

CATALYSIS IN DIRECT COAL LIQUEFACTION : STATUS AND DIRECTIONS FOR RESEARCH

Frank Derbyshire
Sutcliffe Speakman Carbons Limited
Guest Street, Leigh, Lancashire, U.K.

The economic viability and operability of processes to convert coals to useful liquid products is contingent upon the development and application of effective catalysts. New and improved catalysts can lead to more favourable process economics by increasing the rate of conversion and the selectivity to the desired products and by allowing operation at reduced temperatures and pressures.

The processes of primary coal dissolution and coal liquids upgrading are distinguished. The status and limitations of catalysts used to promote these reactions are discussed together with approaches which could lead to the development of improved and novel catalysts.

INTRODUCTION

The production of distillate fuels and chemicals from coal has never been economical in a free market economy. The principal factors which contribute to the high cost of coal-derived liquids are the large amounts of hydrogen which must be added to remove heteroatoms and to convert material containing about 5 wt% hydrogen to products with between 12 to 14 wt% hydrogen, the severe reaction conditions (temperature and pressure) and the relatively low rates of conversion which are experienced.

In spite of these limitations there are valid reasons for pursuing research and development in coal liquefaction. Practically every future energy scenario envisions the development of indigenous fossil fuel resources to supplement and replace materials derived from petroleum crudes. In the short term, situations could arise whereby the supplies of imported crudes to oil-poor industrialised nations are restricted and, in the long term, world petroleum reserves will be eventually be depleted.

As has occurred in the development of the petroleum processing and chemical industries, the route to significant improvements in liquefaction processing lies in the successful development and application of suitable catalyst systems. In this paper some of the more salient aspects of liquefaction catalysts are reviewed in terms of the limitations of our present understanding and approaches which could lead to improved and novel developments. Reference is made to a much more extensive critical review which the author has recently completed for the International Energy Agency under the sponsorship of the United States Department of Energy (1). A companion review on catalysis in syngas conversion has also been prepared by Alex Mills (2).

The recognition that liquefaction takes place in two loosely-defined stages, consisting of coal dissolution followed by upgrading of the solubilised products, has led to the concept of two-stage process configurations. The progression from a single, noncatalytic process to a catalytic - catalytic two stage process is summarised in Table 1 (3). The adoption of a fully catalytic process has led to increases in coal throughput and in the yield and quality of distillate products. In addition, since the construction of the first commercial-scale plants in Germany there has been appreciable progress in lowering operating severity and improving the selectivity to liquid products,

Table 2. Nevertheless there is still a pressing need for innovations which can lead to further gains in process performance and operability. The distinction between the processes of dissolution and upgrading provides a convenient division between dispersed and supported catalysts. While there are exceptions, the former have been applied primarily to promote the process of coal dissolution and the latter to upgrading the solubilised coal liquids. These catalysts cannot really be used interchangeably. It is unlikely that dispersed catalysts could realise the selectivity which is possible with supported catalysts; restricted access to the reaction surface of supported catalysts precludes their being able to directly influence the reactions of coals and high molecular weight coal derived products.

SUPPORTED CATALYSTS

The catalysts which have been applied to coal liquids upgrading comprise a combination of the metals Co, Ni, Mo and W, together with promotional additives, distributed over a porous support of alumina or silica-alumina. The catalysts must be sulphided in order to attain their active form. These catalysts are used extensively in petroleum refining and evolved from catalysts which were originally developed for hydroprocessing distillate coal liquids. No concerted attempts have been made to adapt them for hydroprocessing high boiling coal liquids. Research efforts have focused mainly on catalyst screening and evaluation and little attention has been given to investigating novel formulations.

