2

DOE/PC/90304--4

DE-FG-22-90PC90304-4

DE92 015646

SELECTIVE SOLVENT ABSORPTION IN COAL CONVERSION

Quarterly Report for the Period

July 1, 1991 to September 30, 1991

John W. Larsen, Andrzej Lapucha, Lazarin Lazarov and Jewel Amui

Department of Chemistry

Lehigh University

Bethlehem, Pennsylvania 18015

April 1992

PREPARED FOR THE UNITED STATES DEPARTMENT OF ENERGY

Under Contract DE-FG-22-90PC90304

MAY 14 1992

Objectives:

1. To determine the importance of the presence of added hydrogen donor compounds within the coal in the first stage of direct liquefaction processes.
2. To determine the composition of the solvent absorbed by and present within the coal in the first stage of direct coal liquefaction.

Scope:

Importance of Hydrogen Donors in the Coal

Prepare highly pure 2-t-butyltetralin. Study the conversion of Argonne Premium coals and partially dehydrogenated coals in tetralin and 2-t-butyltetralin and compare the following: conversion to soluble products, product molecular weight distributions, and product structure. Hydrogen donated by both tetralin and 2-t-butyltetralin will be measured by gas chromatography and the same technique will be used to establish the amount of dealkylation of 2-t-butyltetralin. Reactions will be performed at several different temperatures for varying times.

PRESENT WORK:

PART 1: Experimental: Coal Conversions using 2-t-Butyltetralin

2-t-Butyltetralin was synthesized using the procedure of Whitmore et. al.[1] The product purity was higher than 99% by G.C. and ^{1}H nmr. 2-t-butylnaphthalene was prepared by oxidation of 2-t-butyltetralin with excess of sulfur (2:3 mole ratio) at 215°C for twenty hours. This reaction resulted in a 100% conversion.

With cis-decalin as the internal standard, standard solutions of tetralin, naphthalene, 2-t-butyltetralin, 2-t-butylnaphthalene and cis decalin were prepared for the determination of G.C. response factors. A Hewlett Packard Model 5880A gas chromatograph equipped with a flame ionization detector was used. The column used was a 15 meter AT-5 capillary column (polydimethydiphenyl (5%) siloxanes) of 0.25mm I.D. and 0.45 micrometer film thickness. The G.C. conditions were as follows: 1)carrier gas and flow rate: He, 1.06ml/min); oven temperature: (100°C for 1 min., programmed at 3°C/min. to 130°C (5 min); 3) injection port temperature: 250°C 4) detector temperature: 275°C 5) split ratio 113:1.

Parallel liquefaction reactions of tetralin and 2-t-butyltetralin with Argonne Premium Ill #6 coal were carried out for 10 minutes at temperatures ranging from 350 to 400°C (Table 1). The coal and thimbles used for Soxhlet extraction were dried at 110°C in a vacuum oven to constant weight. The solvents used were stored under nitrogen.

Each liquefaction experiment was carried out using two tubing bombs. A 2:1 weight ratio of solvent to coal was used under identical conditions under dry nitrogen atmosphere. The reactors did not leak when charged with 80 psi of dry nitrogen at room temperature. The reactors were shaken at 200 cycles per minute inside the heated fluidized sandbath. The time-temperature profile was measured using a thermocouple attached to the reactors.[2] After the reaction, the reactors were quickly cooled in an ice water bath. The gaseous products were collected in previously evacuated gas traps. In a nitrogen filled glove bag, the contents of each reactor was washed out with pyridine into a beaker. A weighed amount of the internal standard was added and thoroughly mixed using a magnetic stirrer. 0.5mL of each of the pyridine-coal mixture was filtered through a 0.45µm millipore filter and analyzed by G.C. Yields of 2-t-butylnaphthalene and naphthalene are included in Table 2.

Under dry nitrogen atmosphere, each pyridine coal mixture was subjected to Soxhlet extraction. The thimbles containing the extraction residue were dried at 110°C to constant weight.

