BATCH AUTOCLAVE TEMPERATURE-PRESSURE STUDIES ON THE DIRECT CATALYTIC LIQUEFACTION OF VICTORIAN BROWN COAL

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INTRODUCTION

Victorian brown coal is a low rank, low ash lignite with an elemental composition similar to North Dakota lignite (see Table 1).

Table 1: Comparison of Victorian Brown Coal and North Dakota Lignite

	As Received	Daf basis				
	H_2O	C	H	O	N	S
Victorian Morwell Coal (1)	62.5	69.3	5.0	24.5	0.6	0.6
North Dakota Lignite (2)	25.0	69.4	4.3	23.1	0.7	2.5

Previous batch autoclave studies[3,4] using hydrogen gas with tetralin as the vehicle have confirmed that brown coal is suitable for direct catalytic hydrogenation giving high yields of liquid products. Furthermore, brown coal is an excellent ion-exchange medium primarily because a significant amount of the bound oxygen is present in carboxylic ($\sim$2.6 mol kg^{-1}) and phenolic ($\sim$3.2 mol kg^{-1}) functional groups.[5] This property has been exploited to achieve high dispersion of metal catalysts throughout the coal.[5]

The work presented here is aimed at developing catalysts and reaction conditions which maximise the conversion to a low oxygen refinery feedstock. Product distribution dependences on reaction temperature (345-460°C : 6MPa H_2) and hydrogen pressure (1-10MPa : 385°C) using iron, tin and synergistic iron + tin (trace) catalysts are compared to those for untreated Morwell coal.

EXPERIMENTAL

Coal Preparation and Hydrogenation

The coal and catalysts were prepared for hydrogenation by the method of Jackson et al.[3] The coal (3.0 g) was dried under nitrogen at 105°C to constant weight and slurried (1 : 1) with AR grade tetralin as the vehicle. The hydrogenations were performed in a 70 ml rocking autoclave heated to reaction temperature in 11 minutes. Reaction time was one hour at temperature after which the autoclave was quenched in an ice bath.

Catalyst concentrations used for the study were as follows:

Coal	Catalyst	Concentration (mmol/kg daf coal)
untreated	Fe	30
iron treated	Fe	300 ± 40
tin treated	Sn	200 ± 20
synergistic iron-tin treated:	Fe	300 ± 40
	Sn	20 ± 10

Product Analysis

Product gases (CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, n-C_4H_{10}, i-C_4H_{10}) were analysed by GLC using a standard gas mixture for calibration. Hydrogen was determined indirectly by difference. The liquid product was removed from the reaction using CH_2Cl_2 and the water produced was determined by azeotropic distillation. The insoluble material was soxhlet extracted for 12-15 hours with CH_2Cl_2 and the residue dried at 105°C under nitogen to determine the total conversion. The CH_2Cl_2 soluble material was further divided into asphaltene (insoluble in light petroleum) and oil (soluble in light petroleum). Elemental analyses for C, H, O, N, S were performed by the Australian Analytical Laboratories. The direct analysis for oxygen was cross checked by difference (Equation 1)

$$\text{wt\% O} = 100 - \%C - \%H - \%S - \%N \qquad (1$$

Acidic oxygen was determined by non aqueous titration using the method of Brookes and Maher.[6]

TEMPERATURE DEPENDENCE

Total Conversion

The temperature dependences of the product distributions for untreated iron, tin and iron-tin treated coals at 6MPa initial hydrogen pressure are shown in FIGURES 1A-D. The total conversions are compared in FIGURE 2. The temperature range chosen for study was from 345-460°C. At temperatures below 345° conversion was too low for meaningful measurements and at temperatures above 460° decomposition of tetralin can become a significant problem.[7,8]

