

INTERACTIONS IN THE EXTRACTION  
STAGE OF TWO-STAGE COPROCESSING.

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INTRODUCTION.

In recent years there has been a growing interest in liquefaction processes in which coal recycle solvents are replaced by cheaper petroleum fractions.<sup>1-3</sup> In conventional liquefaction processes there is some evidence that a two-stage process is more advantageous than single stage processes. The Liquid Solvent Extraction (LSE) process of the British Coal Corporation is such a process.<sup>4</sup> Firstly, the coal and solvent are heated in an inert atmosphere before the extract is further upgraded in a second stage involving high pressure hydrogen and a catalyst. The work reported in this paper was undertaken to evaluate the viability of replacing the coal solvent with heavy petroleum fractions in the LSE process.

The results presented here are concerned only with the extraction stage, which in coprocessing is the most important stage. If coal cannot be solubilised to an extractable form poor yields will result however good the upgrading in the hydrocracking stage.

Experimental.

The materials used were Point-of-Ayr (POA) coal and a range of petroleum fractions from various sources. Analytical data are given in Table 1. Samples of coal and petroleum fractions were heated in tubing bombs ( $\sim 15 \text{ cm}^3$ ) with agitation in a fluidised sandbath. Runs were carried out in duplicate. The product was extracted with n-pentane to obtain the % pentane insolubles (% PI). Further extractions were carried out to give the % toluene insolubles (% TI) and quinoline insolubles (% QI).

Table 1 : Analysis of Feed Materials.

Source	Fraction	Wt %				
		C	H	N	S	H/C
Crude "O"	VR > 475°C	85.1	10.5	~	2.95	1.48
Crude "M"	VR 475°C	86.6	12.5	0.35	0.9	1.73
Forties	VR	87.4	11.1	0.45	0.8	1.52
Arabian Heavy	AR	84.3	11.2	0.3	3.9	1.59
Marguerite Lake	AR	83.4	10.4	0.7	5.0	1.50
POA Coal		84.1	5.2	1.8	1.0	0.74

A small number of extractions were carried out in a 250 ml stirring autoclave with a heating rate of  $7^{\circ}\text{C min}^{-1}$ .

The products were extracted with dichloromethane (DCM) and both the soluble and insoluble material was collected and analysed.

#### Pretreatment of Petroleum Crudes.

Whole crudes were vacuum distilled at  $475^{\circ}\text{C}$  and the residue used in coprocessing runs. Vacuum and Atmospheric residues were used as obtained.

The asphaltene fraction of two petroleum fractions was removed and the deasphalted samples coprocessed with POA.

Samples of two of the petroleum residues were hydrogenated prior to use at  $375^{\circ}\text{C}$  or  $425^{\circ}\text{C}$  under 80 atm  $\text{H}_2$  (cold pressure) with NiMo catalyst.

### RESULTS AND DISCUSSION.

#### Thermal Stability of Petroleum Fractions.

The petroleum fractions were heated alone under a variety of reaction conditions. The extraction yields are shown and compared with those of the untreated fractions in Table 2.

Table 2.

Crude	Reaction conditions	% PI	% TI	% QI
VR-M	-	0	0	0
VR-M	$410^{\circ}\text{C}/30 \text{ min}$	2.7	-	-
VR-M	$440^{\circ}\text{C}/30 \text{ min}$	5.9	-	-
VR-O	-	-	-	-
VR-O	$380^{\circ}\text{C}/30 \text{ min}$	22.5	-	-
VR-O	$410^{\circ}\text{C}/30 \text{ min}$	21.0	-	-
VR-O	$440^{\circ}\text{C}/30 \text{ min}$	27.4	15.2	5.4
		23.5	10.0	-
HVR-O	None	-	-	-
HVR-O	$410^{\circ}\text{C}/30 \text{ min}$	11.5	6.4	2.7
VR-FF	None	10.9	-	-
VR-FF	$380^{\circ}\text{C}/30 \text{ min}$	11.0	-	-
VR-FF	$410^{\circ}\text{C}/30 \text{ min}$	14.9	-	-
VR-FF	$440^{\circ}\text{C}/30 \text{ min}$	21.8	4.0	1.0
(VR-FF) <sub>da</sub>	$410^{\circ}\text{C}/30 \text{ min}$	3.3	-	-
AR-ML	None	22.2	-	-
AR-ML	$380^{\circ}\text{C}/30 \text{ min}$	19.5	-	-
AR-ML	$410^{\circ}\text{C}/30 \text{ min}$	21.4	-	-
AR-ML	$440^{\circ}\text{C}/30 \text{ min}$	24.0	12.3	3.3
AR-ML	$410^{\circ}\text{C}/10 \text{ min}$	19.2	-	-
AR-ML	$410^{\circ}\text{C}/2 \text{ h}$	19.6	7.3	4.0
(AR-ML) <sub>da</sub>	$410^{\circ}\text{C}/30 \text{ min}$	2.2	-	-
H <sub>1</sub> ARML	$410^{\circ}\text{C}/30 \text{ min}$	8.8	-	-
"	None	0	-	-
H <sub>2</sub> AR-ML	None	0	-	-
"	$410^{\circ}\text{C}/30 \text{ min}$	-	-	-
AR-AH	None	15.0	-	-
AR-AH	$440^{\circ}\text{C}/30 \text{ min}$	13.6	-	-
AR-AH	$440^{\circ}\text{C}/30 \text{ min}$	16.1	4.5	-