One of the important conclusions emanating from a long program of research by Sullivan and co-workers at the Chevron Research Company (4, 5) is that coal liquids can be adequately hydroprocessed over conventional catalysts provided that the end-point does not exceed about 370°C. The presence of higher boiling materials is deleterious to catalyst life which is shortened by the formation of carbonaceous deposits, the adsorption of basic compounds and the deposition of metals. These effects are considerably more pronounced in the presence of non-distillable coal-derived materials. Under these conditions and during continuous processing there is a rapid and massive reduction in catalyst activity during the first 30 to 50 hours on stream, due principally to the deposition of carbonaceous materials which effect a drastic reduction in surface area. Subsequent loss in activity is more gradual and is attributed to the accumulation of metals. Other contributory causes are the loss of active metals and sintering. Substantial research has been conducted at the Sandia National Laboratories and the Pittsburgh Energy Technology Center to investigate the causes and mechanisms of deactivation (see reference 1). The deposition of carbon is generally attributed to the adsorption and reaction on catalyst acid sites of species such as polycondensed aromatics and heteroatom-containing compounds.

It is concluded that the existing generation of supported catalysts cannot adequately meet the exacting requirements for upgrading primary coal liquids. Two prospective approaches to resolving this problem are indicated. The first involves the development of new supported catalysts which are less susceptible to deactivation by the mechanisms discussed. Avenues for research are considered in reference (1). The second approach is to produce materials which are more amenable to upgrading over supported catalysts through effective catalytic control of the process of coal dissolution. While both of these strategies are considered to be important priorities for future research, the remainder of this paper will be given to a discussion of dissolution catalysis.

It is considered that successful research in this area could have an immediate impact on liquefaction process development.

DISSOLUTION CATALYSTS

Although many catalysts have been examined in fundamental studies, large scale investigations have been primarily concerned with two groups of catalyst materials; metal sulphides and acid catalysts. The sulphides of metals such as Mo and Fe are believed to function as hydrogenation catalysts while metal halides like $ZnCl_2$ promote bond cleavage by an ionic mechanism. In both cases, effective control of the dissolution process requires intimate contact between the catalyst and coal. In turn, this means that the used catalyst is associated with the solid reaction products, which complicates its recovery. For this reason, low cost has been a priority in catalyst selection as it allows use on a once-through basis. This has limited the choice of candidate catalyst materials. The development of technologies for catalyst recovery could alleviate the cost constraint and have a major influence on broadening the resource base for the selection of catalysts.

It is also true to state that research on catalytic coal dissolution has been retarded by the persistent and misguided belief that catalysts cannot influence the reactions whereby the solid coal feed is converted to soluble products.

Sulphide Catalysts

For most metals, the thermodynamically stable form under liquefaction conditions is a sulphide or mixture of sulphides. Fortunately, a number of sulphided metals are active catalysts for coal dissolution. A water or oil-soluble catalyst precursor is normally introduced to the coal or coal-solvent slurry in a manner intended to disperse it efficiently. The sulphided catalyst is subsequently produced by the in-situ reaction of the precursor with sources of sulphur. For a given metal, the catalyst activity will be a function of its dispersion and the stoichiometry of the sulphide phase.

Dispersion is very difficult to quantify. It is always described qualitatively and inferred from experimental data. Logically, it will be dependent upon the precursor composition and the mode of its addition. There is a need to develop methods to quantitatively assess catalyst dispersion. Without this information, there is no means to distinguish effects due to differences in dispersion from those caused by changes in other parameters.

The kinetics of formation of the active phase will be determined by the dispersion and composition of the catalyst precursor and the availability of sulphur-containing species. This reaction is of some relevance since, if the rate is slow, the initial and critical reactions within the coal matrix may be thermally controlled, despite the ostensible presence of catalyst.

Increasing the partial pressure of H_2S will promote precursor conversion and can have an important influence on catalyst activity. In the presence of added pyrrhotite, increasing the H_2S partial pressure has been shown to enhance the hydrocracking of diphenylether and diphenylmethane (6). Research on upgrading petroleum feedstocks with unsupported vanadium catalysts showed that the catalyst activity passed through a maximum between 10-25 mole percent H_2S (7). Studies with supported catalysts have demonstrated that increasing the partial pressure of H_2S accelerates the rate of

hydrodenitrogenation (8-11). One explanation of these phenomena is that the H₂S partial pressure serves both to maintain the catalyst in its sulphided state and to control its stoichiometry. However, it has also been found that H₂S alone can promote cracking reactions and its direct participation in hydrogenolysis reactions may well contribute to the effects observed in the presence of catalysts.