The total conversion of untreated coal increases steadily from 37% to 63% between 345°C and 425°C then it levels out to 65% at 460°C. An iron based catalyst results in a rapid increase in total conversion from 37% at 345°C to 63% at 385°C after which it increases steadily to 72% at 460°C. The tin catalyst increases the conversion dramatically from 43% at 345°C to 73% at 385°C after which it increases regularly to 81% at 460°C. The iron-tin catalyst is not as efficient as the tin catalyst up to 385°C as the conversion is only 66% at 385°C. However, above 385°C the conversion rises sharply reaching 85% at 425°C after which it levels out with a maximum of 88% at 460°C. Above 400°C the products from the tin and iron-tin coals are increasingly unstable with increasing amounts of CH_2Cl_2 insoluble material being precipitated during product work up. The result is reduced total conversions at all temperatures compared with findings using a larger 1 litre autoclave.[5,9,10] The results should therefore be viewed as internally consistent, but not directly comparable with work in larger autoclaves with different temperature profiles.

Conversion to Useful Liquid Products (Oil and Asphaltene)

Between 365 and 425°C the three catalysed coals offer significantly improved CH_2Cl_2 soluble liquid (oil + asphaltene) yields compared to untreated coal (FIGURE 3). At 345°C tin gives an 8% improvement while the iron-tin and iron catalysts offer no improvement over the untreated coal yield of 20% (daf coal) at that temperature. In the region 365°-385°C tin continues to be superior giving 4-5% more liquid product than the Fe-Sn, 10-14% better than Fe and 22% more than untreated coal. However, above 405°C the yield of liquid product from tin coal deteriorates significantly from 50% at 405°C to 42% at 460°C. This can be attributed to increased yields of hydrocarbon gases and significant repolymerisation of asphaltenes during product workup. (The total oil + asphaltene yield in these small scale experiments is only 0.5 to 1.5 g.) Above 385°C the Fe-Sn catalyst dramatically increases the yield of useful liquid products from 44% at 385°C to 57% at 425°C after which it decreases slightly to 55% at 460°C. This improvement in yield at higher temperatures is due

to the formation of a more stable product relative to the Sn catalyst system while the slight decrease at 460°C can be attributed to the increased production of hydrocarbon gases and some repolymerisation. The iron catalyst smoothly increases the liquid yield at 41% at 405°C and then levels out. The liquid yield from untreated coal increases steadily to 37% at 425°C after which there is little improvement.

The asphaltene temperature dependence (FIGURES 1A-D) is similar for the four coals with the yield increasing with temperature to a maximum of 405°C for untreated, iron and iron-tin coals and 385°C for tin treated coal after which it decreases regularly with increasing temperature. The iron-tin catalyst is clearly superior to the other three coals for producing oil (FIGURES 1A-D) at all temperatures except in the region of 400°C. The maximum oil production is 35-38% daf coal with the iron-tin catalyst between 425°-460°C. The oil production for the untreated, iron and tin coals is similar reaching a maximum of 30% daf coal at 460°C. The minor variations in the trend can be attributed to the formation and breakdown of the asphaltenes. The major effect of all the catalysts is to produce more asphaltenes at temperatures below 405°C which are degraded to oils at higher temperatures.

Oxygen Distribution in the Products as a Function of Reaction Temperatures

In developing useful catalysts for brown coal liquefaction one major objective is to achieve a high yield of low oxygen content liquid. It is important to know how the oxygen is distributed in the products and in what form (H_2O, CO_2, CO) it is removed from the coal system. The oxygen distributions for products from the four coals are shown in FIGURES 4A-D.

Generally raising the reaction temperature removes more oxygen, primarily as water. In all cases carbon monoxide production increases slightly with increased temperature while CO_2 formation appears to reach a maximum in the region of 385°C after which it decreases slightly for the three catalysed coals. There is no such maximum reached in the carbon dioxide produced from the untreated coal. As the majority of the carbon dioxide is formed at low temperatures (200-300°C) by decomposition of carboxyl groups, any variation on this level is probably a response to changes in the equilibrium of the water gas shift reaction. Tin is clearly the superior catalyst for removing oxygen from the coal products with the general order being

