

EFFECT OF TEMPERATURE PROGRAMMING ON THE LIQUEFACTION
OF INDIANHEAD LIGNITE IN AN INORGANIC (H₂S-H₂O) SOLVENT SYSTEM

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ABSTRACT

High conversions can now be achieved using lower reactor temperatures and a temperature programming technique. Various temperature programs using times between 7.5 and 60 minutes and temperatures from 300° to 480°C were used to liquefy Indianhead lignite. The inorganic solvent system H₂S-H₂O was used in conjunction with CO, H₂ and pyrrhotite as the liquefaction media. Programming the temperature produced higher THF soluble and cyclohexane soluble yields than the use of isothermal temperatures. The maximum overall conversions obtained to date using temperature programming were 94.8% THF solubles, 83.2% toluene solubles and 70.5% cyclohexane solubles. THF-soluble conversions over 90%, were obtained at 350°C with temperature programming.

INTRODUCTION

Most modern coal liquefaction processes consist of heating a coal in the presence of a hydrogen donor solvent and an overpressure of reducing gas. The theory behind such procedures is that coal molecules are homolytically cleaved at the elevated temperature (equation 1) and then hydrogenated by either the solvent (equation 2) or the reducing gases (equation 4) (1-4). Complicating this scenario is the possibility that thermally generated coal radicals dimerize to produce high molecular weight products (equation 5). The occurrence of radical-radical reactions and their deleterious effect on coal liquefaction yields have been reported (5).



When the above mechanism operates during coal liquefaction, maximum liquid yields will be produced when the rate of coal-derived radical formation does not exceed the rate of hydrogen atom donation. If coal radicals are generated rapidly by a sudden thermal jump, then the capability of the solvent/gas system to donate hydrogen atoms by equations 2 and 3 might not be able to compete effectively with the dimerization step (equation 5). The goal of this investigation was to use various temperature programs to match the rate of radical production with the solvent/gas system's ability to cap these radicals and determine if such a procedure could substantially increase liquefaction

yields. Initial reports on the use of temperature programming have been favorable (6,7).

EXPERIMENTAL

A 12-ml batch autoclave (8) was used for the present study. For all reactions, 1 g of as mined Indianhead (Zap, ND) lignite ground to > 200 mesh was charged along with 1 g H₂O, 0.117 g pyrrhotite, Fe₇S₈, ground to > 200 mesh, 250 psi H₂S, 490 psi CO₂ and 490 psi H₂ into the autoclave. The heating block was preheated to the initial temperature, and the autoclave reached the initial temperature 2.0 min after insertion. After reaction, the products were washed with the desired solvent into a glass fiber soxhlet extraction thimble and extracted until constant weight was achieved. The proximate and ultimate analyses of Indianhead lignite are: moisture 29.5%, ash 9.0% moisture free (mf), carbon 65.0% mf, hydrogen 4.2% mf, nitrogen 1.9% mf, sulfur 0.8% mf and O₂ 19.1% mf by difference.

RESULTS

The results obtained from employing various temperature programs to liquefy Indianhead (Zap, ND) lignite are shown in Tables 1 and 2. The temperature programs used are portrayed in Figure 1. Use of Figure 1 in conjunction with Tables 1 and 2 will simplify the correlation of the temperature programs to conversion levels.

Simply increasing the residence time of lignite in the autoclave at 300°C (Figure 1, +A+B+C+D) initially enhanced the conversion to tetrahydrofuran (THF), toluene and cyclohexane solubles (Table 1). When the reaction was continued for longer times, e.g., 60 minutes, the THF-soluble products decreased in amount from that of shorter reaction times at that temperature.

Increasing the temperature from 300°C to 350°C (Figure 1, +E+F+G+H) enhanced the conversion to THF, toluene and cyclohexane solubles. Leaving the autoclave at 350°C for times up to 37.5 minutes (Figure 1, point G) produced increased yields of all three categorized products. Once this time was reached, no further increases in product yields were obtained by extending the residence times; in fact, a slight decrease in THF solubles was noted.

