

EFFECT OF ADDITIVES UPON THE GASIFICATION OF COAL IN THE SYNTHANE GASIFIER

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Introduction

The Synthane process (1)¹, developed by the Bureau of Mines of the U.S. Department of the Interior, is a coal-gasification process in which caking coal is successively decaked and gasified in two individual fluidized beds. The decaked coal is fed from the pretreater directly into the gasifier. Based upon this technique, the Lummus Co. designed a 75-ton-per-day prototype plant, which is presently being built by the Rust Engineering Co. near the Bureau's laboratories at Bruceton, Pa., in South Park Township. In a continuing effort to improve the gasification process, tests are being performed in the original 4-inch-diameter gasifier located at the Pittsburgh Energy Research Center at Bruceton, Pa. Results from the latest gasification tests performed with additives are discussed in this report.

Additives Used

Table 1 shows the analysis of the compounds used as additives in the Bruceton gasifier. The additives were mixed with coal and the mixture then fed to the pretreater-gasifier. Table 2 lists typical gasification tests showing data in which following graphs are based. Lignites and subbituminous coal tests are included for comparison purposes but are not shown in the graphs.

Effect on Carbon Conversion

Figure 1 shows results of tests where we operated with and without additives² showing carbon conversion vs bed temperatures. We used 2%, 5%, and 10% limestone (dolomitic limestone), 2% and 5% hydrated lime, 2% quicklime, and 5% lignite ash. Results show an average increase of about 10% in carbon conversion for the parameter for additive tests above the parameter shown for nonadditive tests.

Effect on Steam Decomposition

Figure 2 shows the effect of the same additives on the steam decomposition. The steam decomposition was increased 5% to 10% above the parameter for nonadditive tests. The highest increases were with CaO and hydrated lime.

Effect on H₂ + CO + CH₄ Yields

As would be expected because of the increased carbon conversion, the yields of H₂ + CO + CH₄ increased about 1 to 2 scf/lb coal (MAF basis) using the additives as shown in figure 3. Again the use of hydrated lime shows the greatest increase.

Effect on Sulfur in the Char

As shown in figure 4, some additives increase the sulfur in the char. What we were interested in especially was a reduction. Agricultural limestone (showing sulfur in char of 0.4% and 0.6%) showed the greatest decrease in the sulfur. Hydrated lime and CaO showed that their use would increase the sulfur in the char. This is an undesirable effect because a low-sulfur char is needed to raise steam needed for the plant, and the stack gas effluent must meet EPA standards. The line shown in this figure is the average for the nonadditive tests.

¹ Underlined numbers in parentheses refer to list of references at end of this paper.

² All tests using additives were made with Illinois No. 6 coal. All nonadditive tests discussed in figures 1 to 5 were made with Illinois No. 6 coal.

Effect on Slag³ Formed in the Gasifier

In Figure 5 the amount of slag (cinder) formed in the gasifier is shown as a function of the maximum temperature in the gasifier. The majority of the tests with the additives show no slag formation. This is an important point since if the slagging temperature can be raised, the gasifier could be operated at a higher temperature, thus achieving a higher throughput in the gasifier. This result has been noted in the literature (2) as has other effects of these additives as discussed in this paper (3, 4).

Effect of Additives on the Water Effluent From the Gasifier

The effect of additives on water effluents resulting from gasification of various coals is shown in Table 3, which shows analyses of water effluents from Illinois No. 6 coal, Wyoming subbituminous, Illinois char, North Dakota lignite, Western Kentucky, and Pittsburgh seam coal. Coke-plant effluent was shown for comparison since it has been successfully treated for over 10 years by Bethlehem Steel Co. at Bethlehem, Pa. (5). Since the coke-plant effluent can be treated, we know the gasifier plant effluent can be also. As shown in the table, compared with Illinois No. 6 coal test without additives, the additive caused higher quantities of phenol, ammonia, and COD (chemical oxygen demand). Reasons for such increases are not known at this time.

Effect of Additives on the Gas Made in the Gasifier

Table 4 shows the effect of CaO and dolomitic limestone on components in the gasifier gas. The largest increase is in the BTX (Benzene-Toluene-Xylene) fraction. Reasons for these changes are not known.

We plan also to examine the tars to see if there is a difference in tar quality with additive tests, but such results are not yet known.

