# MECHANICAL PROPERTIES OF FORMCOKE AFTER REACTION IN $CO_2$ AND $CO/CO_2$ ENVIRONMENTS

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**Abstract**—The mechanical properties of a special formcoke were studied after reaction in $CO_2$ and in $CO/CO_2$ mixtures. The effects of iron- and potassium-catalyzed gasification were also investigated. The Young's elastic modulus, fracture toughness, and fracture surface energy were all observed to decrease with increasing amounts of reaction of the formcoke. These properties were observed to be strongly correlated to the final bulk density rather than to the particular reaction conditions.

**Key Words**—Formcoke, density, mechanical properties, gasification, catalysis.

## 1. INTRODUCTION

As described in an earlier paper, formcoke has been given serious consideration as an alternative fuel for use in blast furnaces and in other metallurgical applications[1]. The ability to prepare formcoke from a wide range of coking and non-coking coals makes it of great interest in light of the decreasing availability and increasing expense of the good coking coals required to prepare conventional metallurgical cokes [2,3]. Although several processing methods have been investigated for the preparation of formcoke, the one most widely considered is that corresponding to the specimens examined in this study. This process involves the low-temperature separation of the tar and char components of the coal, calcination of the char to remove its shrinkage characteristics, recombination of the calcined char with the tar, briquetting, and carbonization [4,5]. Blast-furnace trials that have been completed using formcoke have yielded promising indications.

Many properties of the formcoke are critical to its success as a blast furnace fuel. Some of those which have been studied include its reactivity under various environmental conditions and its mechanical properties before and after reaction [6,7]. The effects of reaction in various $CO/CO_2$ environments on mechanical properties are of particular interest, because of the dynamic nature of the environment in the blast-furnace stack. The mechanical properties of the unreacted formcoke were discussed in a previous publication [1]. This paper addresses the changes in mechanical properties of a specially prepared formcoke after reaction in $CO_2$ at temperatures between 700–850°C. Changes in mechanical properties when the $CO_2$ reaction was inhibited by adding CO were

also investigated. Finally, the effects of catalysis of the reaction by iron and potassium on the mechanical properties of the formcoke are discussed.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Materials

The proximate and ultimate analyses of the original coal and a char prepared from it for use in this study are given in Table 1. The coal is Illinois #6 high-volatile-C bituminous. It was pyrolyzed at 500°C in an $O_2$-steam environment to separate the tar and char fractions. The char was then further heat treated to 815°C in $N_2$, resulting in shrinkage of the particulates as they were further carbonized. After calcination, the char was recombined with the pitch, and rectangular formcoke specimens measuring approximately $127 \times 25 \times 13$ mm were molded at 85°C. Although formcoke is conventionally molded as pillow-shaped briquettes, a rectangular shape was required to facilitate the measurement of mechanical properties for this study. Subsequent to molding, carbonization was carried out at 870°C in $N_2$ to obtain the final specimens.

### 2.2 Physical properties

Before characterizing various physical properties of the formcoke specimens they were dried for 10 hours in air at 120°C because of their highly hygroscopic nature. Physical properties of the formcoke are summarized in Table 2. As shown in the table, the bulk density varied from 0.70 to 0.94 Mg m$^{-3}$. The porosity of the specimens was determined by immersion in water under vacuum, which indicated a pore fraction of 0.497.

### 2.3 Reaction environments

Prior to reaction of the samples, they were dried at 120°C to remove any adsorbed water. After drying, the first two high-temperature exposures of the samples consisted of heating them to the planned

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Table 1. Proximate and ultimate analyses of the coal and char*

| Proximate analysis, (dry basis), wt% | | |
| Component | Illinois no. 6 coal | Char |
| --- | --- | --- |
| Volatile Matter | 35.9 | 3.5 |
| Fixed carbon | 58.2 | 86.8 |
| Ash | 5.8 | 9.7 |
| Sulphur | 0.7 | — |

| Ultimate analysis, wt%* | | | |
| | Illinois no. 6 coal | | Char | |
| Component | ar | db | ar | db |
| --- | --- | --- | --- | --- |
| Moisture | 5.1 | — | 1.8 | — |
| C | 73.0 | 77.7 | 84.2 | 85.8 |
| H | 4.8 | 5.1 | 1.1 | 1.1 |
| N | 0.9 | 1.0 | 1.5 | 1.6 |
| Cl | 0.4 | 0.4 | — | — |
| S | 0.7 | 0.7 | 0.6 | 0.6 |
| O | 9.1 | 9.6 | 2.9 | 2.9 |
| Ash | 5.9 | 6.2 | 7.9 | 8.0 |

*Analyses performed at Inland Steel, East Chicago, Indiana.
*(ar) as received, (db) dry basis

reaction temperature and holding for 5 hours in $N_2$ only. The specimens were cooled to room temperature for observation after each of the 5-hour periods. After the $N_2$ treatments, the samples were exposed to various $CO/CO_2$ environments.

In order to avoid changing the original material characteristics imposed by the initial processing conditions of the formcoke, all reactions were carried out at temperatures below the carbonization temperature of 870°C. Surpassing this temperature would result in the resumption of carbonization, accompanied by structural changes in the formcoke. Three temperatures were included: 700°C, 800°C, and 850°C. Although these temperatures may appear low compared to the temperature extremes present in a blast furnace, the importance of exploring the effects of reaction at these temperatures on the mechanical properties must not be underestimated, especially in the presence of $CO_2$. These conditons prevail in the upper stack of the blast furnace, through which the formcoke must travel before encountering the more severe reaction conditions lower in the blast furnace.

