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Mathematical Analysis of Noncatalytic Coal Dissolution Using Tetralin and the Prediction of Coal Conversion, SRC Yield and Aromaticity of SRC

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Mathematical analyses of noncatalytic coal dissolution using tetralin at 350—460 °C were carried out. Coal conversion, SRC yield and aromaticity of SRC could be predicted fairly well by regression equations using liquefaction conditions as explanation variables. The equation derived from coal conversions in 67 experiments using the C% and volatile matter of 6 coals and liquefaction conditions could predict coal conversions fairly well (R=0.972). The conversions predicted by the proposed equation were also compared with those reported by previous investigators. Although it was suggested that long heating-up period was detrimental to coal conversion, the equation was a good indication of the conversion in solvent extract liquefaction.

There are three alternative processes for direct coal liquefaction (solvent extraction, catalytic hydrogenation and carbonization). In the solvent extraction process coal may be extracted and dissolved at temperatures of 350—450 °C by the action of hydrogen donor solvents with and without catalyst or molecular hydrogen being present.[1] Several solvent extraction process using different modes have been developed. The Pott-Broche process was developed in Germany in 1920s and the process was a prototype of the SCF process in 1950s, the SRC process in the early 1960s and the EDS process in 1960s. It has been well-understood that in noncatalytic coal dissolution, hydrogen from the donor solvents reacts directly with coal molecules to produce hydrocarbon liquids.[2] Therefore, many researchers have attempted to evaluate the hydrogen-donor ability of coal-liquefaction solvents[3] and hydroaromatic compounds such as tetralin are known as donors.[4] In the Pott-Broche and the SCF processes tetralin was used as a solvent. Recently, many laboratory-scale liquefaction processes using tetralin have been intensively investigated.[5–20] Coal conversion has proved to be largely dependant not only on the rank of coal but also on the liquefaction conditions. However, most of the previous studies using tetralin were investigations concerning specific liquefaction conditions[5,7–18] and those using specific coal.[6,19,20] A quantitative evaluation of coal conversion by suitable variables is required for the effective dissolution by establishment of optimal conditions. The object of the present study is to obtain the relationship between explanation variables (coal properties, liquefaction conditions) and observed variables (coal conversion, SRC yield and aromaticity of SRC) and to compare the coal conversions predicted by the proposed relation with the actual conversions obtained in this study and in the previous investigators.[5–16]

Experimental

Coal Sample and Solvent. Seven coals were used in this study. Analyses of these coals are given in Table 1. They were ground to a size that could pass through a 100-mesh (149 μm) screen and were dried at 107 °C in a nitrogen atmosphere. Six types of coal, except Wandoan coal, were used in the study in order to obtain regression equations. Reagent-grade tetralin was used after distillation under reduced pressure.

Coal Liquefaction Procedure. Coal (6—18 g) and tetralin (6—18 g) were placed in a magnetically stirred autoclave and pressurized to ≈5.1 MPa with hydrogen or nitrogen. The autoclave was heated to the reaction temperature and maintained for the nominal reaction time. At the completion of a run, the autoclave was cooled by an electric fan to room temperature. Materials remaining in the autoclave after the liquefaction were extracted with benzene. Conversion to a benzene-soluble material was calculated according to the following equation:

Conversion (wt%, daf coal basis)=
100(coal charged−benzene insoluble material)/daf coal.

Tetralin was recovered from the benzene extract by vacuum distillation at 240 °C and 933 Pa and was analyzed by GC to calculate the transferred hydrogen from tetralin to

Table 1. Analyses of Coals (wt%)

Coal	Ultimate analysis (daf)				Proximate analysis (coal)			
	C	H	N	Odiff	Mois	FC	VM	Ash
Yallourn	69.8	4.0	0.8	25.4	13.3	51.9	32.8	2.0
Wandoan	77.6	6.2	0.8	15.4	9.2	38.6	44.9	7.3
Taiheiyo	77.9	5.8	0.7	15.6	4.8	35.8	47.5	11.9
Horonai	79.4	6.0	1.1	13.4	3.1	44.6	45.4	6.9
Miike-1	80.9	6.4	0.9	11.8	2.1	36.7	37.6	23.6
Minamiohyubari	83.5	6.1	1.3	9.3	1.3	40.8	52.2	5.7
Miike-2	85.9	6.1	1.3	6.7	2.3	46.9	43.9	6.9

coal. The distillation residue was weighed as a solvent refined coal (SRC).

