# SHORT CONTACT TIME DIRECT COAL LIQUEFACTION
# USING A NOVEL BATCH REACTOR

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Quarterly Report
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# INTRODUCTION

The objective of this research is to optimize the design and operation of the bench scale batch reactor (SCTBR) for coal liquefaction at short contact times (0.01 to 10 minutes or longer). Additional objectives are to study the kinetics of direct coal liquefaction particularly at short reaction times, and to investigate the role of the organic oxygen components of coal and their reaction pathways during liquefaction. Many of those objectives have already been achieved and others are still in progress. This quarterly report covers further progress toward those objectives.

Much of the previous quarterly report was concerned mainly in the retrograde reactions occurring during the liquefaction process. This report is largely devoted to the kinetics and mechanisms of the liquefaction process itself and the influence of the liquefaction solvents.

Understanding the mechanisms of uncatalyzed direct coal liquefaction by means of reaction kinetics has been a long sought goal. Curran et al. in 1967 (1) and Wiser in 1968 (2) and Neavel in 1976 (3) measured the rates of liquefaction of various coals and postulated a free radical mechanism to explain the data obtained. The kinetics as determined by these and other workers is described in detail by Gorin in Chapter 27 of Elliott's Second Supplementary Volume to the Chemistry of Coal Series (4). However, it has been well known that most coals contain some material extractable by organic solvents. The solvents used in direct coal liquefaction would of course be expected to also extract soluble material as well as effect the liquefaction reaction. If the extractable material were a significant quantity in the coal, it would seriously affect the kinetics. Cassidy et al. (5,6) used a stirred autoclave with a sampling port at the bottom in their kinetic studies. They observed that hot charging the coal rapidly formed an oil which they considered to originate predominantly from the "guest component", i.e., extractables, in the lignite they studied. Also, the free radical nature of the liquefaction process would be expected to produce secondary reaction products which would complicate the kinetics as well as lead to retrograde products.

With this background, it seemed important to measure the kinetics of direct liquefaction at very short contact times where the extractables would be quickly removed and secondary reactions due to the free radical nature of the liquefaction would be minimized. By the use of our special Short Contact Time Batch Reactor (SCTBR), we have been able to show that direct coal liquefaction occurs both thermally and catalytically in at least two separate and distinct stages: an extraction stage and a slower breakdown and liquefaction of the coal macromolecules themselves (7,8).

It has been known for a long time that the characteristics of the liquefaction solvent has a profound effect on direct coal liquefaction. The amount of hydrogen consumed during the liquefaction process, the degree and quantity of retrograde reactions that occur, and the quality of the liquid products are all influenced by the process solvent (9). A number of analytical approaches have been developed to determine the important characteristics of the solvent for coal liquefaction (9). The hydrogen donor ability has clearly been important (10). However, such

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other characteristics of a liquefaction solvent as solubility parameter (9), content and type of higher aromatic hydrocarbons (11), and phenolic content have also been found to be significant (9). Finseth et al. (12) have shown that the bulk of the hydrogen consumed from an uncatalyzed donor solvent liquefaction above 400 °C is consumed in gas generation, heteroatom removal and hydrogenolysis of the coal matrix. Wilson et al. (13) have also shown that the major role of hydrogen in uncatalyzed liquefaction is consumed by alkyl fission and hydrogenolysis reactions and not with hydrogenating aromatic rings. McMillan et al. (14) have postulated that a radical hydrogen transfer process along with donor solvent capping of thermally produced radicals from the coal as possible processes involved with the hydroaromatic donor solvents in coal liquefaction.

With the development of a short contact time batch reactor (SCTBR) (15,16), it is possible to study the kinetics of each stage and to measure the kinetic parameters of each. The uncatalyzed kinetics of two coals (Illinois #6 bituminous and Wyodak-Anderson subbituminous coals) investigated at reaction times from 10 s to 60 min are reported in this quarterly report. The influence of the processing solvent on the liquefaction rates, conversion profiles and the quality of the liquid product at a particular time is also reported in this quarterly report.

## EXPERIMENTAL

**Coal Studied.** Illinois #6 bituminous and Wyodak-Anderson subbituminous coals from the Argonne Premium Coal Sample program were investigated in this study. Proximate and elemental analyses, together with other analytical data, of these coals are available in the User's Handbook for the Argonne Premium Coal Sample program (17).

**Solvents Used.** Four solvents: 1,2,3,4-tetrahydroquinoline (98%), tetralin (99%), 1-methylnaphthalene (98%), and decahydronaphthalene (99+%) from Aldrich with different hydrogen donor abilities and solubility parameters have been used in the coal liquefaction experiments.

**Catalyst Used.** Molybdenum naphthenate (6.8 wt% molybdenum from Shepherd Chemical Co.) was the liquefaction catalyst used in this study. The catalyst was prepared by dissolving about 0.5 g molybdenum naphthenate (equivalent to about 0.9 wt% Mo based on the amount of the coal charged) in the processing solvent. The catalyst was then sulfided by reacting the solution with about 1 g of methyl disulfide during the transport into the reactor and liquefaction.

**Coal Liquefaction.** All liquefactions were run as mixtures of processing solvent (S) and coal (C) at a mass ratio of S/C = 8 to minimize the effect of changing processing solvent concentration during the reaction. About 4 grams of coal were used for each reactor run, together with the added processing solvent to make up the reactant slurry.

**Workup Procedures of the Reaction Products.** The product mixtures were filtered

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Similar conversion curves are obtained for the liquefaction of the Wyodak-Anderson subbituminous coal in tetralin (8 to one tetralin to coal by weight) (8). These curves show the characteristic stages of extraction, induction period and coal liquefaction similar to the Illinois #6 coal.

**Kinetic Analysis of Coal Liquefaction.** As shown in the previous section, three distinct phases in the coal liquefaction process in the absence of hydrogen and a catalyst are observed. The initial rapid conversion (in the first 30 to 60 s) is due to the extraction of a soluble fraction of the coal into the processing solvent. This is followed by a pseudo-induction period and then the slow conversion of the coal structure to liquid products. This pseudo-induction period is a transition interval which is due to the simultaneous occurrence of these two processes, a very rapid extraction which is ending and a relatively slower liquefaction of the coal matrix which is becoming dominant. Based on this hypothesis, the liquefaction conversion observed in experiments, therefore, is the sum of the conversions of these two processes:

$$ X = X_s + X_r \tag{2} $$

where X is the liquefaction conversion determined in the experiments; $X_s$ is the solubilizing conversion which is due to the extraction of the soluble materials in the coal; and $X_r$ is the liquefaction reaction conversion which is due to the chemical breakdown of the coal structure. From Eq. 2, the liquefaction rate is the sum of the derivatives of these conversions, i.e.,

$$ \frac{dX}{dt} = \frac{dX_s}{dt} + \frac{dX_r}{dt} \tag{3} $$

The extraction rate could be expressed by

$$ \frac{dX_s}{dt} = k_s (X_{s0} - X_s) \tag{4} $$

where $k_s$ is the extraction rate constant; $X_{s0}$ is the equilibrium level of extraction of coal under liquefaction conditions; and $X_s$ is the soluble fraction at time t. The breakdown rate for the coal matrix is given by

$$ \frac{dX_r}{dt} = k_r' \left( (1-X_{s0}) - X_r \right)^\alpha C_t^\beta P_{gas}^\gamma \tag{5} $$

where $k_r'$ is the reaction rate constant; $X_r$ is the liquefaction reaction conversion at time t; $C_t$ is the tetralin concentration; and $P_{gas}$ is the nitrogen or hydrogen pressure. When a large amount of tetralin is used in the liquefaction (for example, 8 to 1 of tetralin to coal ratio was used in this study), $C_t$ is approximately equal to a constant. $P_{gas}$ is held a constant during the liquefaction run in this study. Assuming $\alpha = 1$, Eq. 5 is simplified to

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$$\frac{dX_r}{dt} = k_r((1 - X_{s0}) - X_r) \tag{6}$$

Integrating with boundary conditions of $X_s = 0$ and $X_r = 0$ at $t = 0$ and substituting $(1 - X_{s0})$ by $X_{r0}$ which is defined to be the maximum conversion due to liquefaction reactions, Eqs. 4 and 6 become

$$\ln(1 - \frac{X_s}{X_{s0}}) = -k_s t \tag{7}$$

and

$$\ln(1 - \frac{X_r}{X_{r0}}) = -k_r t \tag{8}$$

respectively.

**Kinetics of Illinois #6 and Wyodak-Anderson Coal Liquefactions.** The plot of $\ln(1-X_s/X_{s0})$ against t for the Illinois #6 coal liquefaction in tetralin under 1000 psig $N_2$ at 390 °C is shown in Figure 2. The slope gives a measured rate constant for extraction of $k_s = 2.81$ with an $r^2$ of 0.97. The plot of $\ln(1-X_r/X_{r0})$ against t for the Illinois #6 coal liquefaction reaction process is illustrated in Figure 3. It shows two distinct reaction stages: a rapid one with a rate constant of 0.027 for the first 5 minutes, and a slower one of 0.0054 for times greater than 5 minutes. The kinetic parameters of the Illinois #6 and Wyodak-Anderson coal liquefactions evaluated by the proposed model are summarized in Table 1. As an example, Figure 4 shows experimental data and modelling curve at the reaction times up to 10 min for Wyodak-Anderson coal liquefaction in tetralin at 390 °C under 1000 psig $N_2$. It shows that the model fits the experimental data very well.