Table 2. Physical properties and characteristics of the formcoke specimens*

| Bulk density, Mg m⁻³ | |
| --- | --- |
| Range | 0.70–0.94 |
| Average | 0.83 |
| X-ray density Mg m⁻³ | 2.07 |
| Surface area, m² g⁻¹ ($CO_2$, 298 K) | 475 |
| Porosity, fraction (open to $H_2O$) | 0.497 |
| Elastic Modulus, GPa | 13 |

*All properties reported on a mineral-matter-containing (mmc) basis.

The environments investigated included the $N_2$ pretreatment, $CO_2$, 50% $CO_2$/50% CO, and 20% $CO_2$/80% CO. In addition, the effects of catalyzed gasification on mechanical properties were investigated, including the presence of iron in an active and inactive state, and the presence of potassium.

### 2.4 Mechanical properties

The mechanical properties investigated in this study include Young's modulus of elasticity, fracture toughness, the fracture initiation energy, and the fracture propagation energy. The elastic moduli were determined using the dynamic mechanical resonance technique discussed by Spinner and Teft[8], and by Davis[9]. Fracture toughness of the formcoke was determined using the notched-beam test[10–11], the specimen geometry is shown in Fig. 1(a). The notches were cut with a 0.03-cm diameter diamond blade, to a depth of approximately half the specimen height. The samples were then broken in three-point-bend with the notch in tension. Two types of fracture surface energy were determined: the fracture initiation and fracture propagation energies. The fracture initiation energies were calculated from the notched-beam test information. The fracture propagation energies were determined via the work-of-fracture test[12]; the latter test geometry is shown in Fig. 1(b). More detailed information on testing procedures and calculations is given elsewhere[6].

### 3. RESULTS AND DISCUSSION

The results are divided into several sections to facilitate their discussion. Changes in mechanical properties after pretreatment in $N_2$ are described in
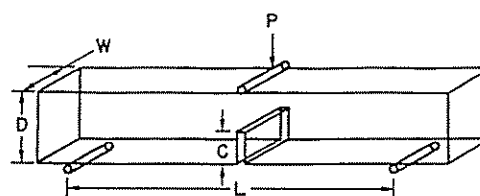


(a.) NOTCHED–BEAM TEST CONFIGURATION
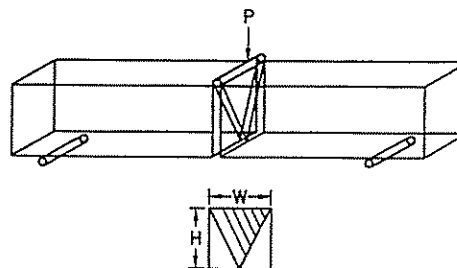


(b.) WORK–OF–FRACTURE TEST CONFIGURATION

Fig. 1. Specimen configurations for (a) the notched-beam test, and (b) the work-of-fracture test.
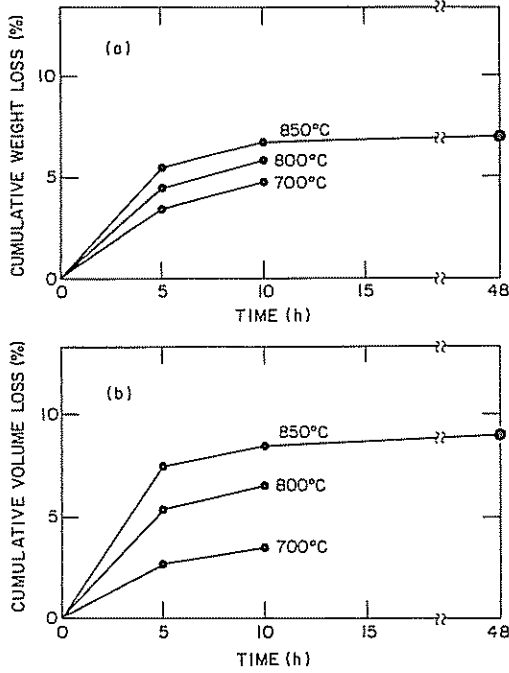
Fig. 2. Effect of heat treatment at various temperatures in N₂ on (a) weight loss and (b) volume loss of formcoke.



Fig. 4. Effect of heat treatment at various temperatures in N₂ on the normalized Young's elastic modulus of formcoke.

the first section, followed by results after reaction of the formcoke in $CO_2$, and also in mixtures of CO and $CO_2$, where inhibition of the reaction was observed. Finally, changes in mechanical properties after gasificaton in the presence of catalysts are presented.

3.1 *Properties after N₂ pretreatment*

As previously described, the specimens were pretreated in N₂ prior to carrying out the actual gasification experiments. The cumulative weight loss and volume loss at 500°, 800°, and 850°C in N₂ are shown in Fig. 2. It is clear that the major changes occurred during the first 5-hour heat treatment and that these changes were more pronounced at higher temperatures. Additional heat treatments in N₂ were not observed to result in significant changes. Recalling that carbonization at 870°C was carried out for only
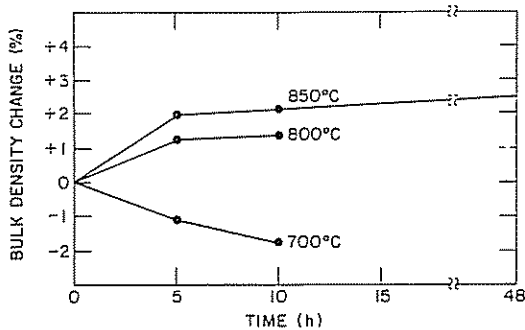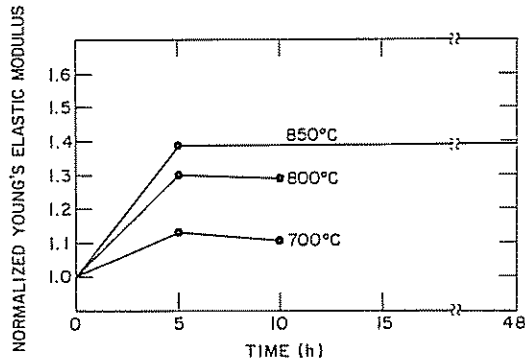
20 min, it is reasonable to assume that the equilibrium structure for this heat-treatment temperature was probably not achieved. An interesting observation made after the N₂ heat treatments were carried out was that an increase in bulk density occurred as a result of the greater decrease in volume than in mass. This in turn resulted in an increase in Young's modulus of elasticity. These two properties are shown in Fig. 3 and Fig. 4, respectively. This indicates that a more rigid and presumably stronger structure is produced by the additional heat treatment of the specimens in an inert environment, and may warrant consideration of such a procedure in the future processing of formcoke.

