

## COAL EXTRACTION BY COMPRESSED FLUIDS: A NEW PARAMETER

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### INTRODUCTION

Extraction of coal and similar materials with dense gases may become an important way of obtaining organic chemicals. The resulting hydrocarbon residue is also a better fuel. Many studies [1-17] were undertaken to understand the effect of a solvent on hydrocarbon yield and nature of the extract; the yield was found to depend on pressure (or density), temperature and extraction time.

To evaluate the potential of a solvent under near liquid densities, a number of parameters were adopted:

1. The first, a gas solubility parameter, which has the following form [15].

$$\delta_g = 1.25 P_c^{\frac{1}{2}} \cdot \rho_g / \rho_l \quad (1)$$

$$= \delta_l \cdot \rho_g / \rho_l \quad (2)$$

where  $P_c$  is the critical pressure,  $\rho_g$  gas density,  $\rho_l$  liquid density of  $\delta_l$  liquid density and  $\delta_l$  the liquid solubility parameter which is constant for a given material [18,19]. Equation (1) was used by several researchers to express the effectiveness of a number of solvents under dense gas [11, 15, 20, 21] and dilute gas [14, 22] conditions. Vasilakos et al. [11] showed that for pure paraffins tested at one temperature there is a linear relationship between yield and increase in solvent molecular weight. However, such a correlation is reduced when different groups of solvents are lumped together [20]. On the otherhand, for a pure solvent, a parabolic expression is necessary to represent the change in yield with solubility parameter i.e. the yield decreased after a point with increase in the solubility parameters. The occurrence of a maximum in the yield curve was also observed when extraction was performed with dilute gases [14,22]. The maximum can be accounted for using equation (3) which was originally derived by Hilderbrand and Scott [18,19] and adapted for gases [16].

$$\phi_1^2 v_2 (\delta_2 - \delta_1)^2 = -RT \ln \frac{Y_2}{Y_1} \quad (3)$$

where  $\phi$ ,  $V$  and  $Y$  refer respectively to volume fraction, molar volume and mole fraction in the gas phase. The subscripts 1 and 2 refer to solvent and solute, respectively. Accordingly, a maximum solubility would occur when  $\delta_1 = \delta_2$ . This did not occur, however in the case of mixed solvents [14,22].

2. The second parameter is derived using the virial equation of state after making a number of approximations [23,24]:

$$\ln \frac{C_2}{C_2^0} = (V_2 - 2B_{12})/V \quad (4)$$

where  $C_2$  is the concentration of the solute in the vapor solvent mixture and  $C_2^0$  that in the absence of the solvent gas both recorded at the same temperature.  $V$  and  $V_2$  refer respectively to the molar volume of the mixture and solute.  $B_{12}$  is the interaction second virial coefficient.

$$1/2 B_{12} = (B_{11} + B_{22})/2$$

$$\text{then } \ln \frac{C_2}{C_2^0} = \frac{(V_2 - B_{22}) - B_{11}}{V} \quad (5) \text{ [ref.1]}$$

$B_{11}$  and  $B_{22}$  are the second virial coefficients for solvent and solute respectively. They represent interactions of pairs of like molecules. They are a function of temperature only. A plot of  $-B_{11}$  against extraction yield for a group of solvents, including alcohols, aromatics and paraffins, resulted in a maximum in the yield curve which seems to shift to lower values of  $-B_{11}$  with temperature. Fong et al. [1] attributed the lower yield at the higher values of  $-B_{11}$  to the size and shape of the solvent molecules.

3) Other parameters have also been suggested:

For example, the critical temperature was reported [10,12,24] to follow closely extraction yield. Kershaw [10] suggested the use of the product of the boiling temperature  $T_b$  (K) and the density of solvent at 20°C.

#### A NEW PARAMETER

A theoretical description of the factors that control the solubility of a hydrocarbon material in a dense gas is rather involved and will invariably contain functions that will be either difficult to measure experimentally or to calculate. Therefore, an intuitive approach was preferred for the sake of simplicity.

There are numerous illustrations in the literature that point to the dependence of the amount of a solute,  $Y_2$ , dissolved in a solvent on both the density,  $\rho$ , and temperature,  $T$ , of a dense gas i.e.:

$$Y_2 = \psi(\rho, T) \quad (6)$$

If a generalized relationship is to be found between temperature and density the above physical properties should be written in their reduced form according to the principle of corresponding states [25].

$$\text{Hence } Y_2 = \psi(\rho_r, T_r, \omega) \quad (7)$$

The acentric factor,  $\omega$ , by Pitzer et al. [25] was included in equation (7) to account for the deviation of a complex fluid from simple fluid behavior due to intermolecular interactions.

