

EFFECTS OF CALCIUM MINERALS ON THE RAPID PYROLYSIS OF A BITUMINOUS COAL

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INTRODUCTION

Previous research at M.I.T. on rapid coal pyrolysis has dealt with the kinetics of evolution of individual products as a function of temperature, pressure, particle size, reactive gas, and coal type (1-5). Since recent studies elsewhere have shown that certain minerals occurring in coal affect significantly other types of coal conversion reactions, the present study was undertaken to determine what effects these minerals may have on rapid coal pyrolysis. This paper presents results on the pretreatment of coal with calcite (CaCO_3) and lime (CaO). These minerals have already been shown to influence fluidized-bed pyrolysis (6), steam gasification (7,8,9), and CO_2 gasification (10,11) of coal. Results obtained with other mineral additives will be reported later.

EXPERIMENTAL

The coal used was a Pittsburgh No. 8 Seam bituminous coal (Table 1) ground to -270+325 mesh (45-53 μm dia.). The native mineral matter was removed from the sample by extraction with HF and HCl followed by float-sink separation, resulting in a coal containing 4.3 percent by weight mineral matter, most of it pyrite. The demineralization procedure was shown to have no effect on the subsequent pyrolysis behavior of the coal (12). A fraction of the demineralized sample was co-slurried in water with 0.1 μm diameter calcite grains for 24 hours and dried at room temperature. The resulting mineral-treated coal contained 20.2 percent by weight CaCO_3 . A second fraction of demineralized coal was similarly treated with CaO , resulting in a sample containing 5.9 percent by weight of a mixture consisting of 74 percent Ca(OH)_2 and 26 percent CaCO_3 . Details of the pretreatment procedures are described elsewhere (12).

The pyrolysis apparatus (Fig. 1) and procedures have been described previously (2,12,13). Briefly, a thin horizontal layer of coal (≈ 15 mg) is sandwiched between the folds of a 325 US mesh stainless steel screen held between two electrodes in either a length of glass pipe or a stainless steel pressure vessel. The coal is heated by electrically heating the screen. The vessel and its gaseous contents remain at close to room temperature throughout the run, and thus the volatiles are quenched almost instantaneously on escape from the coal particles. The entire time-temperature history of the sample is recorded by use of a chromel-alumel thermocouple (75 μm bead diameter) positioned within the folds of the screen alongside the coal particles. Heat transfer calculations show that at pressures of 1 atm and heating rates of 1000 K/s or less, coal particles and thermocouple beads 80 μm or less in diameter closely follow the temperature of the screen and are spatially isothermal.

All reaction products were collected. Gases and low boiling liquids were trapped on lipophilic sorbents and subsequently analyzed by gas chromatography. Char was determined gravimetrically, and was further characterized by elemental analysis. Tar (room temperature condensibles) was collected on a filter at the reactor outlet and by a methylene chloride wash of the reactor internals, and its yield was determined gravimetrically. Total material balances usually exceeded 95 percent.

All runs were performed at heating rates of 1000 K/s with holding times of 0 or 5 s at the maximum temperature attained and cooling rates of about 200 K/s. These elements of the time-temperature history pertain only to the parent sample since the volatiles, once formed, rapidly escape the sample and are quenched as mentioned above. Demineralized and calcite-pretreated samples were heated in 1 atm He to temperatures between 800 and 1400 K. Other demineralized as well as lime-pretreated samples were heated in He at 1 atm or 69 atm to temperatures in the range 1050-1300 K.

RESULTS

Total yields of volatile products from demineralized and calcite-pretreated coals pyrolyzed in 1 atm He for 5 s holding time runs are shown in Fig. 2. The calcite-pretreated sample had lower weight losses, and hence higher char yields, than did the demineralized sample. Tar yields were greatly reduced in the presence of CaCO_3 , as shown in Fig. 3. The CaCO_3 -pretreated coal had a high temperature tar yield of 22 percent by weight dmmf coal, as compared with a yield of 30 percent by weight dmmf coal from the demineralized sample. Yields of lighter hydrocarbons were also reduced in the calcite-pretreated sample, although to a lesser extent than were yields of tar. The results for CH_4 , shown in Fig. 4, are typical for those of the light hydrocarbon gases. The effect of CaCO_3 on these products manifested itself only at temperatures above 1200 K for 5 s holding time runs.

