

COPPER CATALYZED LOW-TEMPERATURE PYROLYSIS AS A MEANS FOR UPGRADING LOW-RANK SOLID FUELS

S. Stournas, M. Papachristos and G. B. Kyriakopoulos

Chemical Engineering Department, National Technical University
42 Patission Street, 106 82 Athens, Greece

ABSTRACT

Low-rank solid fuels (lignite and peat) are characterized by a high oxygen content on a DAF basis, a large proportion of which belongs to carboxyl and hydroxyl groups. These groups being thermally labile, the oxygen content of low-rank coals can be substantially decreased (and their heat content per unit mass correspondingly increased) by subjecting them to simple pyrolytic treatment.

It has been found that the behavior of certain types of lignite and peat is similar to that of simple carboxylic acids, in that the thermal decarboxylation process can be catalyzed by specific metal ions. Thus when lignite and peat, in the presence of small amounts of copper, are pyrolyzed at low temperatures (160°-200° C), they readily undergo decarboxylation and dehydration and their higher heating values on a DAF basis show increases of the order of 30%. When uncatalyzed, these same reactions require temperatures in excess of 300° C.

INTRODUCTION

Among the known fossil fuel reserves those of the low-rank coals (i.e. lignite and peat) remain underutilized, despite their significant potential as a readily recoverable energy resource. The main problem associated with these solid fuels is their low heat content per unit mass, which in turn is due to the high moisture and ash content but also to the relatively low heating value of the DAF coal itself.

It has been a well known fact for many years¹ that, on moving from high rank to low rank coals, the ratio of oxygen content to carbon content increases substantially; it is not unusual for a lignite coal to contain around 30% oxygen on a DAF basis, whereas peat approaches 40%.

It is evident that the upgrading of lignite and peat to forms that come close to hard coal in properties and performance may involve:

- a. Moisture removal through the various drying processes²
- b. Ash removal through processes such as leaching³ and flotation⁴
- c. Oxygen removal from the DAF coal

The first two approaches deal with the separation of the fuel component (DAF coal) from extraneous materials (moisture and ash), whereas the third approach is concerned with the chemistry of the fuel component itself.

The higher oxygen content of low-rank coals is coupled with marked differences in the relative contents of the various oxygen functionalities. This is particularly pronounced in the case of the carboxyl group, which is one of the main oxygen functionalities occurring in lignite and peat but is almost totally absent in coals

of bituminous and higher ranks.^{5,6} An efficient means of decarboxylation, therefore, could lead to a significant improvement of the overall properties, and particularly the heat content of lignite and peat.

The decarboxylation of low-rank coals can be achieved by heating the coal at a high enough temperature. Thus, simple heating of lignite to about 330° C leads to decarboxylation and an increase of about 21% in the gross calorific value of the coal.⁷ Similar results were obtained by heating low-grade solid fuels at about 400° C either in the presence of base⁸ or in the presence of acid,⁹ whereas processes involving even higher temperatures have also been reported.^{10, 11}

It is apparent that, for thermal decarboxylation of low-rank coals to take place to any significant extent, temperatures in excess of 300° C are required. However, it has been known for a long time that copper will catalyze the decarboxylation of carboxylic acids,^{12, 13} and the mechanism of this reaction has been studied in detail.^{14, 15} The purpose of the present study was to assess the possibility of utilizing copper as a catalyst for the decarboxylation of lignite and peat at low temperatures, thus making the process energetically more efficient.

EXPERIMENTAL

Three types of coal were used in this study, Megalopolis lignite, Ptolemais' lignite, and Philippi peat; their characteristics are given in Table I. The experimental procedure was similar to that described in a preliminary report on the heat-treatment behavior of two of the above coals¹⁶ and is summarized below.

Samples of about 10 g of each coal (40 to 200 mesh) were slurried with 20 mL of a dilute aqueous solution of cupric sulfate; the copper content was equal to 1% or 3% of the DAF coal of the sample. An amount of sodium carbonate equivalent to the copper sulfate was dissolved in distilled water and was added to the previous slurry with stirring. The coal was then filtered off under mild suction and washed with distilled water. This method achieved an intimate mixture of the coal under study with copper in the form of cupric carbonate. The treated coal was then transferred to a porcelain crucible and placed in an oven at the desired temperature (140° - 400° C) for a period of 30 minutes. This length of time was found adequate for low temperature pyrolysis after a series of experiments with varying heating durations. For comparison purposes, blank samples of coal (i.e. containing no copper) were subjected to exactly the same procedure, except that the initial slurry was made with distilled water.

