# COAL LIQUEFACTION I. CATALYST POISONS PRESENT IN COAL

By

S. M. Kovach and J. Bennett, Ashland Oil, Inc.
Ashland, Kentucky 41101

## INTRODUCTION

A favorable economic future of coal solvation-hydrogenation technology will depend upon the proper selection of coal feedstocks and upon catalyst life and activity. It is reasonably well established that the reactive character of different coals vary widely in solvation-hydrogenation reactions (1, 2, 3). Some coals appear to have a self-catalytic character (3, 4) while others cause a pronounced deactivation or poisoning of the hydrogenation catalyst (5). In any case, deep hydrogenation to remove organic sulfur from the liquid product will require a catalyst (4, 6). The present maximum catalyst life for certain coal liquefaction processes is of the order of 30 to 90 days. The causes for these varying rates of catalyst deactivation are not clearly understood. These effects are believed to be associated with the various coal characteristics including the nature and concentration of minerals or trace elements in the respective coals, or to large phorphyrin type molecules that fill the catalyst pores and hence cause reduced activity.

Previous investigations of coal liquefaction processes employing a heterogeneous catalyst in a solvation-hydrogenation system have reported catalyst deactivation within the time limits previously mentioned. Catalyst activity is measured by the amount of unconverted coal and by product distribution. As the amount of unconverted coal increases and product distribution shifts to the heavier ends the catalyst is described as being deactivated. At this point in these prior studies the catalysts were removed and analyzed as to surface area, pore size and volume and metals on catalyst. In most cases, surface area and pore structure decreased dramatically with a large pickup of metals on the catalyst surface from the coal ash. Catalyst deactivation has been attributed primarily to these metals, and theories advanced on alkali metal poisoning such as sodium, calcium, magnesium; acidic component poisoning such as boron, titanium, and silica-alumina; and the poisoning effects of iron on hydrogenation metals.

It was felt by the authors that the conversion of coal to coal liquids in such a process is a combination of three mechanisms, namely, thermal, hydrogen donor, and heterogeneous catalysts, and that catalyst activity and deactivation was being masked by the gross effects of this process. To better understand catalyst deactivation a more sensitive method for measuring catalyst activity and decline was required. Since metals disposition on the catalyst surface was occurring throughout the process period and at different rates, this more sensitive technique should allow faster and more accurate catalyst activity measurements. A system was devised for this experimental study to expose the catalyst to a coal-ash-donor solvent system and then isolate the catalyst for activity measurement as related to hydrogenating a pure aromatic hydrocarbon. This pure hydrocarbon is the parent aromatic hydrocarbon for producing this donor solvent.

This paper describes the poisoning effect of the major components present in a Western Kentucky coal on a coal liquefaction catalyst. Their effects on catalyst hydrogenation activity was determined by impregnation techniques and by catalyst exposure to a single inorganic salt in an isolated system. The major inorganic elements studied were sodium, magnesium, calcium, iron, titanium, silica-alumina, sodium silicate and phosphorus.

## EXPERIMENTAL

### Apparatus

The coal liquefaction experiments and reference standard hydrogenation tests were performed in an Autoclave Engineers 2L magnedrive stirred autoclave. The equipment on this autoclave was standard as received from the factory. The cooling coil was removed, and a special 3/8" drain valve was added to the bottom of the reactor for easy and fast dumping of the reactor product. The entire system was properly manifolded for easy and rapid addition of any liquid feed or gas. Liquid product was collected by passage through a cooling coil, pressure was controlled by a regulating valve, and all gases passed through a $H_2S$ scrubber and wet test meter before venting to the atmosphere.

Refractive indices were measured by means of a Bausch and Lomb Refractometer.

Catalyst surface area and pore size-volume were determined by a Micro-Meretics instrument.

Elemental analysis of catalysts before and after treatment with coal and the poison studied were determined by atomic absorption.

Catalyst samples were suspended in a wire mesh basket attached to the baffle plate supplied by the manufacturer.

## Materials

The catalyst chosen for this study was Nalcomo 471. The properties of this catalyst are given in Table 1. This catalyst was chosen because of its extensive use by researchers in earlier studies.

The coal utilized in this project was a Western Kentucky #11 from the Fies Mine, its properties are given in Table 2. This coal was received as run of the mine (large lumps) and stored in double plastic bags inside of a sealed metal can. The coal was crushed, sieved and quartered to pass through a 200 mesh screen as needed. Prior to use the coal was dried in a vacuum oven at 100°C.

The reference standard utilized in our hydrogenation tests to measure catalyst activity is a naphthalene-alkylnaphthalene mixture. The properties of this feed are given in Table 1.

## Test Procedure

A given weight of catalyst was charged to the catalyst basket in the autoclave, the autoclave was sealed and pressure checked at 2500 PSIG. After a successful pressure check the unit was depressured to atmospheric pressure and repressured to 250 PSIG with hydrogen sulfide and heatup started. The catalyst was presulfided at the gas cylinder pressure and 700°F for three hours. After presulfiding the unit was depressured to atmospheric pressure and the temperature dropped to 250°F. At these conditions 1000 cc of tetralin was added followed by coal addition (300 grams) with stirring. The autoclave was then sealed, pressurized to 2000 PSIG with hydrogen and heated to the operating temperature (650 to 775°F). This heat up period required 60 to 90 minutes.