In general, higher reaction temperatures resulted in a small increase in PI but more significantly at 440°C TI were formed. Longer reaction times left the PI unaffected but TI and QI were formed.

Untreated hydrogenated fractions were completely soluble in pentane but on heating considerable PI were formed. These hydrogenated petroleum fractions were less thermally stable than the parent fractions.

#### Effect of Coal/Petroleum Ratio on Extraction Yields.

The extraction yields of compressing runs carried out with a range of coal/petroleum ratios, were measured. During these investigations the reaction conditions were kept constant with a reaction temperature of 410°C and a reaction time of 30 minutes. The results for the coprocessing of VR-FF and AR-ML with POA are shown in Figures 1 and 2 as % insolubles (% INSO) plotted against % POA in the reaction mix. The dashed lines in the figures indicate the % insolubles that would be obtained if the same quantities of coal and petroleum fractions were heated alone under the same reaction conditions. If the experimental points lie on these lines it suggests that no interactions - either positive or negative - have occurred between the coal and petroleum fractions.

In both Figures 1 and 2 it is observed that the experimental points for PI and TI lie on or close to the dashed lines. However, the points for QI lie below the dashed lines. This suggests that VR-FF and AR-ML help to solubilise the coal to a small extent, possibly by providing aromatic radicals that can act as hydrogen shuttlers.

Coprocessing has led to the formation of preasphaltenes and a decrease in the total insoluble material.

Similar results were obtained with other petroleum fractions although the extent of interactions varied with the nature of the petroleum fraction.

The extent of interaction - the difference between the calculated and experimental values of insolubles - was plotted against the % aromaticity of the petroleum fractions (Figure 3). A maximum interaction is noted around 50% aromaticity for coal loadings of 25% and 50%. It might have been anticipated that the greater the aromaticity of the petroleum fractions, the greater the compatibility with coal and so the greater the interaction. The maximum observed at 50% aromaticity might be explained by a concomitant opposing trend. As the % aromaticity of petroleum fractions increases the H/C ratio decreases and so the hydrogen available for shuttling decreases.

#### Effect of Reaction Temperature.

The effect of reaction temperature on the extraction yields of coprocessing runs is shown in Figures 4 and 5. Coprocessing mixes with 25% loading of POA and either VR-FF or AR-ML were heated at 375°C, 410°C and 425°C for 30 minutes. The trends with reaction temperature depend on the petroleum fraction. VR-FF/POA shows a decrease in oil and gas with reaction temperature whereas the changes in oil and gas for the AR-ML/POA runs are very slight. With both petroleum fractions, the total insoluble material decreased as the reaction temperature was increased from 380°C to 410°C but then increased again as the reaction temperature is raised further. In the AR-ML/POA runs the asphaltene content of the product decreased monotonically with reaction temperature but in the VR-FF/POA reactions the variation is <3%. Preasphaltene content in both reactions increased with reaction temperature.

The variations between the petroleum fractions cannot be explained by differences in their thermal stability. They probably result from the complex interactions involved in the reactions between oil and gas/asphaltene/preasphaltene/total insoluble material.

Despite the differences in levels observed the optimum temperature for coprocessing with both petroleum fractions is  $\sim 410^{\circ}\text{C}$ .

#### Effect of Reaction Time.

Coprocessing mixes with 25%, 50% and 75% loadings of POA in AR-ML were heated at  $410^{\circ}\text{C}$  for 10 min, 30 min and 2 h. The results are shown in Figures 6, 7 and 8. The effect of long reaction times was to increase the total insoluble material at the expense of the asphaltene and preasphaltene fractions.

