

CONVERSION OF TETRALIN TO NAPHTHALENE DURING COAL LIQUEFACTION:
A COAL RANK PHENOMENON?

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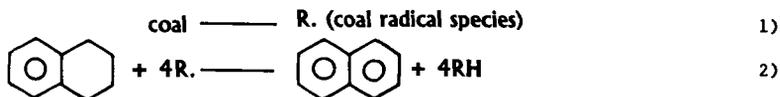
ABSTRACT

Since coal conversion, in the presence of tetralin (a donor solvent), is believed to be a coal rank phenomenon, it seemed worthwhile to determine the role of rank upon conversion of tetralin (T) to naphthalene (N) during coal liquefactions at 385°, 427° and 445°C. The THF soluble fractions, containing T and N, were analyzed using a high performance liquid chromatographic technique. The T/N ratios, for eight coal samples of different ranks, showed a direct relationship between the coal rank and the T/N ratio. The conversion of tetralin to naphthalene was lowest for the highest rank coal, and vice versa. The T/N ratio versus rank relationship was obtained for reaction times ranging from 5 to 65 minutes.

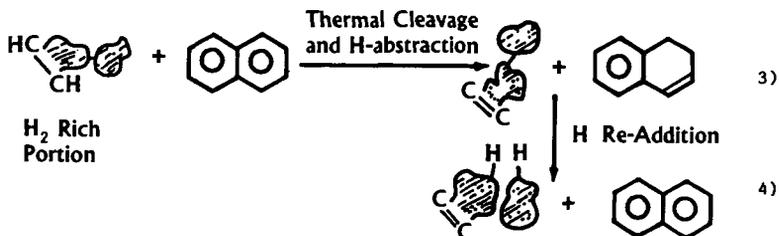
INTRODUCTION

Coal liquefaction processes have been studied in the presence of hydrogen donor as well as non-hydrogen donor solvents during the last five decades (e.g. 1-14). Two generally accepted pathways (5, 6, 14-17) for H-transfer from a donor solvent (tetralin) to coal during coal liquefactions are shown in equations 1) to 4).

Pathway I



Pathway II



Higher coal conversions in the presence of donor solvents have established that no matter which pathway dominates, the solvent hydrogen donor ability plays an important role in the process of coal liquefaction. However, only a small fraction of the research efforts, which are presently being made towards coal liquefaction processes, is being devoted for understanding the fate of H-donor solvent.

Tetralin (a donor solvent) involvement during coal liquefaction processes is indeed highly complex (3, 4, 16, 18) and produces various compounds such as naphthalene, 1-methylnaphthalene, 1-methylindane, indane, indene, butylbenzene, dimers and C₉ - C₁₁ hydrocarbons, etc. However, the major component of tetralin conversion is naphthalene. In order to determine the role of coal rank upon conversion of tetralin (T) to naphthalene (N), we report in this paper our results on T/N ratios for liquefaction of eight coals of different ranks at 385°, 427° and 445°C.

EXPERIMENTAL

The liquefaction experiments were conducted in a microautoclave reactor of 50 ml capacity. The microautoclave was charged with 5g of coal (-100 mesh, dried overnight under vacuum of about 25 inches of Hg at 80-90°C), 7.5g of tetralin and a steel ball (1/4" dia.) for mixing. The system was pressurized with 800 psi of H₂ at ambient temperature (ca. 2000 psi at 445°C) and immersed in a heated sand bath for the desired reaction time. Typically, it required less than two minutes to reach the desired reaction temperature. To ensure thorough mixing of ingredients, the shaker speed (vertical) was set at 400 cpm. At the end of the experiment, the reactor was inserted in a cold sand bath. Once the reactor had come back to ambient temperature (within two minutes), the unreacted H₂ and other gases were slowly released. The products were removed from the reactor using tetrahydrofuran (THF) and were extracted in Soxhlet equipment to obtain the coal conversion. The extraction was continued for about 24 hours or more until the liquid extract obtained was clear.

The THF soluble reactor products were analyzed by a high performance liquid chromatographic (HPLC) technique. The technique requires only the stirring of resulting reactor products overnight with excess of THF and then injecting the THF filtrate into the HPLC system. The ratio of peak areas (number of counts) of tetralin and naphthalene can be used to obtain the T/N ratio directly (without knowing solution concentration) from a linear calibration plot of T_{area}/N_{area} versus T/N (see Figure 1). This technique was developed by optimizing the conditions for the analysis of the THF soluble reactor products:

Column: Supelcosil, LC-PAH (25cm x 4.6mm)
Mobile Phase: THF: H₂O, 40:60
Flow: 0.9 ml/min
Detector: UV, λ 254 (nm)

The performance of the HPLC system was checked against a standard mixture of uracil, acetophenone, benzene and toluene with CH₃OH:H₂O, 60:40 as a mobile phase with a typical flow rate of 1 ml/min.