Conclusions

Additives such as limestone, hydrated lime, and quicklime all have a positive effect on the gasification rate. Limestone, in addition, raises the sintering temperatures and may lower the sulfur contained in the char from the gasifier. More tests are needed to establish the effect on the water and gas from the gasifier. We also plan to perform tests using ashes and chars from various coals as additives. When we have enough data to assess the advantages of the additives, cost studies will be made to determine economic feasibility.

³ This material called "slag" is more like a cinder in that it is not a hard slag.

TABLE 1. - Additives used in the Synthane Gasifier

| <u>Material</u> | <u>Analysis, wt-pct</u> | | | | |
|---|--------------------------------|--|--|-------------------------------|--|
| | <u>CaCO₃</u> | | <u>Mg CO₃</u> | | |
| Limestone (Dolomitic) | 54 | | 44 | | |
| Ca(OH) ₂ Hydrated or Slaked Lime..... | <u>CaO</u> 72. (min.) | | <u>MgO</u> 0.05 | | <u>H₂O</u> 23 |
| CaO Quicklime..... | 97 | | | | |
| Lignite Ash..... | <u>SiO₂</u> 12.3 | <u>Al₂O₃</u> 11.5 | <u>Fe₂O₃</u> 12.5 | <u>TiO₂</u> 0.3 | <u>P₂O₅</u> 0.6 |
| | <u>CaO</u> 23.0 | <u>MgO</u> 8.9 | <u>Na₂O</u> 3.8 | <u>K₂O</u> 0.4 | <u>SO₃</u> 25.4 |

TABLE 2. - Typical data from coal gasification tests

| Test ^{1/} | 11 | 3 | 48 | 83 | 37 | 46 | W-2 | L-7 |
|---|------|------|----------------------|----------------------|----------------------|---------------------|------|---------|
| | Ill. | Ill. | Ill. | Ill. | Ill. | Ill. | Sub- | |
| Coal Type..... | #6 | #6 | #6 | #6 | #6 | #6 | bit. | Lignite |
| Additive..... | None | None | 5% Lime- stone | 5% Lime- stone | 2% Lime- stone | 5% Hydr. lime | None | None |
| Coal Feed | | | | | | | | |
| lb/hr..... | 18.9 | 20.4 | 18.7 | 25.9 | 20.7 | 19.0 | 38.0 | 32.4 |
| lb/hr-ft ² | 221 | 239 | 219 | 304 | 242 | 223 | 446 | 379 |
| lb/hr-ft ³ | 40 | 43 | 40 | 55 | 44 | 40 | 81 | 69 |
| Steam Rate | | | | | | | | |
| lb/lb coal..... | 1.06 | 0.87 | 1.25 | 0.97 | 0.98 | 1.08 | 0.55 | 0.77 |
| Oxygen Rate | | | | | | | | |
| lb/lb coal..... | 0.30 | 0.27 | 0.33 | 0.25 | 0.35 | 0.41 | 0.14 | 0.13 |
| Carbon Conversion, %. | 68 | 65 | 68 | 60 | 93 | 81 | 68 | 75 |
| Steam Conversion..... | 15 | 25 | 15 | 20 | 36 | 30 | 18 | 51 |
| $\frac{SCF H_2 + CO + CH_4}{lb Coal, MAF}$ | 13.3 | 13.9 | 12.8 | 12.1 | 20.4 | 16.7 | 12.7 | 18.2 |
| $\frac{SCF CH_4}{lb Coal, MAF}$ | 3.6 | 3.9 | 3.6 | 3.4 | 4.5 | 4.2 | 3.4 | 4.2 |
| Max. Temp., ° C..... | 970 | 960 | 958 | 965 | 1020 | 1040 | 925 | 880 |
| Av. Temp., ° C..... | 928 | 947 | 920 | 900 | 951 | 919 | 867 | 855 |
| Sulfur in coal, %.... | 3.4 | 3.4 | 3.3 | 3.3 | 3.2 | 3.4 | 0.6 | 1.3 |
| Sulfur in char, %.... | 0.8 | 1.2 | 0.4 | 0.9 | 1.3 | 1.7 | 0.2 | 1.6 |
| Slag, % of coal feed. | 3.0 | 0.6 | 0.9 | 0.0 | 6.0 | 2.6 | 2.7 | 1.0 |

^{1/} All coals are ground to 20 x 0 mesh, about 30% through 200 mesh.