At the end of the coal liquefaction test, which lasted from six to eight hours; stirring was stopped, and hydrogen pressure was shut down. The product was dumped and collected. As the pressure was reduced all gases in the reactor were passed through a cooling coil to collect condensibles.

To remove any traces of heavy hydrocarbons, the catalyst and vessel were washed once with tetralin and once with the reference hydrogenation feedstock at reaction temperature and pressure. This concluded the first coal run of a test series on the same catalyst charge.

The next step in the test procedure was to measure catalyst hydrogenation activity of the aromatic hydrocarbon standard. Prior to the start of the hydrogenation activity test, the autoclave was preheated to 720°F. Upon the addition of 1000 cc of the reference feedstock (Table 1) and pressuring to 2000 PSIG with hydrogen with stirring, the temperature of the contents of the autoclave dropped to 650°F ±5°F which then became the operating temperature of the standard test. At fifteen minute intervals small samples of the hydrogenated feedstock are withdrawn for refractive index measurement. This allows us to obtain a rate of RI decrease and can determine the exact time required to reach the

desired point of hydrogenation. The decrease desired is lowering the index from 1.5877 to 1.5700. This represents approximately a 50% conversion of bicyclic aromatics to the corresponding tetralins. After the hydrogenation test is completed, the unit is prepared for the next coal run by following the test procedure outlined after catalyst presulfiding. This sequence of performing a coal liquefaction run followed by the catalyst hydrogenation activity test can be repeated on the same catalyst charge. In these experiments it was repeated between three and eight times.

The standard conditions utilized in each series of tests are outlined in Table 3. The poison studies in which the catalyst was exposed to a single element present in the coal ash is similar to the technique employed in the coal and reference hydrogenation tests. In these tests, a single ash component was added to the tetralin, its weight corresponding to its concentration in a typical coal run. An example is the use of calcium carbonate. In a typical coal run, 300g of coal is utilized which analyzed at 23.13% ash and 1.37% calcium oxide. This is prorated to show that 1.8g of calcium carbonate would be present in the ash. The catalyst was exposed to this single element in tetralin at conditions corresponding to that employed in a typical coal run. Catalyst washing and the reference feedstock hydrogenation tests are identical to those previously described.

## RESULTS AND DISCUSSION

The apparent deactivation of heterogeneous catalysts employed in coal liquefaction processes (solvation-hydrogenation) is rapid when compared to the use of the same catalyst in petroleum processes. This deactivation rate varies depending upon condition, type of coal, etc. (Figure 1). The cause of catalyst deactivation has been attributed by other researchers to metals poisoning. Analysis of their spent catalysts has shown the presence of high concentrations of alkaline and alkaline earth metals, acidic metal oxides, and iron. However, catalyst activity in these studies was measured by the amount of unconverted coal and product distribution (light vs. heavy ends). We felt that catalyst activity as measured in these systems was being masked by the gross effects of the overall process. That is, coal was being converted to liquids by the three previously mentioned mechanisms operating in any high temperature-donor solvent-heterogeneous catalyst process. To better determine the deactivation mechanism or poisoning elements present, an investigation was instituted to look at catalyst activity during coal liquefaction in the early stages (100-200 hrs.), and to employ a more sensitive test to measure catalyst activity. The best test to measure catalyst activity is the hydrogenation of a pure aromatic hydrocarbon. This test is very sensitive to catalyst poisoning by adsorption or reaction of the hydrogenation metals with other metals present in the reaction media.

Since the coal liquefaction process employs a donor solvent, in this case tetralin, the aromatic hydrocarbon chosen was a methylnaphthalene concentrate (Table 1). Catalyst activity was measured as the time required to hydrogenate this concentrate from the naphthalene to the 50%

tetralin stage. This rate was chosen because at the 50% tetralin stage, the hydrogenation of tetralin to decalin has not occurred which can complicate the rate of reaction (time).

A series of hydrogenation tests were made with the virgin presulfided catalyst and the reference feedstock to establish uncontaminated catalyst activity. A series of six preliminary runs, using the reference feedstock only, established the time necessary to reach the 50% conversion level using the virgin catalyst. A small decline in catalyst activity was recorded between the first two runs. The remaining four runs indicated that an asymptotic value of activity had been reached. The times for these four runs were averaged and this established an equilibrated catalyst activity time of 171 minutes. From these tests initial catalyst activity was determined and assigned a value of catalyst relative activity of 1.0. All other catalyst activities are measured relative to this value and are determined as follows:

$$\text{Catalyst Relative Activity} = \frac{171 \text{ minutes}}{\text{Time (min) to hydrogenate to 1.5700}}$$

Since any significant poisoning of the catalyst by coal constituents will increase Time (1.5700) the denominator will always be greater than 171 minutes. Thus the catalyst relative activity will be between zero and one.