The solvent and coal mass balance for most of the reactions run showed extensive leakage and these data were discarded. We cannot reach any conclusions based on the data in Table 1. Our principal task in now to identify the source of leaks in the tubing bombs and correct it.

Table 1 Data on pyridine soluble Argonne premium Ill#6 Coal for parallel liquefaction reactions using tetralin and 2-t-butyltetralin as donor solvent.

A.

Solvent	Ill#6 coal /g	Solvent /g	Rxn Temp °C	%Pyridine Soluble
2-t-BuT*	1.00	1.93	377	48.0
Tetralin	1.14	2.37	400	83.0
2-t-BuT*	1.08	2.22	400	87.0

* 2-t-BuT is 2-t-Butyltetralin

B.

Original mass of Ill#6 /g	Temp. /°C	Pyridine Soluble coal/g	Pyridine Insolubles (Residue)/g
1.00	377	0.41	0.58
1.14	400	0.85	0.10
1.09	400	0.80	0.21

Table 2 G.C. data on percent conversion to the naphthalene analog, dealkylated products and percent hydrogen per daf of Ill #6 coal. Mole % conversion of tetralin and 2-t-butyltetralin to products are listed below.

Rxn Temp	Tetralin	Naph	2-t-BuT*	2-t-BuNaph@	$\%H_2$/daf
377	0.49	-	87.4	11.0	0.114
400	79.8	10.1	-	-	0.927
400	0.50	-	87.7	19.9	0.968

*2-t-BuT	is 2-t-butyltetralin
@2-t-BuNaph	is 2-t-butylnaphthalene

Table 3 Mass balance of coal and solvent used in this experiment

Rxn Temp. /°C	Solvent	Solvent Mass Balance	Coal Mass Balance
377	2-t-BuTetralin	103%	99%
400	Tetralin	90%	83%
400	2-t-Butetralin	113%	88%

REFERENCES

1. Whitmore, F.C; James, W.H. J. Am. Chem. Soc. (1943), 65, 2088

2. Yamada, O.; Azik, M; and Larsen, J.W. Quarterly Report DE-FG22-87PC79926-9

PART 2 Coal Dehydrogenation

The goal of this work is to prepare coal samples selectively dehydrogenated for liquefaction studies. Studying the effect of removing the easily donatable hydrogen ion coal conversion will provide insight into the role of internal coal hydrogen on direct liquefaction processes.

Dehydrogenation of coals with p-benzoquinone was studied by Peover in an attempt to obtain more information about the non-aromatic portion of the coal structure.[6] More than one-third of the hydrogen of some low rank coals can be removed by boiling with p-benzoquinone in dimethylformamide (DMF) at 153°C for 7-8 hours. The author also concluded that quinone was consumed during the treatment in DMF. Quinone consumption and quinol production were followed polarographically.

In an attempt to dehydrogenate coals without side-reactions, reactions of Illinois #6 coal with p-benzoqinone were examined over a range of temperatures (100-180°C) and solvents. The reaction progress was followed by gas chromatography (GC).

Quantitative GC analysis of p-benzoquinone/hydroquinone

Data on a simultaneous analysis of benzoquinone and hydroquinone by GC were not found in the literature, but reports on the separation of several quinones[7] and of non-derivatized polyhydric phenols[8] were helpful in the choice of an appropriate stationary phase. A Supelco SPB-20 capillary column (15m, 0.25mm ID, 0.25um film thickness) proved to be quite suitable. The gas chromatograph used was a Hewlett Packard model 5880A equipped with a FID detector.

Benoquinone and hydroquinone were injected as solutions in ethanol-chlorobenzene mixtures under the following GC conditions: carrier gas and flow rate: He, 10mL/min); oven temperature: programmed from 100 to 140°C ; 3) injection port temperature:250°C 4) detector temperature:250°C 5) split ratio 100:1. The relative detector response factors were determined using naphthalene as an internal standard. The values, based on 15 injections of test mixtures of different concentrations (0.2-10mg/mL), were 0.5 ± 0.02 for benzoquinone and 0.4 ± 0.03 for hydroquinone, respectively.

