

## PHASE SPLITTING AND SYNERGISM IN COAL OIL COPROCESSING AND COAL LIQUEFACTION

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### ABSTRACT

The phase behaviour of complex hydrocarbon systems relevant to coal-oil coprocessing and direct coal liquefaction was investigated in the temperature range 600 to 700 K, using a batch autoclave apparatus. Bitumen and heavy oil + anthracene mixtures as well as model liquefaction solvents such as pyrene + tetralin are shown to exhibit phase splitting in this region. Gas phase constituents such as H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> were found to influence the size and shape of the phase splitting zone but did not alter the phase behaviour per se. Significant fluctuations in the light oil yield obtained from laboratory and pilot scale models of coal/oil coprocessing and direct coal liquefaction processes are frequently attributed to synergism. In this paper, some aspects of synergism are related to phase splitting and the influence of phase splitting on reaction schemes. Preliminary criteria for solvent/diluent selection and operating conditions are proposed.

KEY WORDS: coprocessing, coal liquefaction, synergism

### INTRODUCTION

Kinetic studies in heavy oil upgrading, coal/oil coprocessing and direct coal liquefaction are frequently conducted without due consideration for the physical properties of solvents or diluents under the reaction conditions employed (650 to 750 K, 4 to 30 MPa). Consequently, significant fluctuations in light oil yields obtained from laboratory and pilot scale studies, arising from apparently minor perturbations in operating conditions, are frequently attributed to synergistic phenomena [1-6]. As the reaction conditions associated with coprocessing and coal liquefaction typically intersect the critical region of one or more of the principal liquid constituents [7], complex phase behaviour can be anticipated [8, 9]. Phase splitting, for example, is a common phenomenon in the critical and subcritical regions [10]. In addition, hydrogen is a principal reagent in both coal dissolution [11] and oil hydrogenation reactions and hydrogen solubility in liquids is sensitive to composition [12]. Phase splitting and hydrogen solubility can have a direct and significant impact on observed rates for coal dissolution reactions [13, 14], for example, and these phenomena provide a satisfactory explanation for 20 wt % fluctuations in coal conversion arising in pyrene-tetralin mixtures under hydrogen [15] which had previously been attributed to synergism [1]. Results obtained by Rincon and Angulo [3, 4] and Fouda et al. [6] are also consistent with phase splitting [16]. The transition of the diluent or solvent from liquid to supercritical fluid is another phenomenon which can have a significant impact on reaction kinetics.

Many of the model compounds and liquids employed are unstable under the operating conditions investigated and the phase data presented are not equilibrium data per se. Catalysts are ubiquitous actors in these systems and their effect can only be minimized. Glass liners reduce the impact of trace pyrrhotite (a well known dehydrogenation catalyst) on reactor walls, but do not prevent catalytic hydrogenation due to catechol adsorption on stirrer surfaces [17]. Homogeneous isomerization, pyrolysis, and other reactions cannot be neglected at elevated temperatures. The degradation of pyrene [2, 15] and tetralin [18-21], for example, has been reported. Compound degradation cannot be ignored or prevented and phase compositions inevitably exhibit a time dependence.

### EXPERIMENTAL

Experiments were conducted in a glass lined PPI autoclave having an inside diameter of 0.095 m and 0.3 m long. The autoclave, equipped with magnetically driven stirrer, internal cooling coil and three heated sample ports, was placed vertically in a 3000 W muffle furnace. All apparatus components were fabricated from type 316 stainless steel. The autoclave temperature was maintained within two degrees of a set point using an Athena temperature controller and a manually actuated internal cooling coil. All model compounds were reagent grade and supplied by Fluka. The anthracene oil was supplied by Allied-Signal and Athabasca bitumen and Venezuela heavy oil vacuum bottoms were supplied by CANMET. Their

properties are listed in Table 1. After loading the autoclave with 150 g of liquid, air was removed by flushing and the autoclave was charged with hydrogen, methane, etc. to a preset pressure and heated at 6 K min<sup>-1</sup> to the first set point. Once the temperature reached the set point, operating parameters were fixed for 0.5 h. Agitation facilitated the acquisition of phase data. However, it proved necessary to cease agitation 0.5 h before sample retrieval so that emulsions, if present, could break [15]. Samples were collected in ice cold sample vials and immediately diluted in toluene. Species that did not condense at 273 K were not collected. Following sample retrieval the autoclave was heated to subsequent set points and the procedure was repeated.

