

TEMPERATURE PROGRAMMED AQUEOUS LIQUEFACTION EXTENDED TO SUPERCRITICAL CONDITIONS

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INTRODUCTION

Since coal contains highly diverse molecular structures with chemical bonds of various dissociation energies, the use of one single preselected reactor temperature to accomplish liquefaction is difficult to defend. Isothermal reactor conditions will likely result in the rapid rupture of weak bonds, a modest rate of cleavage of intermediate strength bonds, and probably leave the strong ones untouched. In attempts to address the chemical diversity within coals, the concepts of staged liquefaction and temperature programmed liquefaction have been devised (1-5) and the success of these efforts are encouraging.

Staged liquefaction is defined as using two or possibly more different temperatures over a specified time period to accomplish liquefaction. Temperature programming is defined as the raising of the reactor temperature through a defined sequence of temperatures over the liquefaction time period. In essence, the latter is staged liquefaction with up to an infinite number of temperature stages. The terminology for the latter is adapted from its common usage in chromatography.

The concept of temperature programming was developed as a technique to match the slurry medium's ability to donate hydrogen atoms with the rate of radical production from the coal. The specific objective is to prevent the newly formed coal radicals from undergoing retrograde dimerization reactions by allowing adequate time for the slurrying medium to donate hydrogens to them.

Temperature programming for liquefaction reactors using H_2O-H_2S and Indian Head lignite in the subcritical temperature region, 300-350°C, gave higher yields than comparable ones using either 300°C or 350°C isothermal conditions (1,2). The temperature program profile was designed with the aid of thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) (1-3,7,8).

The objective of this study is to extend the use of temperature programming of liquefaction reactions beyond the subcritical temperature region of the slurrying liquid, H_2O-H_2S (1,2,9). ESR, TGA and DTA data are employed in the design of the temperature programs. The critical temperature of water in these reactors is approximately 374°C. However, since it is known to vary with the gaseous composition of mixtures.

EXPERIMENTAL

A 12-ml bath autoclave was used for these experiments (10). For all reactions, 1 g of as-mined Indian Head lignite (Zap, ND) ground to 200 mesh was charged along with 1 g H_2O , 0.117 g pyrrhotite ground to 200 mesh, 1.73 MPa H_2S , 3.39 MPa CO and 3.39 MPa H_2 into the autoclave. The heating block was preheated to the initial temperature, and the autoclave, when inserted into the heating block, reached 300°C 2.0 min. after insertion. Then, the heating block temperature was manually varied from 300 to the final temperature with the appropriate temperature program. 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 yields were calculated using the mass of undissolved solid on the moisture- and ash-free basis. The proximate and ultimate analyses of Indian Head lignite are: moisture 29.5%, ash 9.0% moisture-free(mf), carbon 65.0% mf, hydrogen 4.2%, nitrogen 1.9% mf, sulfur 0.8% mg and oxygen 19.1% mf by difference.

RESULTS AND DISCUSSION

The rapid progression of temperature profiles (rapid profiles) employed herein are portrayed in Figure 1, and the slow progression of temperature profiles (slow profiles) used for this study are defined in Figure 2. The results obtained from using various temperature programs to liquefy Indian Head lignite are shown in Figures 3-9. Figure 1 illustrates the rapid profiles used to obtain the yield data of Figures 3-7 (points A through P). Figure 2 similarly portrays the slow profiles used to obtain the yield data of Figures 8 and 9 (points Q through T). Hereafter, when three percentage yields are given as the data from a given set of conditions, the three percentages refer to THF-, toluene-, and cyclohexane-solubility yields, respectively. The selection of the plateau temperatures of the temperature program used herein, 300°, 350°, 400° and 450° is discussed in the preceding article (2).

The isothermal data illustrated in Figure 3 and Table 1 serve as the baseline liquefaction yield data against which the yield data of the temperature programmed runs can be compared for relative effectiveness. When the residence time at 300°C is increased (programs A to D of Figure 1), the conversion to tetrahydrofuran (THF)-soluble products is enhanced (Figure 3).

When the liquefaction reactor temperature is isothermally kept at 350°C for 37.5 minutes, the conversions are improved by 22%, 23% and 11% (program G of Figure 1 Figure 4) from that of the 37.5-minute, 300°C isothermal reaction (program C of Figure 1, Figure 3). No appreciable further increases in the soluble product yields occurred by extending the residence time at 350°C from 37.5 to 60 minutes (programs G to H of Figure 1, Figure 4).

When the liquefaction reactor temperature is temperature programmed to proceed from 300 to 400°C over 60 minutes using the rapid profile (program L of Figure 1, Figure 5), the yields improved from that of the 350°C isothermal reaction (program H of Figure 1) by an additional 9%, 23% and 22%. When compared to the 400°C, 60-minute isothermal reaction, the 400°C programmed reaction gave yields which were improved by 8%, -14%, and 14%. When residence time at 400°C was increased from 0 to 40, minutes the cyclohexane-soluble product yields further improved (programs J to L of Figure 1, Figure 5) but the THF- and toluene-soluble product yields were essentially unchanged.