## Coal Liquefaction Studies

Based upon our initial premise as to catalyst activity, catalyst deactivation, and liquefaction mechanisms, a series of studies on catalyst activity decline during coal liquefaction were initiated. We anticipated that the initial measurements of catalyst hydrogenation activity would remain high (near 1.0) and would show a slight decline in the region of 50-100 lbs. coal per lb. of catalyst. Beyond this point catalyst activity would decline more rapidly and the rate would determine at what point the catalyst would be removed for analysis. Analysis at this point would consist of surface area and pore size-volume measurements and the determination of any trace elements absorbed on the catalyst surface from the coal ash.

As noted in Figure 2 this never occurred. After many repeat tests to correct operating procedure, and mechanical problems, we finally resolved that catalyst deactivation was occurring in the first test upon exposure to coal. This is shown by the curve for coal liquefaction at 675°F. Additional experiments were made at higher temperatures on the premise that too much heavy material was remaining unconverted and required higher temperatures to be cracked and hydrogenated to less viscous material. The curves for operation at 725°F and 775°F show that initially catalyst activity improved but rapidly decreased with subsequent coal liquefaction runs, and approached (within experimental error) the same ultimate asymptotic value of activity.

At this point it was not known if catalyst deactivation was due to carbon laydown or metals poisoning. Analysis of the catalyst by X-ray diffraction and AA showed only traces of ash components present on the catalyst surface. These were only present in 0.1 wt. % or less concentration which was considered insufficient to decrease catalyst activity any significant amount.

The catalyst was then submitted for surface area and pore volume analysis. The results (Table 5) were more dramatic as to reasons for catalyst deactivation.

TABLE 5

| | S.A. $M^2/g$ | P.V. cc/g | % C - Wt. % |
|---|---|---|---|
| Fresh 471 | 260 | 0.46 | 0.0 |
| Used 471 - 675°F | 126.5 | 0.20 | 18 |
| Used 471 - 775°F | 158 | 0.25 | 15 |

These results showed that catalyst deactivation was occurring as soon as the catalyst contacted the coal-solvent system. These heavy carbonaceous materials could include tars, asphaltenes, maltenes, resins, etc. To establish if this theory was correct the catalyst would only need to be regenerated in air to remove the carbon and be restored to virgin activity.

Figure 3 shows the effect of carbon on catalyst and regeneration with air on catalyst activity. The catalyst was contacted with coal for a single pass and its activity measured. It was then regenerated in air at 925°F and its activity measured. This sequence was repeated on the same catalyst with two coal runs in sequence. Regeneration with air again restored the catalyst to virgin activity. The effect of repeated exposure of the catalyst to the coal-solvent system gives catalyst relative activity rates that fall on the original curves shown in Figure 2.

These data show that catalyst hydrogenation activity drops dramatically upon initial exposure to a coal-solvent system. Catalyst relative activity drops to 10-20% of virgin activity when only 20-40 lbs. of coal is processed per lb. of catalyst. Those processes presently showing potential for commercial development that have reported a catalyst operating at a high and constant activity level are in reality operating at a level that is almost near complete deactivation. This is further substantiated by the sudden and rapid decline in activity that they themselves have reported.

## Poisons in Coal Ash - Catalyst Impregnation

The next phase of this program was to determine the major elements present in our coal ash (Table 2) and the type of compound they represent. This was tentatively identified by the Chemical Engineering-Geological Department of the University of Kentucky. The first step was to study the effects of these elements on catalyst activity by impregnation. Figure 4 gives the results of these tests.

The elements were impregnated upon the Nalco 471 catalyst through the use of water soluble salts. These salts were typically nitrates or chlorides. As expected, the alkali salts (Na, Ca, Mg) gave the highest degree of deactivation whereas the acidic components (B, Ti, Si) gave little or no deactivation. Secondly, these curves would give a basis for measuring catalyst deactivation when the catalyst was exposed to a single ash compound.

## Poisons in Coal Ash - Catalyst Exposed to Single Component

Upon completion of the catalyst poison study by impregnation, the next phase was the exposure of the Nalco 471 catalyst to a single component. This was accomplished by employing tetralin as the solvent and suspending the single compound in the donor solvent as a fine powder (as present in the coal ash during a coal run). The compounds utilized in this series are given in Figures 5 and 6 alongside of the appropriate activity curves. In some cases these activity curves are identical to that obtained for the impregnation tests and in others dissimilar.

The best interpretation of these tests and curves are given in Table 4. The grams of each compound utilized represents its concentration in 300g of coal (amount per test run). After this had been exposed to five repeat runs (the equivalent of 60 lbs. of coal per lb. of catalyst), the catalyst was removed and analyzed for the amount of the particular element tested that had been adsorbed on its surface. This figure is reported as % metal oxide on catalyst - AA. The final activity of the catalyst after the poison study is reported under the column catalyst activity. The final column catalyst activity based on Figure 4 is the catalyst activity as estimated from Figure 4 based upon the amount of the poison (ash constituent) analyzed by AA and reported accordingly.