While addition of CaCO_3 to coal reduced the yields of all hydrocarbon products, yields of carbon oxides were strongly enhanced. Carbon monoxide yields, shown in Fig. 5, were larger for the CaCO_3 -pretreated coal than for demineralized coal for all 1000 K and higher runs. At the limit of 1300 K, the yields were three times those from the demineralized sample. Yields of CO_2 for both 5 s and 0 s holding time runs are shown in Figs. 6 and 7, respectively. These plots show yields of CO_2 from demineralized and CaCO_3 -pretreated coals, uncorrected for mineral carbonate decomposition. Yields of CO_2 from pyrolysis of samples of pure CaCO_3 under the same conditions and converted to a basis of percent by weight dmmf coal are shown on the same graphs for comparison. The high temperature, 5 s holding time yields of CO_2 from calcite-pretreated coal are approximately equal to those obtained from pure calcite mineral under the same conditions. For 0 s holding times or low temperatures, however, yields from the CaCO_3 pretreated sample were much higher than the combined yields of CO_2 from separate pyrolysis of demineralized coal and calcite at equivalent conditions. The CO_2 yields in 5 s runs from calcite-pretreated coal have in fact already reached an asymptote in the 1050-1200 K range, where the rate of CO_2 evolution from calcite itself is at its maximum. These results all seem to indicate that calcite in the

presence of coal decomposes yielding CO_2 at lower temperatures than it would when pyrolyzed alone.

Elemental compositions of chars resulting from 5 s holding time runs are shown in Fig. 8. Data are plotted as the percent of the element (C, H, or O) in the original coal sample that is retained in the char. Chars from calcite-pretreated coal have greater retentions of carbon and hydrogen, and much lesser retentions of oxygen, than do chars from demineralized coal.

In Table 2, yields from pyrolysis of CaO-pretreated coal at 1 atm and 69 atm He are compared with those from demineralized coal under similar conditions. Since product yields are temperature independent for 5 s holding time runs at high temperatures, results for several runs have been grouped together and reported by means of an average value and a standard deviation. The effects of CaO pretreating and CaCO_3 pretreating on hydrocarbon yields are similar. The CaCO_3 -pretreated sample, however, gave a much higher CO yield than did the CaO-pretreated sample.

Fewer runs were done at 69 atm than at 1 atm, and the standard deviations are thus much larger for the high pressure data. These uncertainties tend to reduce the significance of the effects observed for CaO addition to coals pyrolyzed at 69 atm. These effects are, however, very similar to those seen for pyrolysis at 1 atm. The effect on tar of CaO addition tends to be obscured at the higher pressure since, as can be seen in the table, increased pressure itself leads to decreased tar yields and hence to less opportunity for an enhancement of tar cracking by CaO.

DISCUSSION

The yields from coal samples pretreated with calcite and those pretreated with lime are quite similar. This is consistent with the indication in Figs. 6 and 7 that for most runs conducted with calcite pretreated coal, the CaCO_3 decomposed to CaO. Thus, lime is the likely active species for the effects observed in either coal.

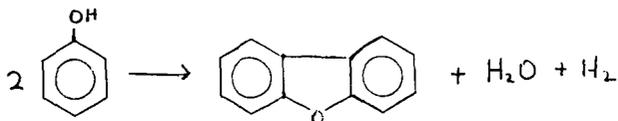
Addition of CaCO_3 to coal reduces the yields of all volatile hydrocarbon products. Yields of heavy hydrocarbons such as tar are reduced considerably at temperatures above 900 K for 5 s holding time runs, while yields of lighter products are reduced to a lesser extent, and only at temperatures above 1200 K. These results point to a catalysis by CaO of secondary hydrocarbon cracking/repolymerization reactions, a conclusion consistent with results of other work. Yeboah *et al.* (6) showed that addition of calcined dolomite or limestone to a fluidized-bed coal pyrolyzer reduces tar yields. No reduction in light hydrocarbon yields was seen, but temperatures in that study did not exceed 1050 K. Solano *et al.* (14) showed that calcite promotes CH_4 cracking to char at 1200 K, while Mead (15) observed that lime is particularly active for the cracking of single-ring aromatic compounds. The latter result may account for the much larger reduction of aromatic-rich liquids obtained by adding calcite, as compared with the reduction of light aliphatic gas products. Some of the tar is converted to CO as well, and thus the amount by which tar hydrocarbon cracking exceeds light hydrocarbon gas reduction is unclear. Since all volatile