Some thoughts are presented here concerning the mechanisms by which sulphide catalysts may promote coal dissolution. Indisputably, they promote hydrogenation of the coal. It is also probable that they provide several other functions although, as yet, there have been no clear indications of these.

McMillen (12-14), and earlier Vernon (15), have described a mechanism by which the addition of H-atoms to the ipso positions of linkages to aromatic systems can induce bond cleavage. Free H atoms could be made available from one of several sources including the catalytic dissociation of molecular hydrogen. However, even at high levels of dispersion, a large proportion of the catalyst centres must be distant in molecular dimensions from the bonds which are broken. The facility with which hydrogen is known to move through the structure of coals suggest that it should be able to diffuse from the sites where it is generated by a spill-over mechanism, Figure 1. Thus the catalyst can be viewed as a means to inject H-atoms into the coal or the coal-solvent mixture and thereby increase the pool of available hydrogen. This hydrogen will be available for aromatic hydrogenation, the promotion of bond cleavage reactions and radical stabilisation.

In the proposed mechanism, the catalyst does not participate directly in bond cleavage which is dependent upon the level of thermal energy input. This could explain why, for a given coal, different catalysts have been found to show evidence of liquefaction activity over the same range of temperature, Figure 2 (16). The threshold temperature will depend upon the types and distribution of connecting linkages and is expected to differ from coal to coal and to show a systematic change with coal rank.

The effectiveness of the catalyst can be strongly influenced by the presence and composition of a liquefaction solvent. While space precludes an extended discussion of this subject, it seems that those solvent characteristics which have been found to be desirable in 'thermal' liquefaction also hold for catalytic coal conversion. The solvent can provide additional routes for the transport of H-atoms produced by the catalytic dissociation of H₂. The presence of polycondensed aromatics in the solvent has been found to be particularly advantageous (see reference 1).

The possibility that there exists a temperature threshold, below which hydrogenation catalysts have little effect on liquid yields places a lower limit on the temperatures required for liquefaction. However this constraint need not hinder the development of more effective catalysts.

Catalysts with higher activities for dissociating molecular hydrogen will increase the availability of hydrogen atoms and may make it possible to operate at more elevated temperatures (thereby increasing the rate of conversion) while suppressing condensation reactions. Reductions in operating pressure may also be realised. A number of single metals and metal compounds which possess the desired attributes have been excluded from research programs because of their

cost. The scope of fundamental research should not be restricted by such considerations. Until the extent of any potential benefits are determined experimentally, judgements of economic viability can only be subjective.

Although catalytic hydrogenation does not appear to significantly enhance the yield of product liquids below a certain temperature range, it has been shown that reaction at lower temperatures can effect structural modifications to the coal which are advantageous to the production of liquids upon subsequent high-temperature reaction (17,18). The influence of the catalyst can thus be augmented by reacting the coal in successive stages of increasing temperature.

Perhaps the most promising approach to the development of novel catalysts lies in research into multicomponent systems which, in comparison to work on single metals, are essentially unexplored. There are good reasons to anticipate that synergistic effects will lead to exciting discoveries. Synergism has been reported for Fe - Mo catalysts (19). It is supposed that the two metals provide complementary functions which results in non-additive behaviour. A further example of this is given below. The use of a second component could also reduce catalyst cost if the concentration of a more expensive component can be reduced.

Acid Catalysts

Acid catalysts can promote the cleavage of the linkages which connect coal structural units and crack the structures which comprise these units. Several of the catalysts of interest for coal dissolution are metal halides, such as $ZnCl_2$, which possess a low melting point and develop significant vapour pressure at sub-pyrolysis temperatures. This facilitates their penetration and dispersion in the coal matrix. Cracking reactions proceed by an ionic mechanism in which protonation of the reactants is the initial and rate - limiting step. The driving force is the strength of the acid. By using stronger acid catalysts the rate of reaction can be accelerated and the reaction temperature can be reduced.

Process development research conducted by Zielke and co-workers at the Consolidation Coal Company in the 1960s and 1970s demonstrated that it is possible to liquefy coals at fast rates of throughput and with high selectivity to gasoline-range products, using a zinc chloride catalyst. The disadvantages were (i) that the use of massive concentrations of $ZnCl_2$ necessitated the development of techniques for catalyst recovery and (ii) that the corrosive nature of the catalyst created problems in plant construction and operation (see reference 1).