Since an increase in pressure will increase the density while an increase in temperature produces the opposite effect, the following dependence of  $Y_2$  on the reduced density and temperature is proposed [ $\rho_r = 1/V_r$ ]:

$$Y_2 = A \exp(-E/RT) \cdot \left( \frac{\omega}{V_r T_r} \right)^n \quad (8)$$

where  $A$  and  $n$  are dimensionless constants;  $E$  is the activation energy;  $R$ , is the gas constant;  $T$  is the absolute temperature;  $\omega$  is the acentric factor;  $V$  the reduced molar volume of the gas mixture and  $T_r$  is the reduced temperature. The exponential term was introduced to account for the effect of temperature on the distribution of the solvent molecules.

#### DISCUSSION

To test the model the experimental results for three combination of solvent-solute system [7,17] were compared: (i) Naphthalene-fluoroform, (ii) Naphthalene-carbon dioxide and (iii) Phenanthrene-carbon dioxide. This choice enabled us to evaluate the effect of the solvent tested on the values of  $E/R$  and the constant  $A$  on the one hand and on the suitability of the proposed form of equation (8) on the other hand. However, the predicted values of  $Y_2$  will also depend on the success of the Soave-Redlich Kwong [26] equation which was used to evaluate the molar volume  $V$  and to a lesser extent on the values of the critical properties, (Tables 1 to 4). A sample of the results for the model compounds is shown in Tables 5 and 6. The values of  $A$  and  $E/R$  in equation (8) were obtained by regression analysis and are given in Table 7.

Several points are worthy of note:

- 1- A and E/R for fluoroform are lower than those for carbon dioxide.
- 2- The values of  $Y_2$  in a phenanthrene-carbon dioxide system were better correlated by equation (8) than in the Naphthalene carbon dioxide system.
- 3- In the Naphthalene-fluoroform system the first set of data at each temperature (e.g.  $P = 60.5 \times 10^5 \text{ N/m}^2$  in Table 5) were omitted because of the large deviation. This did not significantly alter the values of A, E/R or r.

Tables 8-11 shows the results for coal. Because extraction was performed at only one temperature, equation (8) was rewritten as follows:

$$\% \text{ Ext.} = a + b. \frac{\omega/V}{r} T_r \quad (9)$$

The predicted values for the paraffins and aromatics (Tables 8 and 10) are far better than those for the alcohols (Table 9). This is also indicated by the higher values of r in Table 11.

At this stage it is appropriate to compare the predictions with equation (9) to those involving other parameters mentioned before. Table 12 shows the results when the solubility parameter in equation (1) was compared to extraction for the same solvent groups studied in Table 11. The results show that both  $\omega/V T_r$  and  $\delta$  represent well the paraffins and alcohols but that the first  $T_r$  parameter provides a better indicator for the aromatics. The same can be said about  $T_b$  and of a number of other parameters (see Table 13). The suggestion by Kershaw [10] that the product of  $T_b$  and the density at 20°C is a useful parameter to estimate conversion is interesting considering that  $T_b$  is proportional to the enthalpy of vaporization,  $\Delta H_v$ , at 298 K [19]. For a large number of non polar hydrocarbons boiling between 285 and 408 K, the relationship with extraction was as follows:

$$\% \text{ Ext.} = \frac{T_b}{V} = \frac{140 + 0.0269\Delta H_v}{V} ; r = 1.0 \quad (10)$$

which explains the high correlation coefficient recorded in Table 13. The constants in equation (10) will depend on the solvent group regressed. Considering that  $\Delta H_v$  at the critical point is zero, the use of an equation containing room temperature parameters to correlate together data of several groups of supercritical solvents would at first seem questionable unless a significant part of solute was extracted during the heating up stage i.e. below supercritical

conditions. However, most of the parameters discussed in this report can in one case or another be linearly related to extraction yield:

$$\% \text{ Ext.} = a + b \theta \quad (11)$$

where  $\theta$  can be visualized to have the form of the cohesive energy density or internal pressure as defined in Hilderbrand and Scott [18,19].

$$\theta = \frac{c}{V} \quad (12)$$

Therefore, for a function to be successful the value of  $c$  should closely represent molecular interaction which explains the success of room temperature parameters and of simple physical parameters for predicting dense extraction in the case of one group of solvents and its failure when different mixed groups are analyzed together.