hydrocarbon product yields are reduced by CaO, the resulting cracking products must in all cases include char and H₂. Char yields are indeed higher for the calcite-pretreated coal (Fig. 2), and carbon and hydrogen retention in this char is higher than it is in demineralized coal (Fig. 8). High temperature H₂ yields are also higher for calcite-pretreated coals (12). Hydrocarbon yield reductions were almost identical for both calcite- and lime-pretreated samples, despite the fact that the former sample had almost four times as much calcium as the latter. This would seem to point to the presence of a saturation effect for CaO catalysis of hydrocarbon cracking.

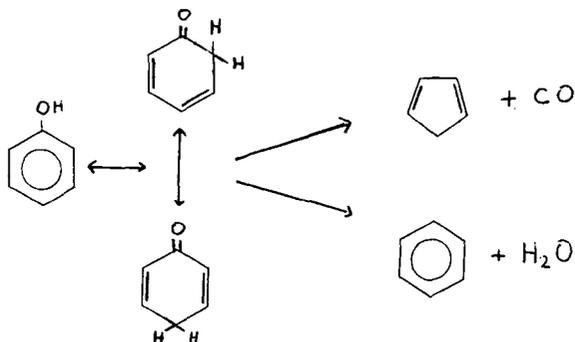
The CO₂ evolution data, shown in Figs. 6 and 7, seem to indicate that the presence of coal in some way catalyzes the decomposition of CaCO₃ to CaO and CO₂. Similar results have been observed in two other recent studies dealing with different carbon-carbonate systems. McKee (11) pyrolyzed mixtures of graphite and alkaline earth carbonates under He and CO₂ atmospheres in a thermogravimetric analyzer. Weight loss of these mixtures in helium occurred at temperatures much lower than the decomposition temperature of the carbonates alone. He postulated, based on the degree of weight loss observed, that the carbonates react with graphitic carbon yielding the corresponding oxide and CO. No analysis of the exit gas was conducted to verify the presence of CO. Other workers (16) heated mixtures of Illinois coal and ¹⁴C labeled K₂CO₃ at 775 K. The carbonate decomposed completely to CO₂ under these conditions, and no carbonate carbon was detected as either CO or hydrocarbon products. The decomposition temperature of pure K₂CO₃ is well above 775 K. The authors proposed that a reaction of K₂CO₃ with the coal forms a surface complex and CO₂, a mechanism said to generate well-dispersed active sites for catalysis of subsequent reactions of the coal or char. This hypothesis is consistent with the data of the present work, although the mechanism for the apparent solid-solid reaction is not yet well-established. One possibility might be the reaction of carbonates with the phenolic groups in coal (21). This would agree with the finding of Sears et al. (10) that CO₂ gasification rates of chars correlate with the cross correlation of char oxygen and calcium contents, an indication of a calcium/coal-oxygen gasification site.

CaCO₃-pretreated samples gave considerably higher yields of CO than did demineralized samples. CO₂ yields from calcite-pretreated coals are always greater than or equal to CO₂ yields from calcite mineral at corresponding conditions, and hence the excess CO cannot be explained by postulating reactions of carbonate CO₂ with the coal or its volatile products. H₂O yields (not plotted) were also increased by calcite addition, thus ruling out steam gasification as a source of the excess CO. The oxygen in this excess CO is therefore organic in origin, and is derived from oxygen groups that end up in the tar and char fractions in demineralized coal pyrolysis. Most organic oxygen in bituminous coals is phenolic (17), and this phenomenon must therefore be examined in terms of decomposition mechanisms for the phenolic groups in coal.