$$Sn > Fe - Sn \cong Fe > \text{untreated}$$

At 460°C tin has removed 98% of the oxygen, iron and iron-tin approximately 80% and untreated coal has lost only 67%. In fact little further oxygen is removed from untreated coal above 405°C. The distribution of acid oxygen in the CH_2Cl_2 insoluble residue is similar for all three catalysed reactions. The dramatic difference is that tin has removed significantly more non acidic oxygen from the residue at lower reaction temperatures. The oxygen content in the asphaltene is similar for the three catalysts, reaching a maximum in the region of 385°C and decreasing at higher temperatures. The oxygen level in the asphaltenes from untreated coal is almost invariant with reaction temperature. Tin is also the best catalyst for the removal of oxygen from the oil fractions at temperatures above 385°C while the iron and iron-tin catalysts have similar activity and are better than untreated coal. At temperatures below 385°C there is, in all cases, an increase in the oxygen level in the oil fraction as the reaction temperature decreases with the trend being most marked for the tin and iron-tin catalysts. This suggests that the catalysts are breaking carbon-oxygen bonds at low reaction temperature but do not have the ability to remove the oxygen completely from the system at low temperatures. It is a reasonable presumption that it is the trace of tin in the synergistic iron-tin catalyst which facilitates the improved bond breaking compared to the iron catalyst. Increasing the reaction temperature to 385°C is sufficient to remove this oxygen from the oil. The increase in total oxygen in the oil fraction

above 385°C for untreated, iron and iron-tin coals suggests that these catalysts have difficulty in removing oxygen from certain classes of oxygen containing functional groups. However, the ability of tin to catalyse the almost total removal of oxygen does lead to problems of product stability. Some of the derived products repolymerise even on standing in dichloromethane solution. It is possible that higher concentrations of reactive poly-enes are formed which are not hydrogenated in the absence of iron or other metals capable of catalysing liquefaction.

HYDROGEN PRESSURE DEPENDENCE

The hydrogen pressure dependence reactions were performed at 385°C for the four coals and at 425°C for the coals with iron-tin synergistic catalyst (see FIGURES 5 to 7). The most significant feature is that in all catalysed reactions the total conversion (FIGURE 5) increases with pressure until a critical pressure is reached above which increasing the hydrogen pressure has a reduced effect. For the iron and iron-tin catalysts at 385°C the critical pressure is 4MPa initial hydrogen while for the tin at 385°C and iron-tin at 425°C 6MPa is the critical hydrogen pressure. Furthermore increasing hydrogen pressure results in significantly more asphaltene being produced for the tin (385°C) and iron-tin (at 385°C and 425°C) catalysts (FIGURE 6) while it has little effect on oil production from both catalysed and non catalysed coals at 385°C (FIGURE 7). However, at 425°C the oil production from iron-tin coal shows a marked hydrogen pressure dependence (FIGURE 7) and these studies suggest that a suitable initial hydrogen pressure for obtaining high conversion in catalysed reactions is not very high e.g. an initial pressure of 6MPa for the iron-tin system for 425°C.

CATALYTIC EFFICIENCY - USEFUL CARBON/HYDROGEN VERSUS OXYGEN REMOVAL

While developing catalysts that remove oxygen from brown coal is a major objective it is also important to ensure that the maximum amount of carbon and hydrogen from the coal be carried through into the useful liquid products, i.e. oil and asphaltene. An additional view of conversion then is a measure of the percentage of carbon and hydrogen carried through to the useful products. Recognising that approximately 4% of the carbon is always lost from the system as carbon dioxide and carbon monoxide and that the coal contains ∿25% oxygen, the maximum yield of carbon and hydrogen can only be 71% of the daf coal. Considered from this point of view the iron-tin catalyst converts 75% of the available carbon and hydrogen into liquid products at 425°C while the tin converts only 63%, iron 53% and untreated coal 46%.

