

MECHANISTIC STUDIES ON THE HYDROLIQUEFACTION OF VICTORIAN
BROWN COAL AND OF COAL DERIVED PRODUCTS

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Introduction

The overall aim of our recent studies has been to obtain a more complete understanding of the mechanisms for the principal reactions which occur during the catalysed hydroliquefaction of low rank, high oxygen containing (ca. 25 wt% db) coals. The results of 70 ml batch autoclave studies with and without added catalysts on Victorian brown coal, on a number of different coal derived products and on related model ether compounds are discussed herein. More complete details of various aspects of this work may be found elsewhere (1-6). On the basis of these investigations a mechanism is proposed for the hydroliquefaction process which emphasises the role of catalysts in inhibiting repolymerisation reactions, the significance of interconvertibility of coal derived products and the importance of hydrogen donation from molecular hydrogen and the vehicle tetralin.

Experimental

Coals: Two samples of dried (105°C, under N₂) Victorian brown coals from the Morwell seam were used in these experiments viz., Drum 66 (1976 100t bulk sample) and Drum 289 (1979 100t bulk sample). The chemical characteristics of the coals on a weight per cent dmmf basis are as follows: Drum 66, C 69.3, H 5.0, O (by diff.) 24.5, N 0.6, S 0.6. Acidic O 9.7 mol kg⁻¹ dmmf coal non-acidic O 5.6 mol kg⁻¹ dmmf coal. Drum 289, C 69.2, H 4.8, O (by diff.) 25.2, N 0.52, S 0.25. Acidic O 9.6 mol kg⁻¹ dmmf coal, non-acidic O 5.3 mol kg⁻¹ dmmf coal. The elemental composition is therefore similar to that of a North Dakota lignite.

The coals (< 250 μm) were hydrogenated in a 70 ml rocking autoclave using a 1:1 slurry of tetralin: coal at initial hydrogen pressures of 1-10 mPa for 1 hour at a reaction temperature of 385°C. In related studies temperatures in the range 345 - 460°C were used at 6 mPa pressure. Both iron and tin-based catalyst systems were examined.

For the work reported herein the catalysts were incorporated by the ion exchange technique (1). In other studies we have shown that impregnation using soluble metal salts is as effective in achieving a comparable level of catalytic activity.

The products from these hydrogenations were separated into gases (analysed by g.c.), water (analysed by azeotropic distillation), insolubles (CH₂Cl₂ insolubles), asphaltene (CH₂Cl₂ soluble/X₄ insoluble), oils (CH₂Cl₂ soluble/X₄ soluble). Hydrogen transferred from the donor solvent was determined by g.l.c. analysis of the ratio of tetralin to naphthalene in the total hydrocarbon liquid product.

Coal derived materials: These products were obtained from our 1 kg h⁻¹ continuous reactor unit (7) as oils (X₄ soluble) asphaltenes (tetralin soluble/X₄ insoluble) asphaltols (tetralin insolubles/tetrahydrofuran (THF) solubles) and THF insoluble materials for subsequent reactivity studies. Methylene chloride was not used in

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the separation because of concern for its potential catalyst deactivation role in the subsequent series of experiments to be undertaken. Experimental continuous reactor conditions were a 3:1 slurry of tetralin:coal to which an iron (278 ± 30 mmol kg^{-1} dc from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and tin (20 mmol kg^{-1} dc from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) catalyst had been added. The reaction temperature was 400°C with a developed pressure of 10 MPa and a residence time from 15 to 40 minutes.

Samples of each of the coal derived materials were reacted separately in the presence of several catalysts in a 70 ml batch autoclave using a 1:1 slurry of tetralin:material at 425°C with an initial hydrogen pressure of 6 mPa for 1 h at reaction temperature. The products from these reactions were separated into oils, asphaltenes, asphaltols and THF insolubles.

Model ether systems: A series of ethers have been examined to assist in the elucidation of the role of the iron and tin catalyst systems investigated. Hydrogenation conditions were 1-2 g ether, initial hydrogen pressure 6 mPa, reaction time 1 h with catalyst loadings similar to those used for coal hydroliquefaction studies. Full details are outlined elsewhere (2,5).

Results

Reactions with coal

Total conversion yields for the temperature range $345\text{--}460^\circ\text{C}$ at 6 mPa hydrogen are summarized in figure 1. Absolute conversions are lower than for work with 1 l autoclaves and the continuous reactor unit because of different reactor temperature profiles and residence time; however, the qualitative conclusions are consistent. The effect of increasing the reaction temperature was to increase the total conversion of all reactions irrespective of the catalyst system.

