

## Coal Liquefaction: Impact of Alkyl Substitution in Naphthalene Model Solvents

R. A. Keogh, B. Chawla, K.-J. Tsai and B. H. Davis  
Kentucky Energy Cabinet Laboratory  
P.O. Box 13015, Iron Works Pike  
Lexington, Kentucky 40512

### ABSTRACT

The solvent 1-methylnaphthalene has a unique ability of being able to effect the use of gaseous hydrogen during coal conversion. This unique characteristic is not universal; rather it is exhibited only for about one-third of the eastern and western Kentucky coals examined in this study. With these exceptional coals, 1-methylnaphthalene may be as, and sometimes even more, effective than tetralin in converting coal to pyridine soluble products.

### INTRODUCTION

One of the features of a process solvent that is believed to be important is the amount of donatable hydrogen that is present in the form of hydroaromatic compounds. Neavel (1), for example, shows that, in the initial stages of the liquefaction of an Illinois high-volatile C bituminous coal, the conversion to pyridine solubles is similar in tetralin, a good hydrogen donor solvent, and in naphthalene, a solvent without donatable hydroaromatic hydrogens. Only after a few minutes does one see a significant difference in the overall conversion. With tetralin, a conversion of greater than 90% is attained rapidly, and this remains constant during the next 100 minutes of residence time (Figure 1a). When naphthalene is the solvent, the early conversion reaches ca. 85% but rapidly declines during the next 40 minutes of residence time to a level below 40% conversion (Figure 1b). Neavel's data dramatically emphasize a concept that has developed over the years as it relates to the need for donatable hydrogen in a liquefaction solvent that inhibits retrograde reactions.

For studies in microreactors, a convenient way to vary the amount of hydrogen donor is to use a model solvent containing tetralin and naphthalene. 1-Methylnaphthalene, a liquid at room temperature, is frequently used instead of naphthalene, a solid at room temperature since this makes the experimental procedure for sample removal and analysis easier. Naphthalene and 1-methylnaphthalene could be interchanged, on a molar basis, without altering the amount donatable hydrogen and, presumably, without altering the conversion for a solvent with a particular donatable hydrogen content.

For example, Pina et al. (2) found that the conversion of a western Kentucky coal was essentially constant as the fraction of 1-methylnaphthalene was increased up to 0.8 to 0.9 range; as the amount of donatable hydrogen was further decreased by increasing the amount of 1-methylnaphthalene a dramatic, rapid decrease in coal conversion was observed. Derbyshire and Whitehurst (3) made a similar observation for the conversion of a Belle Ayr sub-bituminous coal in a mixture of tetralin with 2-methylnaphthalene or pyridine; in this case, a lower concentration of the nondonor methylnaphthalene was required to

cause a decrease in conversion. Chiba et al. (4) have obtained conversion data with 1-methylnaphthalene-tetralin and a Yallourn coal that are intermediate to that of the above two studies. Maa et al. (5) reported that EXXON Research & Engineering Company had developed a solvent-quality index (SQI) to characterize the ability of recycle solvents to effect coal conversion and that, for some coals, below a critical value of SQI, the liquid yields and coal conversions decreased sharply. Furthermore, for the three coals reported, two coals, an Illinois No. 6 bituminous and Wyodak sub-bituminous, showed a much stronger sensitivity to SQI than did a West Virginia Ireland Mine bituminous coal. The implication of the data presented in this study is that all coals do not respond in the same manner to a given SQI.

For some Kentucky coals, a higher conversion may be obtained in a pure 1-methylnaphthalene solvent than in a tetralin. These data indicate that the amount of donatable hydrogen required for a "good" solvent is dependent upon the coal. In view of the expanding use of 1-methylnaphthalene as a model solvent (e.g., Ref. 6) to provide solvents of varying amounts of donatable hydrogen, some of these results are described in this report.

#### EXPERIMENTAL

The coal samples were collected from the working face of the mine and stored under argon prior to analysis and liquefaction. Chemical and petrographic analyses of the coals are given in Table 1. The coals were ground to -100 mesh, stored under argon and dried prior to the liquefaction experiments.