FIGURE 8 compares the ability of the catalyst to remove oxygen and to convert the available carbon and hydrogen into useful products. The most efficient catalyst will be closest to the 45 degree line on the coordinate system. All of the coals lie to the left of the line which shows that all four of the reaction systems have a preference for the removal of oxygen relative to converting the carbon and hydrogen to useful products. This trend is particularly true for high temperature reactions where the shift to the left is associated with greater production of hydrocarbon gases and, in the case of tin catalysed reactions, significant repolymerisation of material which was initially soluble in methylene chloride. The exception is the iron-tin catalyst which lies very close to the line and at one point (corresponding to 425°C) actually shows a slight preference for converting the carbon and hydrogen into liquid products. In order of catalyst efficiency the four coals are ranked in order;

iron - tin > tin >> iron > untreated

CONCLUSION

The development of suitable catalysts and reaction conditions in the liquefaction of brown coal is a compromise of the ability of the catalyst to fulfill the following

requirements;

- Remove all of the organically bound oxygen
- Carry the maximum amount of carbon and hydrogen through to the liquid products
- Minimise production of hydrocarbon gases

Under the reaction conditions chosen for this study (6MPa initial hydrogen pressure and a low (1 : 1) hydrogen donor solvent to coal ratio) the synergistic iron-tin catalyst is superior to the other three coals. It achieves its objectives remarkably well at reasonably low reaction temperatures (425°C) and correspondingly low reaction pressure (14.6 MPa/2190 psi at 425°C). Under these conditions 75% of the available carbon and hydrogen is converted to liquid products and 5% to hydrocarbon gases. A large proportion (60%) of the liquid product is present as oil (X4 soluble) while 73% of all oxygen has been removed as CO_2, H_2O and CO. The tin catalyst is superior at removing oxygen (94% at 460°C) but produces more hydrocarbon gases and is less efficient at carrying the available carbon and hydrogen through to liquid products (63% at 425°C). It is possible that the tin requires higher hydrogen pressures to prevent repolymerisation of the unstable asphaltenes at these temperatures. At 425°C/6MPa hydrogen the iron catalyst is only 7% better than untreated coal for converting available carbon and hydrogen into useful liquids.