The iron-tin catalyst system was the most temperature sensitive of the four coal-catalyst systems studied. Unlike the iron and tin treated coals which were only sensitive to temperature in the range $365\text{--}405^\circ\text{C}$, the iron-tin treated coal was also sensitive to temperature in the range $385\text{--}425^\circ\text{C}$ where the conversion rapidly increased from 66% to 85% (daf coal). Thus the iron-tin system was most efficient at the higher reaction temperatures up to 425°C while the iron and tin treated coals were most effective up to 405°C (see Table 1, reference 2).

The initial hydrogen pressure dependent conversion results in the range 1-10 mPa are given in figure 2 for studies at 385°C . The tin catalysed reactions show most pressure dependence, consistent with previous findings that tin facilitates molecular hydrogen transfer during hydrogenation (4). For the untreated coal and for other catalyst systems there is only a small pressure dependence of product yields beyond 4 mPa.

A detailed study of the chemical constitution of the products revealed that their composition is influenced by temperature but not by pressure or the nature of the catalyst. With increased reaction temperature there was a decrease in total and acidic oxygen concentrations in the asphaltenes and a corresponding increase in both aromatic content and C/H ratio. This observation is consistent with the loss of aliphatic side chains from the polycondensed ring systems

Reactions with coal derived products

Hydrogenation studies were undertaken on the parent iron-tin treated coal (Drum 289) as well as the THF insolubles, asphaltol, asphaltene and oil derived from a continuous reactor run as previously discussed. Studies with no additional catalyst added (case A) and with the addition of a sulphided nickel molybdate catalyst supported on alumina (case B) were performed. The results are presented in table 1. The Ni/Mo catalyst in case B did not increase the conversion of the coal or the THF insolubles beyond that for case A because sufficient amounts of

iron and tin materials were already associated with these reactants to catalyse the reaction. The iron-tin treated coal has of course a much greater reactivity than untreated coal as shown in table 1. It is noteworthy that once isolated the THF insolubles showed a similar reactivity (~ 75 wt% daf) to the coal (~ 80 wt% daf).

The results in table 1 show that for reactions at 425°C significant conversion of the asphaltols and the asphaltenes produced at 400°C to other products was possible. In particular for the asphaltol $> 95\%$ interconversion occurred, while for the asphaltene the interconversion was $> 65\%$. A complete range of products was formed from high oil yields to repolymerised THF insoluble material. This reactivity underlines the inherent instability of these intermediate products. The addition of a sulphided Ni/Mo catalyst led to $\sim 50\%$ improvement in oil yields, however addition of the traditional first stage catalysts iron, tin or the iron-tin mixture did not significantly improve the conversion of asphaltene or asphaltol to oil as compared to the reactions without additive (results not presented here). Tin, and to a lesser extent, iron were successful in reducing the amount of repolymerisation of asphaltols to THF insolubles.

Hydrogenation of the oil fraction resulted in the formation of a small amount of the higher molecular weight products (< 4 wt%), but the recovered oil contained a higher proportion of lower boiling point material.

Reactions with model ether compounds

The reactions of a series of lignin related model ether compounds with iron II acetate and tin metal have been investigated (2,5). The models selected contain phenoxy groups ($\text{PhO}-(\text{CH}_2)_n\text{Ph}$ $n = 1,2,3$), benzyl groups ($\text{PhCH}_2\text{-OCH}_2\text{Ph}$) and alkoxy groups ($\text{PhCH}_2\text{CH}_2\text{-OCH}_2\text{CH}_2\text{Ph}$). Conversion results for the reactions of 2-phenylethyl phenyl ether ($\text{PhO-CH}_2\text{CH}_2\text{Ph}$) and dibenzyl ether ($\text{PhCH}_2\text{OCH}_2\text{Ph}$) are shown in figures 3 and 4 respectively. For the phenylethyl phenyl ether the extent of conversion is significantly reduced in the presence of both metal additives with iron being more effective than tin in suppressing the decomposition. For example at 325°C there was only 13% conversion in the presence of an iron based additive compared with 33% with tin and 43% without additive. In contrast, addition of an iron-based catalyst to a reaction of dibenzyl ether (figure 4) was found to promote the conversion while the tin-based catalyst suppressed it relative to no additive being present. At 300°C the conversion was 96% with iron, 12% with tin and 19% without additive. The thermal decomposition of these ethers is believed to be via a radical chain mechanism. (9) It is postulated that while iron catalysts may facilitate carbon-oxygen bond cleavage, as evidenced by the increased reactivity of benzyl and aliphatic ethers, when phenoxy radicals are produced they are strongly adsorbed on the catalyst surface. They are not therefore readily available to propagate the radical chain reactions. This effect is restricted to the phenoxy radical and not observed for a species such as $\text{PhCH}_2\text{CH}_2\text{O}$ in the reaction of $\text{PhCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Ph}$ because the resonance stabilisation energy associated with the PhO would result in it having a longer half-life and hence time to diffuse to the catalyst surface without being stabilized by hydrogen. The iron catalyst does not show the same affinity for the benzylic radical even though it is also a long-lived species.