Dehydrogenation of Illinios #6 Coal with P-Benzoquinone

Benzoquinone is used widely as hydrogen acceptor in the aromatization of hydroaromatic hydrocarbons. The reaction does not involve substituent groups and is known to be enhanced in polar solvents compared to nonpolar solvents.[9]

Kimble glass tubes with teflon lined screw caps and equipped with small magnetic stirring bars were used as reaction vessels. 0.1g of Illinios #6 coal (100 mesh) and 0.3g of benzoquinone were stirred in 5 mL of solvent at several temperatures (100-180°C) fo different time periods (0.3-24 hrs).

Chlorobenzene (b.p. 132°C) and 1,2-dichlorobenzene (b.p.178°C) were used as solvents. Hydroquinone is not soluble in these solvents but benzoquinione is soluble in and stable at 130°C in chlorobenzene and at 180°C in dichlorobenzene. No G.C detectable reaction products were found after heating benzoquinone in these solvents for 24 hrs. These solvents extracted no more than 0.2% of the coal. Extracted components were not detectable under the chromatographic conditions used. Dimethylformamide, used by Peover as solvent, was not used in this reaction because it is difficult to remove from the coal. It also reacts slowly with benzoquinone at 150°C.[6] We also tested the stability of benzoquinione in commercially available decalin. A 15% yield of hydroquinone was obtained after 24 hours treatment due to reaction with 0.5% tetralin impurity present in decalin.

Most of the reactions were performed using chlorobenzene at 100, 115 and 130°C and dichlorobenzene at 150 and 180°C. At equal temperatures and reaction times, the reaction occurred to essentially the same extent in both solvents. About 0.1g of naphthalene (G.C internal standard) and 10mL ethanol were added to the cooled reaction mixture. The resulting mixture was shaken, centrifuged, and G.C. analyzed. The sample for G.C analysis was carefully withdrawn from above the precipitated coal.

The reaction was monitored by following the formation of the hydroquinone from benzoquinone. The sum of unreacted benzoquinone and hydroquinone was 100% of the starting benzoquinone for reactions at 100 and 115°C for less than 4 hrs. At 130°C the sum of benzoquinone and hydroquinone dropped below 100% after 1 hr. (Fig. 1). Also included in Figure 1 are the oxidant mass balances at different reaction times and temperatures. It is clear that benzoquinone is reacting with the dehydrogenated coal as observed earlier by Peover.[6]

Hydroquinone is formed when hydrogen is removed from the coal. The progress of coal dehydrogenation with time is shown in Figure 2. At 180°C, the coal hydrogen removal approaches a limiting value of about 35%.

Only when temperatures are below 130°C and reaction times are short can hydrogen be removed without benzoquinone incorporation into the coal. Data on hydroquinone formation and benzoquinone incorporation from 28 experiments at different temperatures and reaction times are presented in Fig. 3. As expected, there is a good linear relationship between hydroquinone formation and hydrogen removal from coal. The data for benzoquinone incorporation are scattered, perhaps due to greater experimental error in this difference measurement.

Figure 4 shows the dependence of benzoquinone incorporation on its consumption. The linear dependence strongly suggests that dehydrogenation activates the coal for reactions with benzoquinone.

Benzoquinone consumption and coal hydrogen removal during 24 hr reactions at several temperatures are presented in Table 3. Peover believed that quinone consumption at 153°C in dimethylformamide was due to Diels-Alder addition of the quinone to existing and /or produced structures in the coal.[6] Our data are consistent with this view, but we cannot endorse it. We have no information on the structure of the coal-benzoquinone products and do not speculate on the nature of the reaction.