Rate constants of $k_s$ and $k_r$ at three temperatures (358, 390, and 408 °C) were used to estimate activation energies of extraction and liquefaction reaction processes. The plot of $\ln k_s$ against $1/T$ and $\ln k_r$ vs $1/T$ shown in Figures 5 and 6 give activation energies of 14 and 22 kcal/mol for the solubilization and liquefaction reaction processes, respectively.

It is of interest to compare these results with those obtained by others at higher conversion. Wiser (2) obtained an activation energy value of 28.8 kcal/mol for Utah bituminous coal liquefaction at 63 to 94% conversion. Curran et al. (1) obtained two values for a rapid and a slow rate with mean values of 30 and 38 kcal/mol on Pittsburgh Seam bituminous coal at 2.5 minutes and 2 hours, respectively. They used a process-derived solvent from 325 to 435°C. While the 22 kcal/mole value seems rather low, coal has obviously both weak and strong bonds which will be broken in order of their bond strength. The process derived solvent may strongly affect the relative amounts of the extraction and liquefaction stages in the Curran work. All of these values are low compared to the strength of carbon-carbon bonds and obviously the

activation energies observed by us and others reflects the reaction complexity as well as the particular bonds being broken.

**Effect of Gas Atmosphere on the Coal Liquefaction.** Conversions of the liquefaction of Illinois #6 and Wyodak-Anderson coals in tetralin at 390 °C for 30 min under 1000 psig $N_2$ or 1000 psig $H_2$ is shown in Figure 7. For the Illinois #6 coal, the liquefaction conversion in hydrogen was higher than in nitrogen. However, there was no difference for the Wyodak-Anderson coal liquefied in hydrogen or in nitrogen. The contents of pyritic sulfur in Illinois #6 and Wyodak-Anderson are 2.81 wt% and 0.17 wt%, respectively. This is a strong indication that pyrite in the Illinois #6 provides some catalysis for the liquefaction in the presence of hydrogen.

**Effects of Solvent, Catalyst, and Gas Atmosphere on the Coal Liquefaction.** Conversion vs. time curves of the thermal (without added catalyst) liquefaction of Illinois #6 coal in 1,2,3,4-tetrahydroquinoline (THQ), tetralin, and 1-methylnaphthalene, in decreasing order of hydrogen-donor ability, run under 1000 psig nitrogen at 408 °C are shown in Figures 8a and 8b for two different time intervals. The liquefaction conversions using 1-methylnaphthalene as a processing solvent shows distinct stages of liquefaction kinetics: a very rapid extraction and followed by an extremely slow liquefaction of the coal structure. The equilibrium extraction of the Illinois #6 coal using 1-methylnaphthalene was 30.7 wt%. This value is very close to that using tetralin as a processing solvent. The solubility parameters of 1-methylnaphthalene and tetralin are 20.3 and 19.4, respectively. This suggests that the extraction stage in the coal liquefaction is dominated by the solubility characteristics of the processing solvent used. However, the rates of coal structure breakdown in tetralin and in 1-methylnaphthalene were 0.0458 wt%/min and 0.00168 wt%/min, about 27 times different. For the very strong hydrogen donor solvent of 1,2,3,4-tetrahydroquinoline, the extraction stage becomes indistinguishable from the liquefaction of the coal structure. This is because the rate of coal structure breakdown in the very strong hydrogen donor solvent is close to the rate of extraction. The rate of coal structure breakdown measured in this solvent was 1.41 wt%/min. Comparison of the rates of the coal structure breakdown in 1,2,3,4-tetrahydroquinoline, tetralin, and 1-methylnaphthalene suggests that hydrogen transfer from the solvent may be the rate-determining step in uncatalyzed coal liquefaction. This is consistent with the observations that the activation energies for coal structure breakdown is much less than carbon-carbon bond strength (1,2).

Effects of solvent on the thermal liquefaction of the Illinois #6 coal in nitrogen and in hydrogen are illustrated in Figure 9. These data show that the very strong hydrogen donor solvent, such as 1,2,3,4-tetrahydroquinoline, gives much higher conversion than tetralin. More interestingly, the liquefaction conversion in this very strong donor solvent shows no sensitivity to gas atmosphere (i.e., in nitrogen or in hydrogen), indicating little if any hydrogen is derived from the molecular hydrogen in the case of a very strong hydrogen donor solvent used. On the other hand, the liquefaction in the poor hydrogen donor solvents, such as decahydronaphthalene and 1-methylnaphthalene, shows much lower conversion than in tetralin under nitrogen pressure. However, for these very poor hydrogen donor solvents, the liquefaction conversions of the Illinois #6 coal in hydrogen is much higher than that in nitrogen, showing strong sensitivity to

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gas atmosphere. These results suggest that, in a poor hydrogen donor solvent, the hydrogen needed in the liquefaction process must be mostly derived from molecular hydrogen when a hydrogenation catalyst is present in the parent coal (for example, the pyrite in the Illinois #6 coal) and/or is added (such as sulfided molybdenum naphthenate).

Effect of molybdenum naphthenate catalyst in different solvents on the Illinois #6 coal liquefaction is shown in Figure 10. Liquefaction conversions are always higher in tetralin than in 1-methylnaphthalene for both of the thermal and catalyzed liquefactions. However, with the added catalyst and hydrogen, the conversions in tetralin increased only by a factor of 53%, 31%, and 29% for 30 min liquefaction at 390 °C, 403 °C, and 420 °C, respectively, compared to those in 1-methylnaphthalene by a factor of 123% and 97% for 10 min at 397 °C and 30 min at 410 °C, respectively. These results indicate that the catalysis by an added hydrogenation catalyst in coal liquefaction is more responsive when a poor hydrogen donor solvent is used. They also suggest that a hydrogenation catalyst could be used to compensate for the lack of hydrogen donor ability of a processing solvent.

To quantitatively evaluate the effects of solvent, catalyst, and gas atmosphere for the coal liquefaction, specific liquefaction conversion ratios of $\alpha$, $\beta$, and $\gamma$ are defined using the coal liquefaction conversion in nitrogen as a reference, i.e.,

$$\alpha = \frac{X_{H_2}}{X_{N_2}}$$

$$\beta = \frac{X_{catalyst}}{X_{N_2}} \tag{9}$$

$$\gamma = \frac{X_{catalyst}}{X_{H_2}}$$

where $X_{N2}$ is the liquefaction conversion in nitrogen; $X_{H2}$ is the liquefaction conversion in hydrogen; and $X_{catalyst}$ is the catalyzed liquefaction conversion in hydrogen. The $\alpha$ is selected to evaluate the hydrogen gas effect. The larger the $\alpha$, the stronger the hydrogen gas effect. When $\alpha = 1$, it means there is no hydrogen gas effect in the coal liquefaction. The $\beta$ is calculated to evaluate the catalyst reactivity in hydrogen and the $\gamma$ is used to evaluate the net reactivity of the added catalyst. The data to show the combination of the effects of solvent, catalyst, and gas atmosphere on the Illinois #6 and Wyodak-Anderson coal liquefactions, together with the calculated specific ratios of $\alpha$, $\beta$, and $\gamma$, are summarized in Table 2. Based on the $\alpha$ values, the order of the hydrogen gas effect on the Illinois #6 coal liquefaction for different solvents was decahydronaphthalene $\sim$ 1-methylnaphthalene > tetralin > 1,2,3,4-tetrahydroquinoline. The stronger the hydrogen donor solvent, the less will be the hydrogen gas effect. In fact, there is no hydrogen gas effect on the Illinois #6 coal liquefaction for the very strong donor solvent of 1,2,3,4-tetrahydroquinoline for which $\alpha = 1$. The Wyodak-Anderson coal shows no hydrogen gas effect ($\alpha = 1$) during the liquefaction in tetralin. Based on the $\beta$ values, the order of the catalyst influence on coal liquefaction in different hydrogen donor

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solvents was 1-methylnaphthalene > tetralin. Furthermore, the higher the liquefaction temperature, the lower the catalyst influence on liquefaction conversion. This may be because, as temperature increases, the selectivity to liquid products during the liquefaction decreases. This is also supported by the $\gamma$ values for the liquefaction of the Illinois #6 in 1-methylnaphthalene.

## SUMMARY AND CONCLUSIONS

The direct liquefaction of coal shows distinct stages: an extraction stage and multiple slower stages representing the breakdown of various components of the coal structure. These only become apparent with a reactor system capable of accurately distinguishing conversions at reaction times as low as 10 seconds.

The liquefaction conversion observed in these experiments is the sum of two simultaneous processes of extraction and liquefaction of the coal structure. Based on this model, the liquefaction kinetics in each stage of the entire process can be adequately described.