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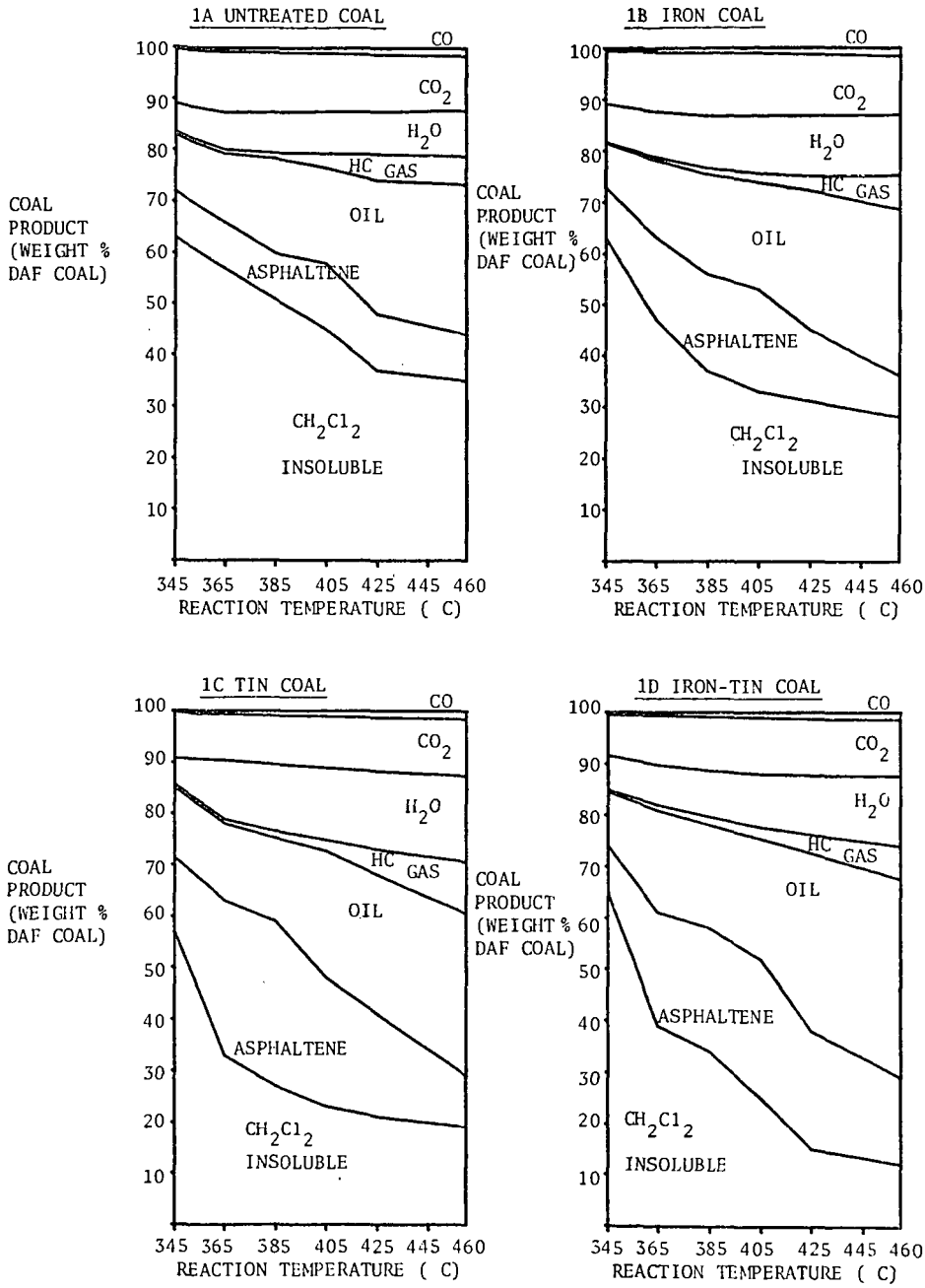
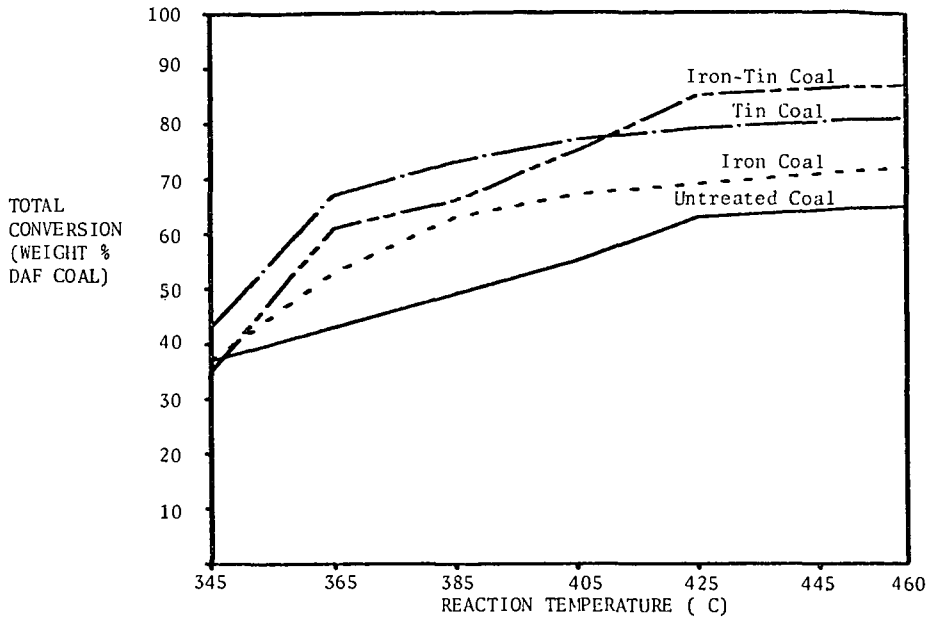
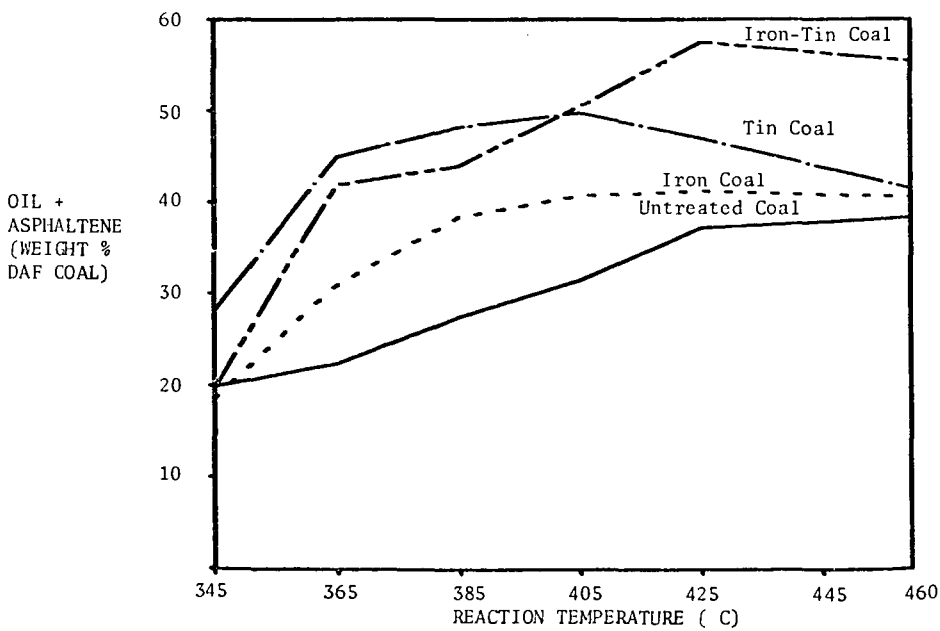
PRODUCT DISTRIBUTION vs REACTION TEMPERATURE FIGURE 1.