#### CONCLUSIONS

1. A new parameter was presented which predicts well the effect of varying the temperature and pressure of a pure solvent on yield, using model compounds.
2. In the case of coal the parameter  $\omega/V_T$  was consistently highly correlated with percent extraction, whereas the linear correlation with  $\delta$  was lower in the case of the aromatics. It was also lower in the case of the alcohols with  $-B_{11}$ .
3. Parameters based on one or two physical properties (e.g.  $T_b$ ,  $T_c$ ) may be useful in predicting the trend produced by one group of solvents. However it is not wise to generalize their usefulness for groups of solvents.

## REFERENCES

1. Fong, W. S., Chan, P. C. F., Pichaichanarong, Corcoran, W. H. and Lawson, D., Chapter 17, pp. 377-394, "Chemical Engineering at Supercritical Fluid Conditions" (Eds. Paulaitis et al.), Ann Arbor Science Publishers, (1983).
2. Scarrah W. P., Chapter 18, pp. 395-407 "Chemical Engineering at Supercritical Fluid Conditions" (eds. Paulaitis et al.) Ann Arbor Science Publishers, (1983).
3. Monge, A. and Prausnitz, J. M., Chapter 7, pp. 159-171 "Chemical Engineering at Supercritical Fluid Conditions" (Eds. Paulaitis et al.) Ann Arbor Science Publishers, (1983).
4. Paulaitis, M. E., Mc Hugh, M. A., and Chai, C. P., Chapter 6, pp. 139-158 "Chemical Engineering at Supercritical Fluid Conditions" (Eds., Paulaitis et al.) Ann Arbor Science Publishers, (1983).
5. Olcay, A., Tugrul, T., and Calimli, A., Chapter 19, pp. 409-417 "Chemical Engineering at Supercritical Fluid Conditions" (Eds. Paulaitis et al.) Ann Arbor Science Publishers, (1983).
6. Pullen J. R. "Solvent Extraction of Coal", Report number ICTIS/TRIS November 1981, IEA Coal Research, London.
7. Reid, R. C., and Schmitt, W. J., "The Influence of the Solvent Gas on Solubility and Selectivity in Supercritical Extraction". Paper presented at the Annual meeting of AIChE, San Francisco, Nov. 25-30, 1984.
8. Kim, S. and Johnston, K. P., "Theory of the pressure Effect in Dense Gas Extraction". Paper presented at the Annual meeting of AIChE, San Francisco, Nov. 25-30, 1984.
9. Sunol, A. K. and Beyer, G. H. "Mechanism of Supercritical Extraction of Coal". Paper presented at the Annual Meeting of AIChE, San Francisco, Nov. 25-30, 1984.
10. Kershaw, J. R., Fuel Processing Technology, 5, pp. 241-246 (1982).
11. Vasilakos, P. N., Dobbs, J. M., and Parisi, A. S., preprint Am. Chem. Soc., Div. Fuel Chem. Vol. 28 (4) pp. 212-227, (1983).

12. Whitehead, J. C. and Williams D. F., J. Inst. Fuel 48, pp. 182-184 (1975).
13. Mortimer, J. Fuel 59, pp. 782-786 (1982).
14. Anglovich, J. M., M. S. Thesis, University of Wyoming, 1968.
15. Giddings, J. C., Science 162, pp. 167-73 (1968).
16. Bowman, Jr. L. M., Ph.D. Thesis, University of Utah, 1976.
17. Kurnick, R. T., Holla, S. J. and Reid, R. C., J. Chem. Eng. Data 26, pp. 47-51 (1981).
18. Hilderbrand, J. H., Prausnitz, J. M., and Scott, R. L., "Regular and Related solutions". Van Nostrand Reinhold Co., 1970.
19. Hilderbrand, J. H., and Scott, R. L. "Solubility of Nonelectrolytes". (Third Edition) ACS Monograph Ser. 17. Reinhold Publishing Corporation, 1950.
20. Jezko, J., Gray, D. and Kershaw, J. R., Fuel Processing Technology 5, pp. 229-239 (1982).
21. Blessing, J. E. and Ross, D. S., Amer. Chem. Soc. Symp. SER., No. 71. pp. 171-185 (1978).
22. Angelovich, J. M., Pastor, G. R. and Silver, H. F., Ind. Eng. Chem. Process Des. Develop. 9, pp. 106-109 (1970).
23. Rowlinson, J. S. and Richardson, J. S., Advances in Chemical Physics, Vol. II, pp. 85-118 (Ed. Prigogine). Interscience Publishers, Inc., New York (1959).
24. Paul, P. F. M. and Wise, W. S., "The Principles of Gas Extraction", Mills and Boon Ltd., (1971).
25. Reid, R. C. J., Prausnitz, J. M., and Sherwood, T. K., "The Properties of Gases and Liquids". (Third Edition) McGraw Hill Book Co., 1977.
26. Soave, G. Chemical Engineering Science, 27, pp. 1197-1203, (1972).
27. Timmermans, J. Physico Chemical Constants of Pure Organic Compounds, Vol. II, Elsevier Publishing Co., 1965.