The petroleum/coal ratio also affected the levels with reaction time. This can be seen in Figure 9 where % INSOL are plotted against % POA for a reaction time of 2 h. This plot is considerably different from Figure 1. There appears to be a very negative synergistic effect that is greatest at high loadings of coal.

It is apparent that longer reaction times are not advantageous.

#### Effect of Pretreatment of Petroleum Fractions.

Deasphalted samples of VR-FF and AR-ML were coprocessed with POA in various ratios at  $410^{\circ}\text{C}$  for 30 min. It is clear that the interactions observed with the parent petroleum fractions are no longer present. Particularly notable was the absence of any preasphaltene fraction. The procedure used to prepare these samples removed most of the aromatic material and consequently seriously impaired the ability of the fraction to solubilise the coal.

It was postulated that prior hydrogenation of the petroleum fraction would increase the hydroaromatic content and so increase its ability to donate hydrogen to the coal. The extraction yields for the reactions of hydrogenated VR-0 and AR-ML with POA are given in Figures 12 and 13.

Hydrogenation of VR-0 appeared to have reduced its ability to solubilise coal. All the experimental points lie on the dashed lines. However, the effect of prehydrogenation of AR-ML on its ability to solubilise coal was dramatic. The total insoluble material at 50% POA was reduced to  $\sim 15\%$ . This extent of solubilisation is comparable to that of coal solvents.

#### Extractions in the Autoclave.

The results of % DCMI obtained from coprocessing AR-ML and POA in an autoclave are given in Figure 12. The two values of the % DCMI shown were calculated as follows:

$$\% \text{ DCMI (min)} = \frac{\text{wt. DCMI}}{\text{wt. mix}} \times 100$$

$$\% \text{ DCMI (max)} = \frac{\text{wt. DCMI}}{\text{wt. recovered}} \times 100$$

It was observed that the results follow a similar trend to those obtained in tubing bombs with a reaction time of 2 h. A major problem with extraction in the autoclave is that short contact times are not possible.

It was noted from the gc traces of the DCMS product of coprocessing runs that a considerable amount of the lighter material was coal derived. The peaks observed were not simply a combination of those observed from runs involving coal alone and AR-ML alone. Some major peaks were missing while others new to either materials appeared. This potentially very interesting observation, which agrees well with SEC results reported by Wallace et. al.,<sup>5</sup> will be further examined by gc-ms.

#### Conclusions.

The extraction stage of a two-stage coprocessing operation is very important. Using untreated petroleum fractions, the best coal conversion (d.a.f.) that was achieved was around 30%. This compares poorly with the performance of coal solvents. However, some considerable reaction between the coal and petroleum fractions must take place as indicated by the gc results from autoclave extractions. The greatest promise lies in the result obtained with prehydrogenated AR-ML. The coal conversions (d.a.f.) that resulted with this solvent stream were of the order of 85%. This compares well with the best of coal solvents.

#### Acknowledgments.

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- Figure 1. Coprocessing of VR-FF with POA at 410°C for 30 minutes.
- Figure 2. Coprocessing of AR-ML with POA at 410°C for 30 minutes.
- Figure 3. Variation of the extent of interaction between POA/Petroleum fractions with % aromaticity of the petroleum fractions.
- Figure 4. The effect of reaction temperature on the coprocessing of VR-FF/POA with 25% POA and a constant reaction time of 30 minutes.
- Figure 5. The effect of reaction temperature on the coprocessing of AR-ML/POA with 25% POA.
- Figure 6. The effect of reaction time on the coprocessing of AR-ML/POA with a coal levelling of 25% and a constant reaction temperature of 410°C.
- Figure 7. The effect of reaction time on the AR-ML/POA mix with % POA = 50%.
- Figure 8. The effect of reaction time on the AR-ML/POL mix with % POA = 75%.
- Figure 9. Coprocessing of AR-ML with POA at 410°C for 2 h.
- Figure 10. Coprocessing of deasphalted VR-FF with POA at 410°C for 30 minutes.
- Figure 11. Coprocessing of deasphalted AR-ML with POA at 410°C for 30 minutes.
- Figure 12. Coprocessing of prehydrogenated VR-O with POA at 410°C for 30 minutes.
- Figure 13. Coprocessing of prehydrogenated AR-ML with POA at 410°C for 30 minutes.
- Figure 14. Coprocessing of AR-ML with POA at 410°C in the autoclave.