The extraction stages in the bituminous and subbituminous coal studied to date are about two orders of magnitude faster than the structure breakdown stages and have correspondingly lower activation energies. The liquefaction of the coal structure itself also consists of multiple steps of different rate constants and activation energies. The rate of breakdown of the coal structure itself however is controlled in large measure by the strength of the hydrogen donor solvent, and the rate determining step in that structure breakdown may be the transfer of hydrogen from the solvent to the coal structure itself.

The extraction stage in the coal liquefaction is dominated by the solubility characteristics of the processing solvent. The liquefaction of Illinois #6 using 1-methylnaphthalene shows distinct stages of liquefaction kinetics similar to tetralin. However, compared to tetralin, it has an extremely slow breakdown rate of the coal structure. The equilibrium extraction for 1-methylnaphthalene was 30.7 wt% at 408 °C, which is very close to that (31.9 wt%) in tetralin. The extraction and coal structure breakdown stages of the Illinois #6 coal liquefaction in 1,2,3,4-tetrahydroquinoline, however, were indistinguishable.

A hydrogen atmosphere increases the thermal (uncatalyzed) conversion of Illinois #6, but had no effect on Wyodak-Anderson subbituminous coal. This is apparently due to the catalytic effect of pyrite (or pyrrhotite derived from the pyrite) in the Illinois #6 coal, since this coal contains substantial amounts of pyrite whereas the Wyodak-Anderson coal contains only trace amounts of pyrite.

The order of the hydrogen gas effect on the Illinois #6 coal liquefaction for different solvents was decahydronaphthalene ~ 1-methylnaphthalene > tetralin > 1,2,3,4-tetrahydroquinoline. The stronger the hydrogen donor solvent, the less the hydrogen gas effect. When a poor hydrogen donor solvent was used and a hydrogenation catalyst either was present

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in the coal itself (for example, pyrite in the Illinois #6 coal) or was added (such as sulfided molybdenum naphthenate catalyst), hydrogen is predominantly contributed by molecular hydrogen.

## PUBLICATIONS

One paper entitled "Kinetics of Coal Liquefaction at Very Short Reaction Times" has been submitted and accepted by *Energy & Fuels*. It is scheduled to issue in May of 1996. Two manuscripts have been submitted and accepted for presentation to the American Chemical Society national meeting in Orlando in August 1996 as follows:

1.  "Coal Liquefaction Kinetics" by Shaojie Wang, Keyu Wang, He Huang, Michael T. Klein and William H. Calkins*.

2.  "Effect of Solvent Characteristics on Coal Liquefaction" by He Huang, Shaojie Wang, Keyu Wang, Michael T. Klein and William H. Calkins*.

## FUTURE PROGRAM

1.  Apply the same kinetic analysis to Buelah Zap lignite, Blind Canyon bituminous coal, and Pittsburgh #8 bituminous coal.

2.  Continue to develop analytical methods to obtain the data on the oxygen species in coal and their reaction pathways during coal liquefaction.

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Table 1 The rate constants of the Illinois #6 and Wyodak coal liquefactions

| Coal | T,°C | time | Liquefaction stage | Rate constant k | $r^2$ |
|---|---|---|---|---|---|
| Illinois #6 | 358 | 0 - 2 min | Extraction | 0.848 | 0.996 |
| | | 0 - 60 min | Reaction | 0.00275 | 0.999 |
| | 390 | 0 - 1.5 min | Extraction | 2.81 | 0.997 |
| | | 0-5 min | Reaction (R1, fast) | 0.0276 | 0.999 |
| | | > 5 min | Reaction (R2, slow) | 0.00541 | 0.998 |
| | 408 | 0 - 1 min | Extraction | 6.05 | 0.998 |
| | | 0-10 min | Reaction (R1, fast) | 0.0458 | 0.972 |
| | | > 10 min | Reaction (R2, slow) | 0.00301 | 0.987 |
| Wyodak-Anderson | 390 | 0 - 0.5 min | Extraction | 11.8 | 0.996 |
| | | 0-15 min | Reaction (R1, fast) | 0.0195 | 0.995 |
| | | > 15 min | Reaction (R2, slow) | 0.0161 | 0.999 |

Table 2 Effect of solvent on the thermal and catalytic liquefactions of the Illinois #6 and Wyodak-Anderson coals in 1000 psig N2 or H2

| Sample | Coal | Solvent | T C | t min | Gas | Catalyst [Note 1] | X wt% [Note 2] | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|---|---|---|---|---|---|
| DOE00 | Illinois #6 | Tetralin | 390 | 30 | N2 | No | 42.6 | 1.09 | 1.53 | 1.41 |
| DOE07 | Illinois #6 | Tetralin | 390 | 30 | H2 | No | 46.3 | | | |
| DOE14 | Illinois #6 | Tetralin | 392 | 30 | H2 | Yes | 65.3 | | | |
| DOE09 | Illinois #6 | Tetralin | 404 | 30 | N2 | No | 54.4 | N.A. | 1.31 | N.A. |
| DOE16 | Illinois #6 | Tetralin | 402 | 30 | H2 | Yes | 71.2 | | | |
| DOE10 | Illinois #6 | Tetralin | 422 | 30 | N2 | No | 59.9 | N.A. | 1.29 | N.A. |
| DOE17 | Illinois #6 | Tetralin | 418 | 30 | H2 | Yes | 77.1 | | | |
| DOE14 | Illinois #6 | 1-methylnaphthalene | 398 | 10 | N2 | No | 24.7 | 1.41 | 2.23 | 1.58 |
| DOE15 | Illinois #6 | 1-methylnaphthalene | 396 | 10 | H2 | No | 34.9 | | | |
| DOE15 | Illinois #6 | 1-methylnaphthalene | 395 | 10 | H2 | Yes | 55.1 | | | |
| DOE18 | Illinois #6 | 1-methylnaphthalene | 409 | 30 | N2 | No | 33.7 | 1.63 | 1.97 | 1.20 |
| DOE18 | Illinois #6 | 1-methylnaphthalene | 412 | 30 | H2 | No | 55.1 | | | |
| DOE18 | Illinois #6 | 1-methylnaphthalene | 412 | 30 | H2 | Yes | 66.4 | | | |
| DOE18 | Illinois #6 | THQ [Note 3] | 412 | 30 | N2 | No | 85.6 | 1.00 | N.A. | N.A. |
| DOE18 | Illinois #6 | THQ | 415 | 30 | H2 | No | 85.5 | | | |
| DOE23 | Illinois #6 | Decahydronaphthalene | 400 | 30 | N2 | No | 22.2 | 1.49 | N.A. | N.A. |
| DOE23 | Illinois #6 | Decahydronaphthalene | 400 | 30 | H2 | No | 33.0 | | | |
| DOE08 | Wyodak-Anderson | Tetralin | 392 | 30 | N2 | No | 39.6 | 1.01 | N.A. | N.A. |
| DOE08 | Wyodak-Anderson | Tetralin | 390 | 30 | H2 | No | 39.8 | | | |

Notes:

