MEASUREMENT OF THE REACTIVITY OF A KENTUCKY 9 AND 11 COAL USING A MICROAUTOCLAVE

Shuji Mori and Burtron H. Davis

University of Kentucky, Institute for Mining and Minerals Research
Iron Works Pike P.O. Box 13015, Lexington, KY 40583

The liquefaction reactivity of Kentucky #9 and #11 coal was measured in a micro-autoclave. The conversions were carried out using a tetralin solvent and 2000 psig hydrogen pressure. The noncatalytic conversion, based on pyridine extraction, exhibited a maximum at less than 15 minutes reaction time; reaction times longer than 15 minutes resulted in conversion lower than 90-95% maximum conversion. The catalytic and noncatalytic conversions showed contrasting behavior at reaction times longer than 15 minutes. The conversion continued to increase with time when a cobalt-molybdena catalyst was and secondary reactions caused the "apparent conversion" to decline at reaction times greater than 15 mintues. The noncatalytic reactivity at the maximum conversion depends on the length of time the coal is presoaked in the tetralin solvent; presoaking at room temperature for four days results in a conversion that is about 5% greater than the conversion obtained after only a two hour presoaking.

INTRODUCTION

Attempts have been made to correlate the liquefaction reactivity of coals to the carbon content (1,2), with the petrography (3,4) or with the "reactive maceral" content (5,6). Also, experimental difficulties (7-9) have limited the data available for short reaction times.

Diffusion is usually not a problem for reaction in a conventional batch autoclave with vigorous agitation, but the heatup period is long for such a system and it is difficult to assess the influence of slow heatup on short time coal conversion experiments.

In the present work, a small glass lined reactor capable of a rapid heatup was used to measure the noncatalytic and catalytic coal conversions at short reaction times.

EXPERIMENTAL

Samples of Kentucky No. 9 and No. 11 were ground to -60 mesh and to 16-36 mesh, respectively. The ultimate and proximate analytical data for these materials are given in Table 1.

The reactor, illustrated in Figure 1, was fabricated from 316 SS. A glass liner of about 10cc volume was placed in the reactor. The reactor was attached to a manifold with a pressure gauge and a valve. A thermowell of 1.59mm o.d. (1/16" O.D.) extended into the liquid contained in the reactor.

Approximately 1.5gr of a Kentucky No. 9 coal was mixed with 1.5gr of ground ceramic material as a filler (16-36 mesh); the solids were slurried with approximately 6gr of test value. For the noncatalytic reaction with Kentucky No. 11 coal was approximately 3gr of the coal mixed with 6gr of tetralin. For the catalytic run approximately 1.5gr of Kentucky No. 11 and the same amount of a prereduced Co/Mo catalyst (American Cyanamid HDS-1442-A, 1/16" extrudate) were mixed with approximately 6gr of tetraline. All of the reaction was initiated at 3.45×10^6 N/M^2 (500 psig) hydrogen pressure.

The reactor was immersed to the "nut" top in a fluidized sand bath (Tecam Model SLB-2) at 435°C. The bath temperature decreased slightly when the reactor was introduced, but the temperature was restored to 435°C within approximately one-half minute by manual adjustments of the heater control, and was maintained at 435 $\pm$ 2°C thereafter. Reactor pressure was recorded at one-minute intervals

and temperatures of the reactor and the sand bath were recorded continuously. At the end of the reaction period the reactor was quickly immersed in a cold sand bath for a period of one minute, then quenched in cold water. No mechanical agitation was applied to the reactor or its contents during reaction.

The reactor contents were transferred to a dry, weighed Soxhlet extraction thimble with the aid of pyridine and Sochlet extraction with hot pyridine (150 ml total) was carried out under an atmosphere of nitrogen for a period of 42 hours. Pyridine was replaced with methanol and extraction was continued for six hours, after which the thimble and its contents were dried overnight in a vacuum desiccator over calcium chloride. Drying of the extraction residue was continued in a vacuum oven at 60°C and was considered to be completed when the weight loss between successive four-hour drying periods less than 10mg. Conversion calculations are based on weights of residues and are given on a moisture-ash-free basis.

In the course of this work it became evident that the methanol extraction step did not remove all of the pyridine from the pyridine insolubles and that some pyridine was strongly retained by the residues at 60°C (vacuum). Thorough removal of pyridine could be accomplished at 150°C (vacuum) but the resulting weight losses were too small to change calculated conversions significantly or alter interpretations given below.