Fig. 1

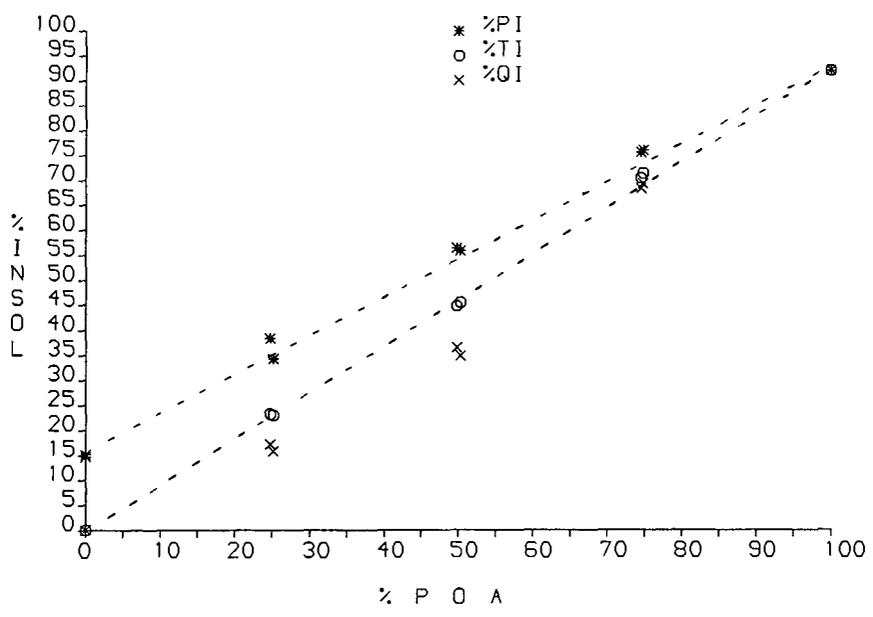


Fig. 2

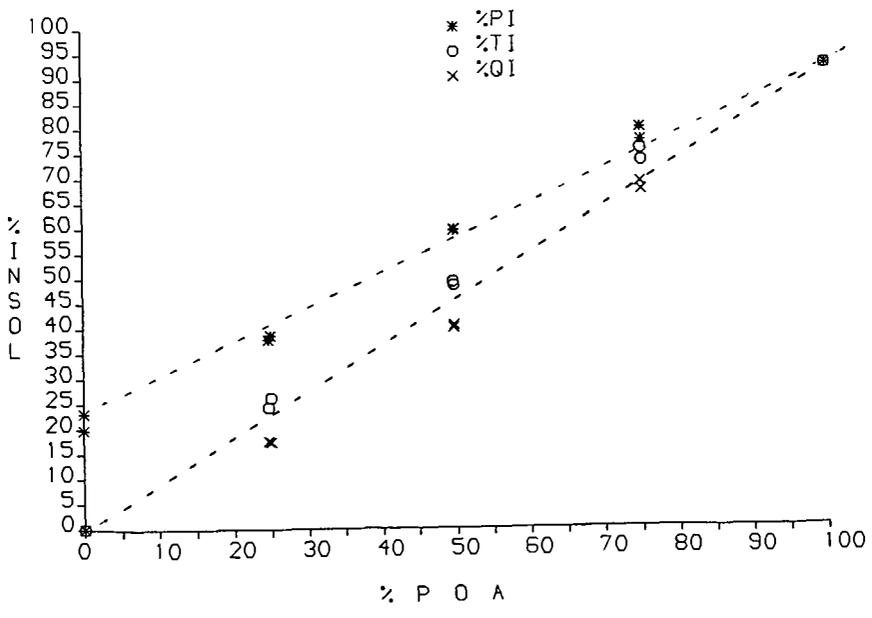


Fig. 3

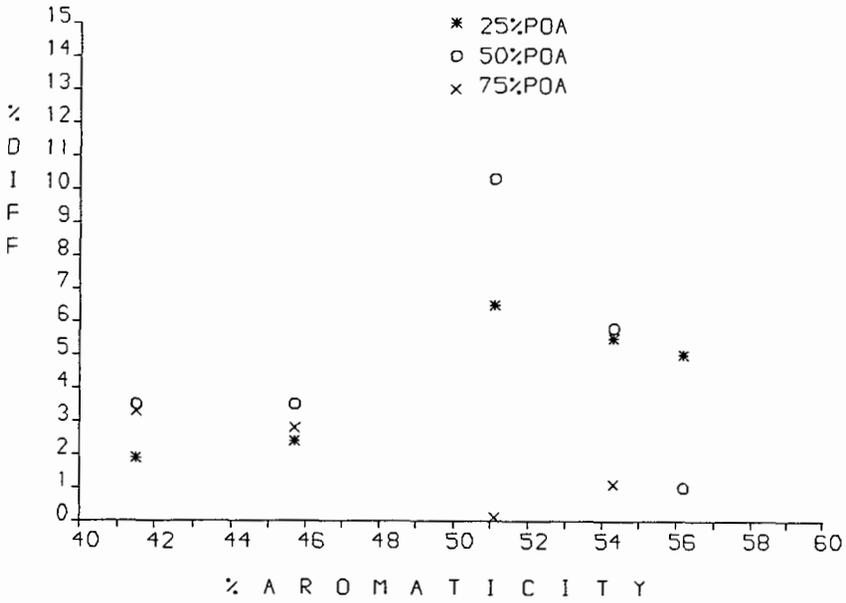