1. Catalyst: Molybdenum naphthenate (equivalent to 0.9 wt% Mo) sulfided in-situ by methyl disulfide.
2. X: Liquefaction conversion on the daf (dry-ash-free) basis.
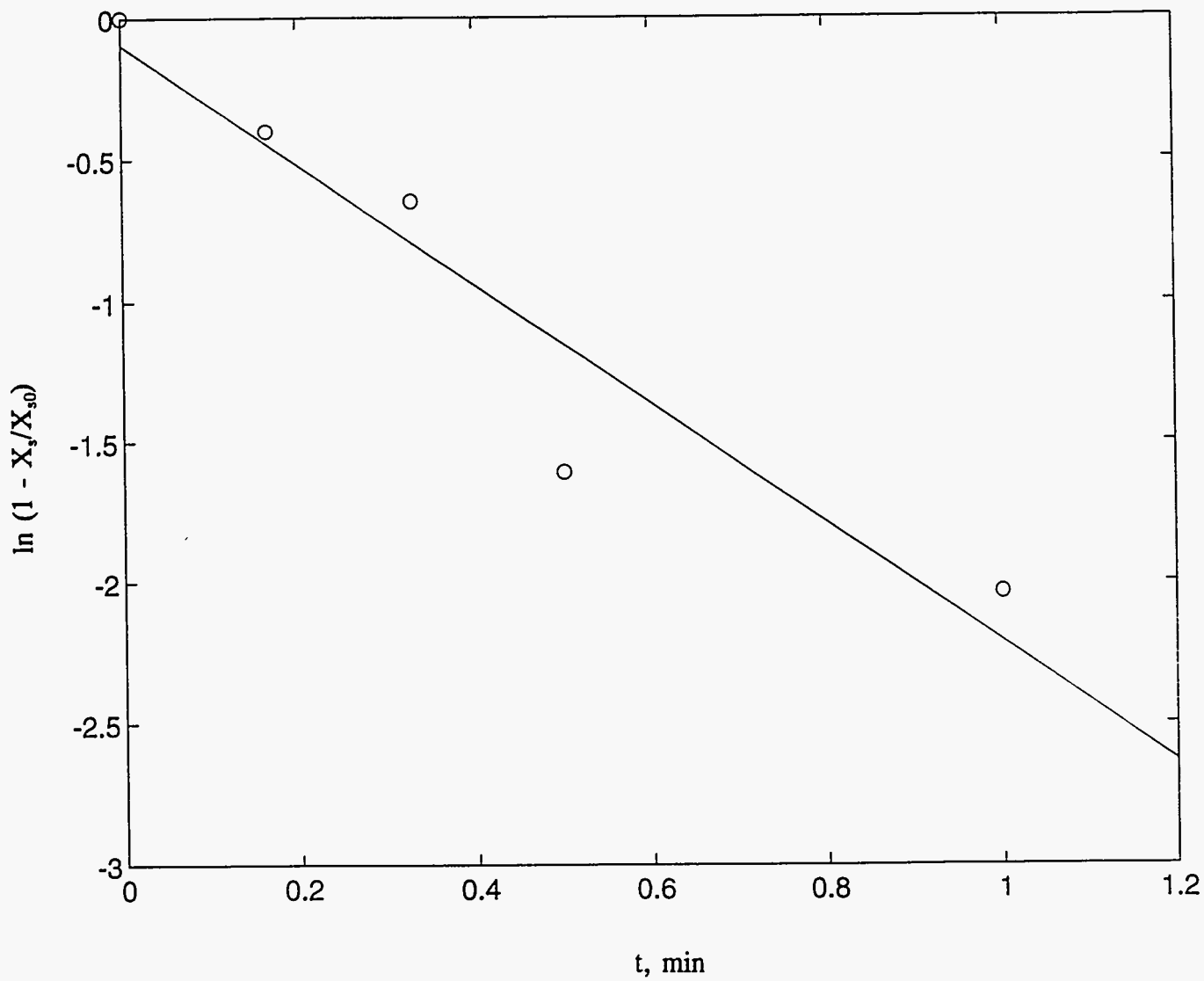3. THQ: 1,2,3,4 - Tetrahydroquinoline
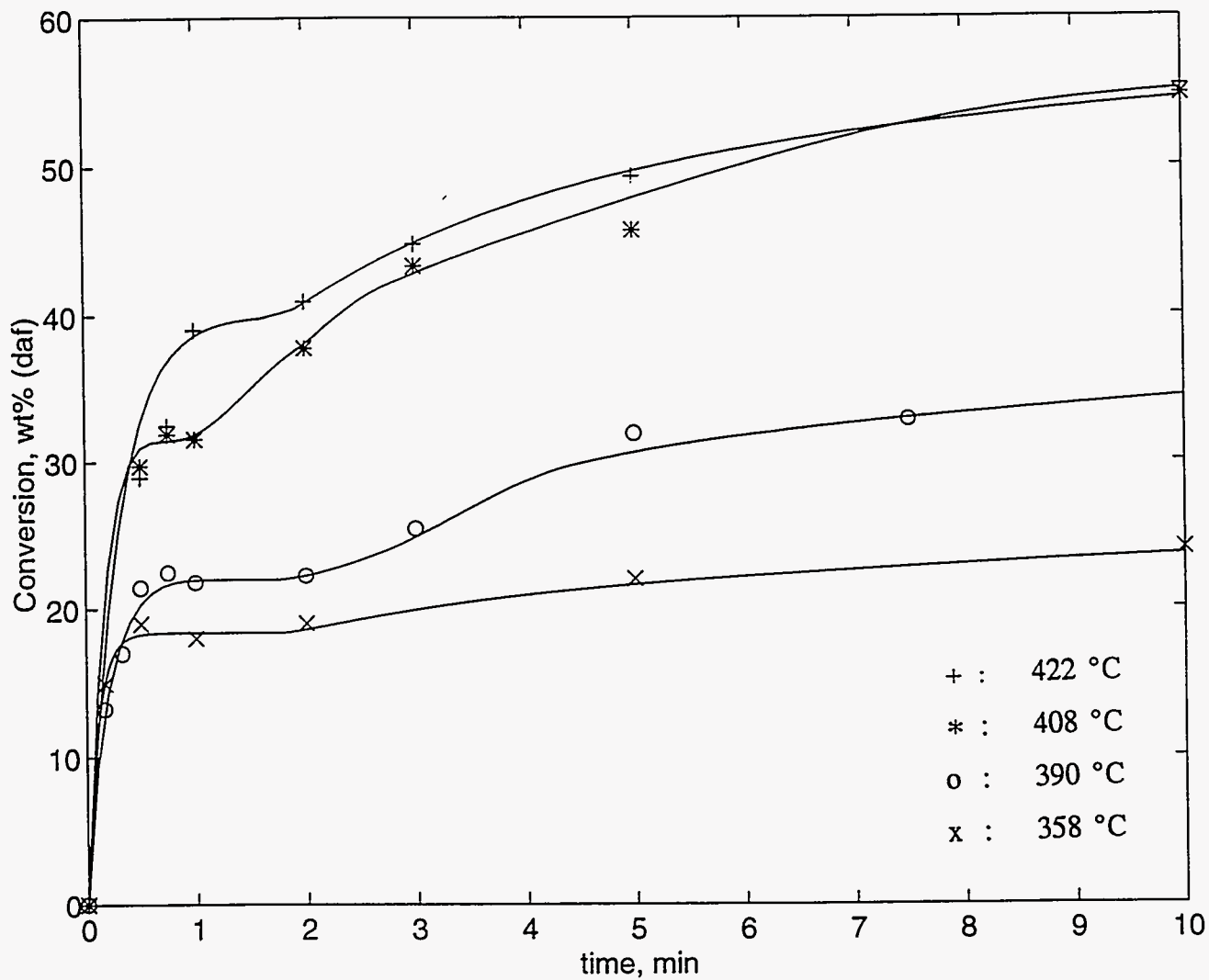
Conversion vs time for Illinois #6 coal liquefaction without added catalyst in tetralin (tetralin:coal = 8:1 mass ratio) under 1000 psig $N_2$ for short contact times.
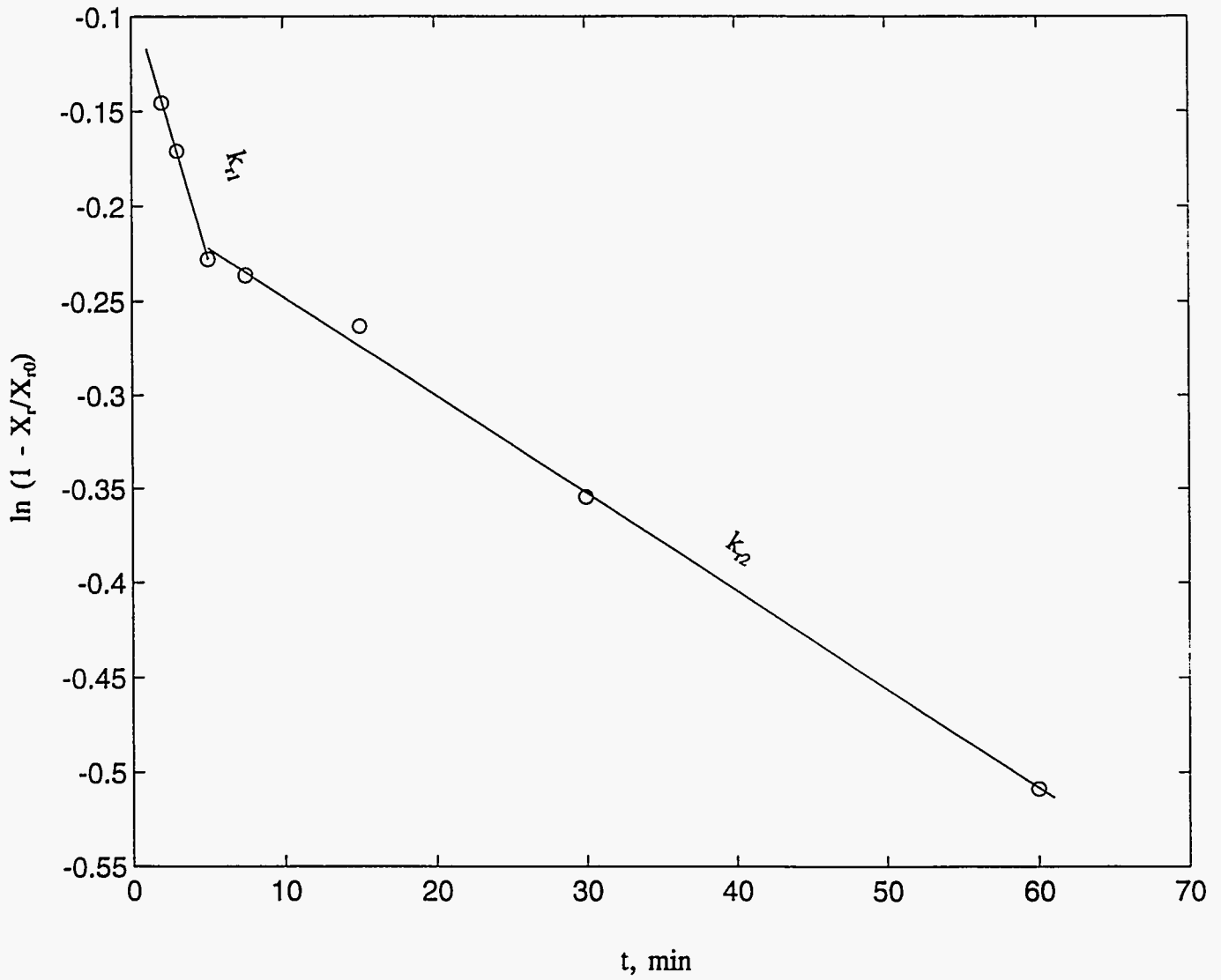
Figure 1a
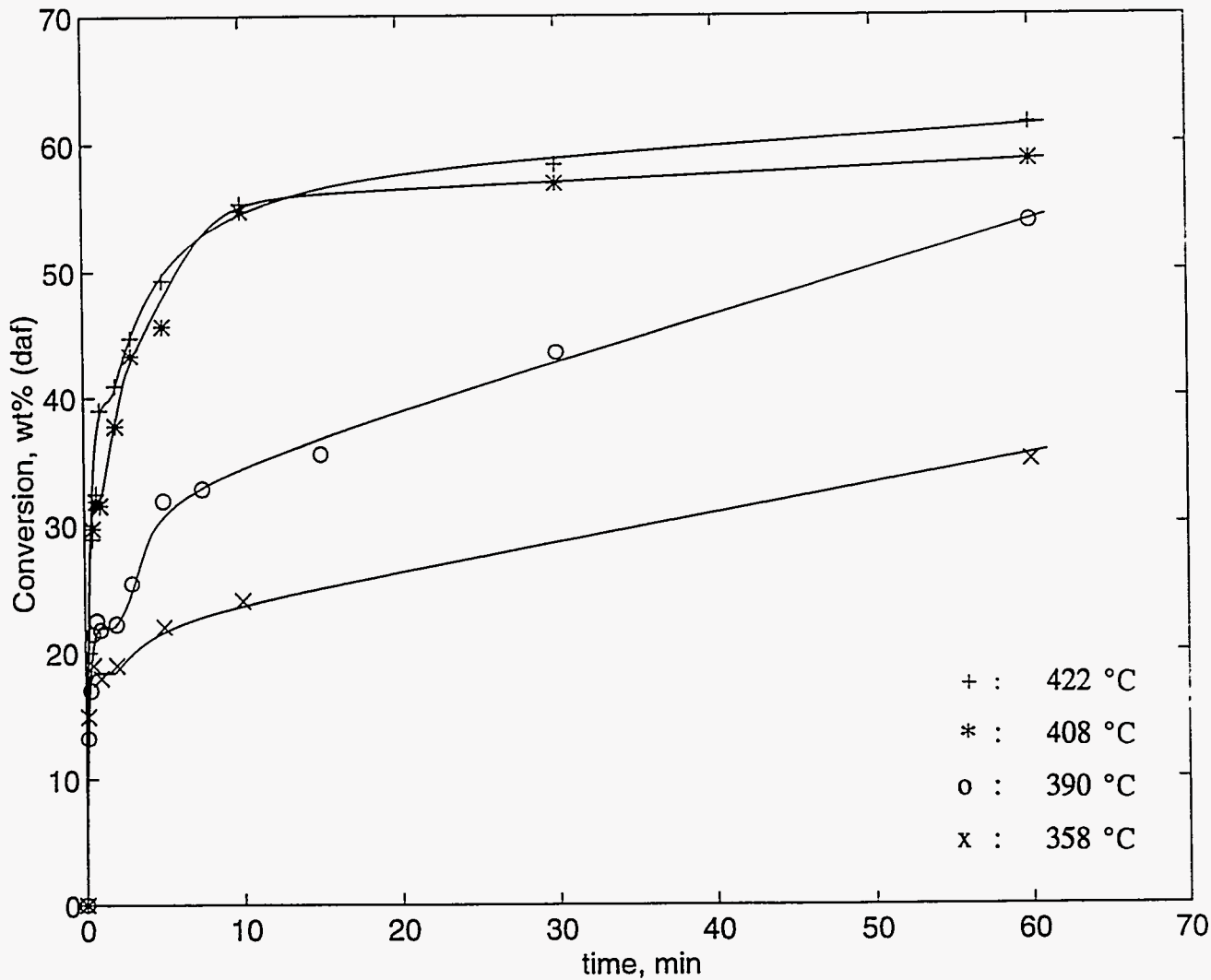
Conversion vs time for Illinois #6 coal liquefaction without added catalyst in tetralin (tetralin:coal = 8:1 mass ratio) under 1000 psig $N_2$ for up to 60 min.
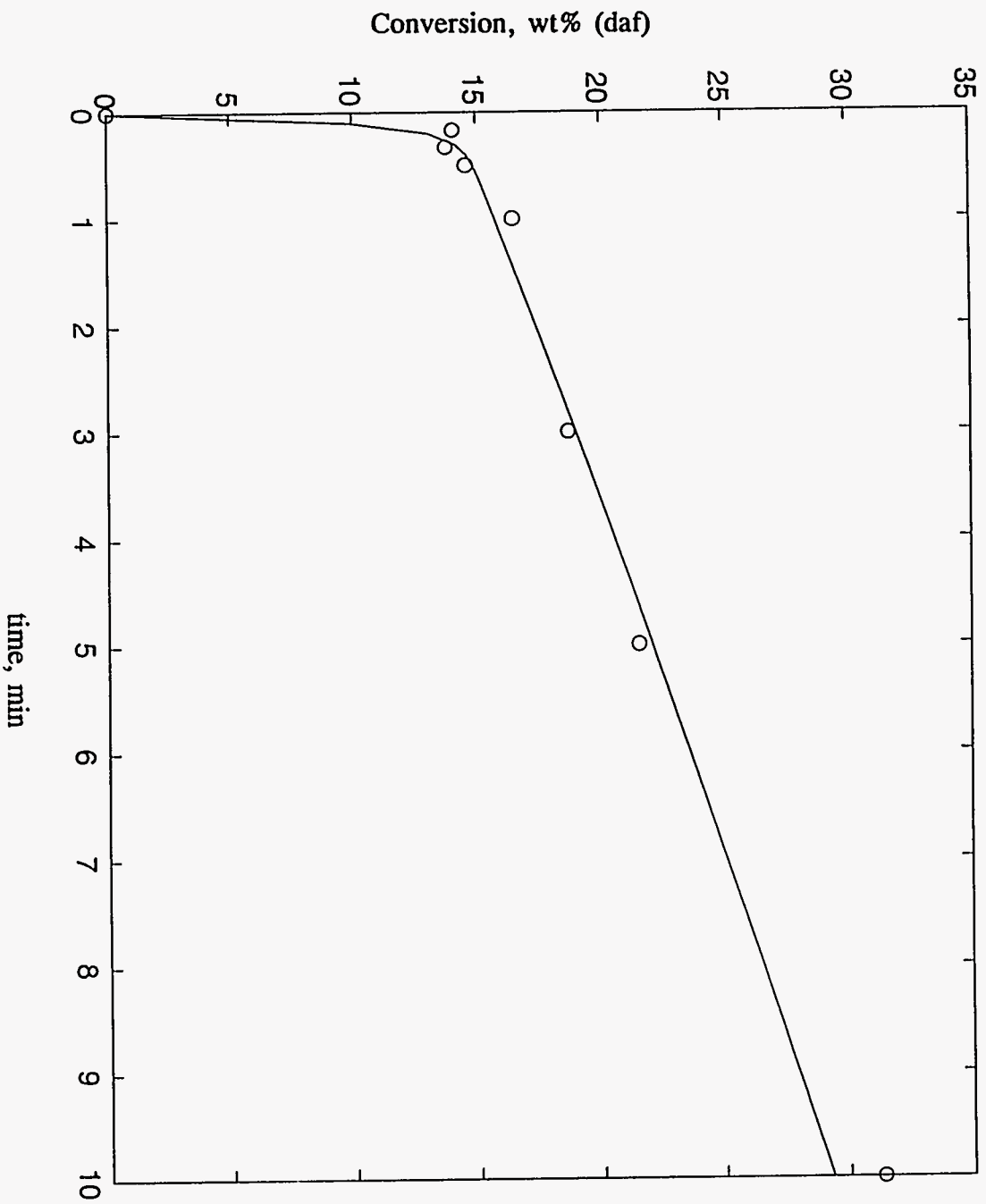
Figure 1b