It is possible that many of these technical difficulties could be resolved. However, there is a further problem relating to the process chemistry. In general, acid catalysts do not promote hydrogenation. As a consequence of their inability to adequately stabilise the cracked products, cracking reactions are accompanied by condensation reactions leading to the production of high molecular weight materials. A possible solution is to introduce a second component which can provide a hydrogenation function, Table 3 (20). As discussed above, there are indications that research into multicomponent catalyst formulations can lead to improved control of the reaction chemistry of coal conversion. In this case, it could bring the more desirable features of acid catalysis closer to practical realisation.

References

1. Derbyshire, F J (1988) Catalysis in coal liquefaction: new directions for research.
IEA Coal Research, London, UK (in press)
2. Mills, G A (1988) Catalysts for fuels from syngas.
IEA Coal Research, London, UK (in press)
3. Weber W, Stewart N (1987) Direct coal hydroliquefaction.
EPRI Journal: 12(1); 40-41
4. Sullivan R F (1986) Transportation fuels from two-stage liquefaction products.
American Chemical Society, Division of Fuel Chemistry, Preprints; 31(4); 280-293
5. Sullivan R F, Frumkin H A (1986) Refining coal liquids: where we stand.
American Chemical Society, Division of Fuel Chemistry, Preprints; 31(2); 325-339
6. Sweeny P G, Stenberg V I, Hei R D, Montano P A (1987) Hydrocracking of diphenyl ether and diphenylmethane in the presence of iron sulphides and hydrogen sulphide.
Fuel: 66; 532-541 (1987)
7. Gatsis J G (1975) Catalytic conversion of hydrocarbon mixtures.
US Patent 3,915,842; 6 pp (28 Oct 1975)
8. Hirschon A S, Laine R M (1985) Catalytic hydrodenitrogenation of an SRC II coal liquid: effect of hydrogen sulphide.
Fuel; 64; 868-872
9. Satterfield C N, Gueltekin S (1981) Effect of hydrogen sulfide on the catalytic hydrodenitrogenation of quinoline.
I&EC Process Design & Development; 20; 62-68
10. Yang S H and Satterfield C N (1983) Some effects of sulfiding of a NiMo/Al₂O₃ catalyst on its activity for hydrodenitrogenation of quinoline.
Journal of Catalysis; 81, 168-178
11. Yang S H, Satterfield C N (1984) Catalytic hydrodenitrogenation of quinoline in a trickle-bed reactor. Effect of hydrogen sulfide.
I&EC Process Design & Development; 23; 20-25
12. McMillen D F, Malhotra R, Chang S-J, Nigenda S E (1985) Solvent radical mediated hydrogenolysis in coal liquefaction.
In: Proceedings - 1985 International Conference on Coal Science, Sydney, NSW, Australia, Pergamon Press pp 91-94
13. McMillen D F, Malhotra R, Hum G P, Chang S-J (1987) Hydrogen-transfer-promoted bond scission initiated by coal fragments.
Journal of Energy and Fuels; 1; 193-198

14. McMillen D F, Malhotra R, Chang S-J, Nigenda S E (1985) Hydrogenolysis in coal liquefaction and pyrolysis: the relative importance of solvent radicals and free hydrogen atoms.
American Chemical Society, Division of Fuel Chemistry, Preprints; 30 (4); 297-307
15. Vernon L W (1980) Free radical chemistry of coal liquefaction: role of molecular hydrogen.
Fuel; 59; 102-106
16. Charcosset H, Bacaud R, Besson M, Jeunet A, Nickel B, Oberson M (1986) On the chemical effects of catalysts in the direct liquefaction of coal.
Fuel Processing Technology; 12; 189-201
17. Derbyshire F J, Davis A, Epstein M, Stansberry P (1986) Temperature-staged catalytic coal liquefaction.
Fuel; 65; 1233-1240
18. Bolton C, Riemer C, Snape C E, Derbyshire F J, Terrer M-T (1988) Effect of low temperature catalytic hydrogenation on pyrolysis and hydroxyrolysis of a bituminous coal.
Fuel; (in press)
19. Garg D, Givens E N (1983) Relative activity of transition metal catalysts in coal liquefaction.
American Chemical Society, Division of Fuel Chemistry, Preprints; 28 (5); 200-209
20. Mobley D P, Bell A T (1980) Hydrogenolysis of dibenzyl ether using zinc chloride-metal co-catalyst systems.
Journal of Catalysis; 64; 494-496