The precision and reproducibility of the data were established by making repeated measurements for completely independent experiments performed on different days. The precision of the T/N data was found to be better than 1%. The accuracy of our results was verified by comparing the T/N ratios obtained by gc and HPLC. The maximum uncertainty in the T/N ratios was determined to be less than 5%.

The HPLC grade THF and water and the commercially available tetralin were used as supplied.

The chemical analyses of the eight coals used in this work are presented in Table 1.

RESULTS AND DISCUSSION

Effect of Coal Rank and Temperature on T/N Ratio

Coal liquefaction runs for eight coal samples were made at three temperatures, 385^o, 427^o and 445^oC, to determine the extent of conversion of tetralin to naphthalene. The tetralin/naphthalene ratios obtained for the THF soluble reactor products are presented in Table 2. The overall variation in T/N values from 1.80 to 18.7 is very significant for the range of coal ranks covered under this study. The following observations result from the data in Tables 1 and 2:

- (a) T/N ratio decreases with an increase in reaction temperature for all the coals studied.
- (b) T/N ratio decreases with an increase in oxygen content of the coal. The decrease of the T/N ratio with the increase in oxygen content is much more systematic at the 427^o and 445^oC thermal severities, the data for 385^oC are somewhat scattered.
- (c) T/N ratio decreases with a decrease in carbon content of the coal and again the decrease in T/N ratio is more systematic at 427^o and 445^oC.
- (d) The percentage coal conversion to THF soluble products (data not given in Table 2) increases with an increase in temperature - consistent with the previous observations (5, 17). Therefore, as the T/N ratio decreases, the conversion of THF soluble product increases. This relationship holds true for a particular coal at the three thermal severities: 385^o, 427^o and 445^oC. However, this relationship does show considerable scatter when one tries to relate the T/N ratios with the conversion data for a series of coals at the higher reactor temperatures such as 445^oC. This is most likely due to the secondary reactions taking place, i.e., asphaltenes and/or preasphaltenes to produce oils and gases.

As the coal rank decreases (the carbon content decreases and oxygen content increases) there will be an increase in hydrogen demand during coal liquefaction process. The higher the hydrogen consumption during the reaction, the higher is the conversion of tetralin to naphthalene. Hence the result is a lower T/N ratio. This is consistent with the observations discussed previously under (b) and (c). Therefore, the lower the coal rank, the lower is the T/N value (or higher H₂ demand).

We have made several attempts to correlate T/N ratios with various other properties of coals. However, there seem to be no other reportable relationships with the limited data base available at present.

Effect of Liquefaction Duration on T/N Ratio

In order to determine the effect of liquefaction residence time (kinetic versus equilibrium conversions) on the T/N ratio, experiments were performed at 445°C for reaction times ranging from 5 to 65 minutes. The T/N ratios obtained using two coals of different ranks (a Western Ky. #9 and a Wyodak) are presented in Figure 2. Figure 2 also displays the T/N results obtained for blank experiments performed on tetralin + H₂ in the presence of a catalyst (Ni/Mo oxide).

As shown in Figure 2, the T/N value decreases sharply with the increase in reaction time until it reaches some pseudoequilibrium value for both the coals and the blank experiments. However, the T/N values obtained for the catalytic tetralin experiments achieve a pseudoequilibrium value faster than those of coals. All reactor conditions were constant in these experiments except different coal samples and a Ni/Mo oxide catalyst for the blank runs were used. Since the pseudoequilibrium values are different for the two coals the pseudoequilibrium T/N value also appears to be coal rank dependent. The relatively low and different pseudoequilibrium T/N values for the two coals (1.3 and 1.9) as compared to that of the catalyzed (Ni/Mo) tetralin conversion reaction (4.0) clearly suggest that the conversion of tetralin to naphthalene is mainly due to the extent of the hydrogen demand during liquefaction rather than some catalytic reactions from the mineral matter. This is further supported by the fact that there was no significant conversion of tetralin to naphthalene when tetralin was heated with or without low temperature ash in presence of H₂ at 385°, 427° and 445°C.

The parallel behavior of T/N ratios of two coals of different ranks over the entire range of reaction time suggests that the T/N ratios (Figure 2) follow a parallel course in both the kinetic (ca. first 35 minutes) and the equilibrium processes (> 35 minutes) and the major contribution to T/N ratio is probably through kinetically controlled processes. This phenomenon is partially supported by the fact that the conversion for most of the coals reaches its maximum value within 5 to 10 minutes (5, 17, 19).