The basic materials follow fairly close to the activity measurements. The large discrepancies occur in the occlusions of the acidic components.

## SUMMARY AND CONCLUSIONS

The liquefaction of coal in a donor solvent-heterogeneous catalyst system leads to catalyst deactivation by two types of poisons. These poisons are of a temporary and permanent type. The temporary poison is a heavy carbonaceous material which acts immediately upon catalyst activity, but activity can be restored to near virgin activity by an air regeneration. The permanent poisons (no known commercial economical method known for its removal) are the components present in coal ash. The degrees of deactivation by these coal ash components on heterogeneous catalysts have been determined and it has been shown that the alkaline materials are more detrimental to catalyst activity than the acidic components.

Our future work will entail studies to find a catalyst that is more active in the presence of these carbonaceous materials.

Also we will determine the rate of deposition of the elements from coal ash on a catalyst and the rate of change of catalyst activity with concentration.

## ACKNOWLEDGEMENT

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TABLE 1

NALCOMO 471
(Cobalt-Molybdenum-Alumina)

CHEMICAL ANALYSES, Wt. %

| | |
|---|---|
| % $MoO_3$ | 12.5 |
| % CoO | 3.5 |
| % $Na_2O$ | .05 |
| % Fe | .03 |
| % $SiO_2$ | .3 |

PHYSICAL PROPERTIES

| | |
|---|---|
| Surface Area, $M^2/gm$ | 260 |
| Pore Volume, $Cm^3/gm$ (C $Cl_4$) | .46 |
| Density, $lbs/ft^3$ | 39 |
| Density, gm/cc | .67 |
| Strength, lbs crush (avg.) | 14 |
| *Attrition Index | 92 |
| Size | 1/16" |
| Form | Extrudate |

* % Retained on a 20 mesh sieve after tumbling one hour.

STANDARD (41 TK) FEED
GC ANALYSIS (Wt. %)

| | | |
|---|---|---|
| 1. | Less than Naph. | 9.61 |
| 2. | Naphthalene | 15.74 |
| 3. | Naph-MN | 4.06 |
| 4. | 2-Methylnaph | 27.44 |
| 5. | 1-Methylnaph | 13.78 |
| 6. | MN-EN | 0.41 |
| 7. | 2-Ethylnaph | 1.91 |
| 8. | Biphenyl | ----- |
| 9. | 1-Ethylnaph | 0.66 |
| 10. | 2,6 + 2,7 DMN | 5.60 |
| 11. | 1,7 DMN | 2.60 |
| 12. | 1,3 + 1,6 DMN | 7.33 |
| 13. | 2,3 + 1,4 DMN | 2.18 |
| 14. | 1,5 DMN | 0.91 |
| 15. | 1,2 DMN | 1.55 |
| 16. | Greater than DMN | 6.22 |
| | Refractive Index (24°C) | 1.5877 |

TABLE 2

COAL SAMPLE 11-000
#11 MADISONVILLE - FIES MINE
Island Creek Coal Company

| | AS RECEIVED | MOISTURE FREE |
|---|---|---|
| Moisture | 4.68 | ----- |
| Ash | 22.05 | 23.13 |
| Volatiles | 33.90 | 35.56 |
| Fixed Carbon | 39.37 | 41.31 |
| Sulfur | 3.68 | 3.86 |
| BTU/lb. | 10,390 | 10,900 |

| ASH ANALYSIS - WT. % ASH | |
|---|---|
| $SiO_2$ | 53.81 |
| $Fe_2O_3$ | 12.11 |
| $TiO_2$ | 0.89 |
| $Al_2O_3$ | 23.48 |
| CaO | 1.37 |
| MgO | 0.80 |

TABLE 3

STANDARD CONDITIONS

COAL RUNS

Figures 2 and 3

| | | |
|---|---|---|
| Temperature °F | - | As Noted |
| Pressure | - | 2,000 PSIG |
| Catalyst | - | 25g Nalcomo 471 |
| Coal | - | 300g |
| Solvent | - | 1,000g Tetralin |
| Stirring Rate | - | 1200 RPM |

STANDARD REFERENCE RUNS

MEASURE RELATIVE ACTIVITY OF CATALYST

Figures 2, 3, 4, 5, 6

1,000 cc of 41 TK Feed

| | | |
|---|---|---|
| Pressure | - | 2,000 PSIG |
| Temperature °F | - | 650°F |
| Stirring Rate | - | 1200 RPM |
| Catalyst | - | 25g Nalcomo 471 |

POISON STUDIES

Figures 5 and 6

| | | |
|---|---|---|
| Temperature °F | - | 675°F |
| Pressure | - | 2,000 PSIG |
| Solvent | - | 1,000g Tetralin |
| Stirring Rate | - | 1200 RPM |