Examination of other Oxidizing Agents

In an attempt to sterically block addition of the quinone to structures in the coal, thymoquinone (2-isopropyl-5-methyl- 1,4-benzoquinone) was used to dehydrogenate Illinois #6 coal. The reactivity of quinones is enhanced by electron withdrawing and reduced by electron-donation substituents. Thymoquinione should be somewhat less reactive than benzoquinone. Thymoquinone (TQ) should penetrate coal slower than the unsubstituted benzoquinone.

The same procedure and similar analytical conditions were used. 20% thymoquinone consumption occurred for reaction at 130°C for 24 hrs. In the case of benzoquinone, there was a 12.9% conversion to hydroquinone and a 38% total consumption of benzoquinone.

REFERENCES

1. Whitmore, F.C; James, W.H. J. Am. Chem. Soc. (1943), **65,** 2088

2. Yamada, O.; Azik, M; and Larsen, J.W. Quarterly Report DE-FG22-87PC79926-9
3. Appell, B.R.; Blaustien, B.D.; Fuel, (1986), **65**, 1085
4. Korda, A; and Larsen, J.W. Quarterly Report DE-FG22-87C79926-13
5. Fowkes, F.M.; Jones, K.L.; Li, G.; Llyod, T.B. Energy Fuels (1989), **3**, 97
6. Peover, M.E. et. al., J. Chem. Soc. (1960), 5020
7. Llobera, A; Garcia-Kaso, A; J. Chromatogr. (1987), **393,** 305
8. Mayer, H.; Nolte, J.; Pashold, B; Fresnius, Z. Anal. Chem. (1983), **315**, 708
9. Braude, E.A.; Jackman, L.M.; Linstead, R.P.; J. Chem. Soc. (1954), 3548

Table 1 Data on pyridine soluble Argonne premium Ill #6 Coal

Solvent	Ill#6 Coal /(g)	Solvent /(g)	Rxn Temp °C	% Pyridine Soluble
Tetralin	1.02	2.03	350	27.9
2-t-BuT*.	1.03	2.06	350	50.7
Tetralin	1.00	1.97	377	80.2
2-t-BuT.	1.00	1.93	377	34.8
Tetralin	1.14	2.37	400	97.5
2-t-BuT.	1.08	2.22	400	73.4

* 2-t-BuT. - 2-t-butyltetralin

Table 2 G.C. data on percent conversion to the naphthalene analog, dealkylated products and percent hydrogen per daf of Ill #6 coal. Mole Percent conversion of Tetralin and 2-t-butyltetralin to the products are listed below.

Rxn Temp °C	Tetralin	Naph.	2-tBu-T*.	2-t-Bu Naph@	%H_2 daf
A. Tetralin as solvent					
350	70.8	2.10	-	-	0.149
377	50.4	4.57	-	-	0.322
400	79.8	10.1	-	-	0.927
B. 2-t-butyltetralin as solvent					
350	0.32	-	68.4	4.12	0.114
377	0.49	-	87.4	11.0	0.532
400	0.50	-	87.7	19.9	0.968

* 2-t-BuT. - 2-t-butyltetralin
@ 2-t-BuNaph - 2-t-butylnaphthalene

TABLE 3. Reactions of BQ and Coal Dehydrogenation for 24 hrs at different temperatures.

Reaction temperature, °C	%BQ reacted to HQ	%BQ incorporated	Coal hydrogen removed	
			%, coal basis	%, coal hydrogen basis
100	4.8	5.9	0.26	5.0
115	5.9	6.5	0.32	6.1
130	12.9	25.6	0.74	14.3
180	30.5	45.8	1.74	33.5