RESULTS AND DISCUSSION

For a Kentucky No. 9 coal, the conversion depends on the reaction temperature as shown in Figure 2. The conversion, in the absence of a catalyst, reached a maximum in 10 to 15 minutes and slowly decreased for longer reaction times due to the pyridine-insoluble "coke" formation. Such conversions at 15 minutes are shown in Figure 1 as a function of temperature between 350° and 500°C. Above 450°C, coking is so severe at the reaction time that the coal conversion, based on pyridine-insoluble, appears to be quite low.

Preliminary work indicated that the length of coal presoaking time in the tetralin solvent prior to reaction may alter the maximum conversion. The influence of room temperature presoaking of the coal sample in tetralin was determined for periods varying from two hours to two weeks. The maximum conversion for a 15-minute retention time was three to four percent lower for the two hour presoaking than for soaking for one day or longer (Figure 3). In the other runs in this report a presoaking of 24 hours was employed.

The conversion with and without a catalyst is presented in Figure 4. For the noncatalytic conversion of the Kentucky No. 9 coal at 435°C, a maximum conversion of about 90% is obtained after a reaction time of 10 to 15 minutes. The reproducibility of the conversion for duplicate runs at each retention time was better than ± 1.5%. At reaction times greater than 15 mintues, the conversion shows a gradual decrease. This conversion decline appears to be due to the formation of "pryidine insoluble coke." Petrographic analysis of the residue from the pyridine extraction confirmed the presence of coke at the later reaction times. Some investigators have reported a similar maximum (10) while others have not observed the maximum (11).

The Kentucky No. 9 coal was obtained as a -60 mesh powder. In order to prevent compaction of the coal particles due to settling, the coal was mixed with ceramic particles 16-36 mesh. The larger particle size Kentucky No. 11 coal was run without the ceramic material. The use of the larger coal particles, as well as the ebullating bed agitation due to the initial heating of the bottom of the tall, narrow, reactor, enabled us to obtain reproducible conversion without mechanical agitation.

The temperature dependence of the noncatalytic conversion of a Kentucky No. 11 coal was presented in Figure 2. The conversion at the 15-minute reaction times was nearly the same in the temperature range 400-450°C and this conversion is represented in Figure 4 by the symbol ⊗. The maximum conversion, based on pyridine solubles, is the same for the Kentucky No. 9 and No. 11 coal; however,

many more coals must be converted to verify whether this is generally the case.

The catalytic conversion of a coal should be more rapid than the noncatalytic conversion. However, the observed fifteen minute catalytic conversion is lower than the noncatalytic conversion. The catalytic conversion also differs from the noncatalytic conversion at longer reaction times since the catalytic conversion continues to increase whereas the noncatalytic conversion decreased with longer reaction times.

The catalytic conversion is more difficult to explain than the noncatalytic conversion. One complication is due to chemical changes in the catalyst during the reaction period. In the present runs the catalyst was prereduced at 500°C and transferred to the reactor in a dry box. However, the catalyst is sulfided to some extent during the reaction period. The catalyst used for the 60 minute run contained, after the Sochlet extraction, one wt.% sulfur. However, this amount of sulfur can account for only a small fraction of the lower conversion observed at the 15 minute reaction time. One possibility is that "coke" deposits on the Co-Mo/Al_2O_3 catalyst are responsible for apparent low conversion much the same as observed in the run with Kentucky No. 9 coal with the ceramic material. The catalyst may cause coke deposition more rapidly than the ceramic material since the catalytic conversion is higher at all times than the noncatalytic conversion at 60 minutes with ceramic material present. In addition, the "coke" on the catalytic material appears to be slowly hydrogenated to yield gaseous and liquid products at higher conversions as the reaction time increases.

There are a number of possibilities to explain why the catalytic conversion is lower than the noncatalytic conversion at early reaction times. Another reason for this may be due to a rapid catalytic conversion to secondary products compared to the conversion of coal to primary products. Since these catalytic conversions of primary liquid products are hydrogen consuming, it is possible that the hydrogen donor solvent (and/or hydrogen) is depleted to the point where the primary coal liquefaction is hindered because of lower hydrogen concentration.

TABLE 1

ULTIMATE AND PROXIMATE ANALYSIS

PROXIMATE ANALYSIS (WT.%)	KY-9 COAL[a]	KY-11 COAL[b]
Moisture	1.7	6.47[c]
Ash	10.9	9.81
VM	42.1	38.4
FC	45.3	45.7
ULTIMATE ANALYSIS (WT.%)		
C	66.5	66.89
H	4.9	4.63
N	0.9	0.54
S	4.3	3.11

[a]Calorific value, 12,230 BTU/lb.