Table 1. Physical Properties of Paraffin Solvents [Ref. 25].

Solvent	$T_c, K$	$P_c, atm$	$V_c, m^3/kgmol$	$\omega$
Pentane	469.6	33.3	0.304	0.251
Hexane	507.4	29.3	0.370	0.260
Heptane	540.2	27.0	0.432	0.351
Octane	568.8	24.5	0.492	0.394
Nonane	594.6	22.8	0.548	0.444
Decane	617.7	20.8	0.603	0.490
Undecane	638.8	19.4	0.660	0.535
Dodecane	658.3	18.0	0.713	0.562

Table 2. Physical Properties of Alcohol Solvents [Ref. 25].

Solvent	$T_c, K$	$P_c, atm$	$V_c, m^3/kgmol$	$\omega$
Methanol	512.6	79.9	0.118	0.559
Ethanol	516.2	63.0	0.167	0.635
Isopropanol	508.3	47.0	0.220	0.424
Isobutanol	547.7	42.4	0.273	0.588
Cyclohexanol	625.0	37.0	0.327	0.550
m-cresol	705.8	45.0	0.310	0.464

Table 3. Physical Properties of Aromatic Solvents [Ref. 25].

Solvent	$T_c, K$	$P_c, atm$	$V_c, m^3/kgmol$	$\omega$
Benzene	562.1	48.3	0.259	0.212
Toluene	591.7	40.6	0.316	0.257
O-xylene	630.2	36.8	0.369	0.314

Table 4. Physical Properties of Solvents Used with Naphthalene and Phenanthrene.

Solvent	$T_c, K$	$P_c, atm$	$V_c, m^3/kgmol$	$\omega$
Fluoroform <sup>a</sup>	299.0	48.8	0.133	0.275
Carbon Dioxide <sup>b</sup>	304.2	72.8	0.094	0.225

(a) Reid and Schmitt [Ref. 7]

(b) Reid et al [Ref. 25]

Table 5. Experimental and Predicted Vapor Mole Fraction,  $Y_2$ , of Naphthalene in Naphthalene - Fluoroform System<sup>2</sup> at  $T = 318^\circ\text{K}$ .

$P \times 10^{-5}$ N/m <sup>2</sup>	$v^a$ m <sup>3</sup> /kgmol	$\omega/V_r T_r$	$Y_2 \cdot 10^3$		%Diff.
			Exp. <sup>b</sup>	Pred. <sup>c</sup>	
60.5	0.238	0.145	0.857	1.187	-38.51
73.3	0.159	0.217	3.300	2.846	13.76
96.1	0.116	0.298	7.040	5.654	19.89
141.3	0.094	0.367	10.090	8.855	12.24
221.0	0.081	0.427	12.300	12.246	0.44
351.3	0.072	0.481	13.400	15.847	-18.26

- (a) Soave Redlich-Kwong [Ref. 26]  
 (b) From Reid and Schmitt [Ref. 17]  
 (c) Using Equation (9)

Table 6. Experimental and Predicted Vapor Mole Fraction,  $Y_2$ , of Phenanthrene in Phenanthrene - Carbon Dioxide System at  $T = 328^\circ\text{k}$ .

$P \times 10^{-5}$ N/m <sup>2</sup>	$v^a$ m <sup>3</sup> /kgmol	$\omega/V_r T_r$	$Y_2 \cdot 10^3$		%Diff.
			Exp. <sup>b</sup>	Pred. <sup>c</sup>	
120.0	0.102	0.191	0.465	0.509	-9.46
160.0	0.077	0.255	1.510	1.370	9.27
200.0	0.068	0.290	2.140	2.114	1.21
240.0	0.063	0.313	2.790	2.769	0.75
280.0	0.059	0.331	3.190	3.356	-5.20

- (a) Soave Redlich-Kwong Equation [Ref.26]  
 (b) From Kurnick, Holla and Reid [Ref. 17]  
 (c) Using Equation (8)

Table 7. Regression Analysis Data for Model Compounds.