Fig. 1. BQ Mass Balance

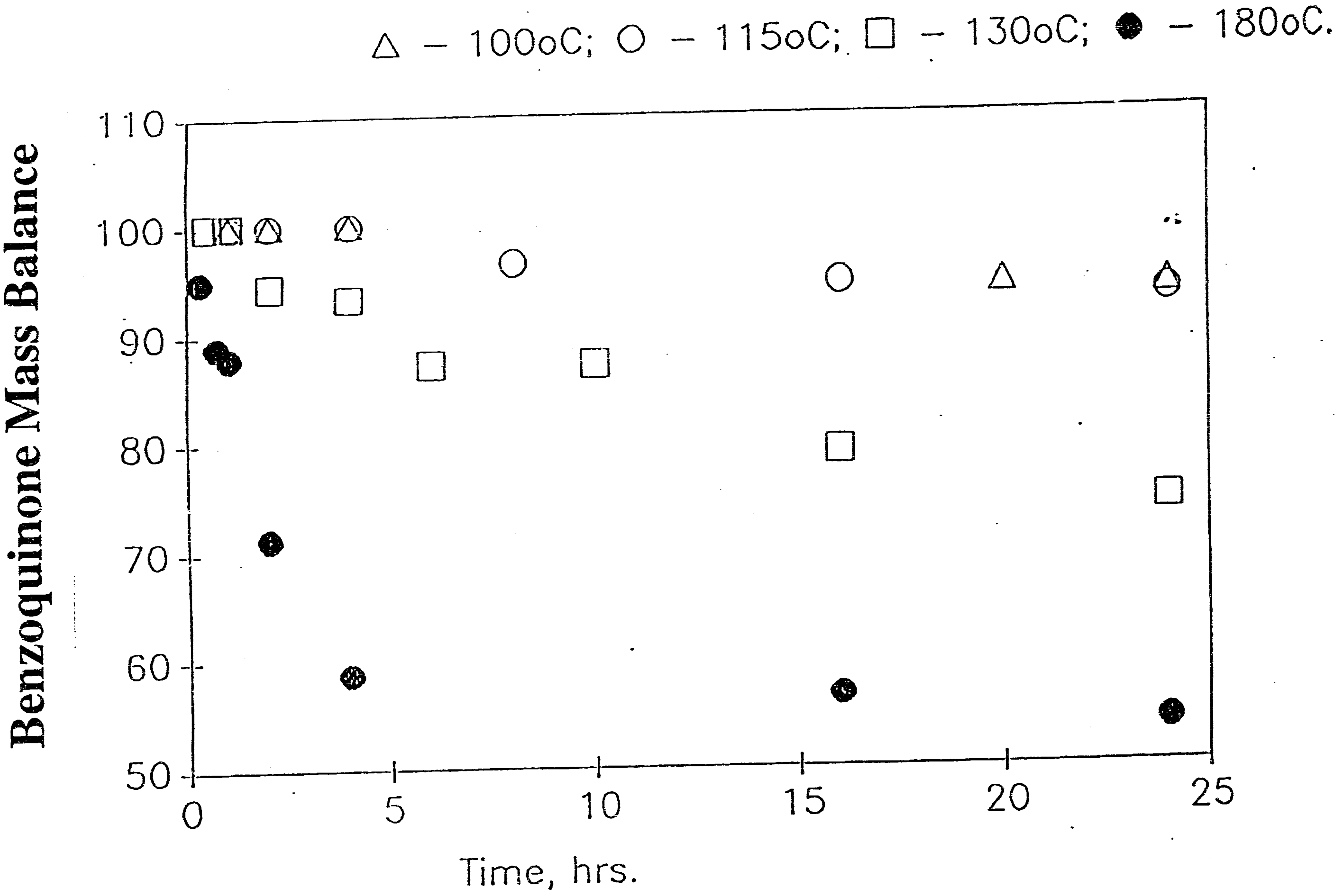


Fig. 2. Coal Dehydrogenation