Evidence that phenol decomposes along two parallel pathways was obtained by Cyprès and co-workers (18,19,20) in a study of the rapid pyrolysis of phenol, cresols, and xylenols using ³H- and ¹⁴C- labeled compounds. One pathway is a condensation of two phenol molecules to form dibenzofuran plus water and H₂.



Dibenzofuran is itself stable at temperatures up to 1150 K. This reaction is important at low temperatures (920–1020 K) at which phenol just starts to decompose, but accounts for only a small fraction of the phenol pyrolysis that occurs at higher temperatures. At temperatures above 1020 K, the major pathway is unimolecular decomposition by way of a keto-enol shift to either H_2O and benzene, or to CO and a C_5 moiety which would then further condense to tetralin, naphthalene, and ultimately char.



The CO pathway is preferred, the molar ratio of $\text{CO}/\text{H}_2\text{O}$ generated at 1120 K being 1.7/1.

Assuming this mechanism for decomposition of phenolic groups in coal, the effect of CaCO_3 addition is predictable. The initial step of the decomposition to CO , the keto-enol shift, is a strongly base catalyzed reaction and the CaO generated by calcite decomposition is a strong solid base. Calcium carbonate or oxide addition will thus promote the decomposition of phenolics to CO at the expense of their evaporation as components of tar, or their condensation to species such as polycyclic furans, which remain in the char. Any of the latter compounds formed may also be cracked by CaO , which has been shown to strongly catalyze the cracking of furan itself (15). These proposed mechanisms are all supported by the results in fig. 8, which show a much lower retention of oxygen in chars from calcite-pretreated coal than in chars from demineralized coal. Tar oxygen contents could not be obtained owing to the small absolute tar yields.

These results seem to conflict with a previous study on fluidized-bed pyrolysis of coal (6) which showed that CO yields from bituminous coal were lower when lime was used as the fluidizing medium than when sand was used. This apparent discrepancy can be explained by the differing conditions present in the two reactors. The temperatures in the fluidized bed were below 1050 K, where CaCO_3 rather than CaO is the stable species. Consequently, the lime removed CO_2 from the gas phase in a secondary reaction independent of the pyrolysis. As a result CO yields were reduced through the water-gas shift which was important in the fluidized bed where the volatiles were not immediately quenched. These gas-phase secondary reaction effects would mask any effects of the lime on the pyrolysis itself.

The calcite-pretreated sample gave much larger CO yields than did the lime pretreated sample. This behavior can probably be explained by the fact that there was 3.8 times as much Ca in the former sample as in the latter. The excess CO yield, that is CO yield from the mineral-pretreated sample less the yield from demineralized coal, is 4.4 times as great for the calcite-pretreated sample as for the lime-pretreated sample. This almost linear relationship between excess CO and Ca content might be due to an association of CaO molecules with the phenolic groups, either during pretreatment (for the lime-pretreated coal) or by reaction of CaCO_3 with the phenolic groups (for the calcite-pretreated coal).

CONCLUSIONS

Addition of CaCO_3 or CaO to coal reduces the high temperature yield of hydrocarbon products and increases the yield of CO in rapid coal pyrolysis. The former effect is probably attributable to lime-catalyzed secondary cracking reactions, while the latter results from base catalysis of a step in the decomposition of the phenolic groups. Calcite in the presence of coal decomposes to lime and CO_2 at lower temperatures than it will when pyrolyzed alone.

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Table 1
CHARACTERISTICS OF COAL EXAMINED

Proximate Analysis		Ultimate Analysis	
Wt. % (as received)		Wt. % (dry)	
Moisture	2.0	Carbon	71.74
Volatiles Matter	36.2	Hydrogen	4.84
Fixed Carbon*	51.0	Oxygen**	6.22
Ash	10.8	Nitrogen	1.14
	100.0	Organic Sulfur**	2.54
		Mineral Matter	13.47
			100.00