Fig. 4

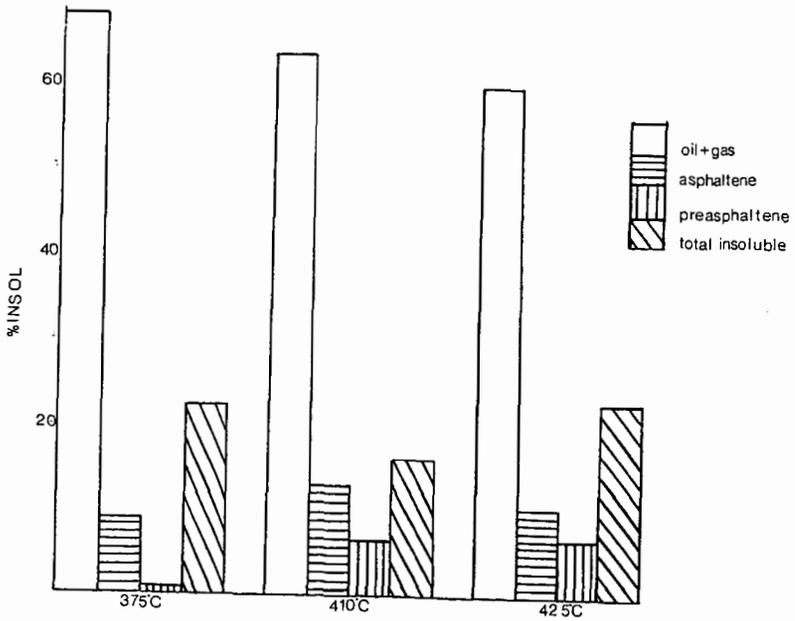


Fig. 5

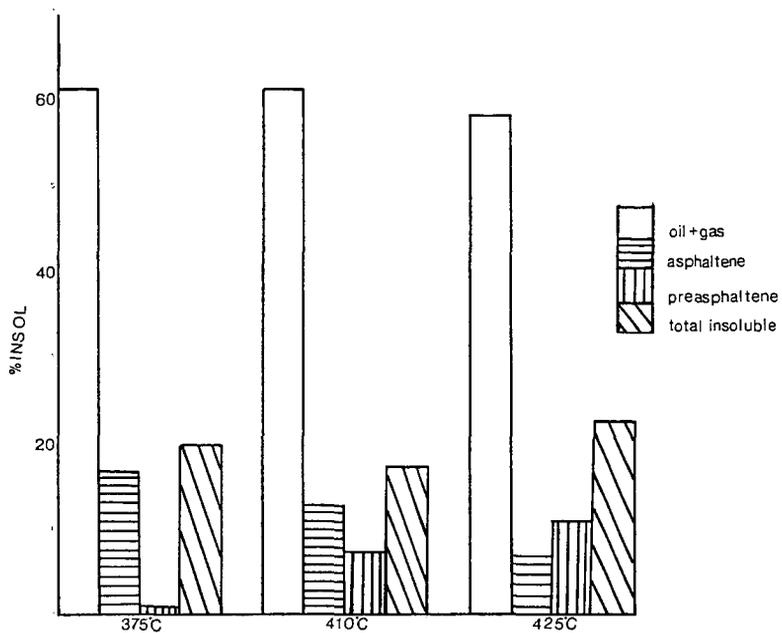


Fig. 6