The liquefaction experiments were conducted in a 50 ml microautoclave reactor. The reactor charge was typically 5 g of coal and 7.5 g of model solvent. The reactor was pressurized with the appropriate gas ( $H_2$  or  $N_2$ ) to 800 psig at ambient temperature. The reactor was immersed in a heated fluidized sand bath for the desired reaction time. Typically, the time required to reach a reaction temperature of  $385^\circ C$  was two minutes, or less. Mixing of the reactor charge was facilitated by a 1/4" steel ball in the reactor. The reactor was vertically shaken (1" amplitude) at a rate of 400 cpm. At the end of the liquefaction experiment, the reactor was immersed in a cold fluidized sand bath to quickly cool to less than  $100^\circ C$  in less than two minutes to quench the reactions.

Once the reactor has reached ambient temperature, the product gases were collected in a sample bomb for g.c. analysis. The remaining products were quantitatively washed from the reactor with benzene into a Soxhlet thimble. The sample was extracted with benzene until the solution was clear or a pale yellow. From the benzene solubles, the asphaltene fraction was separated from the oil fraction by precipitation of the asphaltenes with pentane. The preasphaltene fraction was obtained by a Soxhlet extraction of the benzene insolubles with pyridine. Conversions were obtained by subtracting the weight percent pyridine insolubles (maf basis) from 100%.

The extraction solvents were HPLC grade and obtained from Burdick and Jackson. The liquefaction model solvents were used as received from Aldrich Chemical Co.

## RESULTS AND DISCUSSION

An eastern and western Kentucky coal were converted in tetralin or 1-methylnaphthalene solvent using a reaction time of 15 minutes, a temperature of 385°C and either a hydrogen or nitrogen atmosphere (Figure 2). The data clearly show that molecular hydrogen is utilized in the liquefaction of both coals when 1-methylnaphthalene is the solvent. When tetralin was employed as the solvent, similar conversions were obtained when the reactor vessel was pressurized with either hydrogen or nitrogen. However, when 1-methylnaphthalene was used as the solvent for either coal, the conversion in the hydrogen atmosphere was about double the conversion in a nitrogen atmosphere. Thus, the 1-methylnaphthalene is effecting the utilization of gaseous hydrogen to produce higher conversions. Even more surprising is the observation that, in a hydrogen atmosphere, the 1-methylnaphthalene is as effective as a solvent as tetralin for coal conversion.

The observation that equal conversions are obtained using 1-methylnaphthalene and tetralin as liquefaction solvents does not apply for all coals. Even when a hydrogen atmosphere is used, the expected lower conversions are obtained for ca. 60% of the eastern Kentucky coal samples in Figure 3 (see reference 7 for coal analysis); i.e., the conversion when tetralin is utilized is appreciably higher than when 1-methylnaphthalene is the solvent. The data in Figure 3 indicate that equivalent conversions are obtained for those special coals in both solvents (which span the entire range of conversions). Therefore, this phenomena is not restricted to a set of coals with high or low reactivities. From the data, it may be concluded that some unique coal property, or properties, are responsible for this observation. Similar results have been obtained with western Kentucky coals.

The time dependence of conversions in the two solvents are shown in Figure 4 for a western Kentucky #9 Alston coal. The same conversion is obtained for either nitrogen or hydrogen atmosphere at 15 and 30 minutes with the tetralin solvent. A very different result is obtained with the 1-methylnaphthalene solvent. With this latter solvent and a hydrogen atmosphere, the conversions up to 30 minutes are clearly greater than when tetralin was employed. In addition, the conversions, when a nitrogen atmosphere was used instead of hydrogen, were lower (ca. 30%) and did not increase with longer reaction times. With 1-methylnaphthalene and hydrogen, the conversion at 60 minutes was the same as when tetralin was used as the solvent. Therefore, in addition to the surprising fact that the conversion of the western Kentucky #9 coal is initially greater in the 1-methylnaphthalene solvent, it does not appear that the retrograde reactions, as shown in Figure 1b, have made a measurable contribution in lowering conversions, even after 60 minutes. Again, the data clearly show that 1-methylnaphthalene is able to effect gaseous hydrogen usage and, with this particular coal, appears to be able to provide the hydrogen needed for conversion to pyridine solubles even more effectively than tetralin.