Petrographic Analysis		Mineral Matter Analysis	
Wt. % mineral matter free		Wt. %	
Vitrinite	81.5	Macinite	13
Semi-Fusinite	6.0	Calcite	10
Fusinite	2.5	Quartz	7
Micrinite	3.0	Montmorillonite	14
Macrinite	1.2	Illite	9
Exinite	5.2	Pyrite*	45
Resinite	0.6		100
	100.0		

* by difference
**calculated from total sulfur (5.77% by weight dry coal) and measured pyrite content

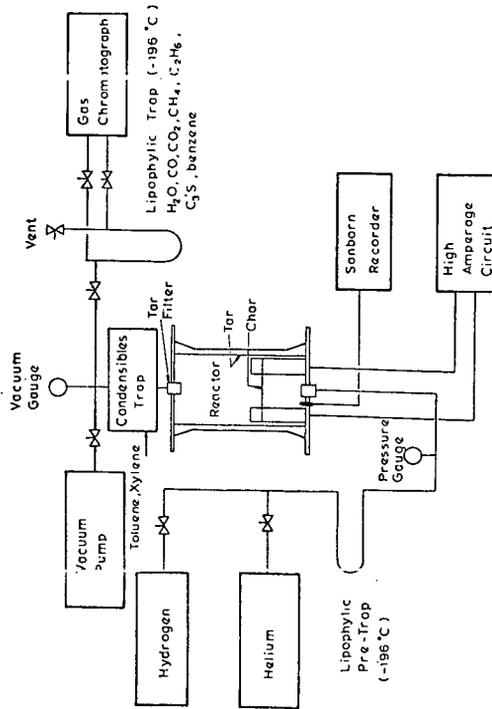


Fig. 1. Schematic of Captive Sample Apparatus

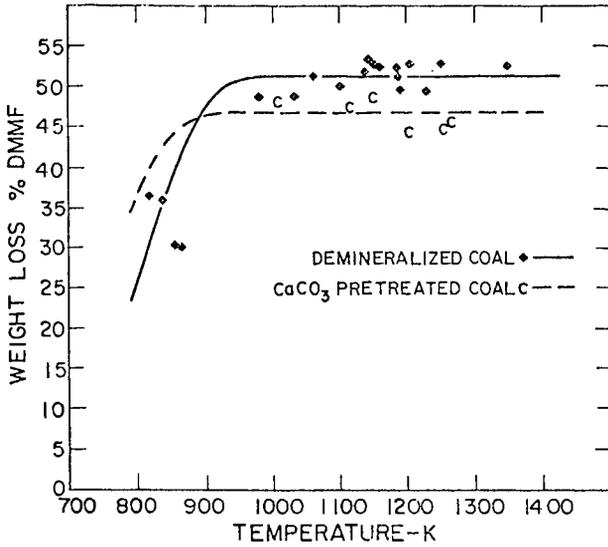


Fig. 2 Total Yield of Volatiles from Pyrolysis in 1 atm He of Demineralized and CaCO₃ Treated Coals, 5 s Holding Times.

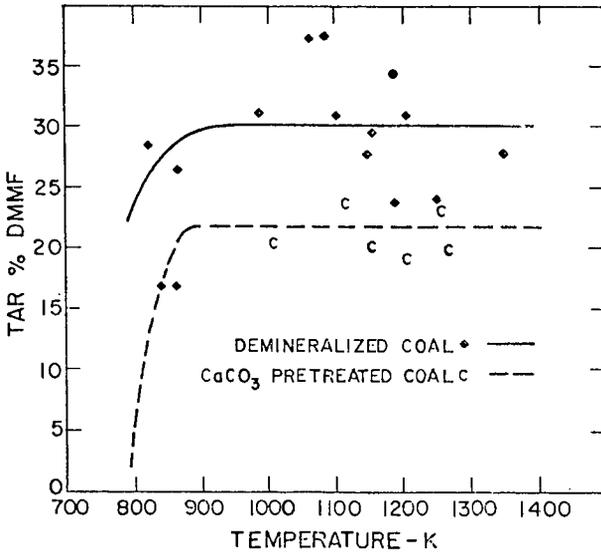


Fig.3 Yield of Tar from Pyrolysis in 1 atm He of Demineralized and CaCO₃ Treated Coals, 5 s Holding Times.