Calculation of Aromaticity of SRC. The aromaticity of SRC was calculated using the Brown–Ladner method.[21] The ^{1}H NMR data required for the calculation were obtained using a Hitachi R 22 apparatus (90 MHz). The distribution of hydrogen was estimated from the intensities of the three different ^{1}H NMR bands (hydrogen on aromatic carbon atoms; δ=6—9, hydrogen on α carbon atoms; δ=2—4.5, hydrogen on other nonaromatic carbons; δ=0.3—2).

Statistical Method. To obtain the relationship between explanation variables (coal properties, liquefaction conditions) and observed variables (coal conversion, SRC yield and aromaticity of SRC), a factorial experimental design was used.[20,22] Thus, the variables of interest were identified and a set of 10 experiments (at least) was performed in which the reaction conditions were changed in a systematic way.[23] The conversion, SRC yield, and aromaticity of SRC were measured under various conditions.

Results and Discussion

Yallourn (a set of 11 experiments), Taiheiyo (15), Horonai (10), Miike-1 (10), Minamiohyubari (11), and Miike-2 (10) coals were liquefied in a hydrogen atmosphere (0—5.1 MPa) using tetralin at 350—460 °C. Under these liquefaction conditions, coal conversion increased linearly with the amounts of transferred hydrogen from tetralin to coal. This indicated that the undesirable regression reaction was minor in these conditions. The observed Yallourn coal conversion, SRC yield and aromaticity of SRC are shown in Table 2. The reproducibility of the data is indicated by the values for duplicate runs at 440 °C under 5.1 MPa for 20 min and at 410 °C under 2.5 MPa for 40 min. This reproducibility shows that application of the data to a regression analysis is possible.[23] Least-squares regression analyses were performed using these data and the resulting equations allowed for a calculation of the conversion, SRC yield and aromaticity of SRC (f_a). The equations derived from the data in Table 2 are given in Eqs. 1—3, where T is the temperature (°C), P the pressure (MPa), and t the time (min):

$$\text{Conversion} = -164.18 + 0.513T - 0.0369P + 0.136t, \tag{1}$$

$$\text{SRC yield} = -59.82 + 0.191T + 0.0221P + 0.0691t, \tag{2}$$

and

$$f_a \times 1000 = -138 + 1.77T - 1.53P + 0.500t. \tag{3}$$

Coefficients of correlation for Eqs. 1—3 were as large as 0.996, 0.936, and 0.934, respectively. Predicted values using the Eqs. 1—3 are also shown in Table 2 (in parentheses). It is clear that the predicted values are close to the observed values.

For other coals, satisfactory results, as well as for Yallourn coal, were obtained. The resulting coefficients for 6 coals for the factors (temperature, pressure, solvent/coal ratio, and time) and correlation coefficients are listed in Table 3. Needless to say, the temperature was main factor for predicting coal conversion and SRC yield. In liquefaction using a catalyst, it was reported that the reaction-rate constant for the liquefaction increased linearly with the reaction pressure.[24] Even in a non-donor solvent like decalin without a catalyst, participation of hydrogen molecules in the liquefaction was suggested.[25] However, it was understood that a donor solvent like tetralin fulfilled the main role of hydrogen donation in the solvent-extraction process.[26] For the equations of conversion, the coefficients in pressure for Yallourn and Taiheiyo coals were negative. However, their absolute values were small. The effect of hydrogen pressure on coal conversion was small under these conditions. Positive values of coefficients in pressure