3.2 *Mechanical properties after $CO_2$ gasification*

After all specimens were pretreated in N₂ for the two 5-hour periods, they were gasified in one atmosphere of $CO_2$. Reactivity plots at 700°C, 800°C, and 850°C are illustrated in Fig. 5. The first two data points for each curve correspond to the two N₂ heat treatments. Gasification was carried out in a stepwise fashion. The samples were cooled to room temperature and removed from the furnace for the determination of various properties after selected periods of time. As can be observed in Fig. 5, the rate of gasification of the formcoke increased with
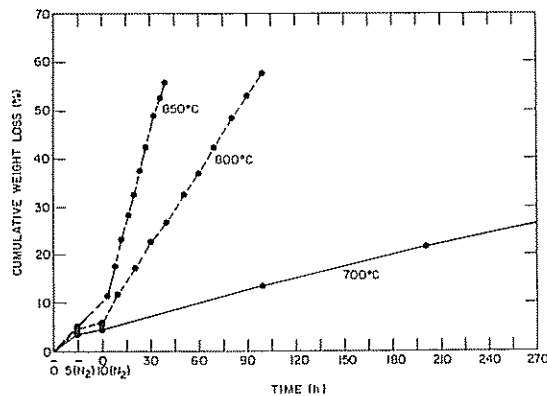


Fig. 3. Effect of heat treatment at various temperatures in N₂ on the bulk density change of formcoke.



Fig. 5. Reactivity plots for formcoke in one atmosphere of $CO_2$ at 700°C, 800°C, and 850°C.

temperature from 0.07 wt%/h at 700°C, to 0.59 wt%/h at 800°C, to 1.52 wt%/h at 850°C. The times required to attain similar weight losses of approximately 55% at the above temperatures were 1000 hours, 100 hours, and 40 hours, respectively. By examining the cross-section of a reacted specimen, the amount of reaction or burn-off occurring externally at the surface and/or internally can be estimated. Density profiles obtained for specimens after reaction at 700°, 800°, and 850°C to approximately 40% weight loss are presented in Fig. 6. The points at the greatest sample thickness correspond to the as-prepared sample. It is clear from these data that the gasification reaction took place uniformly throughout the bulk of the specimens at each of the three temperatures, indicating that any changes in material properties should also be uniform.

Since Young's elastic modulus was measured using a nondestructive technique, progressive changes in this property were readily monitored as a function of the extent of gasification. After gasification in $CO_2$ at 700°C, 800°C, and 850°C considerable decreases in Young's elastic modulus were observed, as illustrated in Fig. 7; the data are presented as a function of the percent weight loss or extent of gasification. For purposes of illustration, these values are normalized to the original elastic moduli of the specimens. Each data point is the average value for six specimens that were reacted simultaneously. The effects of pretreatment in $N_2$ at the reaction temperature for two 5-hour periods can be seen as the first two points on each curve. As described earlier, this pretreatment causes an increase in the elastic modulus, the increase being greater for the higher heat-treatment temperature. The increase corresponds to a slight densification of the specimens. In contrast, gasification in $CO_2$ results in a decrease in the elastic modulus, the rate of which was most rapid in the initial stages of gasification. Reaction to sixty percent weight loss yielded a value of only one tenth of the original elastic modulus. The observed decrease is consistent with the uniform gasification across the specimen thicknesses described earlier.

It should be noted that all of the specimens gasified at the three reaction temperatures were of nominally
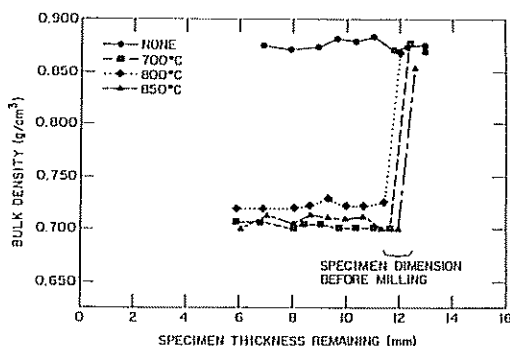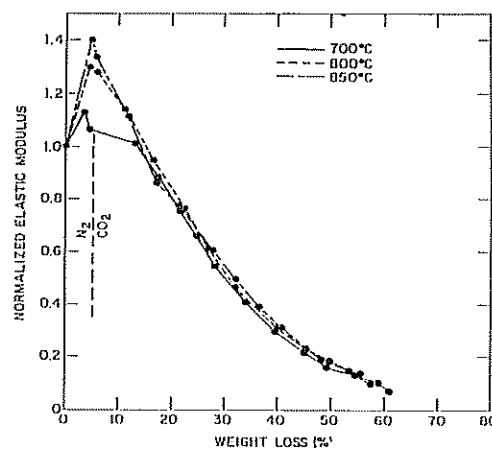


Fig. 7. Young's elastic modulus as a function of extent of reaction at 700°C, 800°C, and 850°C in $CO_2$.

the same initial values of bulk density and elastic modulus. The proximity of the data for the three different reaction temperatures indicates that the decrease in the elastic modulus depends very strongly on the degree of gasification of the specimens, but little on the gasification temperature, as long as gasification through the specimen occurs at a uniform rate.