In order to compare and understand the contributions from kinetically and thermodynamically controlled processes to T/N ratios, liquefaction experiments, using a 45 minute residence time and a 445°C reactor temperature, were performed using the eight coals. The T/N ratios obtained using the longer residence time and the 15 minute residence time are compared in Figure 3. As can be seen, a linear relationship with a slope of greater than unity (1.23) clearly suggest that tetralin is also involved in the

thermodynamically controlled process and the extent of tetralin conversion is controlled by the coal rank. Since coal conversion to THF solubles are somewhat similar (ca. 90%) for 15 minute and 45 minute liquefaction runs, the question arises: what does tetralin do during thermodynamically controlled process? One possible explanation is that during the thermodynamically controlled process, the coal rank dependent conversion of tetralin to naphthalene is due to the hydrogen demand of the secondary reactions of asphaltenes and preasphaltenes to produce the lower molecular weight components - oils and gases. On the other hand, the coal rank dependent conversion of tetralin to naphthalene during kinetically controlled process of coal dissolution is possibly due to the hydrogen demand of the production of asphaltenes and preasphaltenes from the coals. This needs to be clarified further by analyzing the liquefaction products obtained using the different reaction times and is under investigation in our laboratory.

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19. Our unpublished results.

Table 1. Coal Analysis.

	W. Ky. #9 71154	Breckinridge 71160	W. Ky. #9 71072	W. Ky. #11 71064
1. Ash (As-Received)	30.03	6.36	9.04	9.56
2. Volatile Matter, daf	47.83	74.28	42.90	47.47
3. Fixed Carbon, daf	52.17	25.72	57.10	52.53
4. Sulfate S, daf	0.00	0.01	0.14	0.06
5. Pyritic S, daf	1.47	1.23	0.53	1.06
6. Organic Sulfur, daf	2.27	0.55	1.91	3.11
7. Total Sulfur, daf	3.74	1.81	2.57	4.23
8. Carbon, daf	84.99	80.66	79.19	78.80
9. Hydrogen, daf	6.16	8.51	5.44	5.85
10. Nitrogen, daf	1.98	2.13	2.00	1.70
11. Oxygen, daf	3.13	6.90	10.80	9.42

	W. Ky. #11 71081	G. Seam-Co. PSOC866	Wyodak-Wy. 91168	Fort Union Bed-Mt. PSOC833
1. Ash (As-Received)	4.43	17.80	6.64	10.22
2. Volatile Matter, daf	43.23	36.96	52.92	46.86
3. Fixed Carbon, daf	56.77	63.04	47.08	53.14
4. Sulfate S, daf	0.17	0.04	0.05	0.07
5. Pyritic S, daf	0.64	0.06	0.17	0.12
6. Organic Sulfur, daf	2.21	0.52	0.78	0.46
7. Total Sulfur, daf	3.01	0.62	1.00	0.64
8. Carbon, daf	78.28	75.20	71.02	68.64
9. Hydrogen, daf	5.52	5.34	5.42	4.72
10. Nitrogen, daf	1.70	1.18	1.37	1.26
11. Oxygen, daf	11.49	17.66	21.29	24.74

Oxygen by difference.

Table 2. T/N Ratios for 15-Minute Duration Liquefactions at Three Temperatures and THF Soluble Conversions at 445°C.

Coal Sample	Conversion (%)		T/N Ratio		
	445°C 15 min.	445°C 45 min.	445°C	427°C	385°C
71154 (Ky. #9)	—	94.6	4.03 ± 0.21	6.63 ± 0.62	17.40 ± 1.0
Breckinridge	—	90.6	3.51 ± 0.27	5.96 ± 0.18	18.7
71072 (Ky. #9)	—	87.6	2.78 ± 0.12	4.30 ± 0.15	10.3 ± 0.5
71064 (Ky. #11)	—	95.1	2.62 ± 0.06	3.70 ± 0.11	9.14 ± 0.05
71081 (Ky. #11)	93.6	92.7	2.37 ± 0.25	3.99 ± 0.13	11.13 ± 0.22
PSOC 866	77.2	80.2	1.86 ± 0.06	—	—
91648 (Wyodak)	89.5	90.0	2.07 ± 0.06	2.60 ± 0.04	—
PSOC 833	—	84.0	1.80 ± 0.05	2.86 ± 0.05	6.30 ± 0.10