Employing a final reaction temperature of 400°C (Figure 1, +I+J+K+L) yielded higher levels of conversion products than 300° or 350°C. Increasing the residence time at this temperature to a total time of 20.0 min (Figure 1, point J) increased all product yields. Further increases in the residence time had little effect on the THF-soluble product yield while the toluene solubles increased then decreased with residence time and the cyclohexane solubles increased slowly.

When 450°C was the final reaction temperature (Figure 1, +M+N+O) prolonged residence times increased the toluene soluble products but had no effect on the THF and cyclohexane-soluble yields. Increasing the temperature to 480°C (Figure 1, +P) enhanced the cyclohexane solubles but did not increase THF-soluble yields.

The use of temperature programming (varied heating rates up to a maximum temperature) enhanced liquefaction yields over isothermal employment of this maximum temperature (Table 2). The THF- and cyclohexane-soluble yields at 450°C are both much greater in the programmed runs than in the isothermal ones.

Results obtained from temperature programs at which an initial heating period at 300°C was employed are shown in Table 3 and Figure 2. The conversions to THF solubles so obtained were larger than the those already

described. This demonstrates that the heating rate of the initially chosen program was too fast to produce maximum conversions. The toluene and cyclohexane solubles were also generally but not uniformly higher when the second program was used instead of the first.

DISCUSSION

The results of the temperature programmed runs demonstrate that the rate at which a liquefaction system is heated can dramatically vary the extent of conversion observed. The temperature program to 480°C produced slightly higher yields than the isothermal case. The temperature program to 450°C produced higher conversions than the isothermal use of this temperature. With temperature programming to 350°C in the more refined mode of Figure 2 (data in Table 3), THF-soluble products were produced in yields of 91.6-94.6%. These results are consistent with the hypothesis that enhanced liquefaction yields can be obtained if the coal-derived radicals are generated slowly in order to enhance the efficiency of the hydrogen donating media. Therefore, high conversion levels can be obtained through the employment of lower temperatures via the temperature programming technique.

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Table 1. Effect of Temperature Programming on the Liquefaction of Indianhead Lignite in H₂O-H₂S.

Final Temp. °C	Total Time (min)	Temp. Program ^f	Conversion % ^e		
			THF	Toluene	Cyclohexane
300	7.5	A	14.8	13.8	13.0
	20.0	B	50.2	16.4	17.2
	37.5	C	50.4	14.4	19.0
	60.0	D	28.2		
350 ^a	7.5	E	33.0	17.2	20.5
	20.0	F	71.8	24.9	24.1
	37.5	G	76.9	33.6	27.8
	60.0	H	72.2	32.8	28.5
400 ^b	10.0	I	47.2	29.6	26.5
	20.0	J	79.1	48.5	35.4
	37.5	K	77.7	60.1	42.4
	60.0	L	80.8	54.6	48.9
450 ^c	22.5	M	77.1	49.7	38.1
	37.5	N	82.8	58.3	56.7
	60.0	O	84.9	81.8	56.9
480 ^d	60.0	P	82.6	-	70.4

- a. Temperature programmed by ramping from 300-350°C for 2.5 min.
- b. Temperature programmed by ramping 300-350°C for 2.5 min, 5 min @ 350°C, ramping 2.5 min to 400°C.
- c. Temperature programmed by ramping 300-350° 2.5 min, 5 min @ 350°C, ramping 2.5 min to 400°C, 5 min @ 400°C, 20 min to 450°C.
- d. Temperature programmed by ramping from 300-350°C in 2.5 min, 5 min @ 350°C, ramping 2.5 min to 400°C, 10 min @ 400°C, 2.5 min ramp to 450°, 15 min @ 450°C, 22.5 min ramp to 480°C.
- e. The % of MAF lignite soluble in stated solvent.
- f. See figure 1.

Table 2. Comparison of Isothermal and Programmed Reactions.