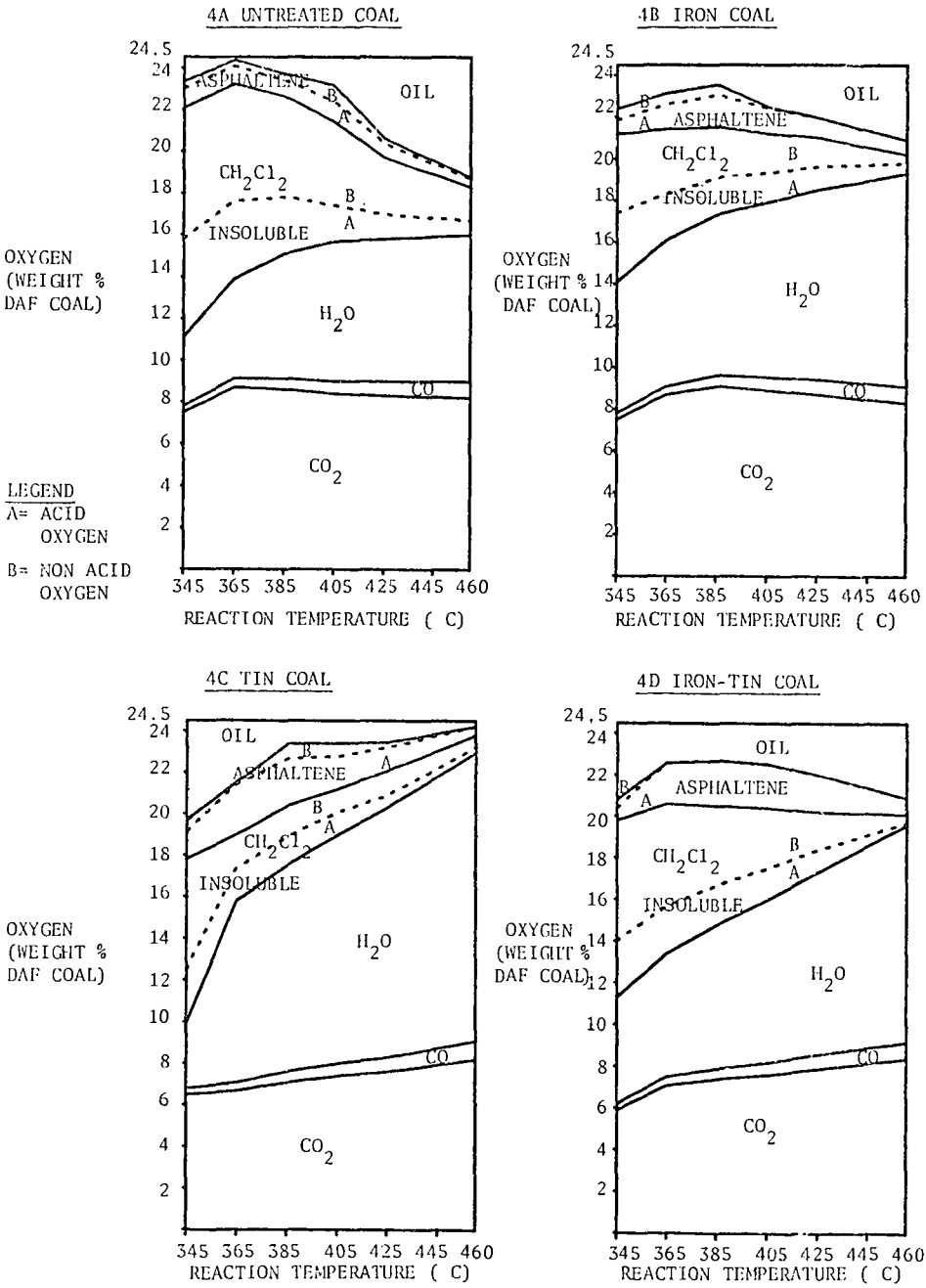
TOTAL CONVERSION vs REACTION TEMPERATURE FIGURE 2.