Solvent class	A	E/R	n	Data Points	r
Naphthalene Fluoroform <sup>a</sup>	$26.90 \times 10^3$	-4058.±567	2.16	18	0.97
Naphthalene Fluoroform <sup>a</sup>	$29.73 \times 10^3$	-4215.±342	1.76	15	0.98
Naphthalene Carbon Dioxide <sup>a</sup>	$29.58 \times 10^5$	-4822.±504	2.98	36	0.96
Phenanthrene Carbon Dioxide <sup>b</sup>	$14.69 \times 10^5$	-5289.±366	3.44	15	0.99

(a) Reid and Schmitt [Ref. 7]

(b) Kurnick, Holla and Reid [Ref. 17]

Table 8. Experimental and Predicted Values of Material Extracted from Coal Using Paraffin Solvents

Solvent	$\omega/V_r T_r^a$	% Extraction		% Difference
		Exp. <sup>b</sup>	Pred. <sup>c</sup>	
Pentane	0.146	18.43	18.73	-1.47
Hexane	0.227	19.26	19.18	0.42
Heptane	0.335	19.70	19.79	0.40
Octane	0.451	20.70	20.44	1.26
Nonane	0.625	21.17	21.42	-1.18
Decane	0.745	22.75	22.10	2.36
Undecane	0.921	23.16	23.10	0.26
Dodecane	1.079	23.56	23.98	-1.78

(a) V from Reference 11.

(b) Vasilakos et al [Ref. 11] at T=673K and V=0.364 m<sup>3</sup>/Kgmol

(c) from Equation (9)

Table 9. Experimental and Predicted Values of Material Extracted from Coal Using Alcohol Solvents.

Solvent	$/V_r T_r^a$	% Extraction		% Difference
		Exp. <sup>b</sup>	Pred. <sup>c</sup>	
Methanol	0.191	18.90	18.15	3.97
Ethanol	0.313	25.50	28.71	-12.59
Isopropanol	0.261	28.80	24.28	1.57
Isobutanol	0.544	45.30	48.73	-7.57
Cyclohexanol	0.741	61.80	65.80	-6.47
m-Cresol	0.839	79.70	74.34	6.73

(a) V from reference 20.

(b) Jezko et al [Ref. 20] at T=723 K and P=20MPa

(c) from Equation (9)

Table 10. Experimental and Predicted Values of Material Extracted from Coal Using Aromatic Solvents.

Solvent	$\omega/V_r T_r^a$	% Extraction		- % Difference
		Exp. <sup>b</sup>	Pred. <sup>c</sup>	
Benzene	0.209	37.90	37.01	2.35
Toluene	0.319	39.20	40.70	-3.83
O-xylene	0.480	46.70	46.09	1.31

(a) V from reference 20.

(b) Jezko et al [Ref. 20] at T=723K and P=20MPa

(c) from Equation (9)

Table 11. Regression Analysis Data for Coal.

Solvent Group	%Ext = $a + b(\omega/V_r T_r)$		Data Points	r
	a	b		
Paraffins <sup>a</sup>	17.90±0.27	5.63±0.42	8	0.98
Alcohols <sup>b</sup>	1.63±4.22	86.65±7.81	6	0.98
Aromatics <sup>b</sup>	30.0±3.38	33.5±9.56	3	0.92

(a) Vasilakos et al. [Ref. 11] (b) Jezko et al. [Ref. 20]

Table 12. Regression Analysis Data for Coal using Solubility Parameter  $\delta$  from equation (1).

Solvent Group	%Ext = $a + b\delta$		Data Points	r
	a	b		
Paraffins <sup>a</sup>	11.21±0.68	3.05±10.21	8	0.98
Alcohols <sup>b</sup>	-12.37±1.95	15.40±0.50	6	1.00
Aromatics <sup>b</sup>	-16.53±37.63	13.04±8.47	3	0.64

(a) Vasilakos et al. [Ref. 11] (b) Jezko et al. [Ref. 20]

Table 13. Regression Analysis Data for Selected Physical Properties with % Extraction

Solvent Group	Linear Regression Coefficient, r						
	$T_b^a$	$\rho_{25}^b$	$\rho_{exp}^c$	$T_b \rho_{25}$	$T_b \rho_{exp}$	$T_c^a$	$-B_{11}^d$
	K	kg/m <sup>3</sup>	kg/m <sup>3</sup>	K.kg/m <sup>3</sup>	K.kg/m <sup>3</sup>	K	m <sup>3</sup> /kgmol
Paraffins	0.98	0.86	0.99	0.97	0.99	0.98	0.98
Alcohols	0.99	0.93	0.99	0.96	0.99	0.96	0.96
Aromatics	0.55	0.00	0.73	0.49	1.00	0.90	0.93

- (a)  $T_b$  and  $T_c$  from Reid et al [Ref. 25];  
 (b)  $\rho$  at 25 °C, from Timmermans [Ref. 27];  
 (c)  $\rho_{exp}$ , from experimental data in references [11,20]  
 (d)  $B_{11}^{exp}$  calculated according to ref. 25.