RESULTS AND DISCUSSION

The measured higher heating values of the various samples, before and after heat treatment, are shown in Tables II, III, and IV. It can be seen that thermal treatment invariably increases the heat content of Megalopolis lignite and Philippi peat; the magnitude of the increase, however, depends both on the temperature of the treatment and on the presence of copper as the decarboxylation catalyst. This behavior can be more easily visualized if one refers to figures 1 and 2, which illustrate the increase in higher heating value as a function of temperature and copper content.

TABLE I
COAL CHARACTERISTICS

	<u>Megalopolis</u> <u>Lignite</u>	<u>Philippi</u> <u>Peat</u>	<u>Ptolemais</u> <u>Lignite</u>
<u>As Received Basis</u>			
Moisture (%)	45.0	16.1	56.3
Volatile Matter (%)	24.4	45.8	18.0
Fixed Carbon	12.5	16.7	12.1
Ash (%)	18.1	21.4	13.7
HHV (MJ/Kg)	9.02	12.72	7.05
<u>DAF Basis</u>			
C %	60.4	56.7	63.2
H %	5.9	5.5	5.2
S %	2.9	1.1	1.6
N %	1.8	1.8	1.6
O % (by difference)	29.0	34.9	28.4
HHV (MJ/Kg)	24.42	20.36	23.43

TABLE II
CHANGE IN CALORIFIC VALUE (DAF BASIS) AS A FUNCTION OF TREATMENT
TEMPERATURE AND COPPER CONTENT
MEGALOPOLIS LIGNITE

<u>Treatment Temperature</u> (°C)	<u>Higher Heating Value</u> (MJ/Kg)		
	<u>No Cu</u>	<u>1% Cu</u>	<u>3% Cu</u>
No Heat Treatment	24.42	24.25	24.28
140	24.45	24.64	24.70
160	26.06	30.43	30.08
200	26.74	30.98	31.24
250	27.67	31.62	31.82
300	33.34	34.07	33.16

TABLE III
CHANGE IN CALORIFIC VALUE (DAF BASIS) AS A FUNCTION OF TREATMENT
TEMPERATURE AND COPPER CONTENT
PHILIPPI PEAT

<u>Treatment Temperature</u> (°C)	<u>Higher Heating Value</u> (MJ/Kg)		
	<u>No Cu</u>	<u>1% Cu</u>	<u>3% Cu</u>
No Heat Treatment	20.36	20.25	20.38
140	20.38	20.39	20.56
160	20.44	20.57	21.83
200	20.55	23.87	25.63
250	21.38	24.36	26.12
300	25.84	28.05	28.79

In the case of Megalopolis lignite (Figure 1) it is evident that the presence of copper is of minor significance up to about 140° C. the temperature being too low even for the catalyzed decarboxylation to take place. Starting at around 160° C. however, the catalytic effect of copper becomes significant and an increase of the order of 20% is observed in the higher heating value of the heat-treated lignite. Increasing the concentration of copper from 1%

to 3% appears to have essentially no effect on its catalytic activity. When the heat-treatment temperature reaches 300° C. the role of copper becomes much less significant, inasmuch as the rate of decarboxylation is quite fast even in the absence of catalyst.

In the case of Philippi peat (Figure 2) the experimental results display a similar pattern, except that the onset of significant catalytic activity of the added copper does not occur until the heat-treatment temperature has reached about 200° C. It is also worth noting that in this particular case the catalytic effect of copper is more pronounced at the higher metal concentration (3%).