The data in Figure 5 indicate the effect of alkyl substitutions in aromatic and hydroaromatic rings on the conversions obtained for a Western Kentucky #9 and Eastern Kentucky Peach Orchard coal. The conversions obtained by these two coals, using naphthalene as the solvent, are lower than those obtained when tetralin was employed as the liquefaction solvent; this is anticipated from previous reports. Liquefaction of the two coals using 2-methylnaphthalene as a solvent produce significantly lower conversions when

compared to those obtained in 1-methylnaphthalene. However, the conversions in 2-methylnaphthalene are essentially the same as those observed for the liquefaction of the coals in naphthalene. One explanation for the above data may be the physical state of the model solvents employed. Naphthalene and 2-methylnaphthalene are solids at room temperature while 1-methylnaphthalene is a liquid. Poor mixing during the initial stages of liquefaction using the solid model solvents could be a factor in the lower conversions observed using these compounds. However, this does not appear to be the case as shown by the data in Figure 6. With the two solid liquefaction solvents, 2-methylnaphthalene and 2,3-dimethylnaphthalene, the microautoclave was preheated to a temperature slightly above the melting point of the solvent and mixed prior to immersion in the sand bath to obtain the reaction temperature. As shown by the data in Figure 6, the conversions, within experimental error, are the same regardless of the physical state of the model solvent prior to heating to reaction temperature.

Dihydronaphthalene is a more effective solvent than tetralin, and this has been observed frequently (e.g. Ref. 8). In fact, Virk et al. (8) propose that Woodward-Hoffmann rules apply so that 1,2-dihydronaphthalene will be more effective for transferring hydrogen to phenanthrene type structures while 1,4-dihydronaphthalene will be more effective for hydrogen transfer to anthracene compounds. These authors present data to show that, at 400°C and 30 minutes reaction time, 1,2-dihydronaphthalene provides essentially the same conversion as tetralin, and the conversion of in these two solvents is about twice that obtained in naphthalene (ca 70 vs. 30%). However, the conversion in 1,4-dihydronaphthalene is greater than in tetralin (81 vs. 70%). Our data differ from since the conversion in 1,2-dihydronaphthalene is much greater than in tetralin (Figure 5).

It is surprising that both methyltetralins used in this study produce significantly higher conversions of these two coals when compared to the results obtained using tetralin. In fact, the two methyltetralin compounds produce as high a conversion as 1,2-dihydronaphthalene does. One could argue that in 1-methyltetralin the tertiary hydrogen provides a relatively weak C-H bond, and this could provide a lower activation energy reaction pathway for hydrogen transfer. However, this argument does not apply for 5-methyltetralin.

At this time, we have no ready explanation how the 1-methyl substituent promotes the use of gaseous hydrogen so much more effectively than does the 2-methyl substituted naphthalene during coal conversion. Likewise, the effect must be specific since 1-ethylnaphthalene does not appear to be a better solvent than the unsubstituted solvent, naphthalene (Figure 5). The coal properties in Table 1 do not provide a ready explanation as to why some coals have equivalent or better conversion, thorough utilization of gaseous hydrogen, in the 1-methylnaphthalene case when compared to the tetralin case.

These results clearly show that 1-methylnaphthalene is a unique liquefaction solvent for some coals and may produce results that are not typical of all nondonor solvents. At the same time, the results suggest that some coals have a unique property or properties which promote the utilization of gaseous hydrogen through nondonor solvents, and that it may be possible to take advantage of this property to improve hydrogen usage through coal selection. Finally, 1-methylnaphthalene, as a model solvent, may have utility

in identifying those coals, such as Ireland Mine coal, that appear to be able to be converted in a low SQI recycle solvent.

#### ACKNOWLEDGMENT

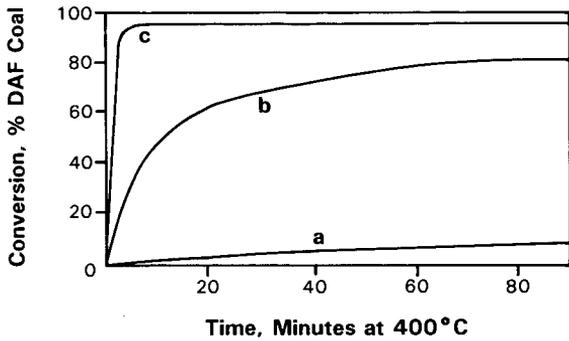
This work was supported by the Commonwealth of Kentucky, Kentucky Energy Cabinet and DOE Contract No. DE-FC-22-85PC80009 as part of the Consortium for Fossil Fuel Liquefaction Science (administered by the University of Kentucky).