Amount of Single Poison Added per run - See Table 4

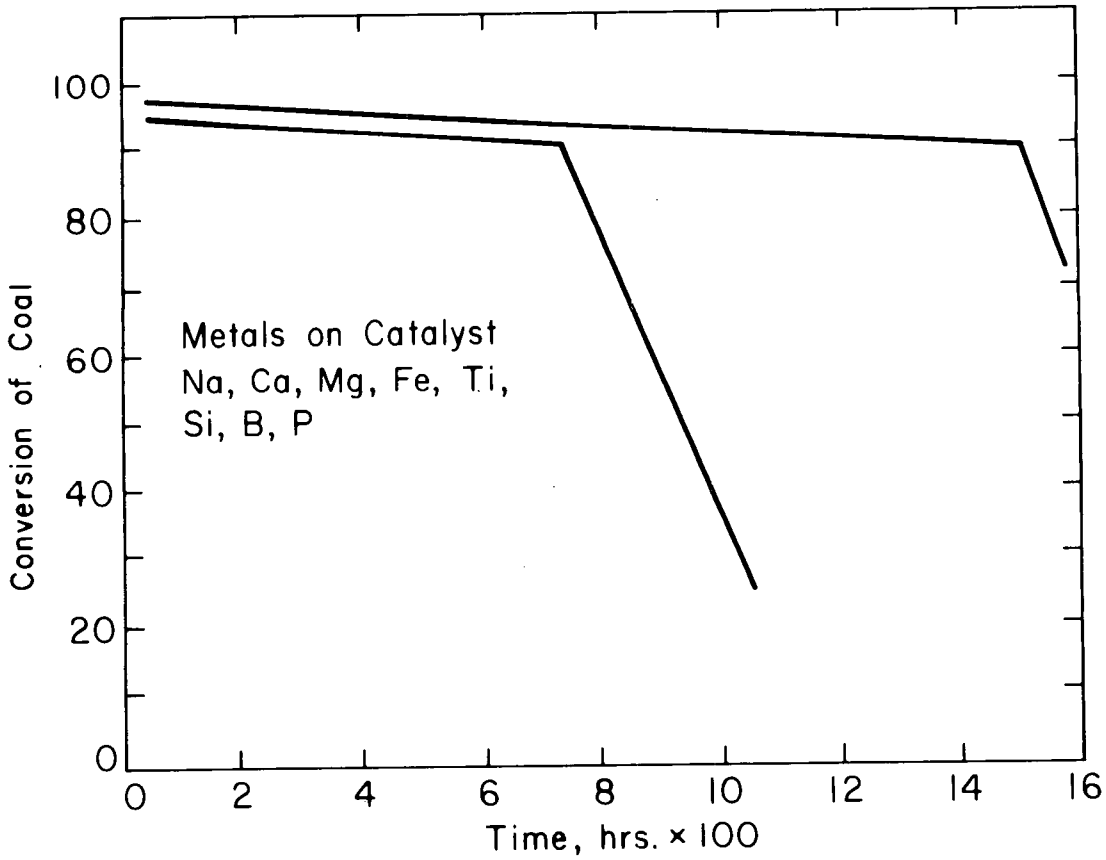


Fig. 1 Catalyst Deactivation

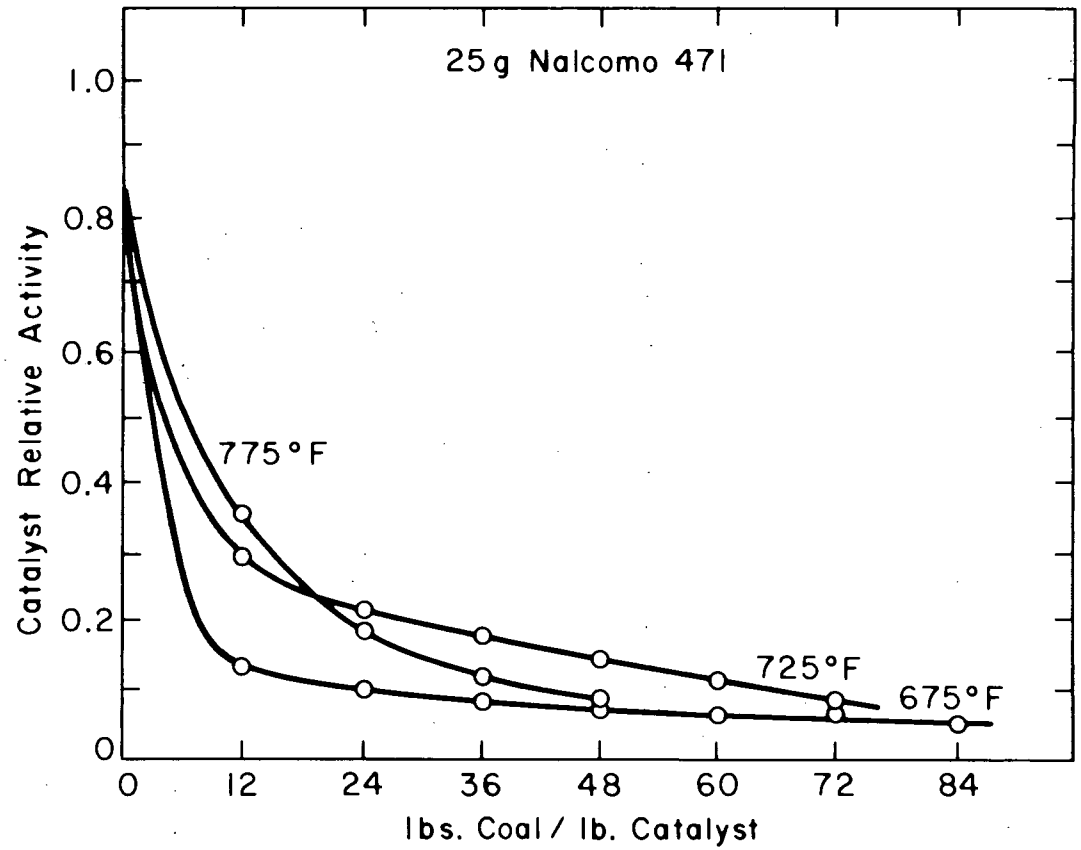


Fig. 2 Effect of Temperature

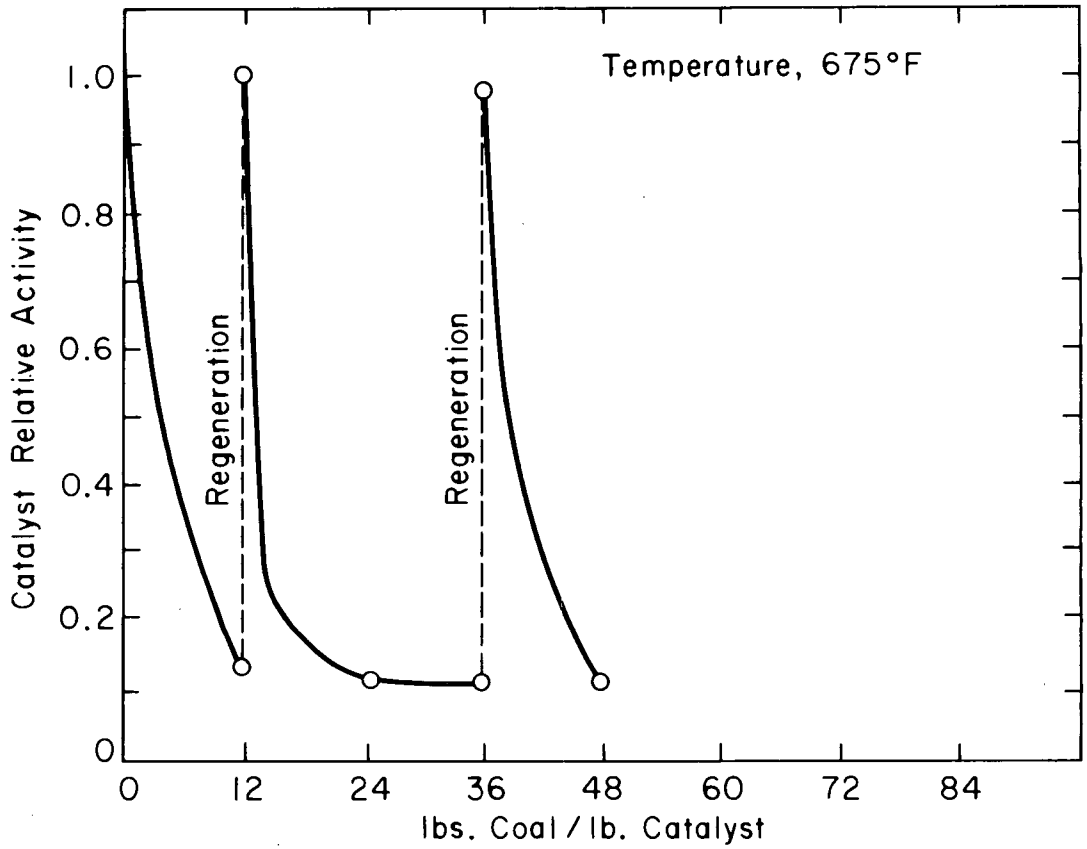


Fig. 3 Effect of Heavy Ends