by Benzoquinone

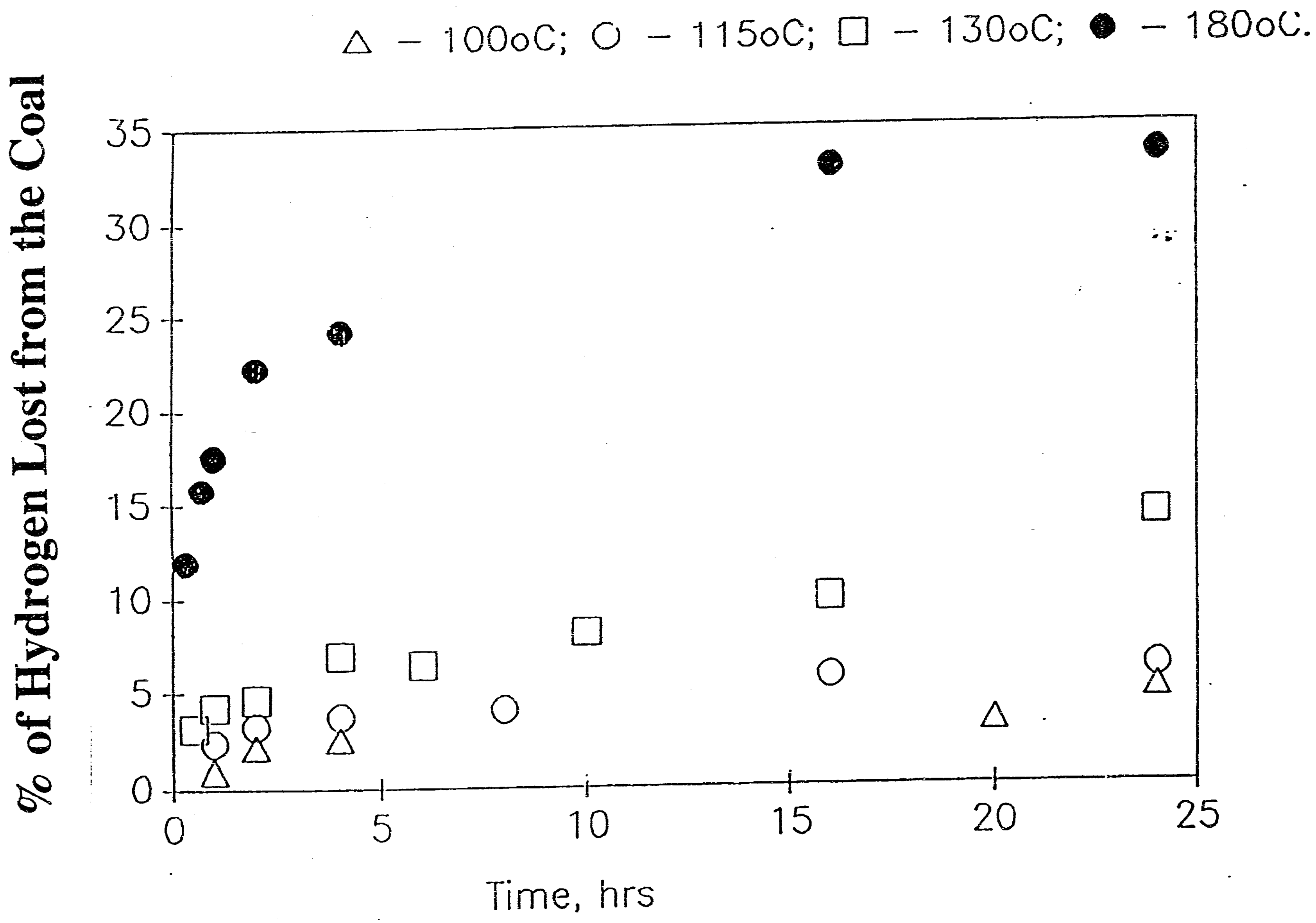


Fig. 3. Reactions of Coal with Benzoquinone