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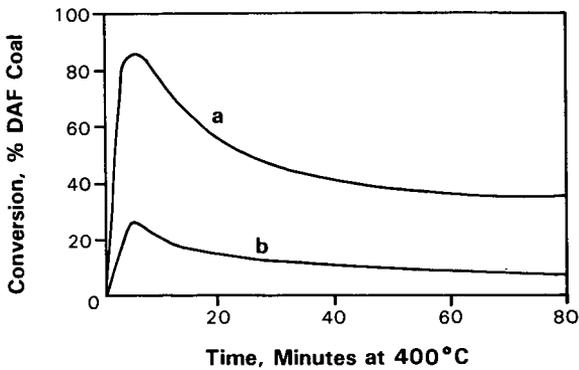
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TABLE 1. Coal Properties

	<u>W. Ky. #9</u>	<u>E. Ky. Peach Orchard</u>
ASH (dry)	11.71	5.29
VM (daf)	43.21	40.11
FC (daf)	56.79	59.89
C (daf)	76.80	83.24
H (daf)	5.41	5.54
N (daf)	1.90	1.70
S (daf)	8.41	.96
O (diff, daf)	7.48	8.56
Pyritic S (daf)	5.22	.08
Organic S (daf)	2.87	.87
Sulfate S (daf)	.32	.01
Vitrinitis	90.9	65.1
Intertinites	7.1	22.5
Liptinites	2.0	12.4



**Figure 1a.** Conversion of Coal reacted at 400°C in tetralin; (a) noncondensable gas; (b) benzene-soluble material + gas; (c) pyridine-soluble material + gas. DAF = dry ash-free (from Reference 1).



**Figure 1b.** Conversion of coal reacted at 400°C in naphthalene: (a) pyridine-soluble material; (b) benzene-soluble material. DAF = dry ash-free (from Reference 1).

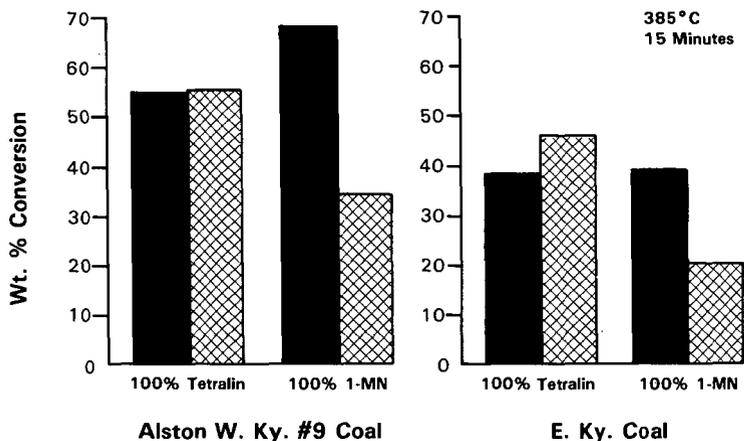


Figure 2. Conversion in a donor (tetralin) or nondonor (1-methylnaphthalene) solvent using hydrogen (■) or nitrogen (⊠) atmosphere.