TABLE 3. - Byproduct water analysis¹ from Synthane gasification of various coals

| | Coke plant | Illinois No. 6 | Ill. #6 | | Ill. char | N. Dak. lignite | W. Ky. | Pgh. Seam | Wyoming sub-bit |
|-----------------------|---------------|-------------------|----------------|-------------------------|--------------|--------------------|--------|--------------|--------------------|
| | | | lime- stone | w/20% lime- stone | | | | | |
| pH..... | 9 | 8.6 | 8.4 | 9.2 | 7.9 | 9.2 | 8.9 | 9.3 | 8.7 |
| Suspended solids | 50 | 600 | 136 | 92 | 24 | 64 | 55 | 23 | 140 |
| Phenol..... | 2,000 | 2,600 | 3,500 | 4,950 | 200 | 6,600 | 3,700 | 1,700 | 6,000 |
| COD..... | 7,000 | 15,000 | 22,000 | 22,134 | 1,700 | 38,000 | 19,000 | 19,000 | 43,000 |
| Thiocyanate..... | 1,000 | 152 | 196 | 102 | 21 | 22 | 200 | 188 | 23 |
| Cyanide..... | 100 | 0.6 | 0.8 | 0.5 | 0.1 | 0.1 | 0.5 | 0.6 | 0.2 |
| NH ₃ | 5,000 | 2,8,100 | 15,100 | 10,400 | 2,500 | 7,200 | 10,000 | 11,000 | 9,520 |
| Chloride..... | | 500 | 435 | | 31 | | | | |
| Carbonate..... | | 3 6,000 | | | | | | | |
| Bicarbonate..... | | 311,000 | | | | | | | |
| Total Sulfur.... | | 4 1,400 | | | | | | | |

¹ Mg/liter (except pH)² 85% free NH₃³ Not from same analysis⁴ S⁼ = 400SO₂⁼ = 300SO₄⁼ = 1,400S₂O₃⁼ = 1,000

Table 4. - Components in gasifier gas¹

| Ill. #6 No. 6 | Ill. #6 lime- stone | Ill. #6 w/5% CaO | | Ill. #6 w/2% CaO | | Ill. char | Wyoming sub-bit | W. Ky. | N. Dak. lignite | Pgh. Seam |
|-----------------------|---------------------------|------------------------|-------|------------------------|-----|-----------|--------------------|--------|--------------------|--------------|
| | | | | | | | | | | |
| H ₂ S..... | 9,800 | 3,600 | 7,480 | 8,100 | 186 | 2,480 | 2,530 | 1,750 | 860 | |
| COS..... | 150 | 70 | 10 | 330 | 2 | 32 | 119 | 65 | 11 | |
| Thiophene..... | 31 | 134 | 40 | 260 | 0.4 | 10 | 5 | 25 | 55 | |
| Methyl thiophene.. | 10 | 50 | 6 | 37 | 0.4 | -- | -- | -- | 7 | |
| Dimethyl thiophene | 10 | 11 | 5 | 37 | 0.5 | -- | -- | 11 | 6 | |
| Benzene..... | 340 | 1,890 | 510 | 2,790 | 10 | 434 | 100 | 1,727 | 1,050 | |
| Toluene..... | 94 | 230 | 85 | 720 | 3 | 59 | 22 | 167 | 185 | |
| C8 Aromatics..... | 24 | 36 | 20 | 160 | 2 | 27 | 4 | 73 | 27 | |
| SO ₂ | 10 | 20 | 9 | --- | 1 | 6 | 2 | 10 | 10 | |
| CS ₂ | 10 | -- | 5 | --- | -- | -- | -- | -- | -- | |
| Methyl mercaptan.. | 60 | 125 | 50 | 330 | 0.1 | 0.4 | 33 | 10 | 8 | |

¹PPM by volume.