TABLE IV
CHANGE IN CALORIFIC VALUE (DAF BASIS) AS A FUNCTION OF TREATMENT
TEMPERATURE AND COPPER CONTENT
PTOLEMAIS LIGNITE

<u>Treatment Temperature (°C)</u>	<u>Higher Heating Value (MJ/Kg)</u>		
	<u>No Cu</u>	<u>1% Cu</u>	<u>3% Cu</u>
No Heat Treatment	23.51	23.22	23.43
160	23.56	23.90	24.06
200	25.26	25.54	26.36
250	25.66	26.34	26.58
280	-	-	25.64
300	26.35	27.34	23.73
320	26.88	28.35	22.95
340	-	-	22.50
370	29.66	29.27	22.59
400	-	-	22.66

As can be seen in Table IV and Figure 3, the behavior of Ptolemais lignite is quite different than that of the other two coals under the experimental conditions that were employed. In the presence of 1% copper, the increase in higher heating value of the pyrolysis residue is only slightly higher than the one occurring in the absence of catalyst. In the presence of 3% copper the results are even more remarkable, in that the higher heating value of the residue starts decreasing at around 250° C and falls below that of the unheated sample at temperatures above 300° C. It thus appears that, in the case of Ptolemais lignite, the presence of copper can lead to the evolution of combustible gases in addition to carbon dioxide and water. The exact nature of this reaction is currently under investigation in our laboratory.

Due to the loss of volatiles (mostly carbon dioxide and water), the mass of the fuel that is recovered after heat treatment is lower than the original one; this loss of mass increases with increasing temperature. The recovery of total heat content, however, is almost quantitative (over 98% in most cases) up to a treatment temperature of 200° C. At higher temperatures the observed heat loss is more pronounced, due to evolution of combustible gases such as carbon monoxide. In the case of Ptolemais lignite the loss of both mass and heat content is much more significant in the presence of 3% copper. Figure 4 is an illustration of typical heat recovery patterns, i.e. the total heat content of the pyrolyzed coal as a percentage of the amount that was contained in the sample before thermal treatment.

The process described in this paper appears to offer the possibility of additional improvements in the quality of the treated coals, including:

a. Lowering of the ash content of the treated coals, probably due to the leaching of the water-soluble components during the slurring operation.

b. Lowering of the sulfur content.

c. Decrease of the hydrophilicity of the coal, thus making it potentially more amenable to ash-removing processes such as flotation and gravity separation.

The magnitude and mode of occurrence of the above effects are currently under study.

CONCLUSIONS

In two of the three samples of low-rank coals that were studied in the course of this work, the addition of small amounts of copper appears to catalyze decarboxylation of the coals in a manner reminiscent of the copper catalyzed decarboxylation of carboxylic acids. As a result, low temperature (160°-250° C) heat treatment in these cases leads to an increase of about 25-30% in the higher heating value of the DAF coal.

The third coal, Ptolemais lignite, offers a different picture. Decarboxylation in the presence of copper is more sluggish, and it appears that other reactions are also being catalyzed, leading to the evolution of combustible gases at comparatively low temperatures.

REFERENCES

1. Van Krevelen, D.W., 1950. Fuel, 29: 269
2. Rozgonyi, T.G. and Szigeti, L.Z., 1985. Fuel Processing Technol., 10: 1
3. Wang, Z.Y., Ohtsuka, Y. and Tomita, A., 1986. Fuel Processing Technol., 13: 279
4. Mitchell, D.R. and Charmbury, H.B., 1963. Chapter 8 in Lowry, H.H., (Ed.), "Chemistry of Coal Utilization", Suppl. Volume. J. Wiley, New York
5. Whitehurst, D.D., Mitchell, T.O. and Farcasiu, M., 1980. Coal Liquefaction. Academic Press, New York, p. 18
6. Doolan, K.R. and Mackie, J.C., 1985. Fuel, 64: 400
7. Elliott, D.C., 1980. Fuel, 59: 805
8. Sharma, D.K., 1983. NSTA Technol. J., 8(2): 93
9. Van Raam, L. and Ruyter, H.P., 1981. Eur. Patent 26011. Chem. Abstracts, 95: 45957
10. Mitsubishi Heavy Industries, 1981. Jap. Patent 157494. Chem. Abstracts, 96: 126107
11. Koppelman, E., 1977. U.S. Patent 4,052,168
12. Dougherty, G., 1928. J. Am. Chem. Soc., 50: 571
13. Fieser, L.F. and Fieser, M., 1967. Reagents for Organic Synthesis. J. Wiley, New York, pp. 157, 158, 163
14. Schambach, R., 1980. Ph.D. Thesis, Univ. of Pittsburgh
15. Cohen, T., Berninger, R.W. and Wood, J.T., 1978. J. Org. Chem. 43: 837
16. Stournas, S., Papachristos, M., and Kyriakopoulos, G.B., 1987. Fuel Processing Technol., in press