Table 2. Observed (Obs.) and Predicted (Pred.) Yallourn Coal Conversion, SRC Yield and Aromaticity of SRC Using Tetralin in a Hydrogen Atmosphere

Temp °C	Press MPa[a]	Time min	Conversion obs.	Conversion (pred.)	SRC yield obs.	SRC yield (pred.)	Aromaticity obs.	Aromaticity (pred.)
440	5.1	20	65.9	(64.2)	24.6	(25.7)	0.665	(0.646)
440	5.1	20	62.3	(64.2)	23.9	(25.7)	0.646	(0.646)
440	5.1	60	68.2	(69.7)	32.7	(28.5)	0.634	(0.666)
440	0.0	20	64.4	(64.4)	27.6	(25.6)	0.644	(0.653)
440	0.0	60	70.3	(69.9)	25.5	(28.3)	0.707	(0.673)
380	5.1	20	33.0	(33.4)	13.3	(14.3)	0.556	(0.540)
380	5.1	60	39.8	(38.9)	17.1	(17.0)	0.568	(0.560)
380	0.0	20	33.0	(33.6)	16.4	(14.1)	0.532	(0.546)
380	0.0	60	37.9	(39.1)	15.9	(16.9)	0.568	(0.566)
410	2.5	40	53.9	(51.7)	20.9	(21.3)	0.585	(0.606)
410	2.5	40	52.2	(51.7)	21.1	(21.3)	0.604	(0.606)

a) Total pressure was 5.1 MPa (2.5 MPa and 0 MPa mean 2.5 MPa of hydrogen + 2.5 MPa of nitrogen and 5.1 MPa of nitrogen, respectively).

were obtained for the equations of SRC yields, except for Taiheiyo coal. This indicated that increasing pressure suppressed the formation of gaseous products.[19]

The aromaticity of SRC tended to increase with the reaction temperature, except for Miike coal-2 in which negative coefficient (−0.167) was obtained although its absolute value was small. From the increasing aromaticity of SRC, two reaction mechanisms were considered: In one mechanism, the value of aromaticity increased owing to a further reaction of the liquefaction products. In the other mechanism, compounds having higher values of aromaticity were liquefied proceeding liquefaction. The aromaticity of SRC scarcely changed upon a thermal treatment.[27] This indicated that the latter mechanism in which, as the liquefaction proceeded, compounds having more condensed-ring were cleaved and liquefied, was reasonable.

If the coefficients were well correlated with the coal properties, the meaning of the coefficients might be clear; however, we could find no good correlations between the coefficients for the factors and the coal properties. Figure 1 is a plot of the conversion predicted from the regression equation against the actual conversion for the 6 coals. The predicted conversions are in fair agreement with the observed conversions over the wide conversion range (5—90%). Figure 1 also shows the conversions under a nitrogen atmosphere (12 experiments) as a closed key. They were also in good agreement with the predicted values. It is evident that the role of molecular hydrogen to increase coal conversion is minor under these mild liquefaction conditions with no catalyst.[19]

Similar satisfactory relationships between predicted and observed SRC yield were also attained. However, a smaller coefficient of correlation than that for conversion was observed in the case of the relationship between predicted and observed aromaticity of SRC. As shown in Table 2, the difference of aromaticity in repeated runs at 440 and at 410 °C were 0.19 and 0.19 (not small). The smaller coefficient of correlation is partly due to an experimental error in determining the aromaticity of SRC.