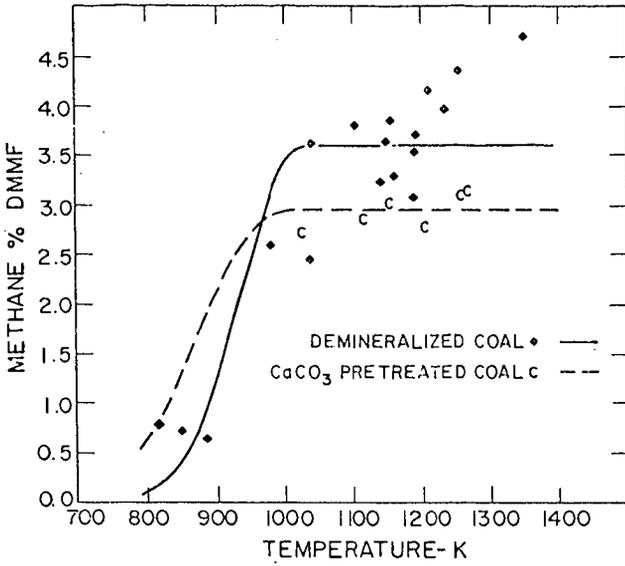


Fig. 4 Yield of Methane from Pyrolysis in 1 atm He of Demineralized and CaCO₃ Treated Coals, 5 of Holding Times.

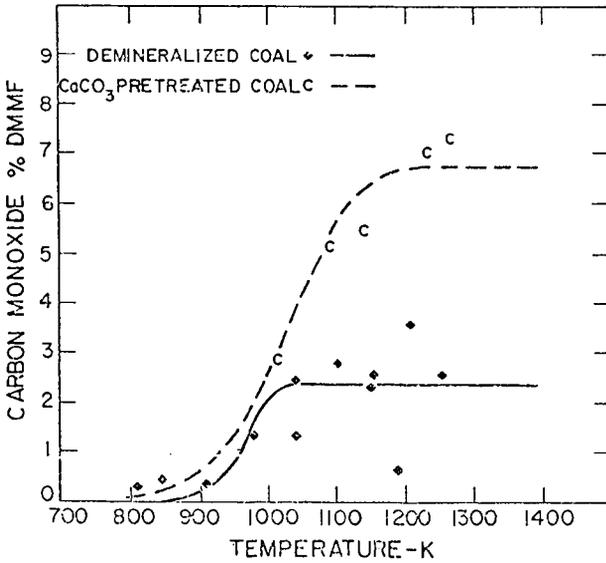


Fig. 5 Yield of Carbon Monoxide from Pyrolysis in 1 atm He of Demineralized and CaCO₃ Treated Coals, 5 s Holding Times.

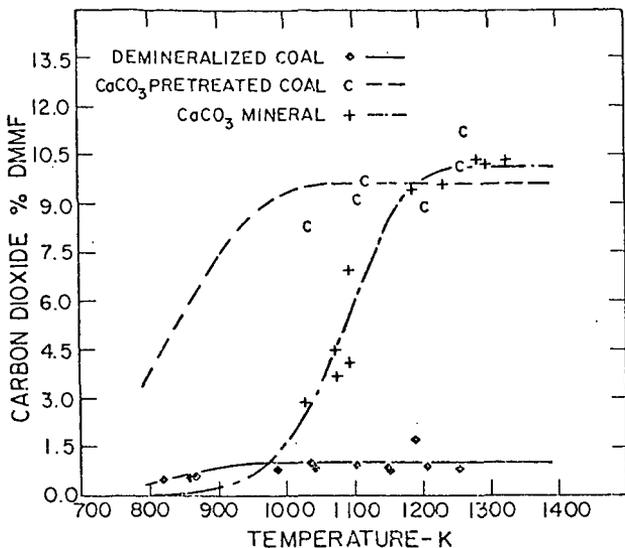


Fig. 6 Yield of Carbon Dioxide from Pyrolysis in 1 atm He of Demineralized and CaCO₃ Treated Coals, CaCO₃ Mineral, 5 s Holding Times.