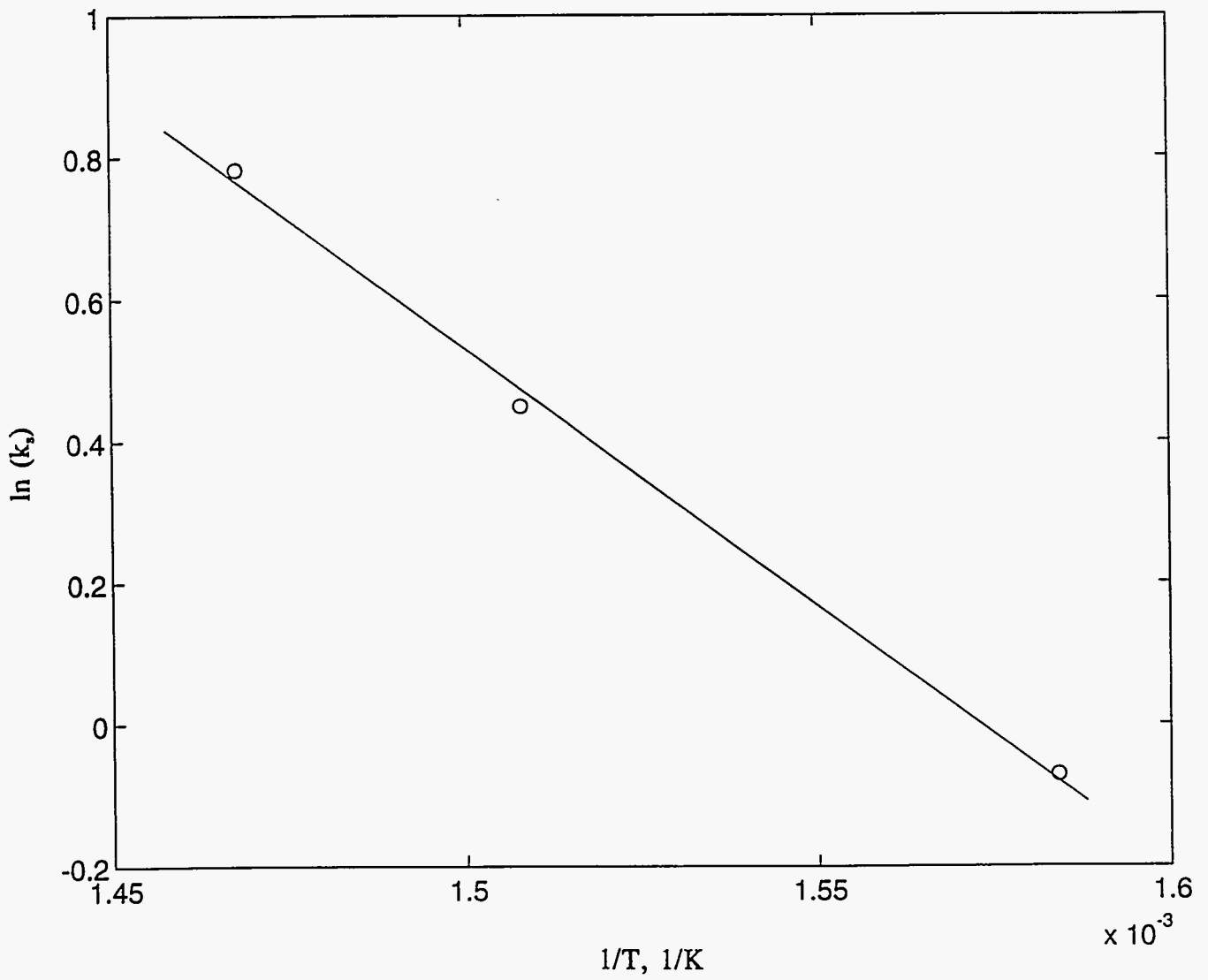ln(1-$X_s$/$X_{s0}$) vs t for the Illinois #6 coal liquefaction in tetralin under 1000 psig $N_2$ at 390 °C