The tin additive is present in the liquid state under the conditions of the present experiments. It has a smaller inhibiting effect than iron on the reactivity of the phenoxy and benzyl ethers. Two explanations are plausible. Hydrogen dissolved in the tin may react with the benzyl and phenoxy radicals which are the chain propagators and remove them from the system. The rate of bond cleavage is therefore lowered. Alternatively, tin may promote radical recombination reactions. By either route the tin would be acting to inhibit propagation reactions.

Mechanistic considerations

Many reaction schemes have been proposed to interpret the results of hydro-liquefaction experiments following the pioneering work of Weller et al. in 1951 (8). Factors to be taken into account when considering the complex liquefaction process include

1. Coal-solvent interactions leading to swelling and dissolution of the coal. (10,11)
2. The radical production resulting from thermal degradation of coal molecules. (12,13)
3. Capping of radicals by molecular hydrogen and by hydrogen abstraction from the solvent inhibiting polymerisation of intermediate radical species.
4. Thermal instability of coal derived materials leading to interconvertibility between products including retrograd reactions and the establishment of steady state conditions. The principle of reversibility is of importance in these processes.
5. The role of the catalyst at various stages of the process. Principally in coal dissolution reactions, in stabilisation of reactive radical intermediates against polymerisation, in promotion of bond cleavage reactions and in facilitating the transfer of hydrogen to coal derived materials. It is most unlikely that any single catalyst will have significant activity in all of these steps.

On the basis of our present knowledge of the role of iron- and tin-based catalysts and of the role of the sulphided nickel molybdate catalyst the mechanism shown in figure 5 is proposed to summarize the essential steps in the hydroliquefaction of low rank coals.

At temperatures $> 360^{\circ}\text{C}$ brown coal is rapidly dissolved in the vehicle without significant chemical reaction forming coal (reaction 1) which corresponds to the pyridine soluble material observed by Neavel. (10) At increasing reaction time coal¹ is thermally converted into reactive radical intermediates (reaction 2) which in the absence of a suitable hydrogen donor, either molecular hydrogen or the vehicle, rapidly repolymerises (reactions 3,4,5). In the presence of a good hydrogen donor, hydrogen abstraction reactions (reactions 6,7) compete with polymerisation reactions leading to the formation of oils and asphaltenes. The important concept of reversibility is included in this scheme by the two way arrows between the radical pool and the respective products. It is possible therefore for polymerised material to re-react (reactions 2,8,9) and form lower molecular weight oils and asphaltenes. Thus the system reaches a dynamic equilibrium after a period of time which is primarily dependent on the reaction temperature, the concentration of available hydrogen, and the metal catalyst.

At temperatures greater than 400°C , the asphaltenes rapidly degrade (reaction 10) and can either repolymerise or in the presence of hydrogen, form oil. At higher temperatures ($> 425^{\circ}\text{C}$) thermal cracking of oils, asphaltenes and repolymerised products leads to increasing yields of hydrocarbon gases (reaction 12).

In the presence of a high pressure of hydrogen, tin metal facilitates the stabilisation of radicals formed by initial coal depolymerisation leading to the formation of asphaltols and asphaltenes (reactions 5 and 6). The stronger pressure dependence of the tin catalysed reactions compared with other systems investigated here may be linked to the fact that the amount of hydrogen dissolved in liquid tin is also pressure dependent.

In the absence of tin less asphaltene is produced which manifests itself as increased yields of THF insolubles and asphaltols. At this time the activity of iron is not completely certain as no effects have been observed on the reactions of the coal derived products. However the proven ability of iron to both catalyse the reactions of some ethers while suppressing propagation reactions of phenoxy radicals suggest that its major activity is probably restricted to the first minutes of reaction (reactions 1,2) and to the slow catalytic degradation of polymerised material. The iron-tin synergism can be interpreted as a co-operative action between the catalytic and radical stabilisation activities of iron with the hydrogen utilisation and radical stabilisation activities of tin which allows the radical intermediates to be stabilised as oil and asphaltene.