[b]Calorific value, 12,310 BTU/lb.

[c]As received basis.

The SRC conversion data in Figure 5 was obtained in the Wilsonville, Alabama 6 ton/day demonstration plant (10) and the H-coal data was obtained in the 3 ton/day PDU at Hydrocarbon Research, Incorporated (11). The conversion, compared on a hydrogen consumption basis, is lower for the runs without a catalyst than when a catalyst was used. The conversions in both runs were based on pyridine soluble materials. Thus, it appears that the data obtained in the microautoclave show the same trend as obtained in the much larger reactors.

REFERENCES

1. Storch, H.H., L.L. Fisher and G.C. Sprunk, "Hydrogenation and Liquefaction of Coal," U.S. Bureau of Mines, 1941, Tech. Paper 622.
2. Fisher, C.H., G.C. Sprunk, A. Eisner, H.J. O'Donnel, "Hydrogenation and Liquefaction of Coal," U.S. Bureau of Mines, 1942, Tech. Prog. Report 642.
3. Stopes, M.C., Roy. Soc. London, Proceedings, Series B, 1919, V, 90.
4. Storch, H.H., Industrial and Engineering Chemistry, 1937, 29, No. 12, 1376.
5. Given, P.H., D.C. Cronauer, W. Spackman, H.L. Lovell, A. Davis and B. Biswas, Fuel 1975, 54, 34.
6. Given, P.H., D.C. Cronauer, W. Spackman, H.L. Lovell, A. Davis and B. Biswas, Fuel 1975, 54, 40.
7. Given, P.H., W. Spackman, A. Davis, P.L. Walker, H.L. Lovell and M. Coleman, "The Relation of Coal Characteristics to Liquefaction Behavior," 1976, FE 2494-1.
8. Given, P.H., W. Spackman, A. Davis, P.L. Walker, H.L. Lovell and M. Coleman 1977, FE 2494-2.
9. Schall, J., "Compilation and Assessment of SRC Experience: Data Book," 1979, EPRI AF-1019.
10. Weber, W.H., J.W. Roberts, G.B. Vsnick, B.H. Cottle, Jr., C.T. Harwell, W.R. Hollenack, C.R. McIlwain, A.K. Rao, C.G. Churchman, F.L. Pate and G. Haider, EPRI AF-918, Nov., (1978), page 191.
11. H-Coal Integrated Pilot Plant, Phase 1, Final Report, Vol. II, July (1977).

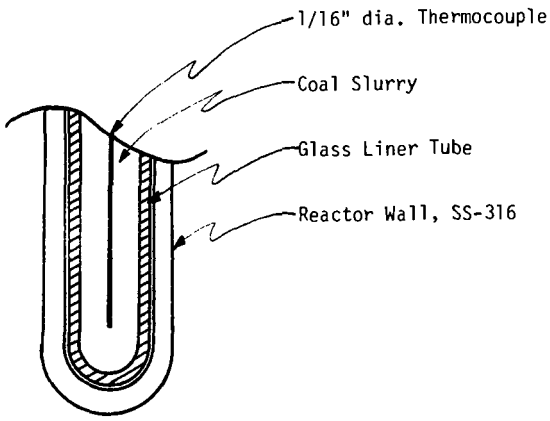

Figure 1. A schematic drawing of the bottom portion of the microautoclave reactor.