A useful way for attaining an effective solvent extraction of coals is to obtain an equation which can describe the change in coal conversion by using the properties of the coals. Regression analyses using coal properties (C%, H%, N%, H/C, volatile matter, fixed carbon, and ash) and liquefaction conditions as explanation variables were carried out in various combinations. We choose C%, volatile matter and liquefaction conditions since the coefficient of correlation was largest when they were used. The equations derived from the 67 experiments using 5 explanation variables (2 coal properties and 3 liquefaction conditions) are given in Eqs. 4—6, where C is the C% of coal (wt%), VM the volatile matter based on dry coal (wt%), T the temperature (°C), P the pressure (MPa), and t the time (min):

Table 3. Results of Multiple Regression Analyses

Coal	Observed variable[a]	Factor				Constant	R[c]
		Temp °C	Press MPa	S/C[b]	Time min		
Yallourn	Conv	0.513	−0.0369		0.136	−164.18	0.996
	SRC	0.191	0.0221		0.0691	−59.82	0.936
	f_a	1.77	−1.53		0.500	−138	0.934
Taiheiyo	Conv	0.606	−1.26			−197.67	0.993
	SRC	0.376	−0.193			−117.37	0.986
	f_a	1.44	−7.00			−6	0.939
Horonai	Conv	0.768	0.610		0.280	−279.64	0.994
	SRC	0.462	0.0659		0.187	−164.54	0.992
	f_a	1.45	0.549		0.494	−58	0.979
Miike-1	Conv	0.722	1.44	−1.63		−233.24	0.980
	SRC	0.449	2.36	2.34		−150.31	0.927
	f_a	0.781	6.78	−22.6		409	0.810
Minamiohyubari	Conv	0.831	0.274		0.148	−308.80	0.993
	SRC	0.538	0.514		0.0565	−197.17	0.975
	f_a	1.03	−1.98		8.07	167	0.747
Miike-2	Conv	0.713	0.835	0.625		−245.94	0.994
	SRC	0.479	1.06	3.61		−168.25	0.982
	f_a	−0.167	2.25	−5.86		673	0.987

a) Conv=Conversion, SRC=SRC yield, f_a=Aromaticity of SRC$\times 10^3$. b) Solvent/Coal ratio. c) Correlation coefficient.

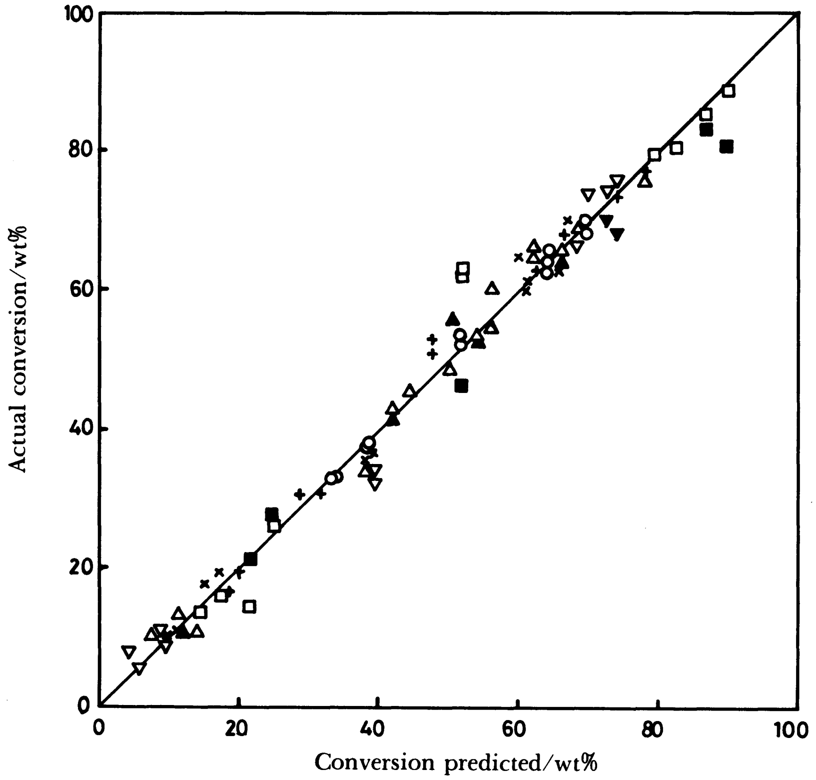

Fig. 1. Comparision of conversions predicted by the six regression equations for each coal and actual conversions obtained: ○, Yallourn (H_2); △, Taiheiyo (H_2); ▲, Taiheiyo (N_2); +, Horonai (H_2); □, Miike-1 (H_2); ■, Miike-1 (N_2); ×, Minamiohyubari (H_2); ▽, Miike-2 (H_2); ▼, Miike-2 (N_2).