References

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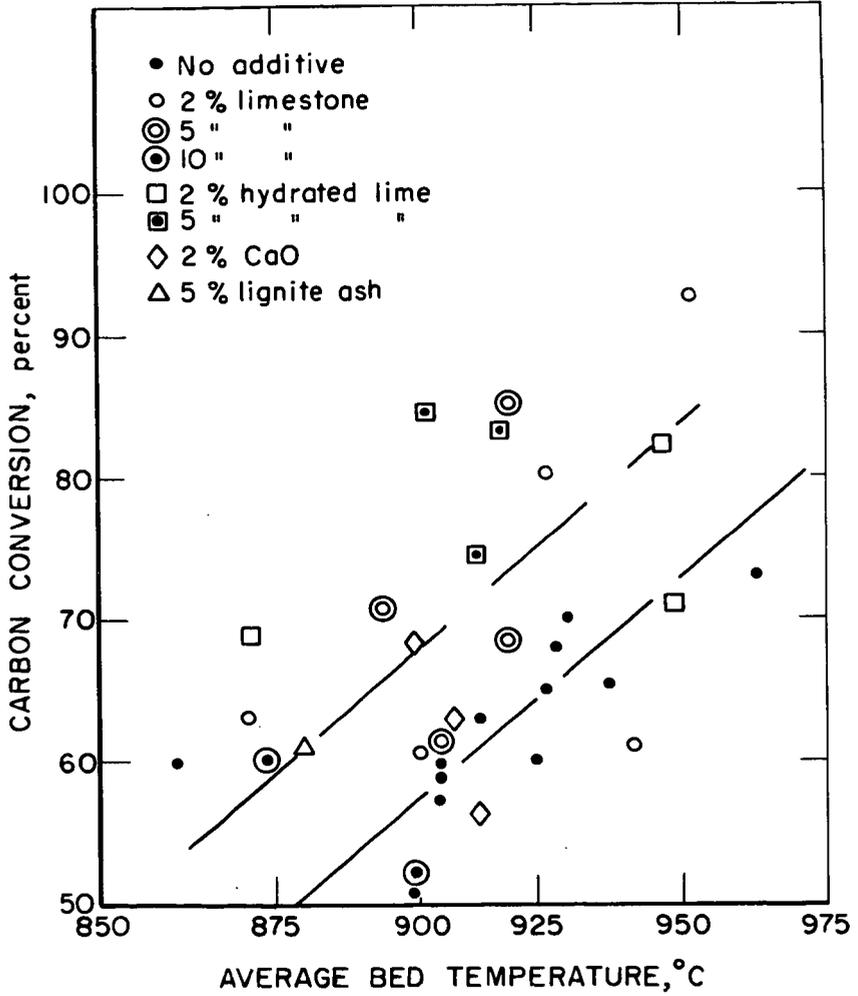