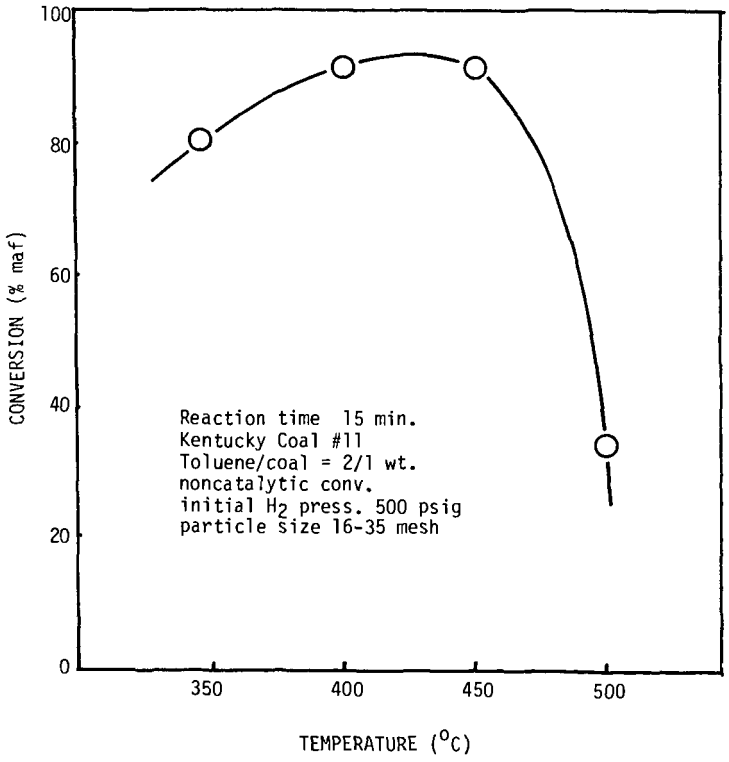

Figure 2. The dependence on the conversion for the noncatalytic reaction at fifteen minutes reaction time.

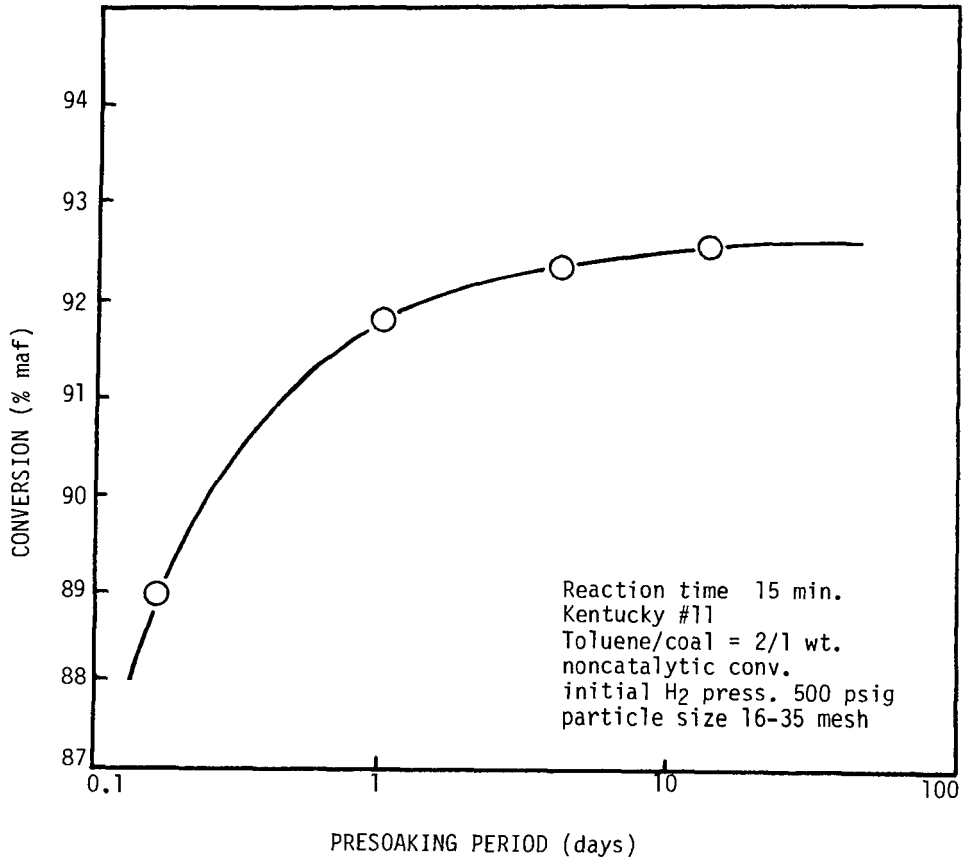

Figure 3. The effect of presoaking on the noncatalytic conversion.