### 3.3 *Effects of CO—CO₂ environments on mechanical properties*

The inhibition of the carbon-$CO_2$ reaction in the presence of CO has been well-documented in the literature[13–15]. Results of the present study confirm a decrease in the reaction rate when CO is added to the reactant gas stream. Figure 8 illustrates the extent of weight loss as a function of time at 850°C in three different $CO_2$/CO environments. The rate decreases systematically from 1.52 wt%/h in 100% $CO_2$, to 0.44 wt%/h in 50% $CO_2$, to 0.22 wt%/h in 20% $CO_2$ (the remainder being CO). The first two data points on each curve correspond to the initial $N_2$ heat treatments. The percentages of CO present in these experiments were much greater than



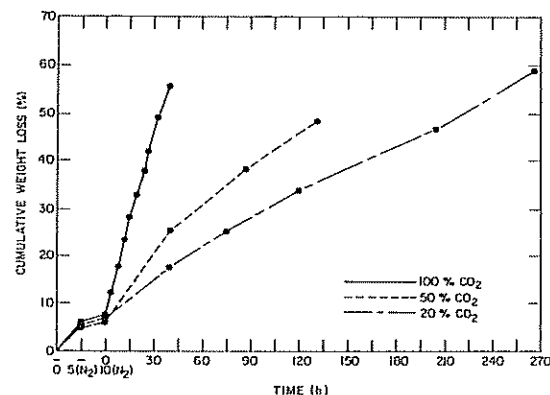Fig. 6. Bulk density profiles of specimens reacted in $CO_2$ at 700°C, 800°C, and 850°C.



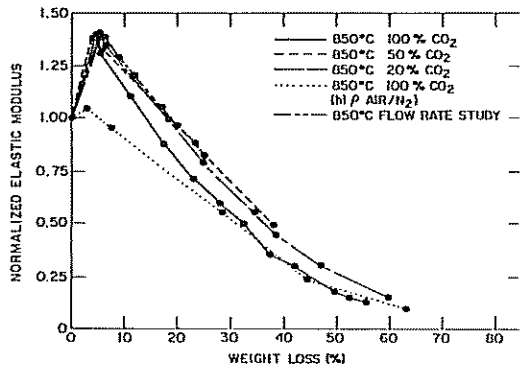Fig. 8. Reactivity plots for formcoke gasified at 850°C in various $CO_2$/CO environments.

Fig. 9. Normalized Young's elastic modulus versus extent of reaction at 850°C for formcoke specimens reacted in various environments.



Fig. 10. Fracture toughness of the as-prepared and reacted formcoke specimens as a function of bulk density.

in the previous studies, where the formcoke was gasified as a function of temperature in $CO_2$ only.

Specimens reacted in different gasification environments exhibit decreases in Young's elastic modulus similar to those described previously for samples reacted in $CO_2$ only. Figure 9 illustrates the normalized values as a function of the extent of reaction (%weight loss) for specimens reacted at 850°C in three different environments: 100% $CO_2$, 50% $CO_2$/50% CO, and 20% $CO_2$/80% CO. As already discussed, the first two data points correspond to the $N_2$ pretreatment. The elastic modulus increased about 40% after the $N_2$ treatments at 850°C. It is immediately apparent that samples reacted in 50% $CO_2$ and 20% $CO_2$ exhibit an overall slower decrease in elastic modulus than samples reacted in 100% $CO_2$, and therefore lie at higher modulus values after the same amount of weight loss. A possible explanation of this behaviour could be a greater inhibition of gasification of the binder phase by CO relative to the filler phase. The binder phase might be expected to control the stiffness characteristics and therefore the elastic moduli of the specimens. Unfortunately, the composite nature of the samples does not permit separate determinations of the reactivities of the two components.

The fracture toughnesses of the reacted formcoke specimens were measured using the notched-beam test, which requires fracturing the specimens at an artificial flaw. Because of the destructive nature of this test, fracture toughness was only determined after specimens were reacted to the fullest extent of interest. For this reason, most of these data lie at relatively low specimen bulk densities. The relationship between fracture toughness and bulk density is illustrated in Fig. 10 for both the reacted specimens and the as-prepared specimens. It is clear that the gasification-related decrease in bulk density also results in a significant decrease in fracture toughness. This change corresponds to a decrease in the load-bearing capacity or strength of the material, as the bulk density is decreased by gasification. A linear
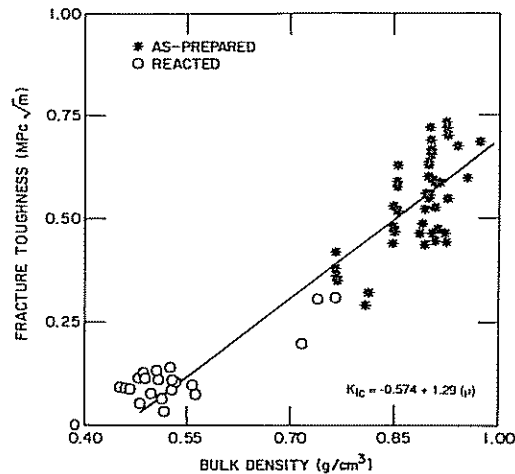
regression line is drawn through the data, and the regression equation is included on the plot.