Table 1 - History of Process Development and Performance for Bituminous Coal Liquefaction

	<u>Configuration</u>			
	Single stage noncatalytic (1982)	Single stage catalytic (1982)	Two stage noncatalytic/catalytic (1985)	Two stage catalytic/catalytic (1986)
Distillate (wt% coal maf)	41	52	62	70
Distillate quality/gravity °API	12.3	20.2	20.2	26.8
Nonhydrocarbons (wt%)				
S	0.33	0.20	0.23	0.11
O	2.33	1.0	1.9	<1
N	1.0	0.50	0.25	0.16

Source: Weber and Stewart, 1987 (3)

Table 2 - Impact of Catalysis on Process Conditions and Selectivity

<u>Process</u>	<u>Temp oC</u>	<u>Pressure MPa</u>	<u>Liquid/gas ratio</u>
Single Stage			
I G Farben	480	30-70	2.4
Ruhrkohle	475	30	2.3
H-coal	450	12	4.0
Two Stage (noncatalytic/catalytic)			
British Coal	400-425	20	4.8
Lummus	410-460	18	10.8
Two Stage (catalytic/catalytic)			
HRI	400-440	17	12.0

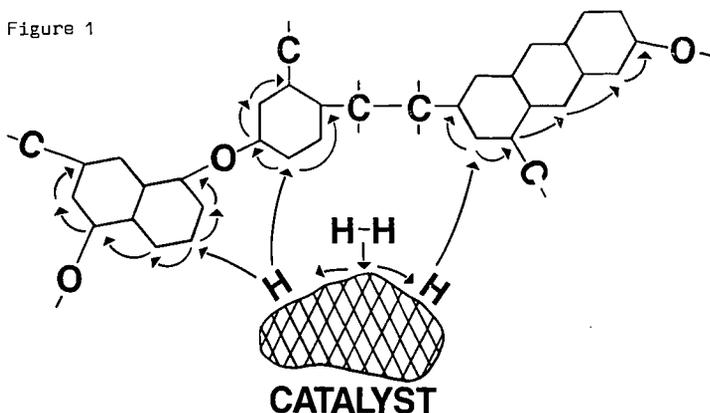
Source: various

Table 3 - Effect of hydrogenation component on ZnCl₂ - catalysed cracking of dibenzylther

Catalyst	% Ether Conversion	% Yield	
		Toluene	Insoluble Resin
None	3.8	1.4	-
ZnCl ₂	100.0	3.9	97.0
Ni	38.2	19.5	2.5
Ni+ZnCl ₂	96.5	65.6	6.0

Source: Mobley and Bell, 1980 (20)

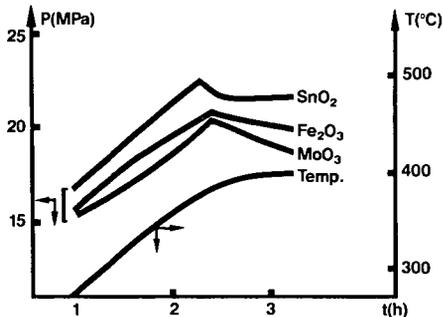
Figure 1



**DISTRIBUTION OF H-ATOMS BY
HYDROGEN SPILLOVER**

*Produced by catalytic dissociation of H₂.
H-Atoms induce bond cleavage and stabilise radicals.*

Figure 2



**EVIDENCE FOR EXISTENCE OF A
THRESHOLD TEMPERATURE IN
CATALYTIC COAL LIQUEFACTION**

**(BITUMINOUS COAL: TETRALIN: CATALYST =
40: 95: 0.8; HEATING RATE 3°C/MIN)**

H. Charcosset and others (1986), Fuel Processing Technology, 12, 189-201