Figure 2

$\ln(1-X_r/X_{r0})$ vs t for the Illinois #6 coal liquefaction in tetralin under 1000 psig $N_2$ at 390 °C

Figure 3

Plot of the experimental data and modelling curve at the reaction times up to 10 min for Wyodak-Anderson coal liquefaction in tetralin at 390 °C under 1000 psig $N_2$.

Figure 4

lnk$_s$ vs 1/T for the thermal liquefaction of Illinois #6 coal (Extraction stage)

Figure 5
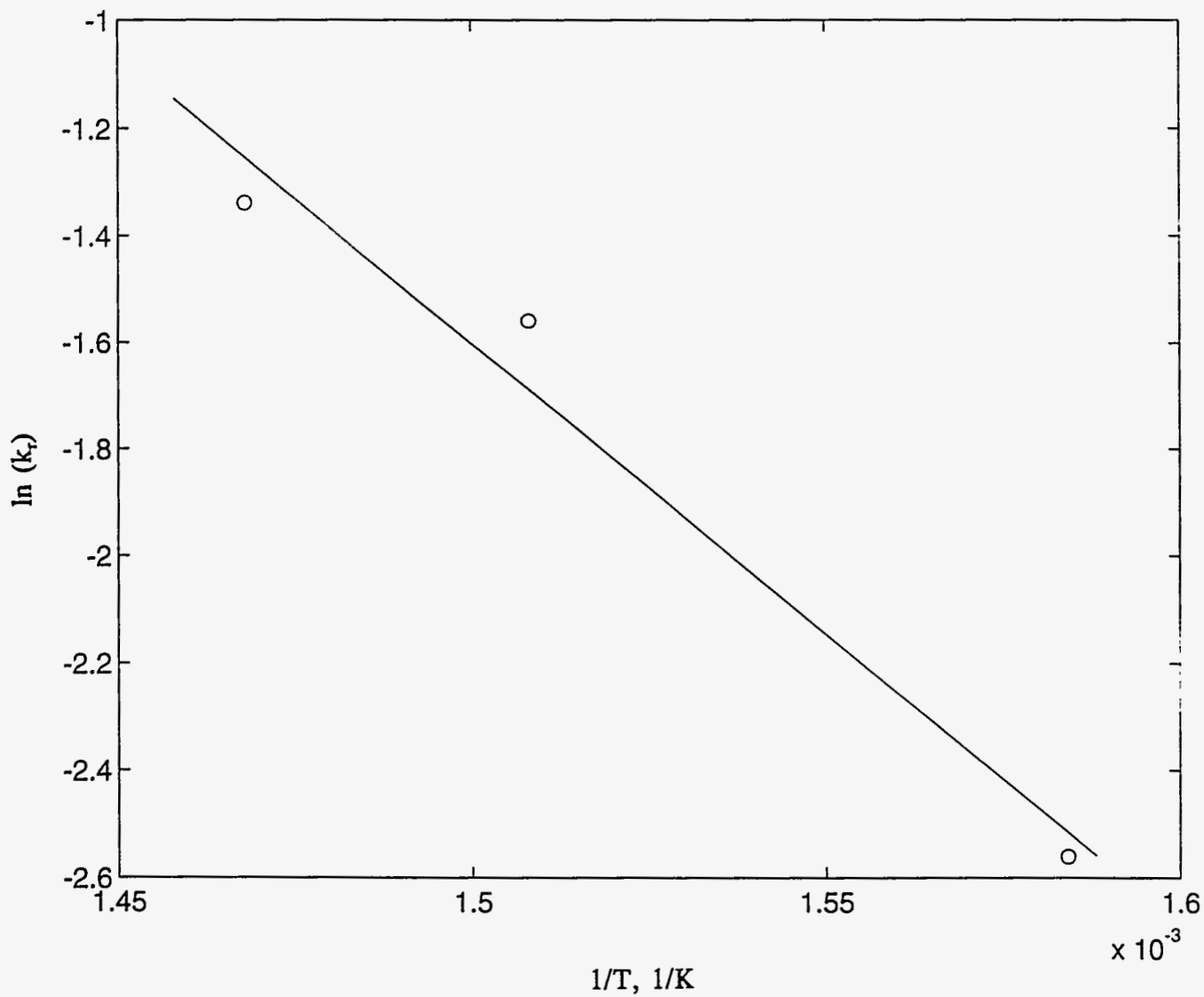
lnk$_r$ vs 1/T for the thermal liquefaction of Illinois #6 coal (Reaction stage)