The conversion of asphaltene to oil is not catalysed by either iron or tin but it is facilitated by increased reaction temperature and the availability of a good H-donor solvent. The resulting oil formed at high temperatures ($> 400^{\circ}\text{C}$) contains much less oxygen (especially acidic oxygen) and the conversion probably is the result of the loss of polar phenolic groups as well as cleavage of carbon-carbon bonds joining aromatic clusters together. Vernon (14) has shown that dibenzyl thermally decomposes above 400°C .

Formation of hydrocarbon gases principally results from thermal cracking although tin catalyses the formation of methane at temperatures $> 425^{\circ}\text{C}$. Weller (15) has also shown that tin II chloride catalyses the formation of methane in the reaction of 1-methylnaphthalene with hydrogen.

The action of sulphided Ni/Mo catalyst was to dramatically increase the yield of oil from the reactions of asphaltol and asphaltenes. It is believed that the mechanism of the Ni/Mo catalyst involves a more conventional dissociative adsorption of both hydrogen and reactant molecule to the catalyst surface followed by hydrogenolysis and hydrogenation reactions. The mechanistic pathway thus differs from both iron and tin and is shown in figure 5 by reactions 13 and 14.

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Table 1: Product distribution from the catalysed and uncatalysed reactions of Victorian Morwell coal and coal derived reactants.

Reactant	P R O D U C T D I S T R I B U T I O N						
	(wt. % reactant)						
	Oil	Asphaltene	Asphaltol	THF Insoluble	H ₂ O	CO/CO ₂	Hydrocarbon Gases
Untreated coal A	26	7	1 ^c	36 ^c	9	13.0	8.0
Iron-tin treated coal ^a A	42	14	1	17	9	12.6	6.6
Iron-tin treated coal B	40	10	2	20	13	12.5	7.1
THF ^a insolubles A	39	13	2	25	11	5.7	6.0
insolubles B	39	14	3	26	12	5.0	6.3
Asphaltol ^a A	44	28	5	13	4	2.2	5.5
Asphaltol ^a B	63	19	3	5	6	1.5	6.0
Asphaltene ^a A	37	41	7	6	3	1.4	5.3
Asphaltene ^a B	67	22	1	3	5	0.5	4.5
Oil ^b A	96	4	tr.	1	0	0.1	1.2
Oil ^b B	97	tr.	1	3	0	0.1	1.0

A No catalyst added. B Sulphided Ni/Mo catalyst (10% by weight reactant)

^a Reactions at 425°C for 1 h using 3 g reactant and 3 g tetralin with initial hydrogen pressure of 6 mPa.

^b Reactions as for a except 1 g oil and 5 g tetralin.

^c Estimated values (asphaltol + THF insoluble = 37).

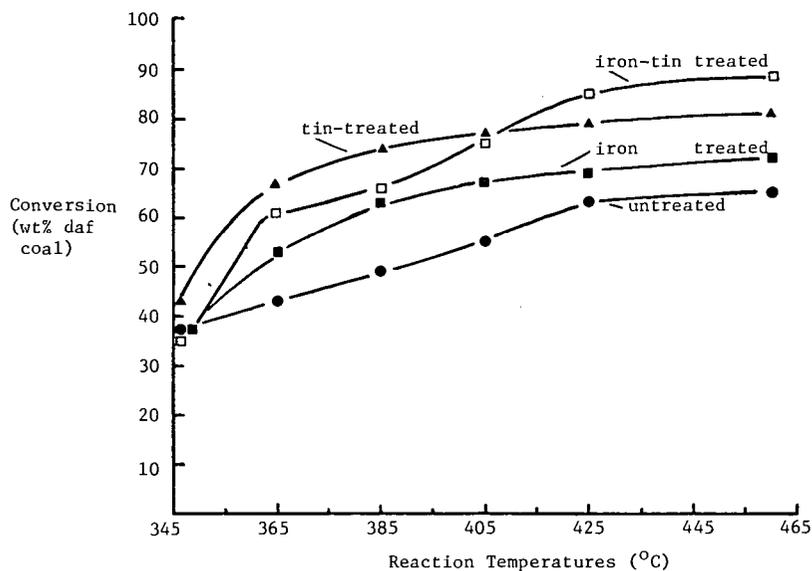


Figure 1: Total conversion versus reaction temperature. Reaction conditions: 6 mPa initial H₂ pressure, 1 h at temperature 1:1 tetralin to coal ratio.