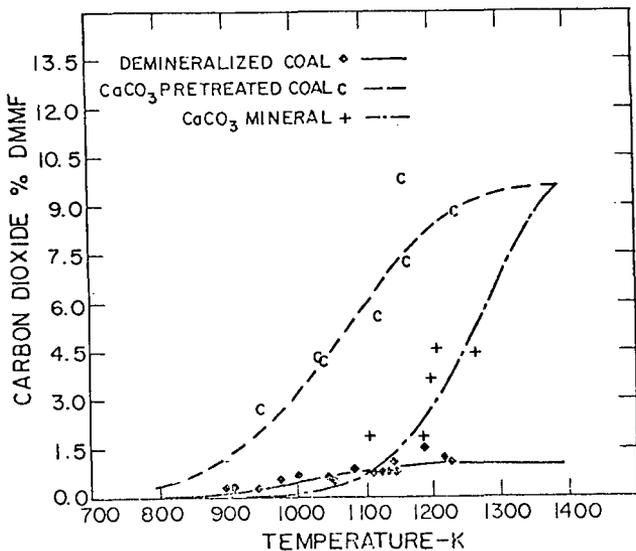


Fig. 7 Yield of Carbon Dioxide from Pyrolysis in 1 atm He of Demineralized and CaCO₃ Treated Coals, CaCO₃ Mineral, 0 s Runs.

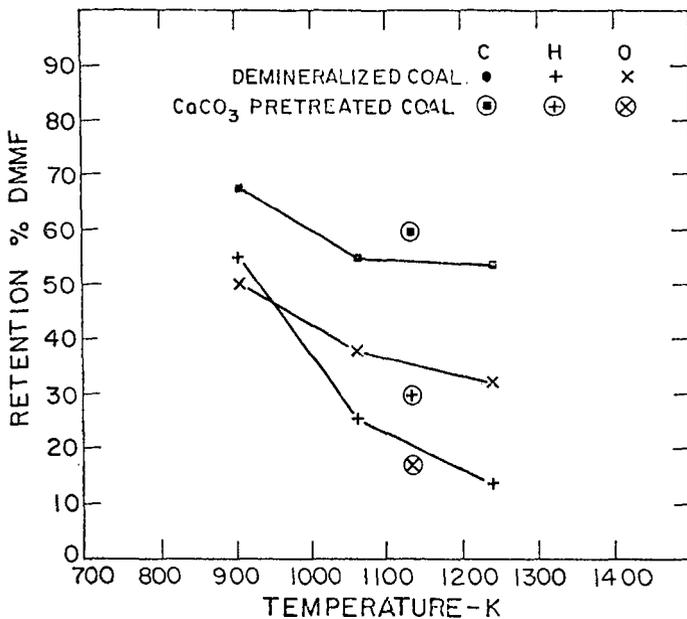


Fig 2 Fraction of Elements in Demineralized and CaCO₃ Treated Coals that Remain in Chars from Pyrolysis in 1 atm He, 5 s Holding Times.

TABLE 2

YIELDS FOR 5 S RUNS IN He 1050 K - 1300 K

	1 ATM		69 ATM	
	<u>DEMIN</u>	<u>CaO</u>	<u>DEMIN</u>	<u>CaO</u>
ΔW/W	51.38±1.13	47.95	35.12±1.47	35.93
TAR	30.24±1.35	23.67	16.76±2.27	14.03
CH ₄	3.62±0.11	2.93	5.79±1.11	5.36
C ₂ H ₄	0.96±0.04	0.87	1.12±0.11	1.03
C ₂ H ₆	0.74±0.03	0.73	0.83±0.21	0.73
C ₃	0.89±0.03	0.75	0.67±0.15	0.58
C ₄ +	1.26±0.04	0.79	0.69±0.19	0.48
LIQ HC	3.37±0.10	2.23	2.50±0.46	1.82
CO	2.40±0.15	3.42	3.73±0.92	4.36
CO ₂	1.03±0.07	2.50	1.15±0.17	2.71
H ₂ O	3.01±0.30	--	2.91±1.76	3.76