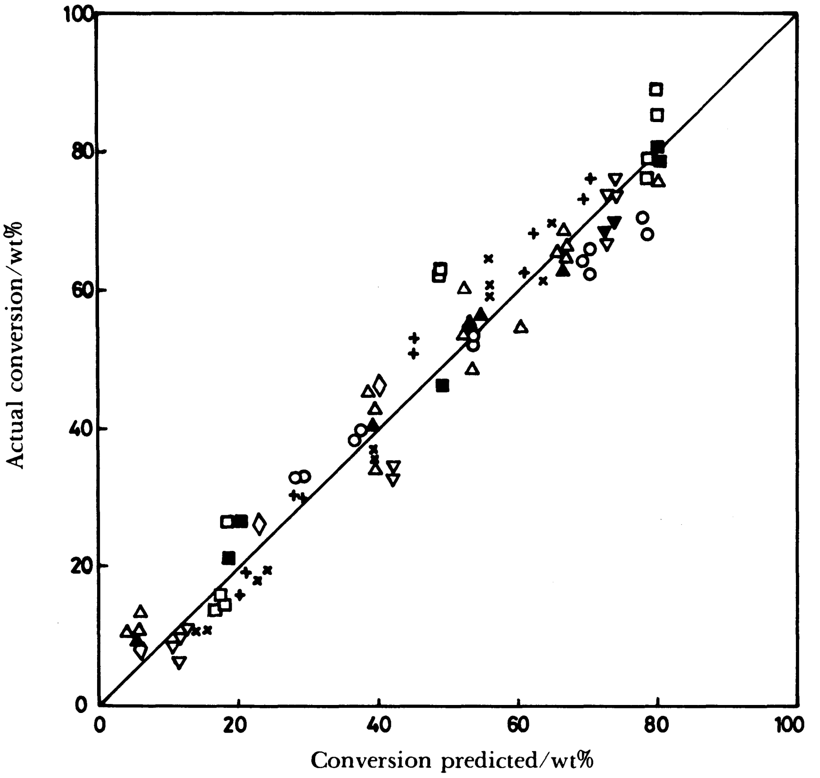

Fig. 2. Comparision of conversions predicted by the regression equation and actual conversions obtained: The key is as in Fig. 1; ◇, Wandoan (N_2).

$$\begin{aligned}\text{Conversion} &= -208.01 + 0.188C - 1.08VM + 0.684T \\ &\quad + 0.210P + 0.212t, \qquad (4)\\ \text{SRC yield} &= -203.93 + 0.868C - 0.367VM + 0.417T \\ &\quad + 0.571P + 0.242t, \qquad (5)\end{aligned}$$

and

$$\begin{aligned}f_a \times 100 &= -9.523 + 0.708C - 0.685VM + 0.108T \\ &\quad - 0.220P + 0.0332t. \qquad (6)\end{aligned}$$

Coefficients of correlation for Eqs. 4—6 were 0.972, 0.900, and 0.795, respectively. A smaller coefficient of correlation (0.948) was obtained when the regression equation was derived using *C, T, P, t* as explanation variables (except for *VM*). Volatile matter is known to decrease with an increase in the coal rank;[28] however, volatile matters of higher-rank coals in this study (Miike coal-1 and -2) are smaller than those of lower-rank coals (Taiheiyo and Horonai coals). The present study, in which volatile matter and coal rank are two important variables, indicates the possibility that they are significant independant properties of coal. The possibility that volatile matter concerned well with the amounts of linkages which were easily cleaved and the resulted radical consumed hydrogen was not excluded. Comparision of predicted values and actual values using the Eqs. 4—6 are shown in Fig. 2—4. Figure 2 shows that the conversions obtained with wide-range conditions and coal ranks can be well predicted only from one Eq. 4. We also added to Fig. 2 the conversions obtained in the liquefaction of Wandoan coal (a set of 3 experiments). The difference between observed and predicted conversions of Wandoan coal were only 3—6%. Although there are small scatter in Figs. 3 and 4, especially in Fig. 4, the equations are sufficient for predicting SRC yield and aromaticity of SRC.