Samples were analyzed chromatographically and mass spectra were obtained using a Hewlett Packard 5987A radio frequency quadrupole mass spectrometer. Many peaks were not identified unambiguously. Samples (1 µl) were injected directly into a 30 m DB-17 column. Column operating conditions were: carrier gas, helium; temperature program, 373 K for three minutes, 373-548 K at 20 K min<sup>-1</sup>. Additional GCMS analysis and ASTM standard boiling point data were provided by Shell Canada Ltd. Compositions are repeatable to within 2 to 3 mole %.

## RESULTS AND DISCUSSION

Partial phase diagrams for the model systems pyrene + tetralin + (ethane, no gas, nitrogen, or methane) are shown in Figures 1 through 3 respectively. At low gas pressures a liquid-liquid zone appears in all cases at temperatures exceeding 640 K. This zone grows with temperature and at 698 K is quite broad eg. the zone is bounded by 0.25 and 0.60 mole % pyrene when no gas is added. Only ethane causes this zone to shrink at elevated temperatures Figure 1a. Phase splitting can also arise at elevated pressures. For example, with nitrogen (Figure 2), phase splitting arises from splitting of the liquid phase. The high pressure and low pressure zones combines at elevated temperatures. With methane, Figure 3, the vapour phase splits at elevated pressures but these two phases do not coexist with a third phase. Key transitions arising in these systems include: gas-liquid to gas-liquid-liquid at low or high pressure, gas-liquid-liquid to gas-liquid, fluid-fluid or fluid at elevated pressures. These systems are most susceptible to phase splitting at low pyrene contents.

Dukhedin-Lalla et al. [16] reported that the model solvent system indene-decalin did not undergo phase splitting and that the synergism observed by Chiba et al. [2] could not be explained by phase splitting of solvent components. However, decalin is unstable in mixtures with indene, or indene + anthracene oil, as shown in Table 2, and forms naphthalene or naphthalene derivatives at elevated temperatures. The solubility of pyrene like coal liquids in naphthalene at 673 K is 15 to 20 wt % depending on pressure and gas composition as shown in Figures 1 through 4. Chiba et al. [2] reported coal conversions of 53, 65, and 35 wt % in indene, indene (50 wt %) + decalin, and decalin at this temperature and attributed the fluctuation to synergism. The corresponding concentrations of the coal derived liquids in the solvents are 18, 22, and 13 wt %. These concentration values are based on the initial charges of coal (6 g) and solvent (18 g), to a 0.1 litre reactor and the physical properties of naphthalene. The impact of solvent expansion, and evaporation was included in the calculations. While the operating conditions and compositions for the phase and liquefaction experiments were not identical, the conversion of coal in "decalin", which corresponds to a coal derived liquid concentration in the solvent of 13 wt % compares favourably with the solubility limit for pyrene in naphthalene. The coal conversions reported by Chiba et al. [2] are consistent with phase splitting resulting from exceeding the solubility of coal derived liquids in the solvent where the solubility limit is a function of solvent composition. The decrease in coal conversion in solvents with a high "decalin" content can be explained in a manner analogous to the explanation of synergism in the pyrene-tetralin solvent system [15].

Complex mixtures of aliphatic and aromatic compounds also exhibit phase splitting as shown in Figure 4. Venezuela vacuum bottoms + anthracene oil and Athabasca bitumen + anthracene oil mixtures both exhibit phase splitting above 640 K for compositions in the 30 to 70 wt % range. As many of the species present could not be identified unambiguously or were retained by the column, the compositions shown in figure 4 are incomplete. Simple model systems do not mimic the behaviour of complex systems in this case. Pyrene-hexadecane mixtures, for example, only begin to phase split at 698 K for pyrene contents in excess of 75 wt %. Curtis et al. [5] reported coal conversions for a series of experiments which simulate the transition from coprocessing to coal liquefaction with complex solvents. The solvents comprised mixtures of Maya TLR (petroleum based) and V1067 (a bottoms recycle solvent from the