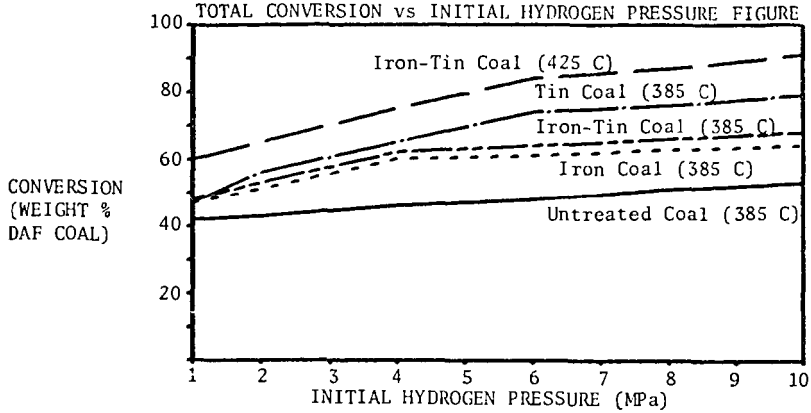
OIL + ASPHALTENE vs REACTION TEMPERATURE FIGURE 3.



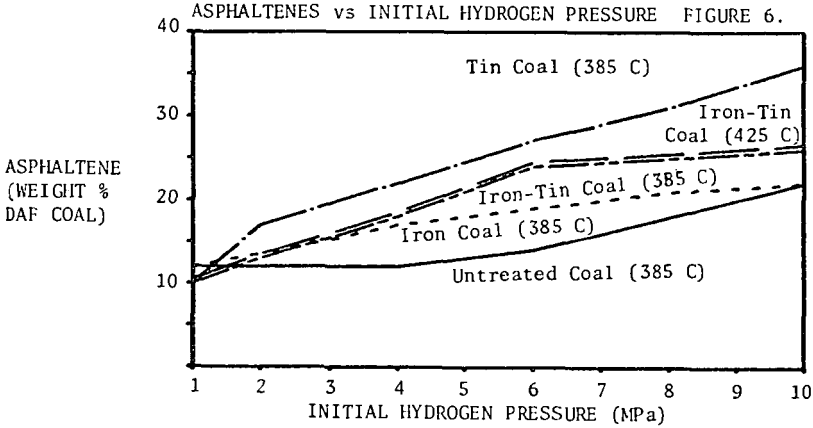
PRODUCT OXYGEN DISTRIBUTION vs REACTION TEMPERATURE FIGURE 4.