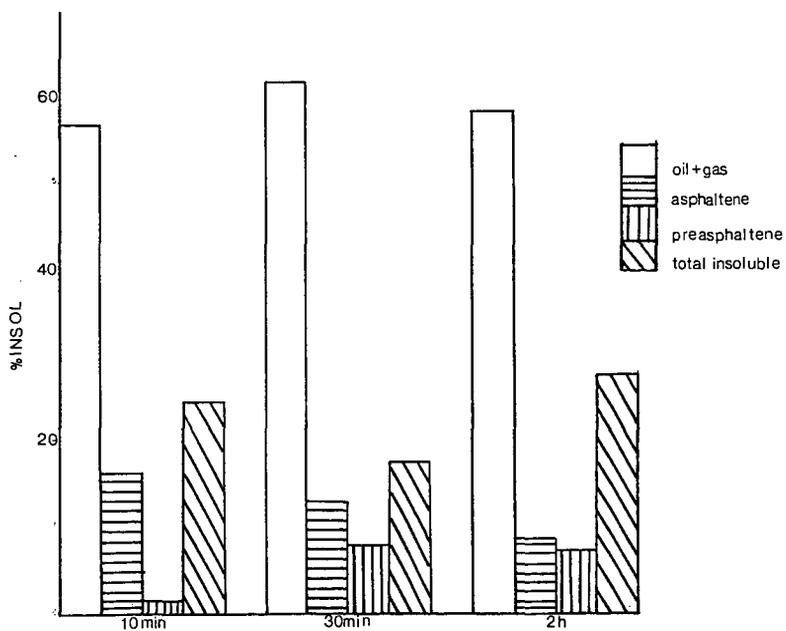


Fig. 7

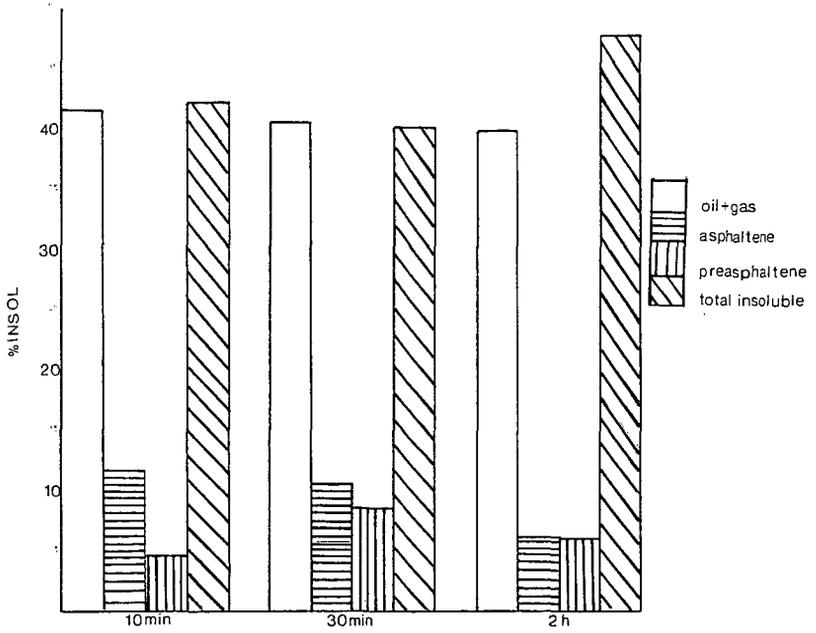


Fig. 8

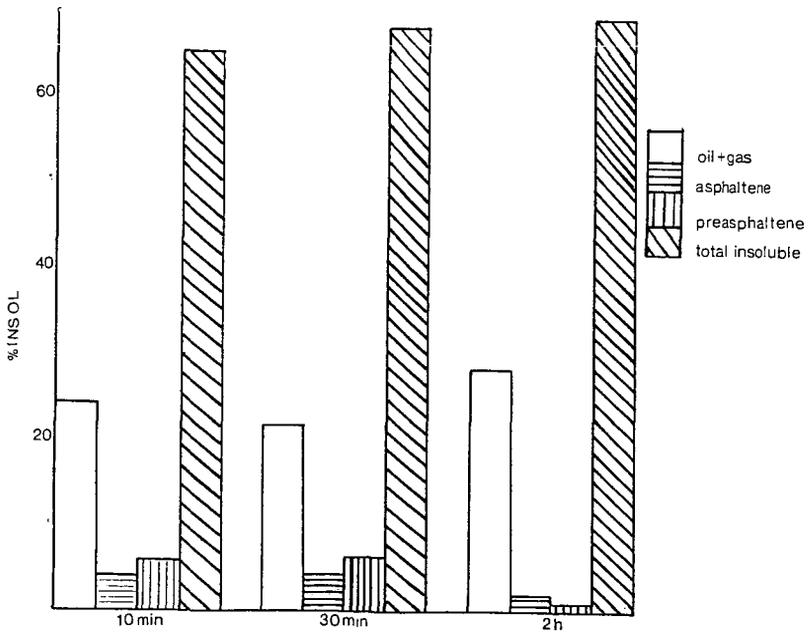