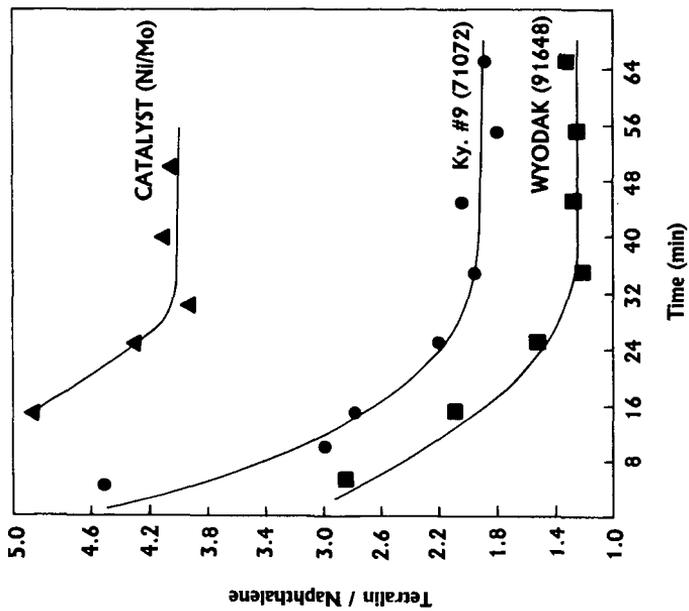


Figure 2. T/N Ratios at 445°C.

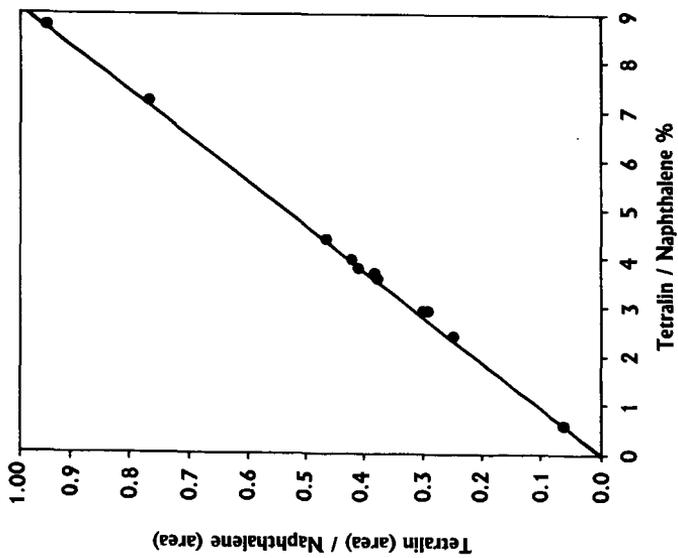


Figure 1. Ratios of Peak areas versus T/N (wt. %) Ratios.

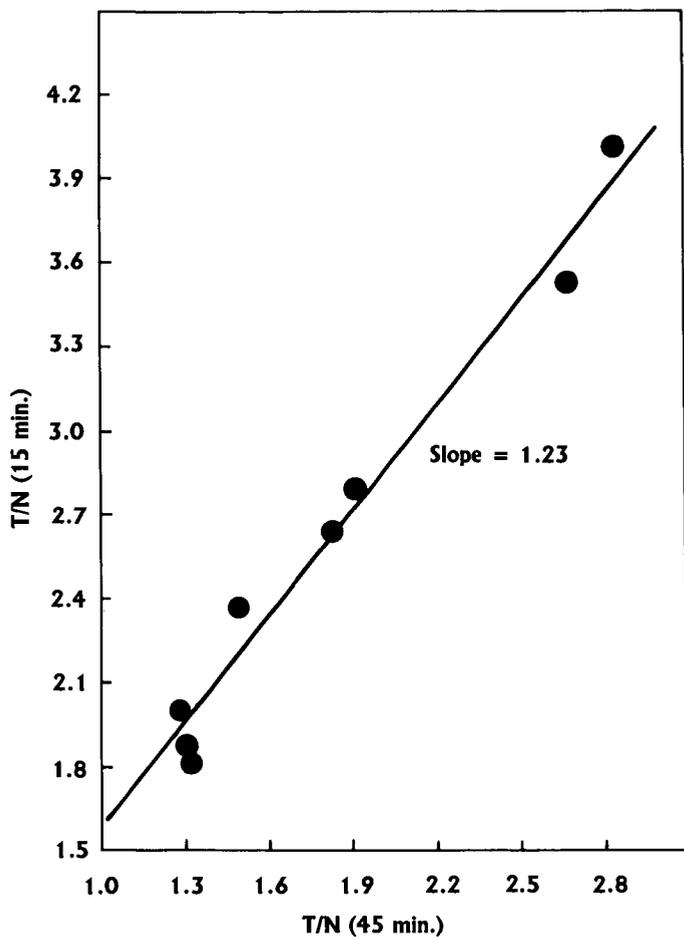


Figure 3. Comparison Between the T/N Ratios of 15 and 45 Minutes Residence Time Runs at 445°C .