Figure 1. Effect of Additives on Carbon Conversion

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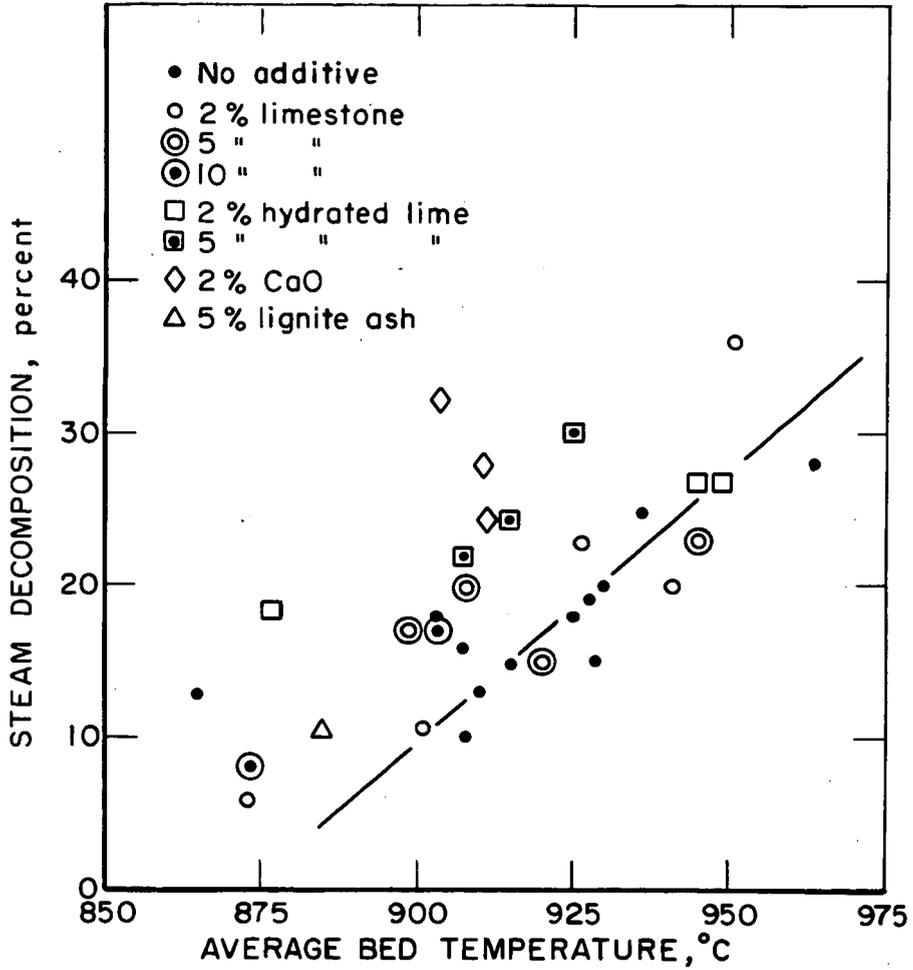
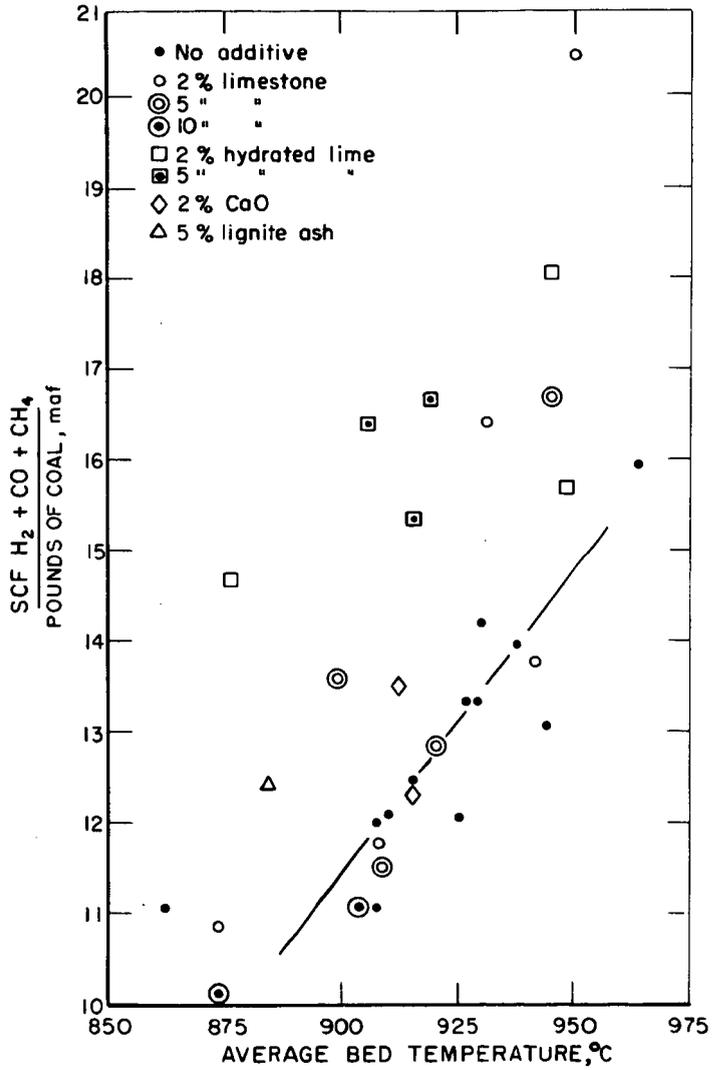


Figure 2. Effect of Additives on Steam Decomposition

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Figure 3. Effect of Additives on H₂ + CO + CH₄ Yields