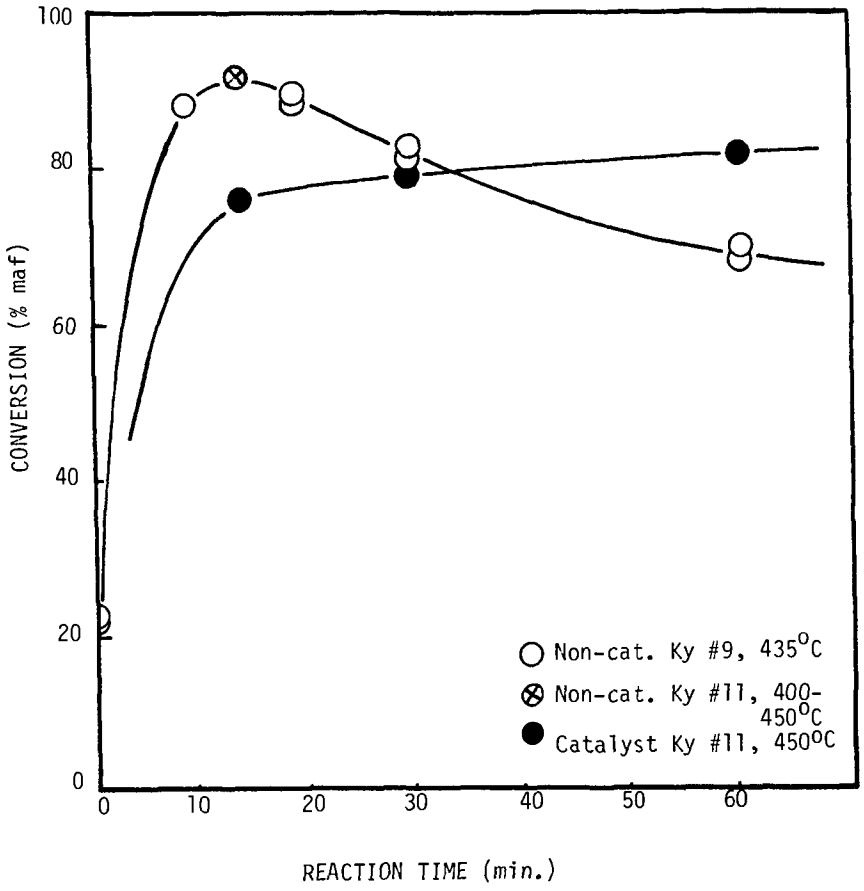

Figure 4. The time dependency of the conversion with and without catalyst.

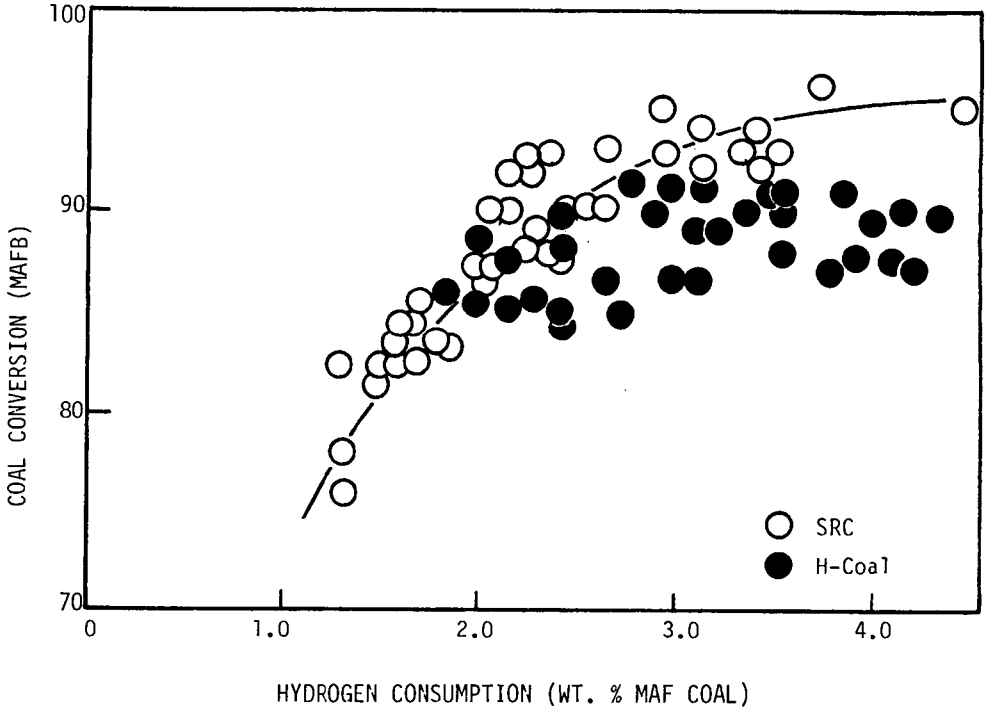

Figure 5. A comparison of the conversion of Illinois #6 coal with and without a catalyst in 3-6 ton/day size reactors in the SRC-I and H-Coal processes.