When the liquefaction reactor temperature was programmed to proceed from 300 to 450°C over 60 minutes using the rapid profile (program O of Figure 1, Figure 6), the product yields further increased from that of the 60-minute, 300 to 400°C program L by an additional 4%, 30%, and 9% (Figure 5). The residence time at 450°C (programs N to O of Figure 1) enhanced the toluene-soluble yield but had little effect on the THF- and cyclohexane-soluble product yields. The 300 to 450°C temperature programmed product yields at 37.5 minutes are +20%, -4%, and +8% changed from the yields obtained under comparable 450°C isothermal conditions (Table 1).

When the liquefaction reactor temperature is programmed from 300 to 480°C over 60 minutes using the rapid profile (program P of Figure 1, Figure 7), the cyclohexane-soluble product yield is enhanced and the THF-soluble product decreased from that of the 300-450°C reaction (program O of Figure 1, Figure 6). The 300-480°C, 60-minute programmed reaction provides 7% greater THF-soluble product yield than that of isothermal reaction of 480°C for 60 minutes (Table 1).

When the liquefaction reactor temperature is programmed from 300 to 350°C over 37.5 minutes using the slow profile (program Q of Figure 2, Figure 8), the product yields are 4%, 2%, and 1% increased from that of the comparable 350°C, 37.5-minute isothermal reaction (Figure 4). However, the differences are not statistically significant. At 60 minutes (programs Q to R of Figure 2), the corresponding yields are increased by 14%, 13%, and 6% from that of the related isothermal program H of Figure 1 (Figure 4).

When the liquefaction reactor temperature is temperature programmed to proceed from 300 to 400°C using the slow profile (program T of Figure 2, Figure 9), the yields are increased by 7%, 14%, and 4% from that of the comparable related rapid profile (program L of Figure 1, Figure 5) and 14%, 9%, and 20% from that of the 60-minute, 400°C isothermal reaction (Table 1). Residence time at 400°C was valuable in enhancing both the toluene- and cyclohexane-soluble yields (Figure 9).

In summary, the slow 300-400°C profile gives 95%, 83%, and 57%, the rapid 300-400°C profile gives 88%, 59%, and 53%, and the 400°C isothermal run produces 81%, 72% and 37% soluble product yields for the 60-minute reaction time.

CONCLUSIONS

Temperature programmed liquefaction gives superior yields compared to the corresponding isothermal counterpart and is dependent upon the nature of the temperature program profile. In a H₂O/H₂S medium using CO/H₂/pyrrhotite/Indian Head coal over the 300-450°C temperature range, the use of two designed temperature program profiles is examined: one with a rapid progression of temperatures and a second with a slow progression. The liquefaction efficiency is measured by the yields of cyclohexane-, toluene-, and tetrahydrofuran-soluble products formed. The relative liquefaction yields for 60-minute reactions are: slow profile > rapid profile > isothermal. The rate of temperature progression through the three sequential 50-degree temperature segments influences the three yields differently. The residence time at 300°C is important in producing respectable yields of THF-soluble products, the 300-350°C temperature range further improves all three product yields, the 350 to 400°C temperature range primarily improves the yields of toluene- and cyclohexane-soluble products, and the 400-450°C temperature region further improves the toluene-soluble product yields. No special yield effects are observed on going from subcritical to supercritical aqueous conditions in the course of the temperature programs.

ACKNOWLEDGEMENT

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Table 1. Conversion Yields Using Isothermal Conditions

Temp. °C	Time, min	Conversion yields, % ^a		
		THF	Toluene	Cyclohexane
300	60	68	10	10
350	60	81	10	10
400	60	81	72	37
450	37.5	70	67	54
480	60	76	na	na

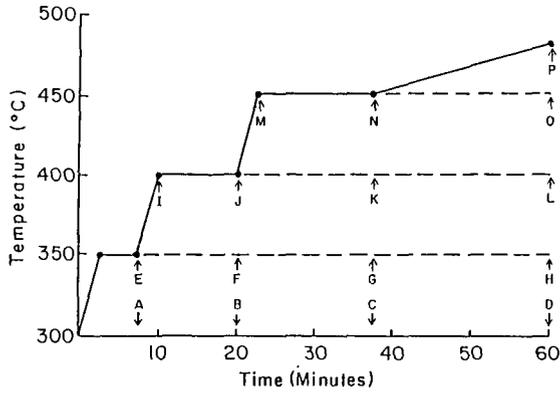


Figure 1. Rapid temperature progression programs (rapid profile) used to liquefy Indian Head lignite.