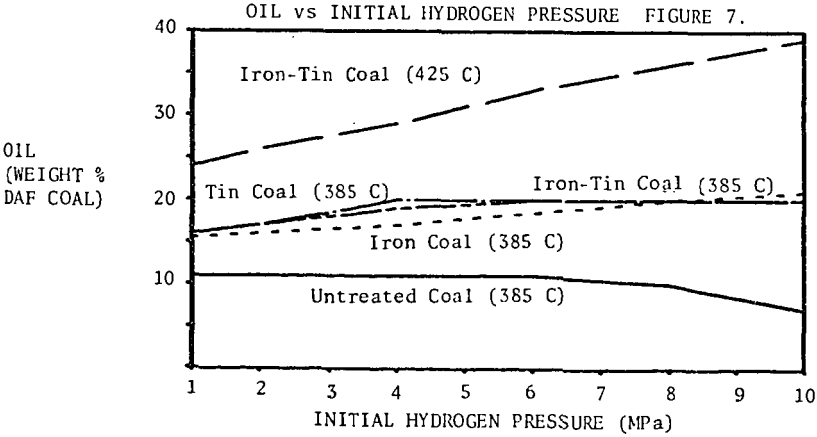
TOTAL CONVERSION vs INITIAL HYDROGEN PRESSURE FIGURE 5.



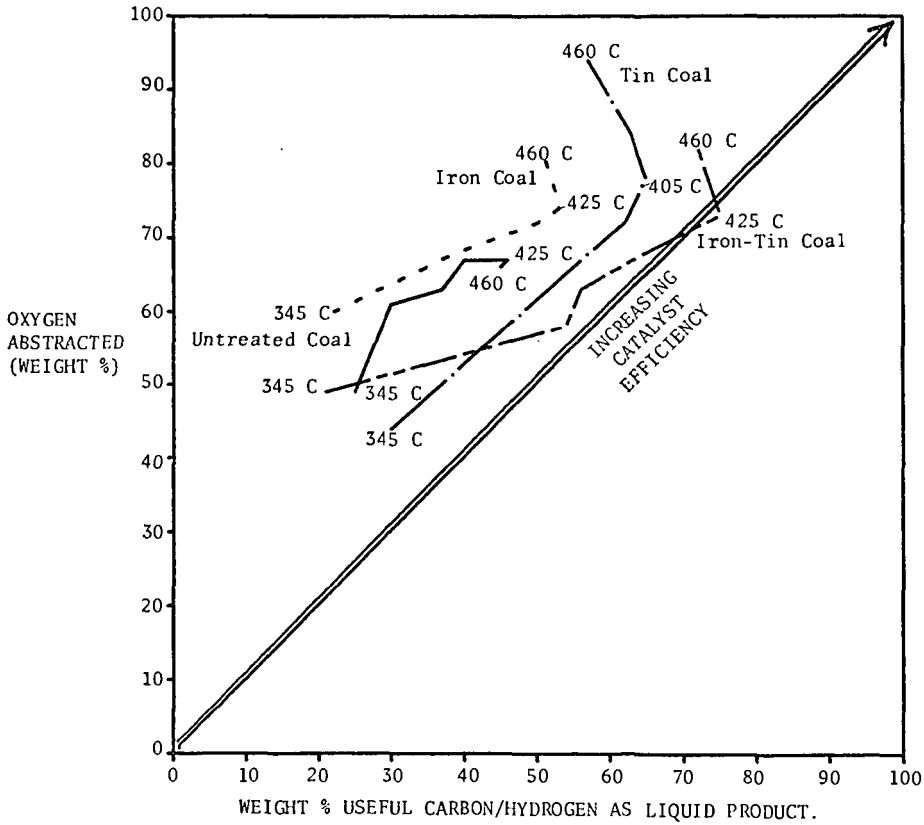
ASPHALTENES vs INITIAL HYDROGEN PRESSURE FIGURE 6.



OIL vs INITIAL HYDROGEN PRESSURE FIGURE 7.



CATALYST EFFICIENCY FIGURE 8.



Note: Temperatures quoted on the graph are the reaction temperatures for the areas of interest.