Final Temperature °C	Total Time (min)	Temp. Program ^d	Conversion % ^a		
			THF	Toluene	Cyclohexane
480 ^b	60	Isothermal	76.4		
480 ^b	60	P	82.6		
450 ^c	37.5	Isothermal	64.7	61.1	49.6
450 ^c	37.5	N	82.8	58.3	56.7

- The % of MAF lignite soluble in stated solvent.
- Temperature programmed by 2.5 min ramp 300-350°C, 5 min @ 350°C, 2.5 min ramp to 400°C, 10 min @ 400°C, 2.5 min ramp to 450°C, 15 min @ 450°C, 22.5 min ramp to 480°C.
- Temperature programmed by 2.5 min ramp to 350°C, 5 min @ 350°C, 2.5 min ramp to 400°C, 10 min @ 400°C, 2.5 min ramp to 450°C.
- See Figure 1.

Table 3. The Conversion of Indianhead Lignite Using Initial Heating at 300°C.

Final Temp. °C	Total Time (min)	Temp. Program ^d	Conversion % ^c		
			THF	Toluene	Cyclohexane
350	40 ^a	Q	91.6	41.3	32.2
350	80 ^a	R	94.6	51.7	39.3
400	37.5 ^b	S	93.1	44.8	34.5
400	57.5 ^b	T	94.8	83.2	56.6

- Temperature programmed by 17.5 min @ 300°C, 2.5 min ramp to 350°C.
- Temperature programmed by 17.5 min @ 300°C, 2.5 min ramp to 350°C, 15 min @ 350°C, 2.5 min ramp to 400°C.
- The % of MAF lignite soluble in stated solvent.
- See Figure 2.

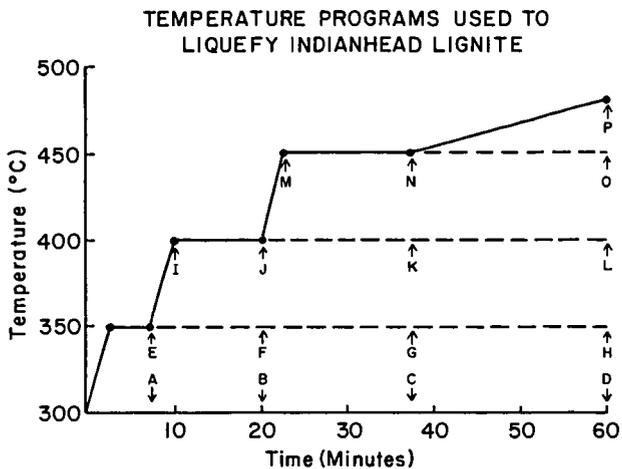


Figure 1. Temperature programs used to obtain the data in Table 1.

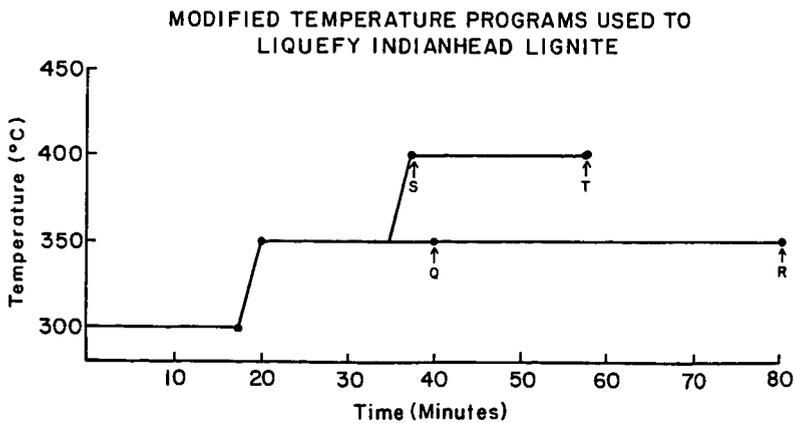


Figure 2. Temperature programs used to obtain the data in Table 3.