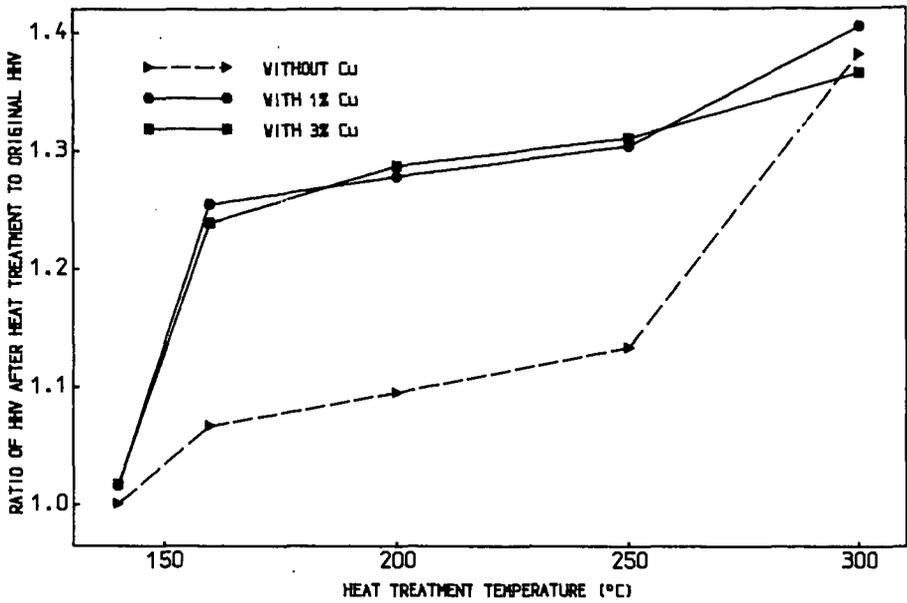


FIGURE 1. LOW TEMPERATURE PYROLYSIS OF MEGALOPOLIS LIGNITE

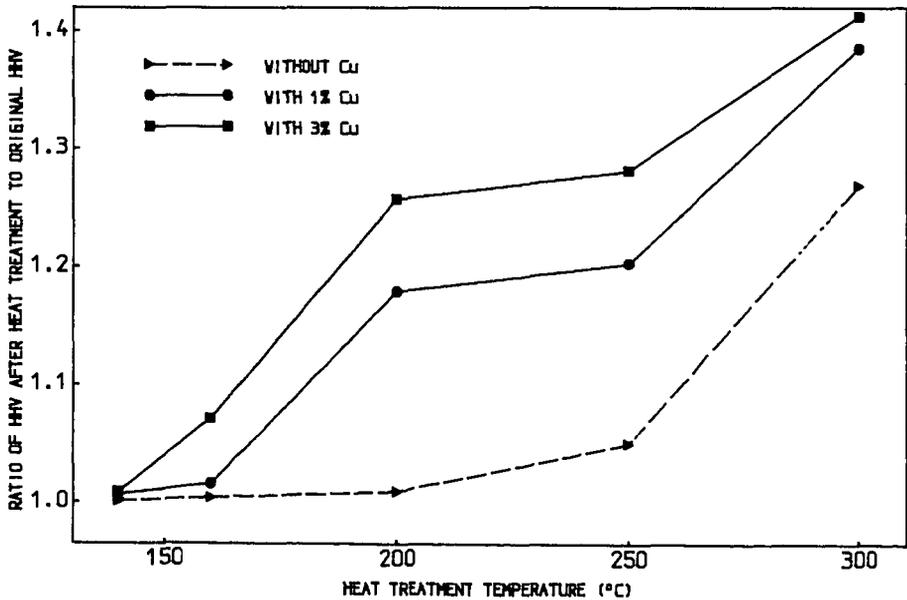


FIGURE 2. LOW TEMPERATURE PYROLYSIS OF PHILIPPI PEAT