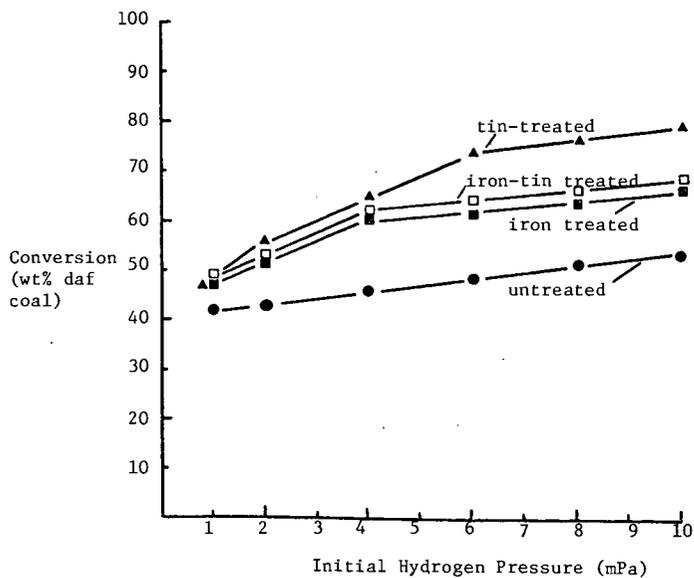


Figure 2: Total conversion versus initial hydrogen pressure. Reaction conditions: 385°C, 1 h at temperature, 1:1 tetralin to coal ratio.

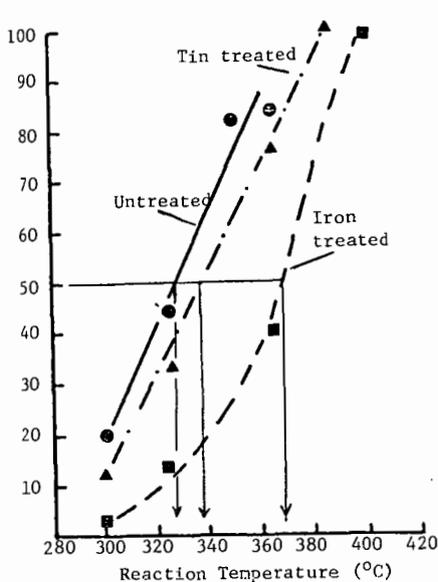


Figure 3: The conversion of 2-phenylethyl phenyl ether versus reaction temperature. Reaction conditions 6 mPa initial H₂ pressure, 1 h at temperature.

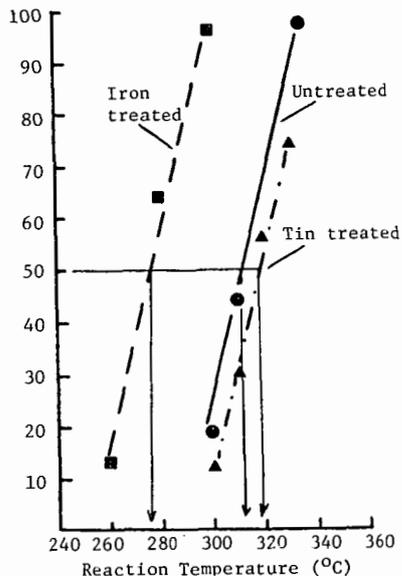


Figure 4: The conversion of dibenzyl ether versus reaction temperature. Reaction conditions 6 mPa initial H₂ pressure, 1 h at temperature.

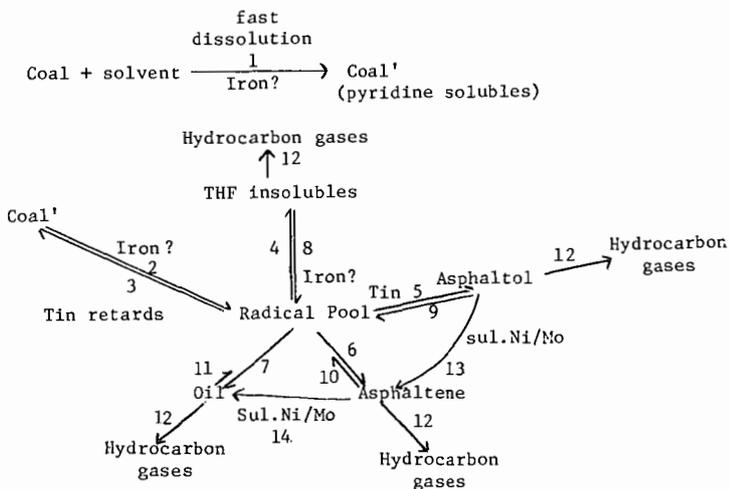


Figure 5: The proposed reaction mechanism of the catalytic hydroliquefaction of Victorian brown coal.

Note: The length of the arrows in reactions 8,9,10,11 indicate the relative reactivities of the respective fractions.