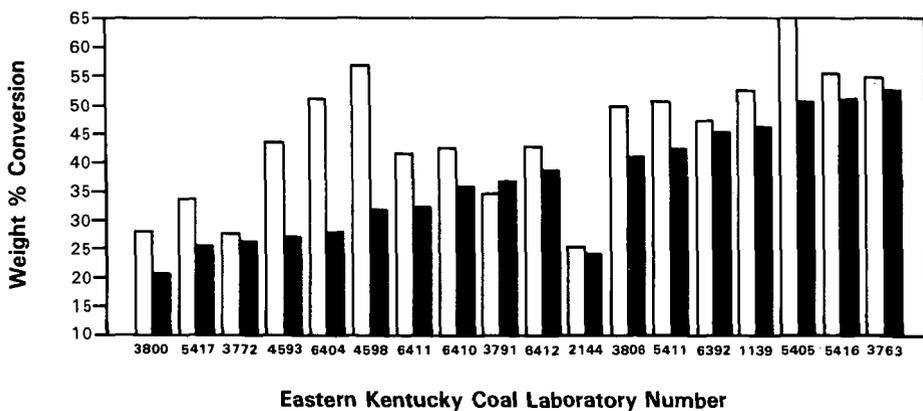
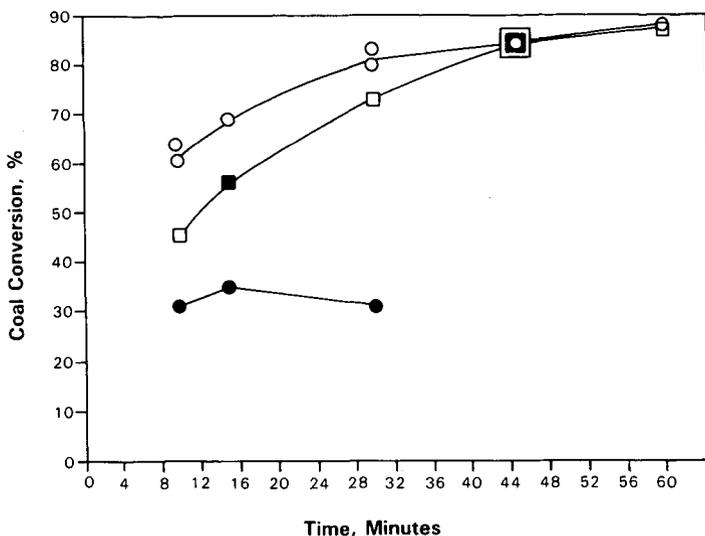
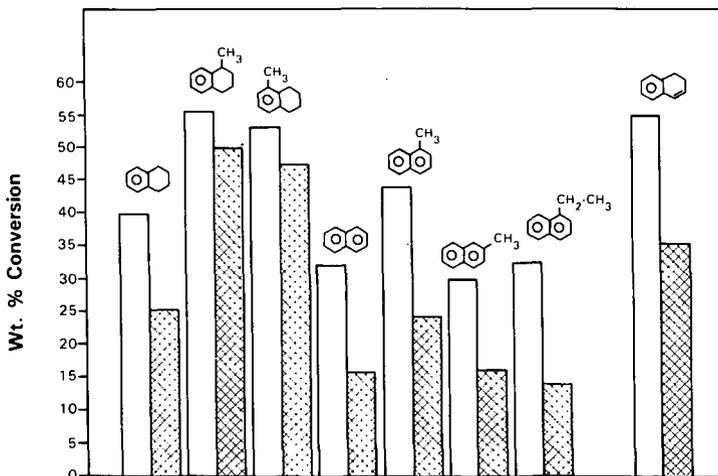


Figure 3. Comparison of conversions at 385°C and 15 minutes for eastern Kentucky channel samples in tetralin (□) and 1-methylnaphthalene (■) solvents.



**Figure 4.** Time dependence of conversion of a Western Kentucky No. 9 Alston coal at 385°C utilizing (1) gaseous (□) hydrogen or (■) nitrogen with a tetralin solvent or (2) gaseous (○) hydrogen or (●) nitrogen with 1-methylnaphthalene solvent.



**Figure 5.** Coal conversion at 15 minutes at 385°C in the presence of gaseous hydrogen for a Western Kentucky No. 9 Alston coal (□) or Eastern Kentucky Peach Orchard coal (▨) and with the indicated solvent.

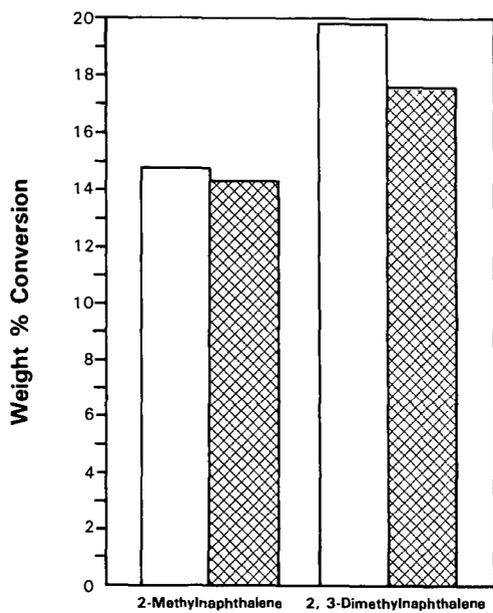


Figure 6. Comparison of the conversion of a Peach Orchard coal starting with a solid (□) or in liquid (▣) solvent.