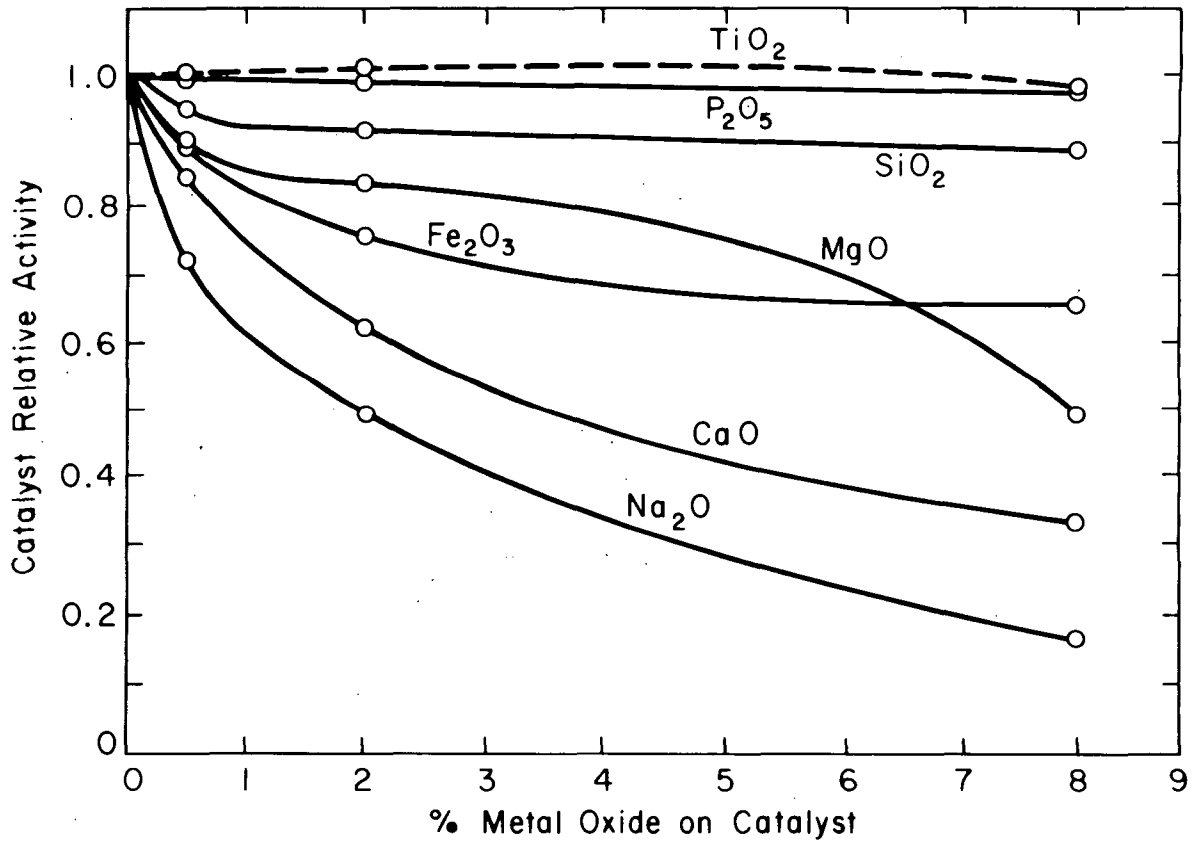


Fig. 4 Single Ash Component by Impregnation

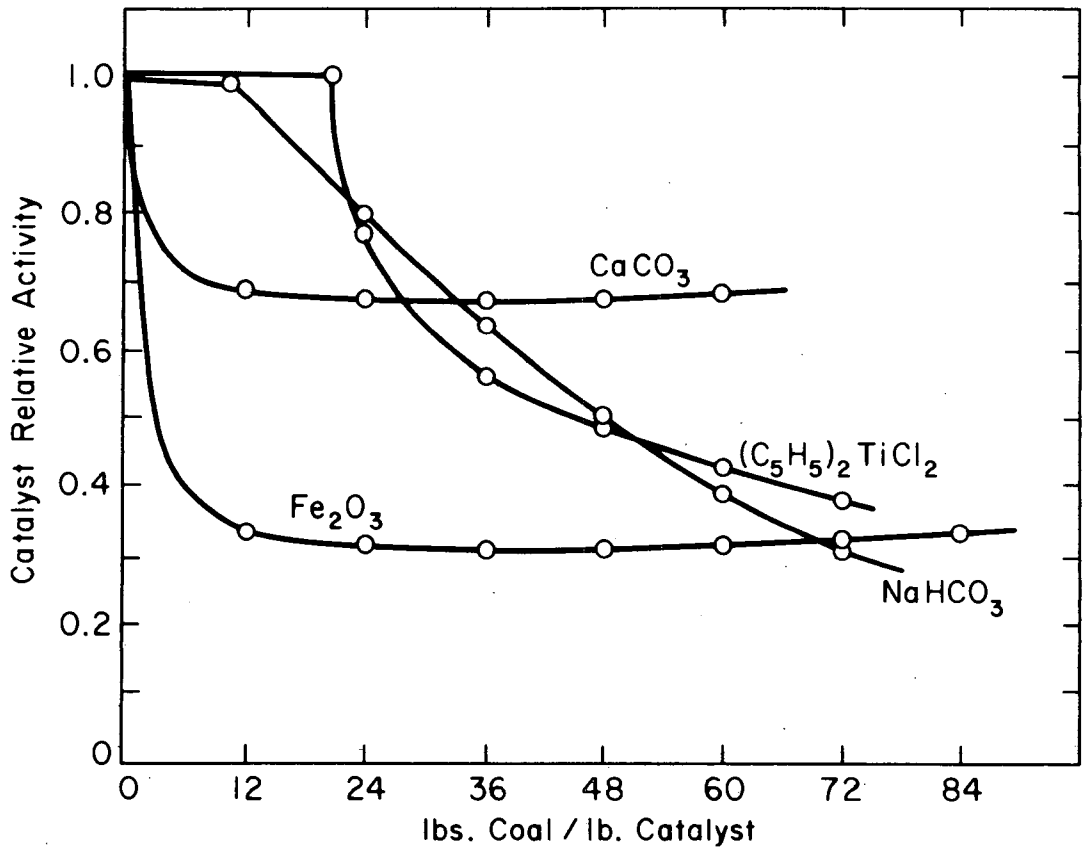


Fig. 5 Catalyst Exposed to Single Ash Compound

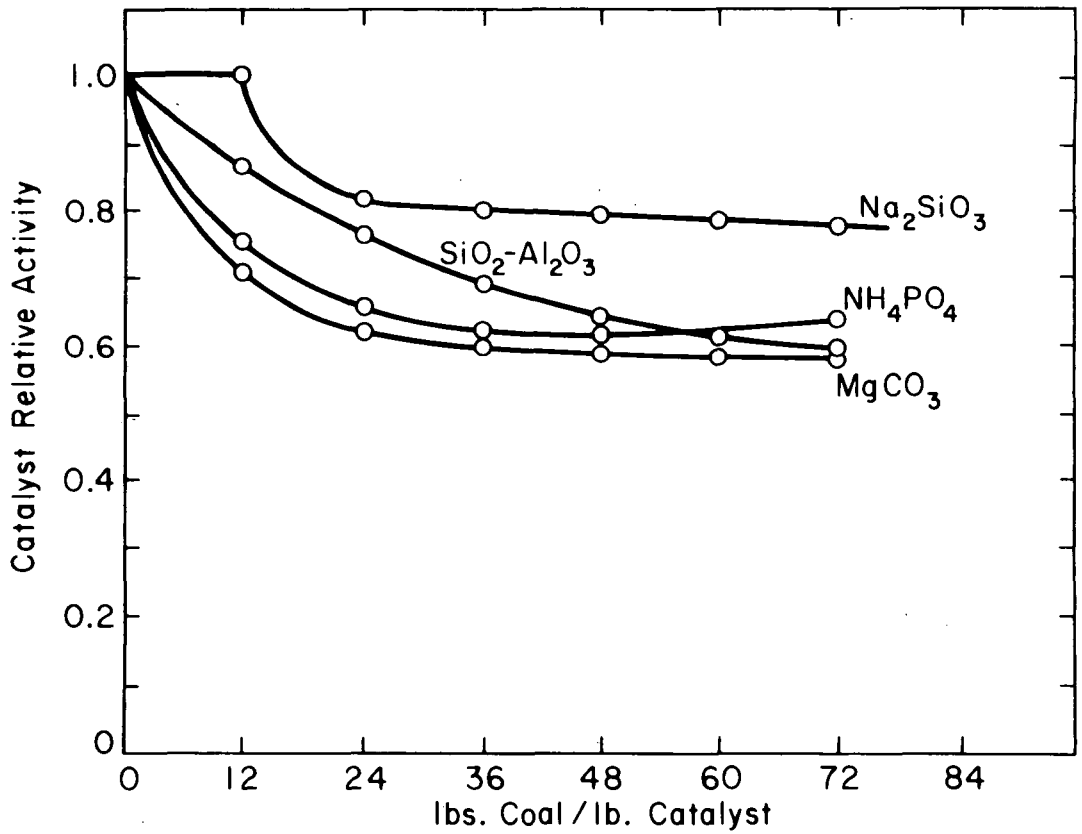


Fig. 6 Catalyst Exposed to Single Ash Compound

TABLE 4

| ASH CONSTITUENT | g/RUN | CATALYST ACTIVITY | % METAL OXIDE ON CATALYST-AA | CATALYST ACT. BASED ON FIG. 4 |
|---|---|---|---|---|
| $NaHCO_3$ | 1.0 | 0.53 | 2.2 | 0.51 |
| $CaCO_3$ | 1.8 | 0.69 | 0.44 | 0.79 |
| $MgCO_3$ | 1.3 | 0.60 | 3.0 | 0.72 |
| $Fe_2O_3$ | 8.0 | 0.34 | 10.0 | 0.38 |
| $TiCl_2$ $(CP)_2$ | 2.0 | 0.82 (R) | 2.2 | 0.98 |
| $NH_4PO_4$ | 0.5 | 0.80 (R) | | |
| $Na_2SiO_3$ | 1.0 | 0.75 | 1.1 Total<br>0.45 Na | 0.9 - $SiO_2$<br>0.80 - Na |
| $SiO_2$-$Al_2O_3$ | 50 | 0.69 | 7.3 | 0.90 |

(R) = CATALYST REGENERATED IN AIR TO REMOVE CARBON OR AMMONIA