Fig. 9

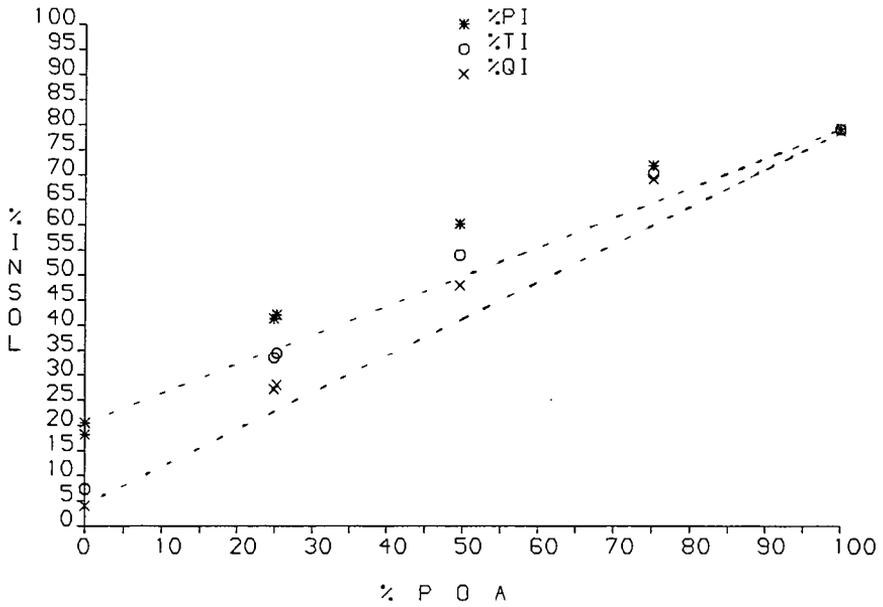


Fig. 10

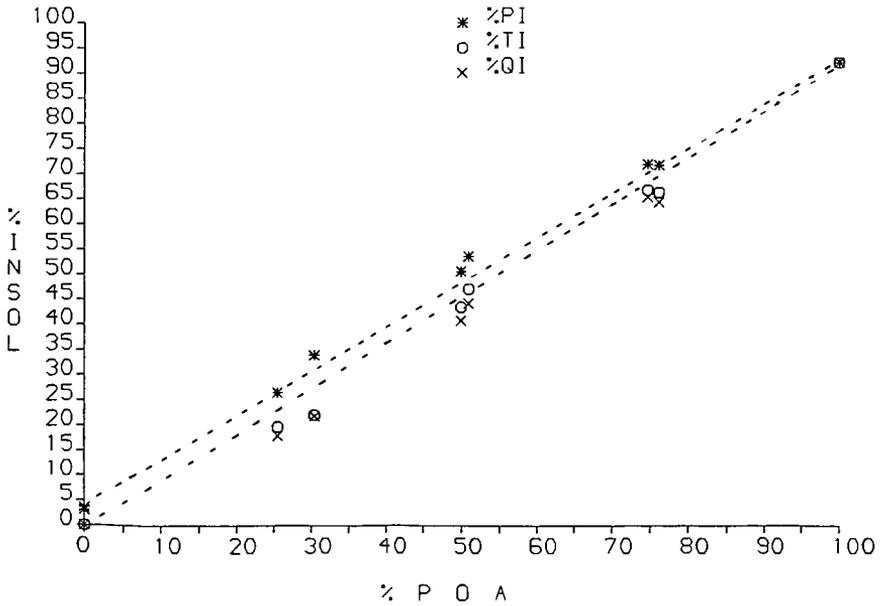


Fig. 11

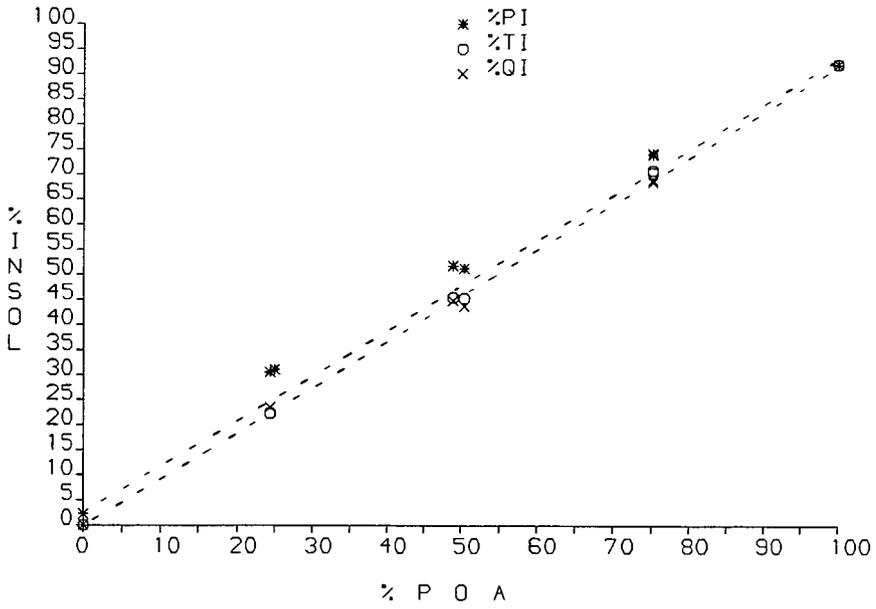