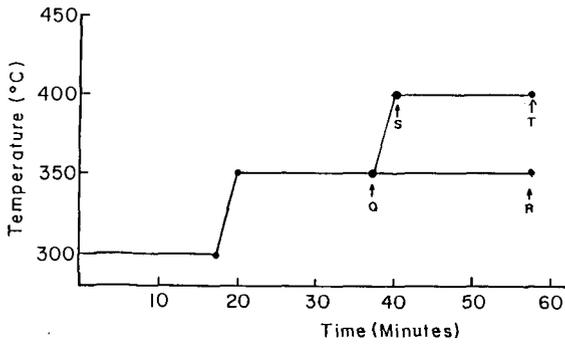


Figure 2. Slow temperature progression programs (slow profile) used to liquefy Indian Head lignite.

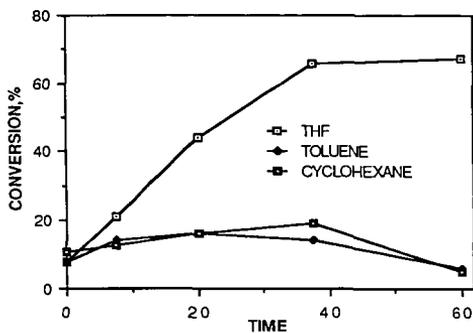


Figure 3. The yields of soluble products obtained as a function of time isothermally at 300°C.

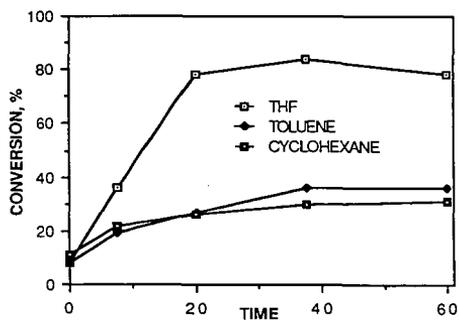


Figure 4. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 350°C.

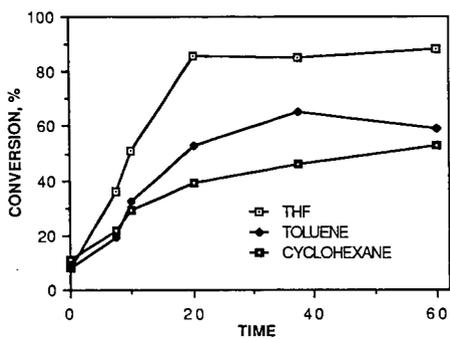


Figure 5. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 400°C.

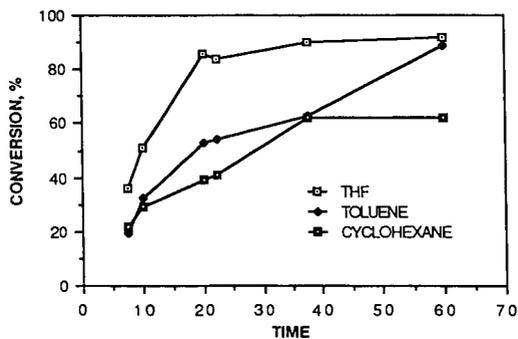


Figure 6. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 450°C.

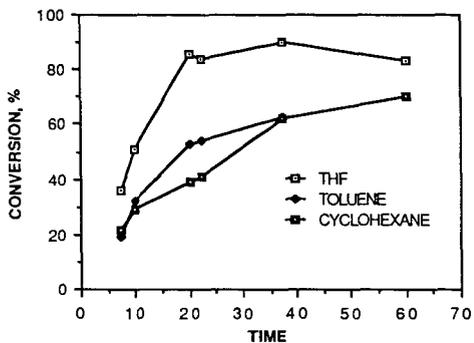


Figure 7. The yields of soluble products obtained as a function of time using the rapid profile from 300 to 480°C.

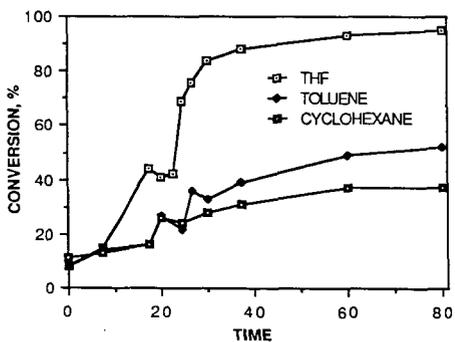


Figure 8. The yields of soluble products obtained as a function of time using the slow profile from 300 to 350°C.

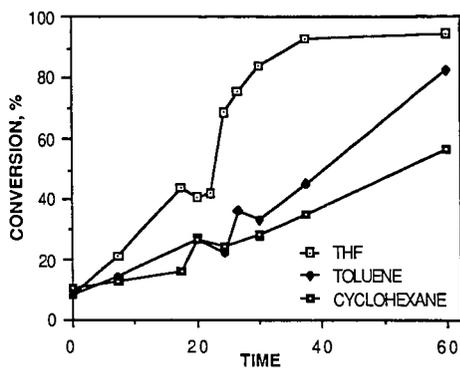


Figure 9. The yields of soluble products obtained as a function of time using the slow profile from 300 to 400°C.