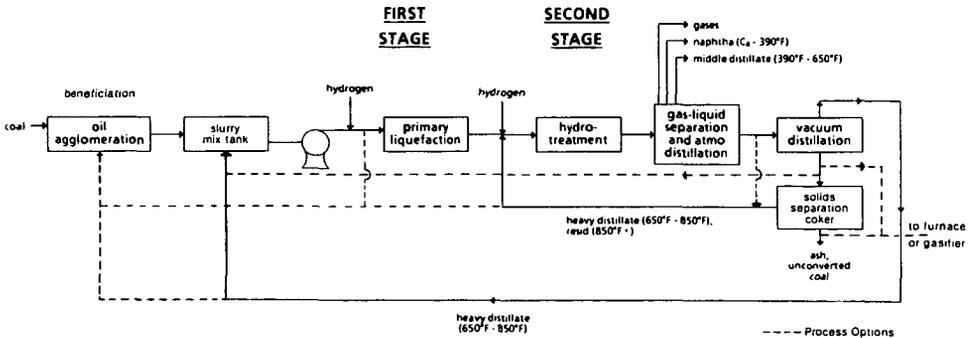


Figure 2. Process Options with Beneficiation and Coking.

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