We compared the conversion predicted by the proposed Eq. 4 with the results obtained by previous investigators,[5—16] as shown in Fig. 5. There is considerable scatter. Actual conversions by investigators 4, 8, and 10 were fairly larger than predicted; however, those by investigators 2, 3, and 5 were smaller than predicted. Here, we must note the difference of liquefaction apparatus among investigators as shown in Table 4. Investigators 4, 8, and 10 used tubing bomb as the reactor which did not require so long heating up period (0.5—1.5 min). Investigator 5 used 4 l autoclave and required 120 minutes to reach reaction temperature (400 °C). In addition, investigators 2, 3, and 6 used 300 ml and investigator 12 used 500 ml autoclave. We used 100 ml magnetically stirred autoclave and required 60 minutes to 400 °C. These facts indicate that in a prediction using Eq. 4, the conversion is overestimated for a larger reactor which requires a long heating-up period and is underestimated for a smaller reactor like tubing bomb. It is well-known that coal liquefaction is proceeded even in the course of heating-up period.[29] However, our results suggest that extending the heating-up period

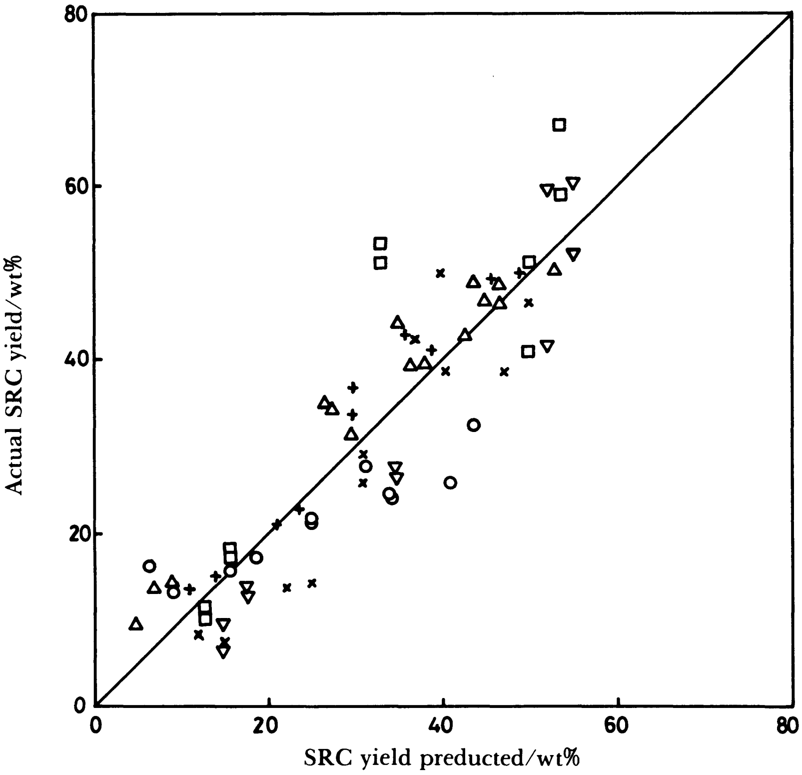

Fig. 3. Comparision of SRC yield predicted and actual SRC yields. The key is as in Fig. 1.