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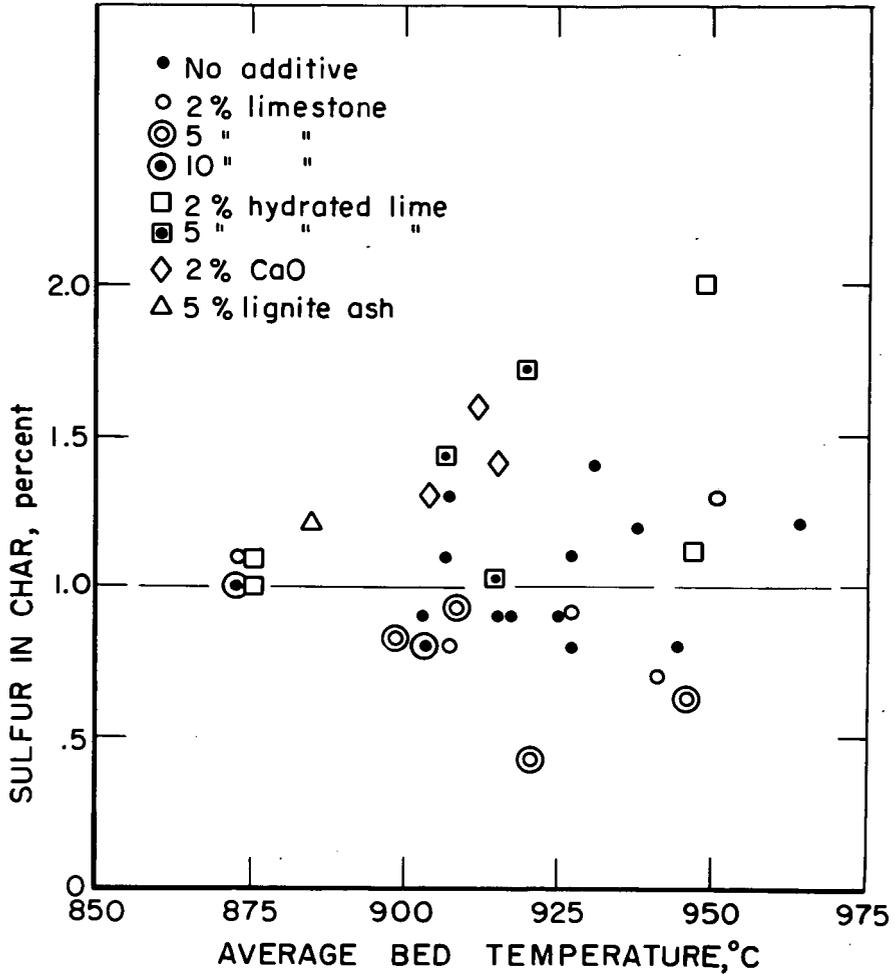


Figure 4. Effect of Additives on Sulfur in Char

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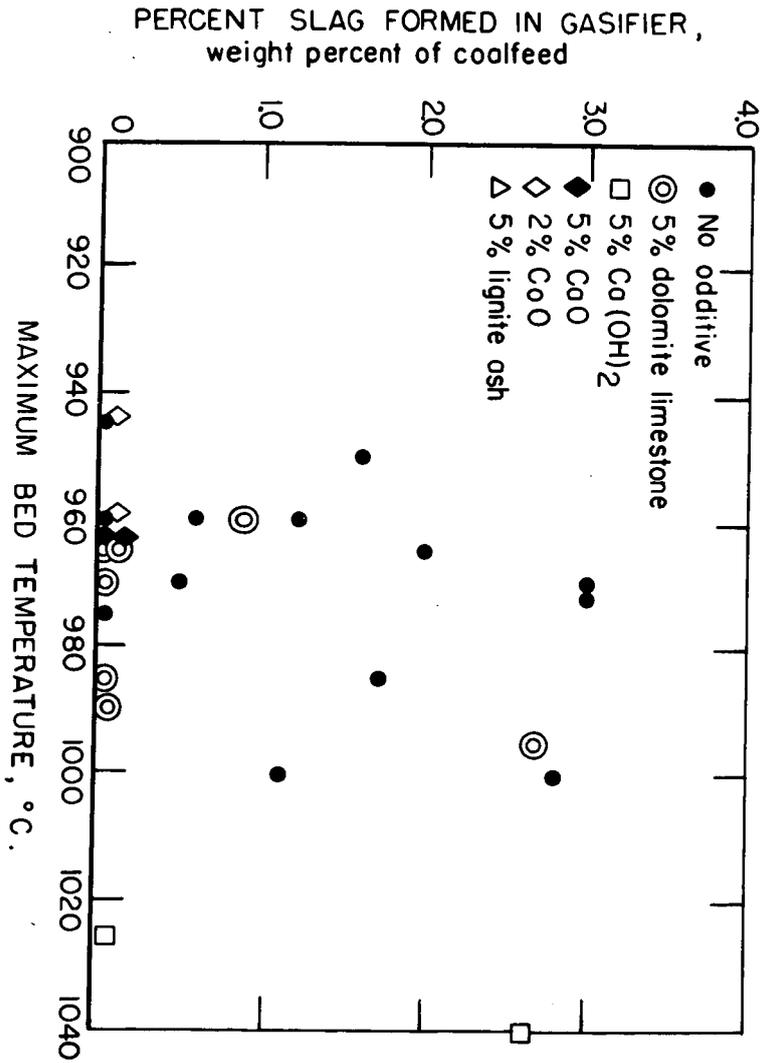


Figure 5. Effect of Additives on Slag Formation