Wilsonville coal research facility). The authors showed that coal conversion decreased slightly, from 65 to 60 wt %, at 698 K as the V1067 content of the solvent increased from 0 to 35 wt %, with a large coincident increase in insoluble organic matter derived from the solvent. Then coal conversion began to increase rapidly to 75 and 90 wt % conversion at solvent compositions of 50 and 100 wt % V1067. The coal derived liquid content at the end of each of these experiments is 25, 50, 64, and 100 wt % respectively. These results are also consistent with phase splitting. The coal derived liquid content in the experiment where Maya TLR was used as a solvent is 25 wt %. Our results show that at 30 wt % mixtures of coal liquids and petroleum feed stocks phase split. So adding coal liquids to the solvent saturates the solvent with coal liquid thus inhibiting coal dissolution. A separate dispersed liquid phase is then formed which leads to an increase in the production of insoluble organic matter (IOM) as the dispersed liquid becomes hydrogen starved due to poor liquid-liquid mass transfer and polymerization reactions dominate in this phase. If sufficient coal liquid is added to the solvent it becomes the continuous liquid phase and there is a sharp increase in coal solubility at this point because it is more soluble in coal derived solvent than in petroleum derived solvent. Consequently a greater fraction of the coal is solubilized and hydrogenated, coal conversion increases and the IOM produced by the coal based solvent decreases. In this case the continuous phase appears to change over at a coal liquid content of approximately 50 wt %.

Phase splitting is a fundamental characteristic of the coprocessing and coal liquefaction reaction environment and cannot be neglected in the design or interpretation of experiments, or the design of processes. In coprocessing, for example, care must be taken to ensure that the anticipated coal derived liquid concentration in the diluent does not exceed the solubility limit. Extant data [5, 6] and the present work place the solubility limit in the 25 to 30 wt % range but more dilute systems are preferred. Coal liquids exhibit phase splitting between 2 and 4 ringed compounds. Thus, in direct coal liquefaction, two optima appear to exist from the point of view of solvent selection which lead to different reactor design choices:

1. a heavy recycle solvent operated at a pressure sufficient to ensure adequate hydrogen availability,
2. a middle distillate operated at a pressure high enough to avoid the phase split zone.

The first optimum is best exemplified by the so-called German technologies whereas the second optimum has received little attention [22].

## CONCLUSIONS

Phase splitting has been shown to arise in both simple and complex mixtures of aromatic, polynuclear aromatic and aliphatic compounds. This phenomenon is shown to account for fluctuations in coal conversions arising in coal oil coprocessing and coal liquefaction previously attributed to synergism. In particular, liquid yields from coal in coprocessing appear to be limited by the solubility of coal liquids in petroleum based solvents. In coal liquefaction the situation is more complex and a minimum of two solvent optima exist.

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TABLE 1: Physical Properties and Compositions of Oils (wt %)

	Anthracene Oil	Athabasca Bitumen	Venezuela (blend 24)
Specific gravity	(288.5 K) 1.092	(297 K) 1.046	(294 K) 1.026
Water, %	0.2	-	-
Xylene insoluble, %	0.08	-	-
Pentane insoluble, %	-	38.4	21.4
Distillation, % to			
498 K	0.0	-	-
543 K	7.9	-	-
588 K	43.7	-	-
628 K	30.5	-	-
+628 K	19.0	-	-
+798 K	-	99.3	95.1
Elemental analysis			
C		84.3	84.3
H		10.9	9.6
N		0.8	0.7
O		0.3	0.7
S		3.5	6.0
Aromatic carbon, %		35.4	30.0
Mean molar mass		983	848

TABLE 2: Sample compositions obtained from ports located at the top (1) middle (2) and bottom (3) of the reactor for the system indene (25 wt %) + decalin (25 wt%) + anthracene oil (50wt %) + hydrogen (5 MPa)