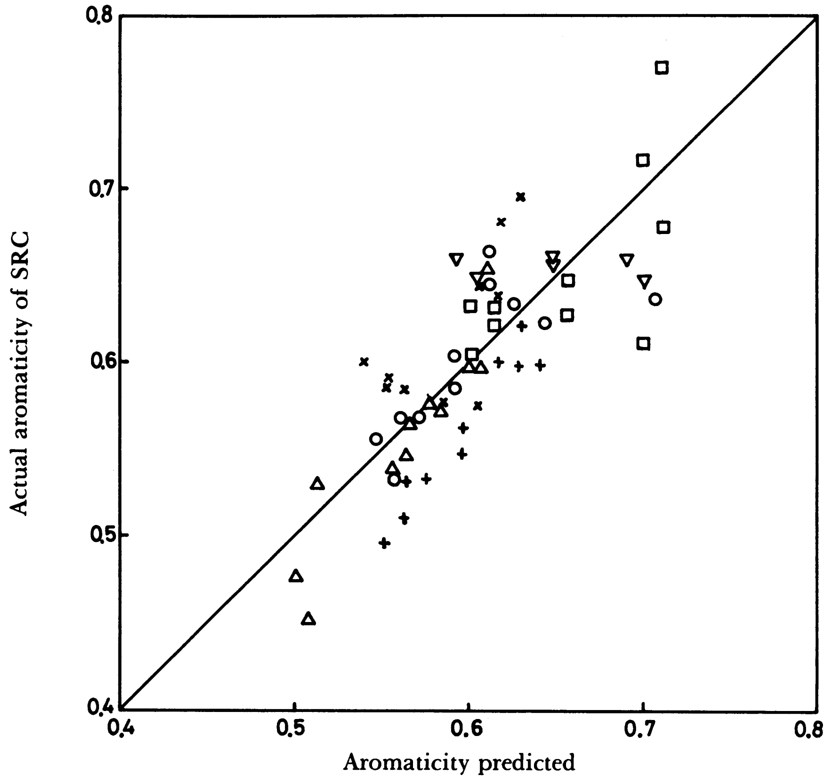

Fig. 4. Comparision of aromaticity of SRC predicted and actual aromaticity of SRC. The key is as in Fig. 1.

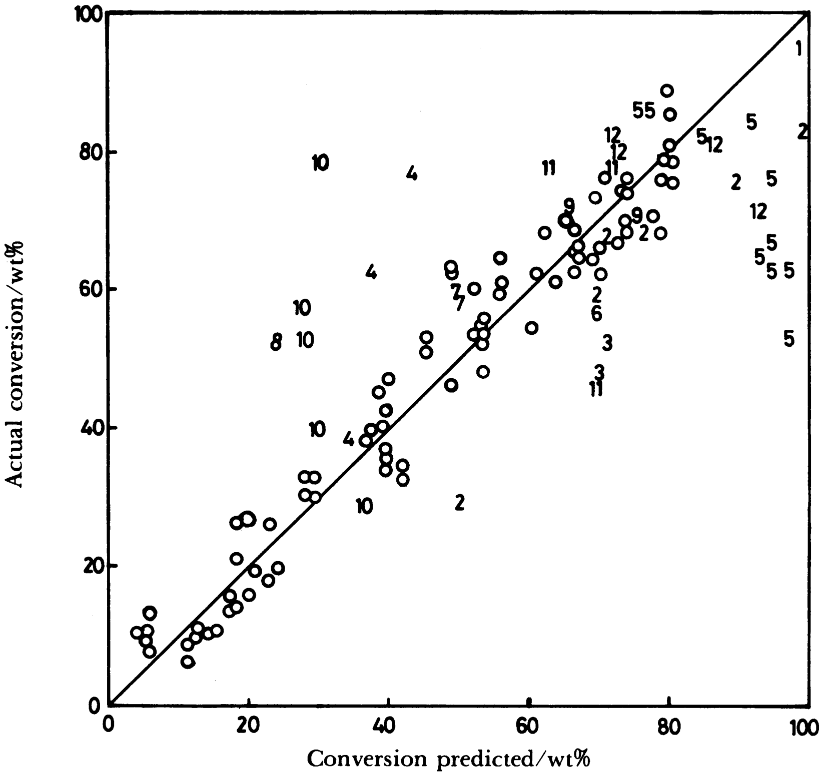

Fig. 5. Comparision of conversions predicted and actual conversions in this study (O) and conversions obtained by other investigators. The key is as in Table 4.