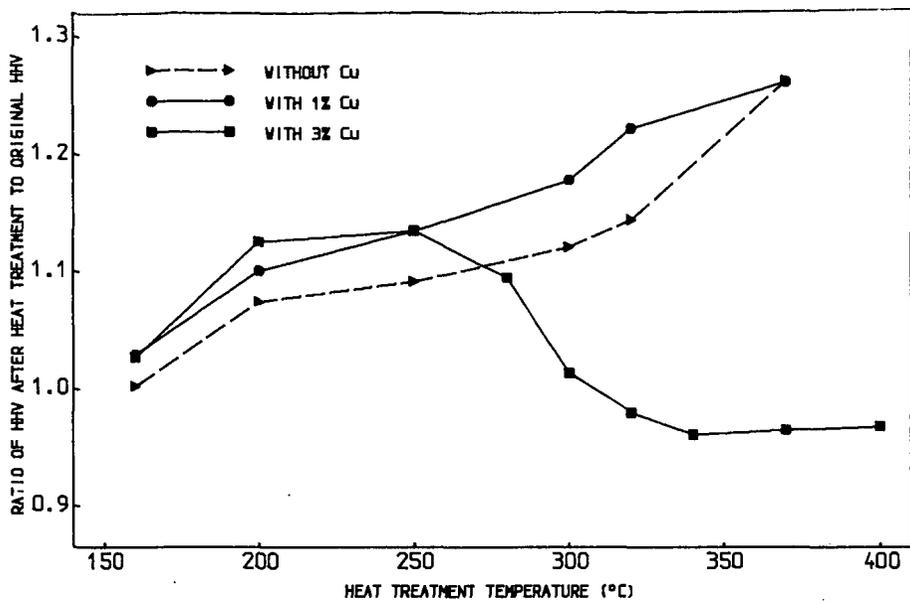


FIGURE 3. LOW TEMPERATURE PYROLYSIS OF PTOLEMAIS LIGNITE

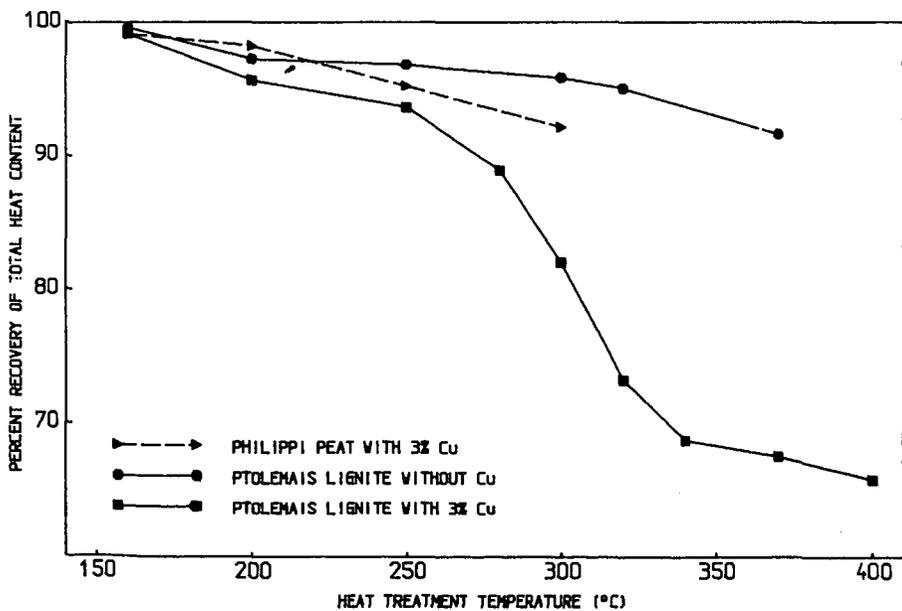


FIGURE 4. RECOVERY OF TOTAL HEAT CONTENT IN THE PYROLYSIS RESIDUE