Figure 6

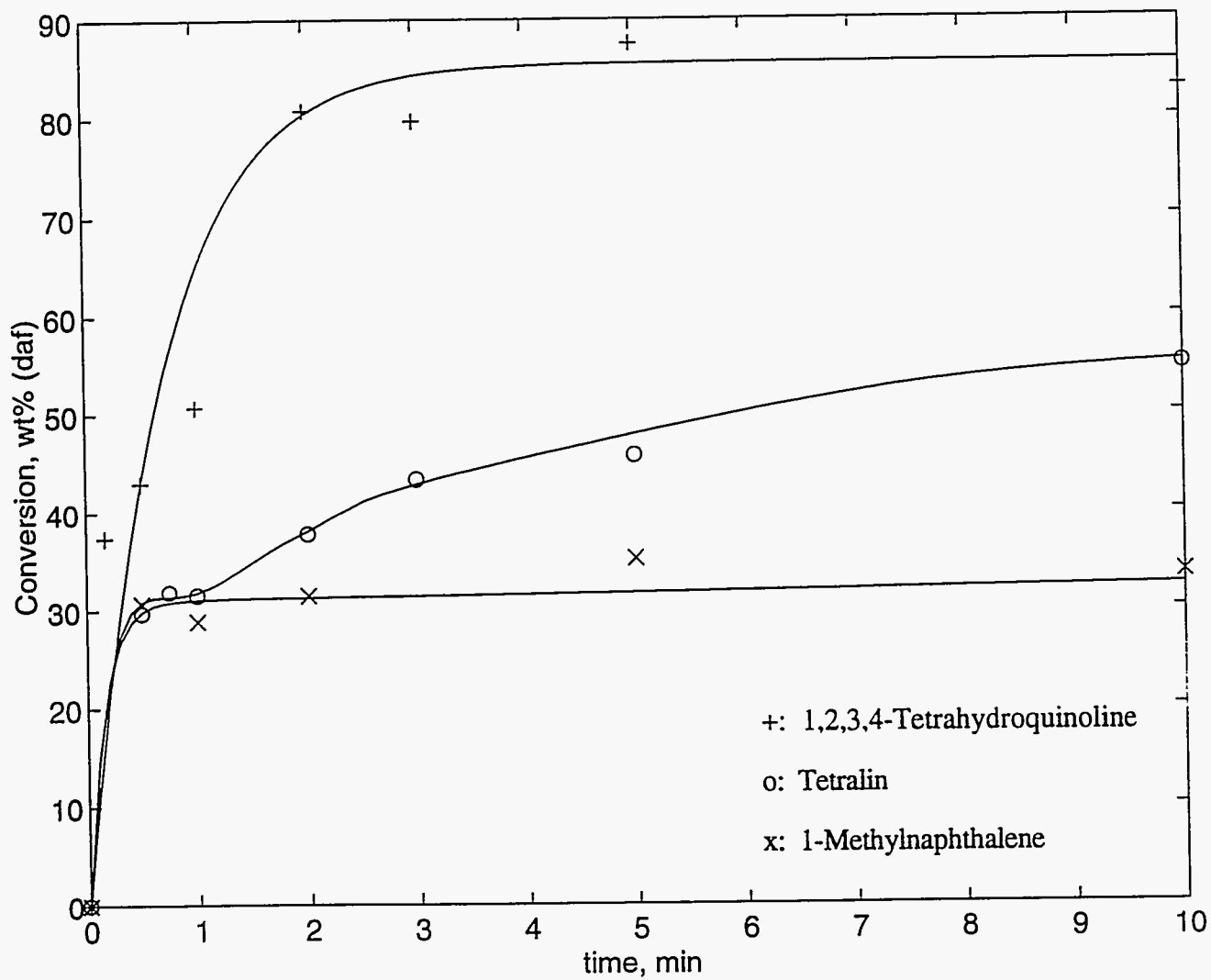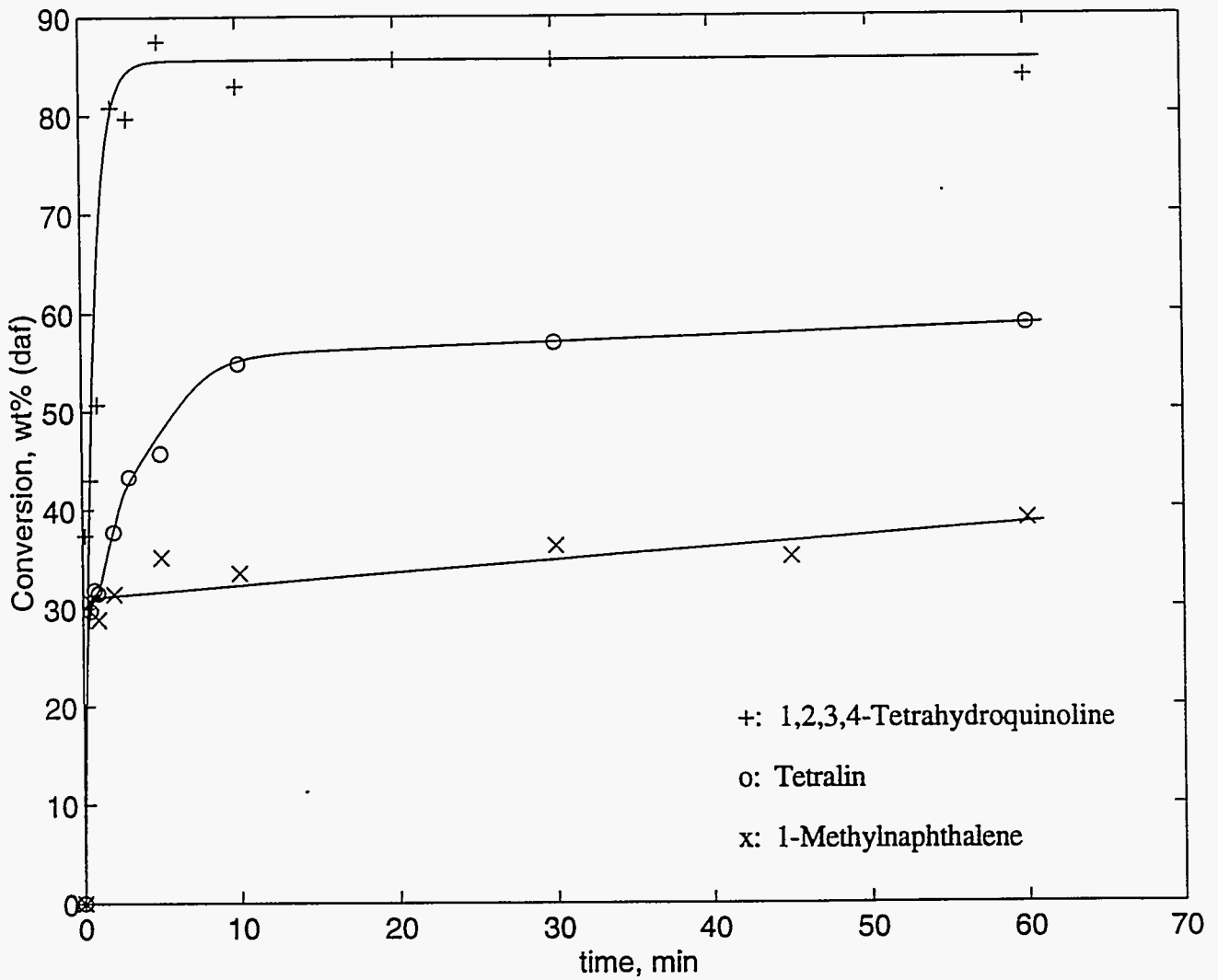**Eeffect of gas atmosphere on the Illinois #6 and Wyodak-Anderson coal liquefactions in tetralin**
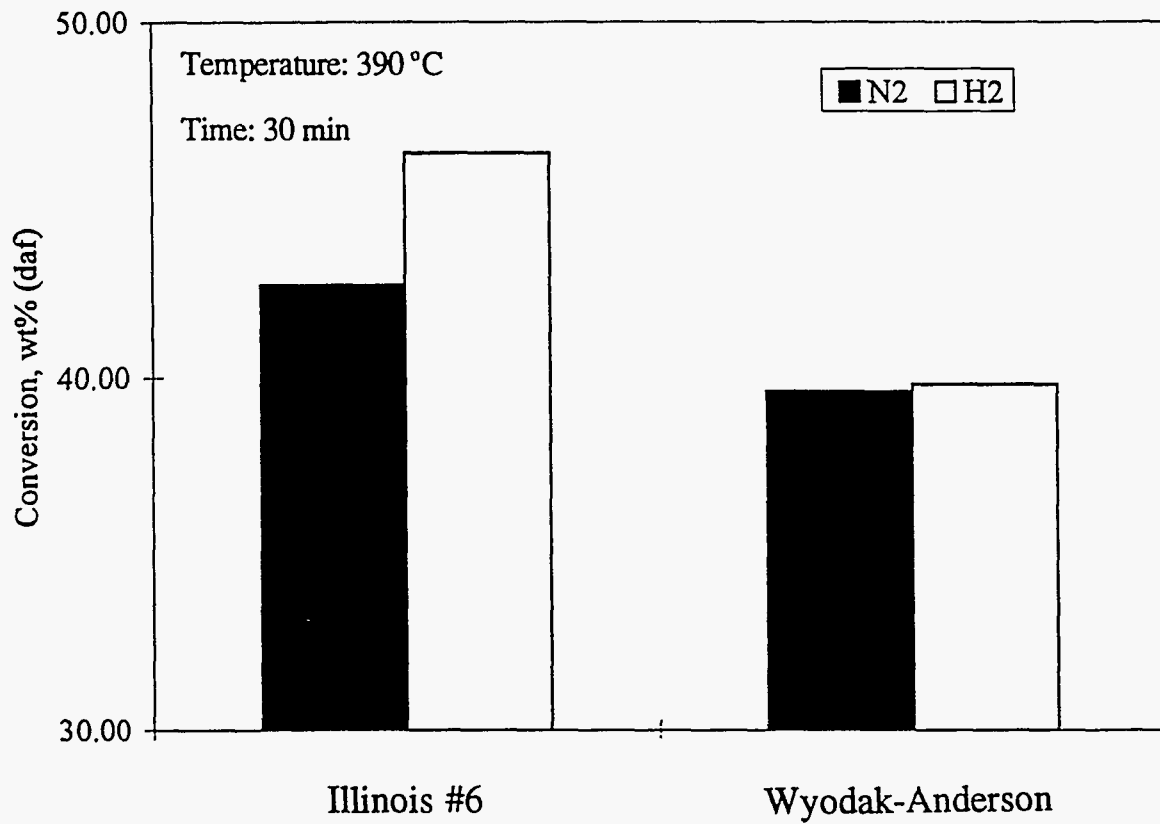