COMPOUND (MOLE FRACTION)	648 K			673 K			698 K		
	PORT 1	PORT 2	PORT 3	PORT 1	PORT 2	PORT 3	PORT 1	PORT 2	PORT 3
INDENE or BENZENE derivative (C <sub>9</sub> H <sub>8</sub> )	0.641	0.556	0.533	0.542	0.543	0.269	0.269	0.224	0.205
DECALIN (cis & trans) (C <sub>10</sub> H <sub>18</sub> )	0.186	0.161	0.171	0.039	0.116	0.031	0.000	0.000	0.000
INDENE or BENZENE derivative (C <sub>9</sub> H <sub>8</sub> )	0.000	0.014	0.016	0.023	0.013	0.000	0.000	0.000	0.000
SPIRO (4,3) DECANE (C <sub>11</sub> H <sub>16</sub> )	0.030	0.033	0.033	0.000	0.013	0.000	0.000	0.000	0.000
TETRALIN (C <sub>12</sub> H <sub>10</sub> )	0.000	0.031	0.012	0.010	0.000	0.000	0.000	0.000	0.000
NAPHTHALENE (C <sub>10</sub> H <sub>8</sub> )	0.073	0.091	0.119	0.229	0.171	0.450	0.575	0.584	0.640
NAPHTHALENE derivative (C <sub>10</sub> H <sub>8</sub> )	0.011	0.013	0.018	0.032	0.021	0.046	0.040	0.020	0.034
NAPHTHALENE derivative (C <sub>10</sub> H <sub>8</sub> )	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000	0.000
ACENAPHTHENE (C <sub>12</sub> H <sub>10</sub> )	0.017	0.028	0.028	0.016	0.023	0.000	0.000	0.000	0.009
DIBENZOFURAN (C <sub>12</sub> H <sub>8</sub> O)	0.009	0.016	0.013	0.019	0.023	0.039	0.000	0.032	0.028
9-H FLUORENE (C <sub>13</sub> H <sub>10</sub> )	0.011	0.024	0.015	0.030	0.030	0.033	0.036	0.033	0.033
DIBENZOFURAN derivative (C <sub>13</sub> H <sub>10</sub> O)	0.000	0.002	0.002	0.000	0.000	0.000	0.000	0.000	0.000
ANTHRACENE (C <sub>14</sub> H <sub>10</sub> )	0.021	0.017	0.031	0.024	0.028	0.061	0.080	0.025	0.059
PYRENE or FLUORANTHENE (C <sub>16</sub> H <sub>10</sub> )	0.000	0.012	0.008	0.013	0.016	0.051	0.000	0.042	0.018
2 RINGED	0.941	0.899	0.903	0.896	0.879	0.796	0.884	0.858	0.847
3 RINGED	0.028	0.089	0.089	0.089	0.104	0.133	0.116	0.100	0.111
4 RINGED	0.000	0.012	0.008	0.015	0.016	0.051	0.000	0.042	0.041