Fracture surface energies were also determined for the reacted specimens. The fracture initiation energies, $\gamma_{NBT}$, were determined using the notched-beam test, and the fracture propagation energies, $\gamma_{WOF}$, were determined using the work-of-fracture test. Since both tests are destructive in nature, these surface energies were only obtained for the as-prepared specimens and for specimens which had been gasified to the fullest extent of interest. The fracture initiation energy ($\gamma_{NBT}$) as a function of the bulk density is shown in Fig. 11. Values for both the as-prepared and the reacted formcoke specimens are included on the plot. It should be noted that the scatter in the data for this particular property is compounded by the fact that it is calculated from two experimentally determined parameters, the elastic modulus and the fracture toughness. Whereas the
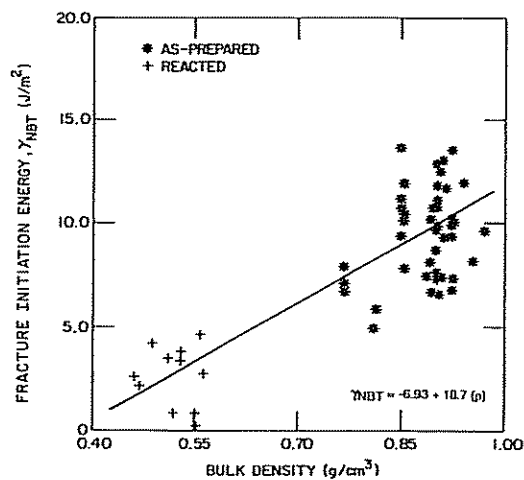


Fig. 11. Fracture initiation energy of the as-prepared and reacted formcoke specimens as a function of bulk density.

fracture initiation energy for the as-prepared spec-imens ranged from approximately $3 J/m^2$ to $14 J/m^2$, after extensive gasification the fracture energy never exceeded about $5 J/m^2$, indicating much easier frac-ture initiation after gasification. It must be noted, of course, that the gasified specimens are of signif-icantly lower density. A regression line based on the unreacted and reacted data is included on the plot.

A similar plot is shown in Fig. 12 for the work-of-fracture (fracture propagation energy) as a func-tion of bulk density. The values for the reacted spec-imens are slightly higher than those observed for the fracture initiation energies. They range from ap-proximately $3 J/m^2$ to $7 J/m^2$. These values are again much lower than those observed for the as-prepared formcoke. The linear regression equation describing the combined as-prepared and reacted formcoke data is included on the plot. The close proximity of the fracture initiation energy and the work-of-frac-ture noted for the as-prepared specimens still exists after extensive gasification. This indicates little re-sistance to fracture propagation once fracture has been initiated. It also implies poor thermal shock damage resistance[16].

## 3.4 Effects of catalyzed gasification on mechanical properties

The changes in mechanical properties after the gasification of the formcoke in the presence of iron and potassium catalysts were investigated. A brief description of the iron catalysis experiments is pre-sented first with the corresponding effects on me-chanical properties, followed by the effects of ca-talysis by potassium on mechanical properties.

3.4.1 Investigation of catalysis by iron. Catalysis of gasification by iron is of special interest, because iron or one of its compounds is frequently a major component of many coal ashes and is, of course, present throughout the entire blast-furnace process. Consideration of the mineralogical analysis of the

precursor coal used to produce the formcoke reveals that iron is indeed present in the coal in the chem-ically combined form of pyrite, $FeS_2$. Approximately 5–10% of the ash (which comprises about 6% of the coal) is pyrite. It has been shown in the literature that iron is effective as a catalyst only when in the elemental or reduced state[17]. For this reason, the pyrite in the specimens was reduced to metallic iron by heating the specimens to 850°C for 60 hours in flowing $H_2$, resulting in the removal of sulphur as $H_2S$. It was of interest to examine the reactivity of the iron-metal-containing formcoke in a $CO/CO_2$ environment for comparison with the results de-scribed previously. In order to avoid conversion of the metallic iron to iron oxide, gasification was nec-essarily carried out in an environment of 80% CO and 20% $CO_2$. Although ratios of other than 4:1 for the $CO/CO_2$ environment could have maintained iron in the metallic state, excessive amounts of CO would have resulted in its disproportionation, such that carbon deposition would have taken place rather than carbon gasification.

Reactivity plots for specimens with and without the activated iron catalyst are shown in Fig. 13. In-cluded on this plot of cumulative weight loss versus reaction time are the data presented earlier for as-prepared formcoke specimens reacted in 100% $CO_2$ and in 20% $CO/80\%$ $CO_2$ environments. The first two data points for each curve correspond to the heat treatments in $N_2$. Comparison of these reaction curves clearly indicates the catalytic activity of the iron metal. In the absence of the reduced iron the reaction rate was approximately 0.22 wt%/h, while the initial rate of reaction in the presence of the activated catalyst increased by a factor of five to 1.15 wt%/h. Although CO was shown to be an inhibitor for the $CO_2$ reaction, it acts as an accelerator for the $CO_2$ reaction catalyzed by iron because of its ability to maintain the metal in the reduced and, therefore, active state.