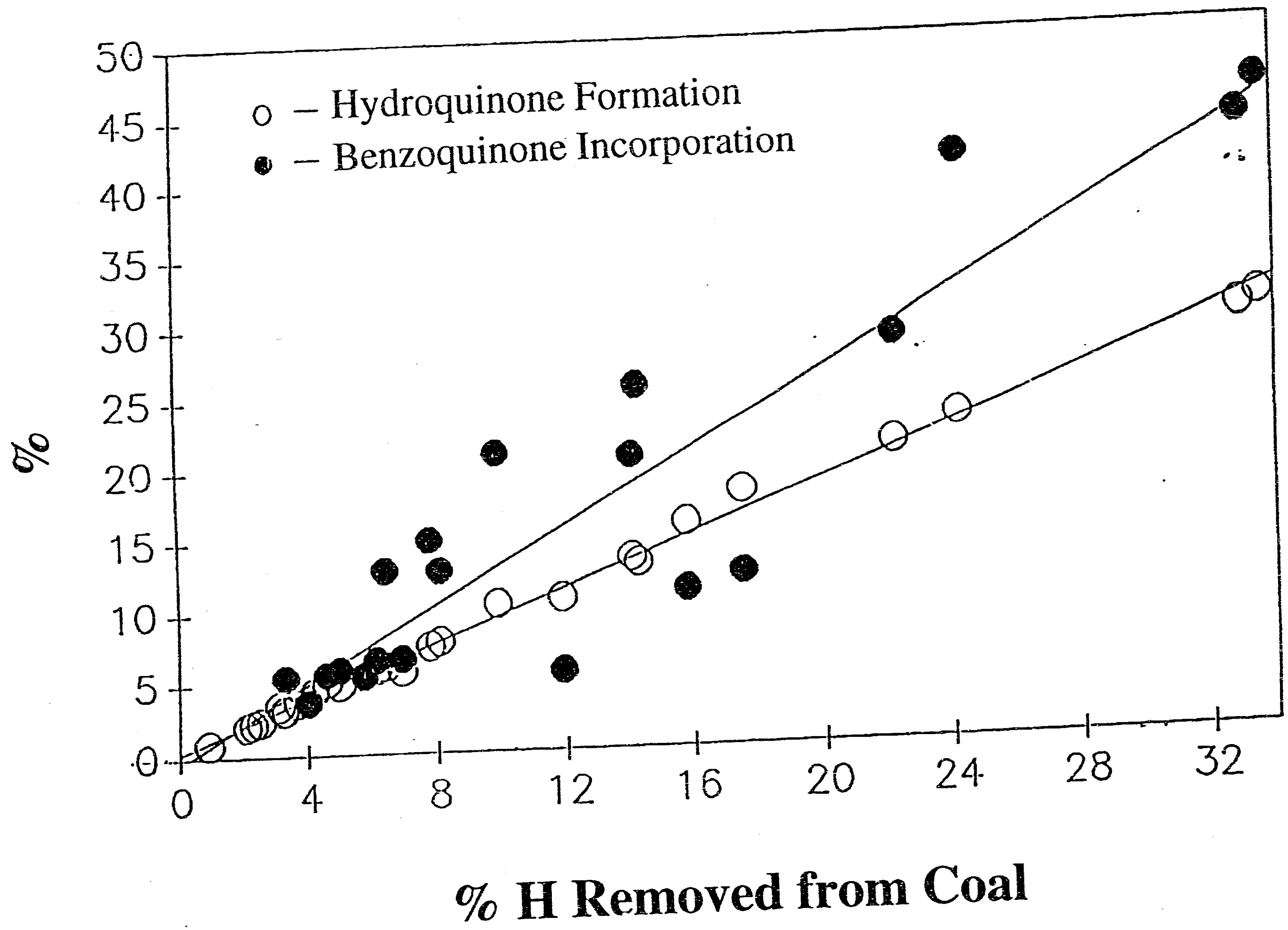
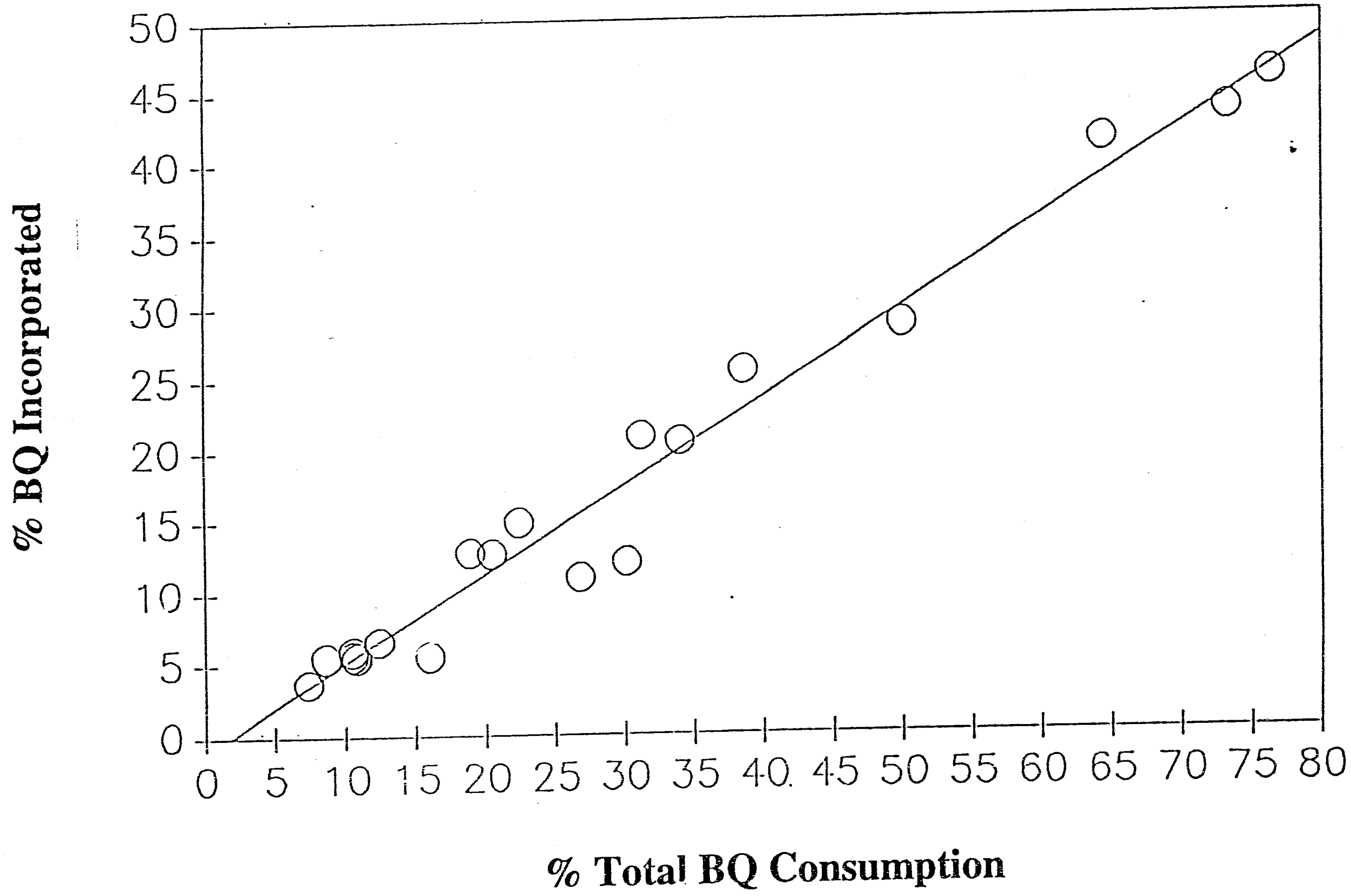


Fig. 4. BQ Incorporation depending on the total BQ Consumption



DATE FILMED

8 / 28 / 92