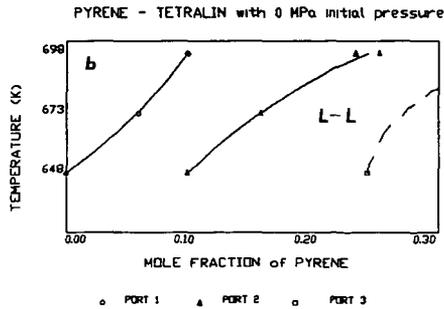
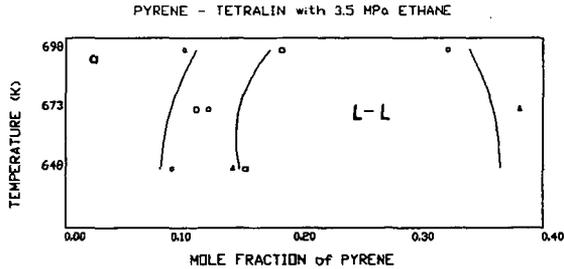
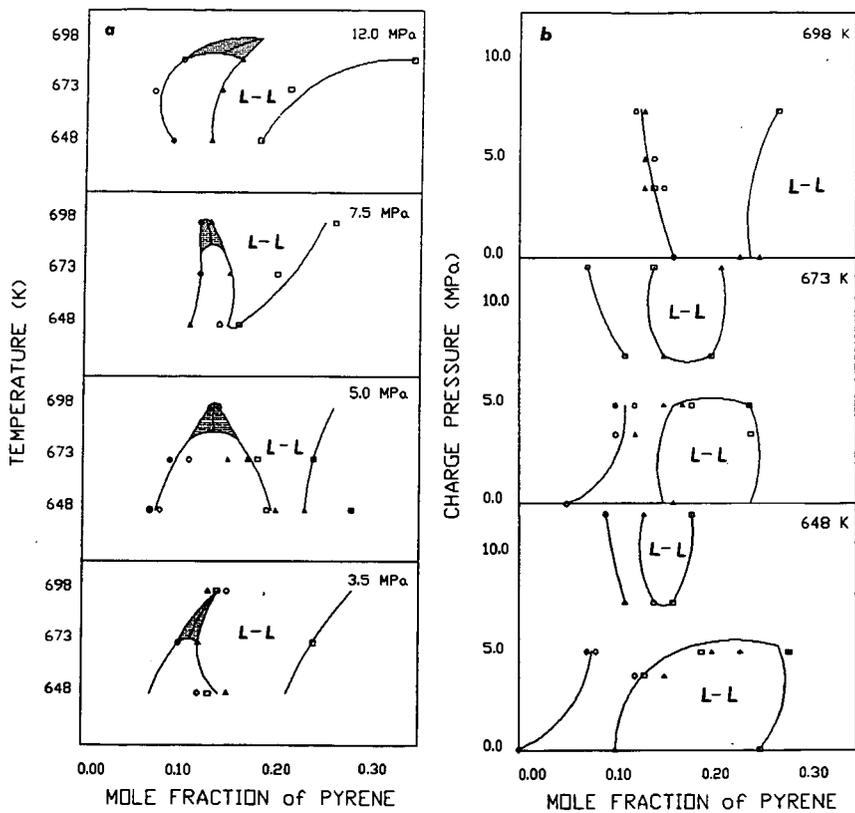


FIGURE 1: Partial phase diagrams for the systems pyrene + tetralin + ethane (a), and pyrene + tetralin (b)

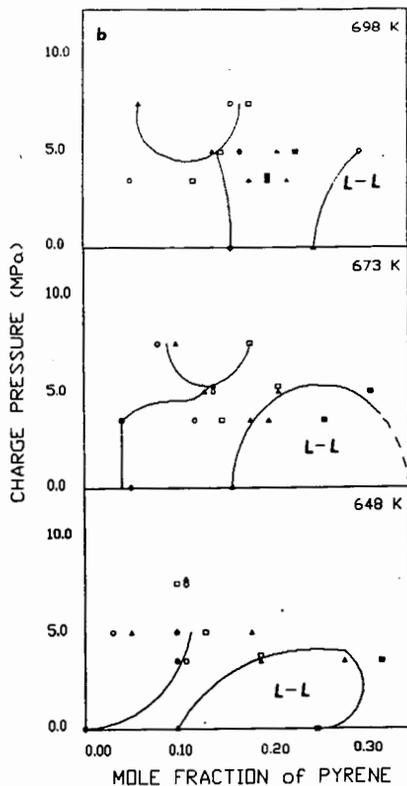
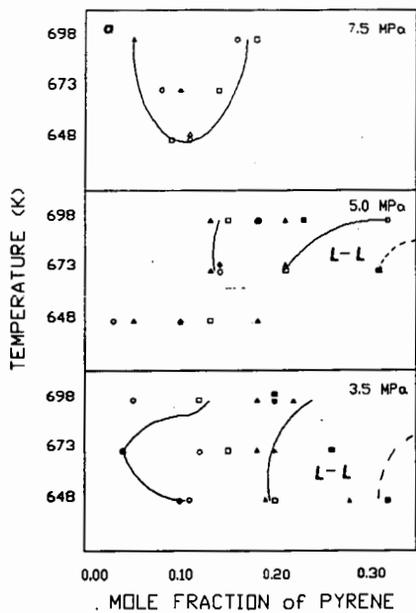