In order to carry out various measurements as a function of extent of reaction, the catalyzed speci-mens were periodically removed from the furnace
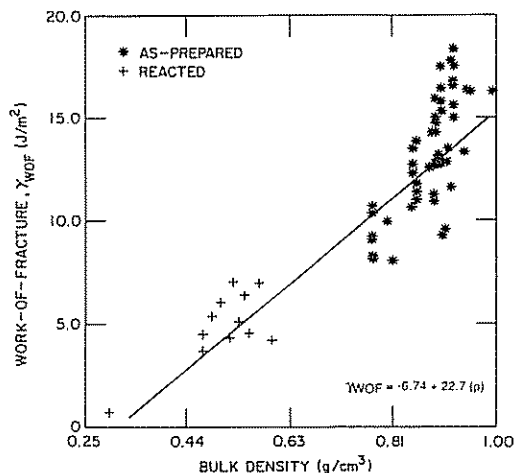


Fig. 12. Work-of-fracture of the as-prepared and reacted formcoke specimens as a function of bulk density.
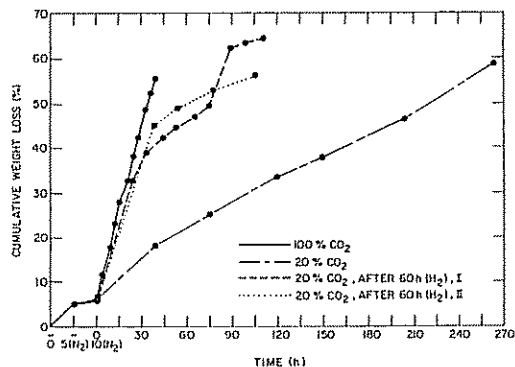


Fig. 13. Reactivity plots for specimens both with and with-out the activated iron catalyst, reacted at 850°C.

and then returned for further gasification. It is apparent from Fig. 13 that after a period of time the catalyst became deactivated. The reaction rate eventually decreased to 0.21 wt%/h, nearly identical to that for gasification carried out in the same environment for the uncatalyzed specimens. In an attempt to reactivate the catalyst, the specimens were again held in $H_2$ at 850°C, for 22 hours. Subsequent reaction in the 20% CO/80% $CO_2$ environment resulted in an increase in reactivity to 1.18 wt%/h, indicating that reactivation of the iron catalyst was indeed possible. Further reaction showed a similar decrease in reactivity to a rate of 0.20 wt%/h as a result of a second deactivation of the catalyst.

Two possibilities are suggested which may account for the lack of catalytic activity after a certain period of reaction. The first is redistribution of any sulphur remaining in the formcoke specimens onto the surfaces of the reduced iron particles. A second possibility is oxidation of the free iron by air when the specimens were removed from the furnace intermittently for property measurements. Since the second heat treatment in $H_2$ could serve to reduce either the sulphide or the oxide back to the free metal, a second experiment was carried out to investigate the deactivation phenomenon. This involved identical treatment of the specimens through the 60h heat treatment in hydrogen. The specimens were then gasified in 20% $CO_2$/80% CO for 33 hours, rather than the 25 hours used for the first group. If deactivation was due to redistribution of sulphur during gasification, then the longer initial period of gasification should have resulted in a slower apparent gasification rate. The results of this experiment are shown as the curve marked II in Fig. 13. It is apparent that similar gasification behaviour was exhibited by both sets of specimens after heat treatment in $H_2$. The initial gasification rates differ only slightly: 1.15 wt%/h for the first group and 1.12 wt%/h for the second group. The proximity of these values suggests that deactivation of the iron is probably not a result of sulphur redistribution. Also in favour of this conclusion is the immediate decrease in reactivity of the second group of specimens after removal from the furnace, analogous to the behaviour of the first group. The catalytic behaviour of the iron was quickly diminished by exposure to air and oxidation of the catalyst.

As for the as-prepared specimens and those gasified without any active catalyst present, the Young's elastic modulus of the iron catalyst-containing specimens was monitored as a function of the extent of gasification. The data for both sets of specimens gasified at 850°C. in 20% $CO_2$/80% CO in the presence of the active iron catalyst, are shown in Fig. 14. Also included are the elastic modulus data for specimens gasified at 850°C in 100% $CO_2$ and in 20% $CO_2$/80% CO in the absence of an active catalyst. Behaviour similar to that exhibited by the specimens reached in 100% $CO_2$ was observed, even though the catalyzed specimens were reacted in 20% $CO_2$/80% CO.
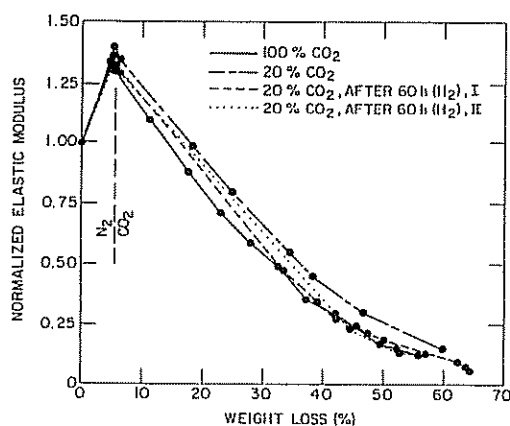


Fig. 14. Normalized Young's elastic modulus versus extent of reaction for specimens gasified in the presence of the active or inactive iron catalyst at 850°C.

Although the exact behaviour at low values of weight loss is not known because the initial periods of reaction were long, at greater than 40% weight loss the three curves fall together. This behaviour suggests that at lower values of weight loss the change in the elastic modulus would also be similar to that for specimens gasified in 100% $CO_2$.

3.4.2 *Investigation of catalysis by potassium.* This investigation was slightly different from that involving catalysis of gasification by iron, in that the iron was already present in the formcoke as a constituent of the mineral matter and was reduced from its chemically combined form of pyrite. The potassium was intentionally added to the formcoke by means of a solution of potassium carbonate. Potassium is present in the blast-furnace operation because of the accumulation of alkali from the slag, and the potential effects on mechanical properties after catalyzed reaction in CO/$CO_2$ is, therefore, of interest.