Figure 7

Conversion vs. time curves of the thermal liquefaction of Illinois #6 coal in 1,2,3,4-tetrahydroquinoline (THQ), tetralin, and 1-methylnaphthalene under 1000 psig nitrogen at 408 °C (Solvent:Coal = 8:1) for short contact times

Figure 8a

Conversion vs. time curves of the thermal liquefaction of Illinois #6 coal in 1,2,3,4-tetrahydroquinoline (THQ), tetralin, and 1-methylnaphthalene under 1000 psig nitrogen at 408 °C (Solvent:Coal = 8:1) for up to 60 min

Figure 8b

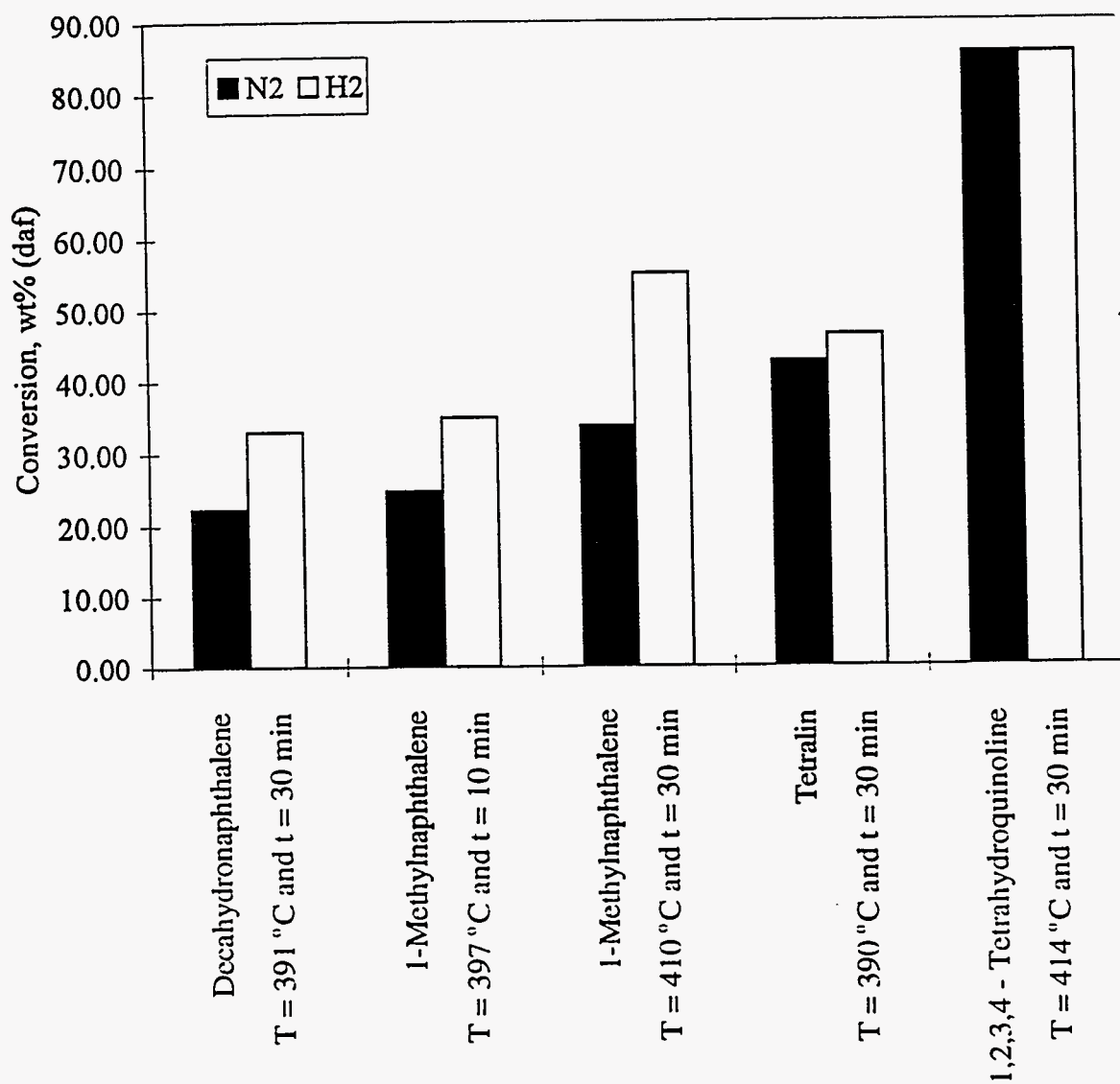# Effect of solvent on the Illinois #6 coal liquefaction in different gas atmosphere



Figure 9

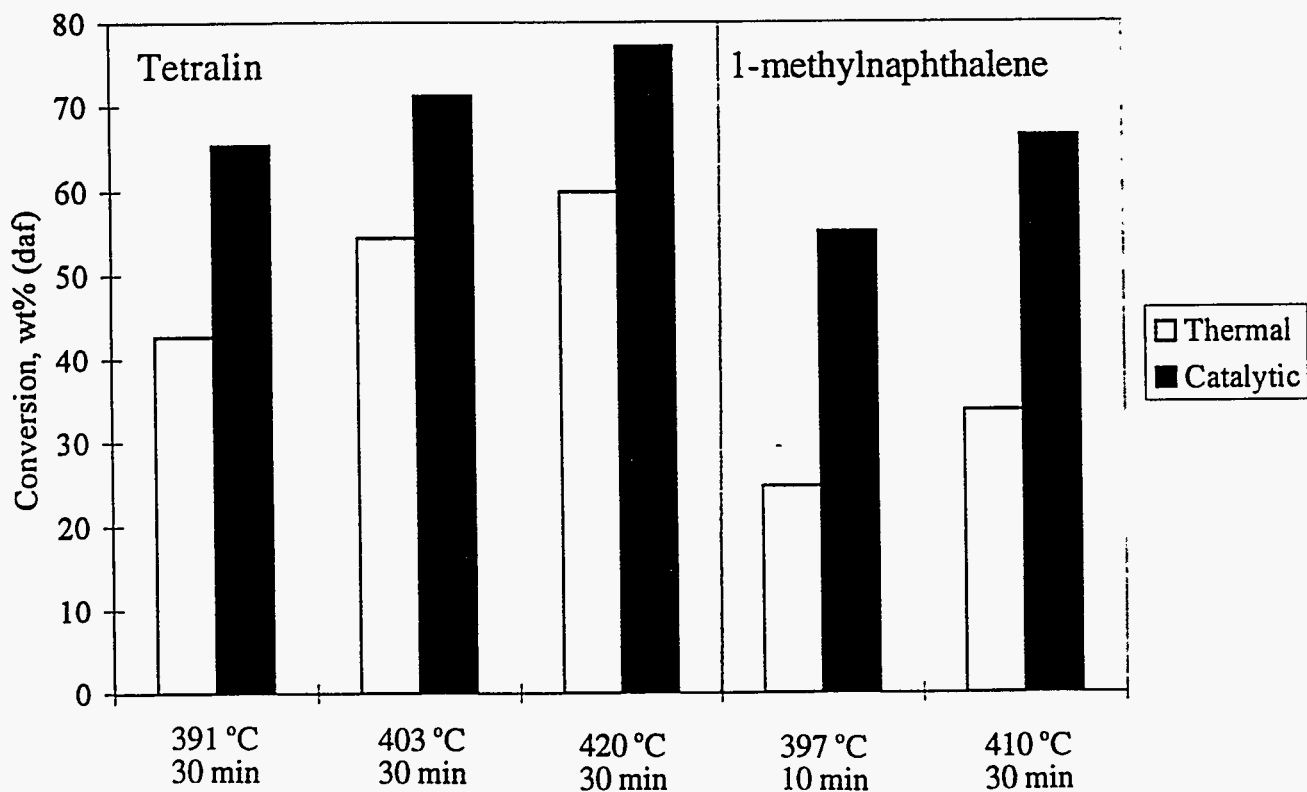**Effect of solvent on the thermal and catalytic liquefaction of the Illinois #6 coal**



Figure 10