○ PORT 1    △ PORT 2    □ PORT 3

□ Open symbols are 18% mole PYRENE and 82% mole TETRALIN

● Solid symbols are 30.4% mole PYRENE and 69.6% mole TETRALIN

FIGURE 2: Partial phase diagram for the system pyrene + tetralin + nitrogen showing isobars (a) and isotherms (b)



○ PORT 1    △ PORT 2    ◻ PORT 3

Open symbols are 18% mole PYRENE and 82% mole TETRALIN

Solid symbols are 30.4% mole PYRENE and 69.6% mole TETRALIN

FIGURE 3: Partial phase diagram for the system pyrene + tetralin + methane showing isobars (a) and isotherms (b)

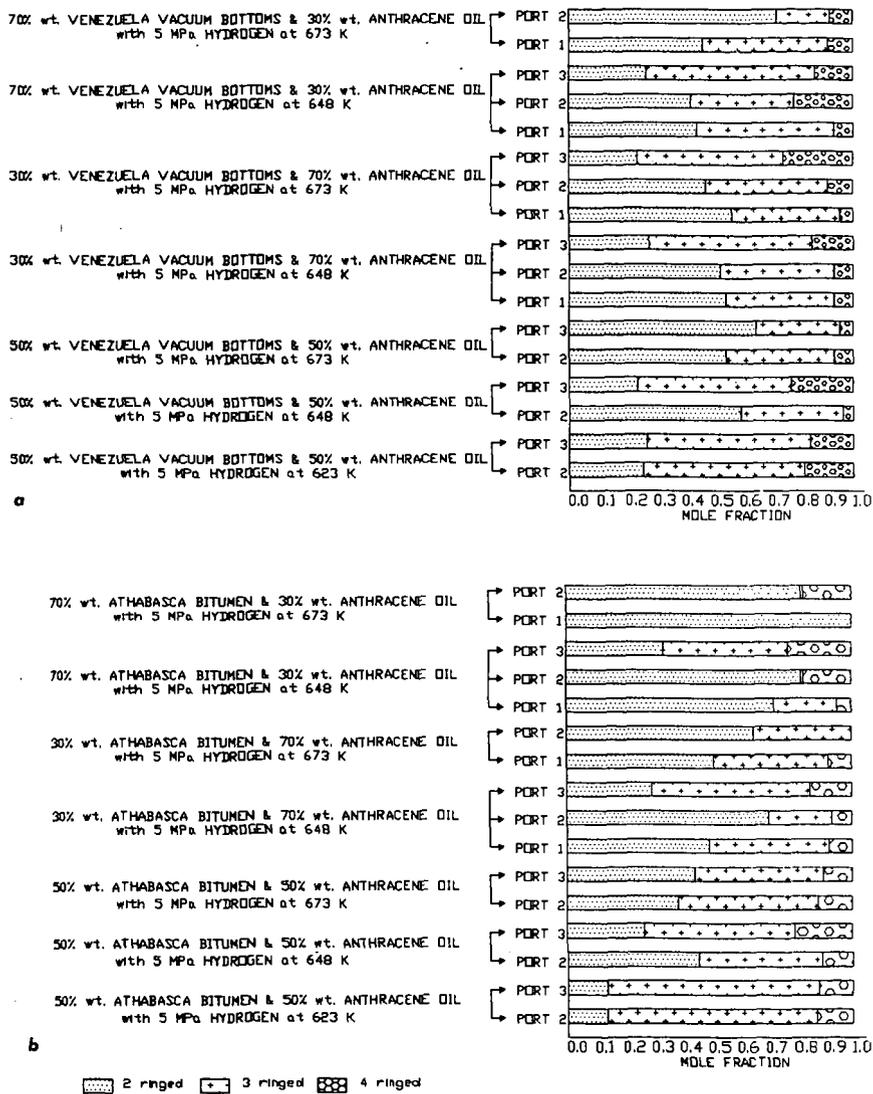


FIGURE 4: Sample compositions obtained from ports located at the top (1) middle (2) and bottom (3) of the reactor for Venezuela vacuum bottoms + anthracene oil + hydrogen mixtures (a), and Athabasca bitumen + anthracene oil + hydrogen mixtures (b)