Reactivity plots for specimens containing intentional additions of approximately 4.5 wt% of potassium (on an elemental potassium basis) are illustrated in Fig. 15. This plot of cumulative weight loss versus time includes data for specimens reacted
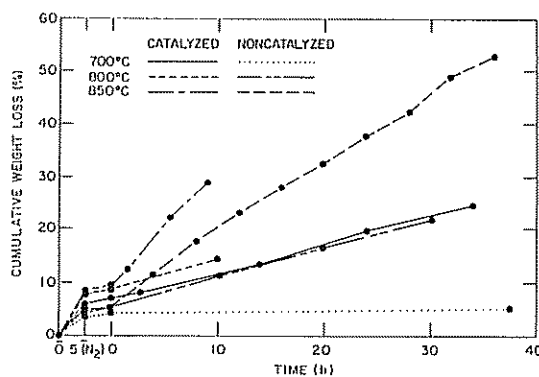


Fig. 15. Reactivity plot for the specimens gasified in the absence or presence of the potassium catalyst.

in 100% $CO_2$ at 700°C, 800°C, and 850°C, both with and without the addition of potassium. It is clear that at all reaction temperatures, the reactivity is substantially increased upon addition of potassium, confirming its catalytic activity. The reaction rates increased from 0.07 to 0.49 wt%/h at 700°C. 0.59 to 1.46 wt%/h at 800°C, and from 1.52 to 2.35 wt%/h at 850°C. The slightly greater weight loss during the two five-hour heat treatments in $N_2$ is attributed to the volatilization of a small amount of the potassium carbonate during these heat treatments.

Unlike the reaction catalyzed by iron, no deactivation of the potassium catalyst was observed. This is because of the direct role of both potassium and potassium carbonate in the mechanism for the catalyzed reaction, as described by McKee and Chatterji[17]. In this mechanism, the recycled carbonate again reacts with the substrate carbon resulting in further gasification. Rather than becoming deactivated after periodic removal of specimens from the furnace for measurements, the reaction rates remained constant.

The effects of catalysis of gasification of the formcoke by potassium on the Young's elastic modulus are shown in Fig. 16. The presentation of these data was made rather complicated because of the addition of potassium carbonate to the specimens. This addition yielded an increase in mass of approximately 7 wt% and, therefore, an apparent increase in the bulk density of the same percentage. In effect, the density of the carbon portion of the formcoke was not really increased, but the simple addition of the potassium carbonate did have a substantial effect on the elastic modulus of the formcoke. An increase of about 30% in the elastic modulus was observed. This is apparently due to the increased stiffness of the formcoke afforded by the presence of potassium carbonate. The extra mass was likely located in pores and microcracks in the specimen. As discussed earlier, these microstructural features are highly deleterious to the elastic modulus, and a reduction in their quantity would result in an increase in Young's elastic modulus.
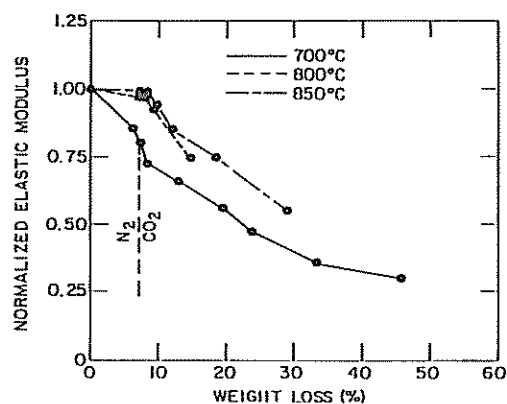
Rather than incorporating this effect into the data presented in Fig. 16, these data were normalized to the final elastic moduli of the specimens before the reactivity experiments were started. This corresponds to the values for the potassium-containing specimens. As a result, the effects of the two 5-hour heat treatments in $N_2$, which again correspond to the first two data points of each curve in Fig. 16, are not the same as observed previously. It appears that the presence of potassium carbonate, presumably occupying micropores and microcracks, discounts any further increase in Young's elastic modulus that may have been anticipated from the two heat treatments in $N_2$. The changes observed correlate well with the changes in bulk density. The greatest decrease in the elastic modulus and in the bulk density during the $N_2$ heat treatments occurred for the specimens heated at the lowest temperature, 700°C. This indicates that there is indeed still some effect due to temperature, even after the potassium carbonate is added.

3.4.3 *Fracture toughness and fracture surface energy after catalyzed gasification.* Because of the limited amount of data, the fracture toughnesses and surface energies of specimens gasified with either the iron or potassium catalyst are combined and presented together. The relationship between the fracture toughness and the bulk density is shown in Fig. 17 for the as-prepared formcoke specimens and the specimens gasified in the absence of a catalyst taken from Fig. 10, as well as for those specimens reacted with either the active iron or potassium catalyst present. It is clear that these additional data follow the same general trend as exhibited earlier, whether reacted to intermediate densities or very low densities. No unusual behaviour was observed as a result of the presence of the catalyst. The regression equation describing the relationship between fracture toughness and bulk density is modified slightly from above, when the additional data for specimens containing a catalyst are included in the analysis. The