Fig. 12

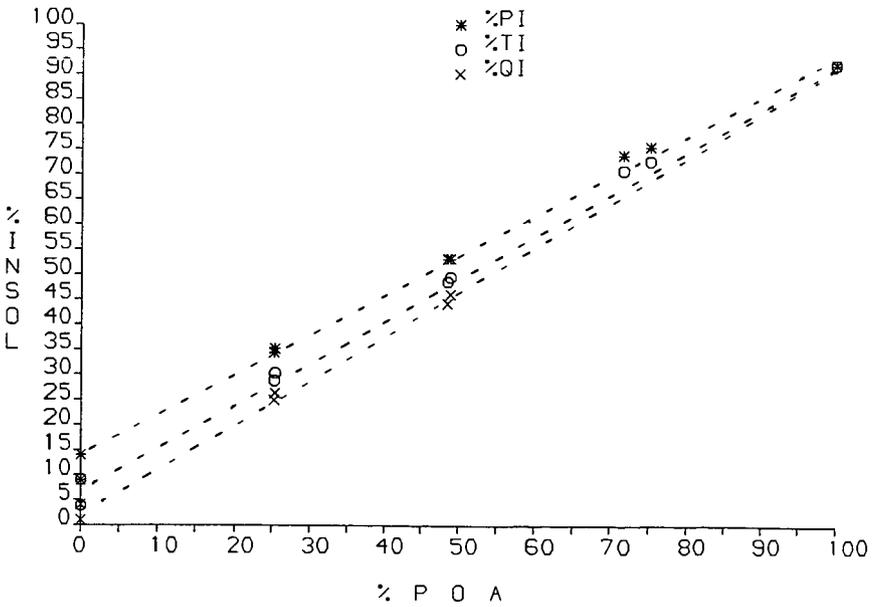


Fig. 13

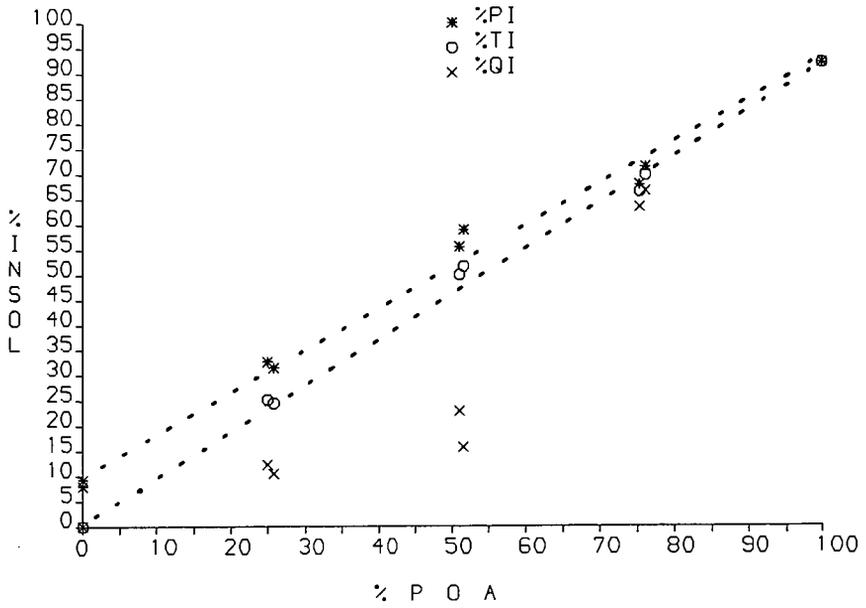


Fig. 14