Table 4. Liquefaction Conditions Employed for the Present Study and Previous Investigations

Key	Investigator	Temperature °C	Reactor ml	Heating-up period/min
○	Present authors	350—460	100	60 to 400 °C
1	Angelovich et al.5)	440	2000	≈140
2	Kamiya and Sato6)	378—465	300	45 to 436 °C
3	Sato et al.7)	436	300	45
4	Neavel8)	400	8.1	0.5
5	Cudmore9)	400	4000	120
6	Sato and Kamiya10)	435	300	45
7	Awadalla and Smith11)	400	50	90
8	Kawai et al.12)	400	14.5	1.5
9	Moritomi et al.13)	450	27	≈3
10	Kawai et al.14)	400	14.5	1.5
11	Miyamoto et al.15)	450	Micro-flow reactor	
12	Nakada et al.16)	450	500	≈110

does not contribute to an increase in coal conversion. The influence of the heating-up period on brown coal carbonization was reported by Mochida et al.30) They found that the occurrence of some fusion of the coal was evident at rapid heating rates (600 °C/3 min and 2 s) whereas that did not occur at low heating rates (600 °C/1 h). They also concluded that the rapid heating rates and high liquefaction temperatures might allow the rapid transfer of reactive, and relatively inert, hydrogen in the solvent to the thermal decomposition fragments of the coal to stabilize them. A detrimental effect, involving pretreatment at low temperatures, on the conversion was confirmed during the liquefaction of Miike coal-2. Conversion of pretreatment coal (pretreatment at 200 °C for 60 min in tetralin) at 400 °C for 60 min (35.9%) was almost similar to 35.4% of no pretreatment coal. However, the conversion of pretreatment coal at 250 °C for 60 min in tetralin was 29.0%, about 6% lower than that of no pretreatment coal. This is directly related to the bad influence of the long heating-up period on coal conversion. In the conversion prediction using Eq. 4, the influence of the heating-up period was not considered. Including the influence of the heating-up period into the prediction is difficult, however, qualitative discussion as long heating up period is detrimental is possible. It is clear that the Eq. 4 is a good indication of the conversion in solvent extract liquefaction.

Conclusion

Conversion, SRC yield and aromaticity of SRC of six kinds of coals (Yallourn, Taiheiyo, Horonai, Miike-1, Minamiohyubari and Miike-2) at 350—460 °C under hydrogen atmosphere were fairly predicted by 18 regression equations (coefficients of correlation were 0.747—0.996) using liquefaction conditions as explanation variables. Conversions under nitrogen atmosphere were also in good agreement with the predicted. Following equation was derived from coal conversions in 67 experiments using 2 coal properties (C% and Volatile matter) and 3 liquefaction conditions having a high coefficient of correlation (0.972):

$$\begin{aligned}\text{Conversion} &= -208.01 + 0.188C\% \\ &\quad - 1.08\ \text{Volatile matter} + 0.684\ \text{Temperature} \\ &\quad + 0.210\ \text{Pressure} + 0.212\ \text{Time}\end{aligned}$$

Coal conversions of previous investigators using small reactor as tubing bomb were underestimated by the above equation and those using large reactor were overestimated. It was suggested that a long heating up period was detrimental. Above equation is a good indication of the conversion in solvent extract liquefaction. Sufficient prediction of SRC yield and aromaticity of SRC were attained by regression equations using same 2 coal properties and 3 liquefaction conditions as explanation variables.

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