Fig. 16. Normalized Young's elastic modulus versus extent of reaction for formcoke specimens gasified in the presence of the potassium catalyst.
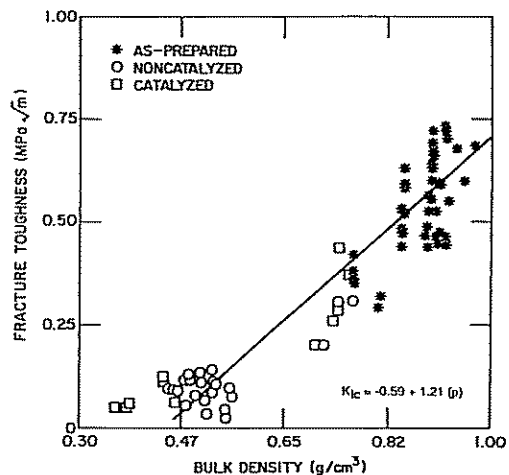
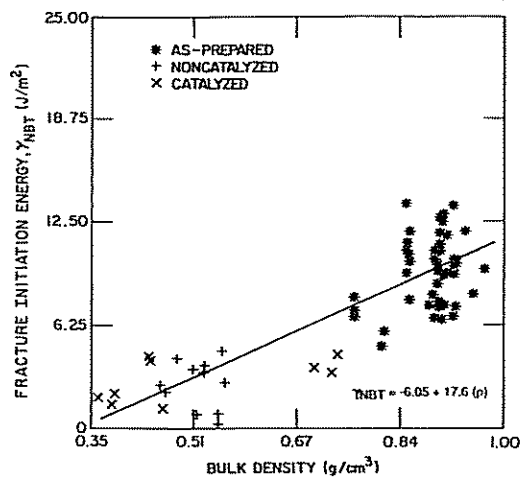Fig. 17. Fracture toughness versus bulk density for all specimens.

Fig. 18. Fracture initiation energy versus bulk density for all specimens.

regression line for all of the data is included on the plot along with the regression equation.

The fracture initiation energies shown earlier in Fig. 11 for the as-prepared formcoke and the reacted formcoke are shown again in Fig. 18 in combination with the specimens reacted in the presence of a catalyst. The additional data provided by the specimens that were gasified in the presence of a catalyst fit logically on the plot with the other data. No eccentric behavior was observed for data at either very low or intermediate post-reaction densities. A regression analysis incorporating all of the data and the regression line are shown on the plot.

The work-of-fracture or fracture propagation energies are presented in Fig. 19 in an analogous fashion to those energies discussed earlier. Again, the data reveal nothing unusual in the behaviour of this parameter after gasification in the presence of a catalyst. The relationship between the work-of-fracture and the bulk density is relatively linear, similar to the previous plot of the fracture initiation
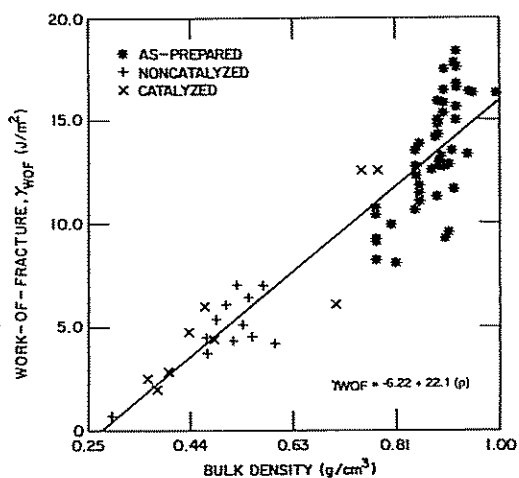


Fig. 19. Work-of-fracture versus bulk density for all specimens.

energies. The work-of-fracture is an independently determined parameter, whereas the fracture initiation energies are calculated from the Young's elastic modulus and fracture toughness, which tends to compound the scatter in the results. The regression line and equation are included on the plot. The similarity of the regression equations for the fracture initiation and fracture propagation energies indicates little resistance to crack growth once fracture has been initiated.

### 4. SUMMARY AND CONCLUSIONS

During preliminary heat treatment in a $N_2$ environment, shrinkage of the formcoke was observed that was temperature dependent. This suggests that complete carbonization to an equilibrium structure was not attained during the 20 min/870°C processing schedule. This resulted in further carbonization and structural changes in the formcoke at temperatures lower than the 870°C carbonization temperature. After approximately 10 hours in $N_2$ at each reaction temperature, the mass and volume of the specimens stabilized. All specimens were, therefore, heat treated at the reaction temperature for this period of time before reactivity experiments were carried out. This heat treatment resulted in an increase in both the bulk density and Young's elastic modulus of the formcoke.

Subsequent gasification in $CO_2$ and $CO/CO_2$ environments was carried out at 700°C, 800°C, and 850°C to substantial amounts of weight loss or burn-off. Reaction was found to occur uniformly throughout the bulk of the specimens. It was found that additions of CO into the entering $CO_2$ gas stream significantly reduced the rate of reaction, and that progressive increases in the concentration of CO resulted in corresponding decreases in the reaction rate. A continuous decrease in Young's elastic modulus was observed as a function of increasing burn-off. The decrease was greatest after the initial periods of gasification; however, a slower rate of decrease was exhibited when large quantities of CO were introduced.

Gasification of the formcoke also resulted in substantial decreases in fracture toughness and fracture surface energy. Regression analyses indicated that these data could have been predicted based on the properties of the as-received formcoke and would correspond to lower density samples. The fracture initiation and and fracture propagation surface energies were close in magnitude at all levels of gasification, indicating little resistance to fracture propagation once fracture has been initiated.

Catalysis of gasification of the formcoke by iron and potassium was studied. The iron catalyst was inherent to the formcoke, being present in the chemically combined and, therefore, inert form of pyrite. Desulphurization of the pyrite in a $H_2$ atmosphere activated the iron metal catalyst. Unlike the specimens involved in experiments for catalysis by iron,

those involving potassium were infiltrated with the catalyst prior to gasification. Accelerated reactivity was observed at all temperatures. Determination of the mechanical properties after catalyzed gasification did not indicate any eccentric behavior. The magnitudes of the Young's elastic modulus, fracture toughness, and fracture surface energy after catalyzed gasification were as would be predicted, based on the final bulk densities of the specimens according to relationships determined empirically for the as-prepared formcoke.

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