Effect of Solid Additives on Pyrolysis Behaviour of Makerwal Coal

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Summary: The method used in this study provides a quantitative description of the relationship between the chemical structure of coal and the physical and chemical properties of the resultant pyrolysis products (gas, tar, liquid, and char). The purpose of this study is to investigate the effect of inorganic solid additives (Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, Fe_2O_3 and $CaSO_4$), on flash pyrolysis of high volatile bituminous coal samples from Makerwal coalfields by using open tubular type pyrolyzer coupled with gas chromatography. Two different coal samples were selected for this purpose. The sampling apparatus consisted of two traps in order to separate the products into fractions on the basis of their volatility such as tar, liquid, and gaseous fractions. The product yields released from each sample in their raw, de-mineralized and salt treated form were monitored. The gaseous fractions were directly introduced to GC for identification. The gases were C_1-C_5 hydrocarbons. The pyrolysis was carried out at 690°C. Some evaluations and comparisons, from the results obtained, are presented.

Introduction

Coal has been used as an important source of fuel for thousands of years, but it is a complex, heterogeneous fuel that is difficult to burn or process without serious environmental implications. Coals can vary significantly among different geographic areas in important properties such as rank, ash, sulfur and nitrogen content, mineral impurities, and maceral constituents. Substantial worldwide attention is being focused on more efficient and cleaner methods for utilization of this important energy resource. Since, coal pyrolysis is the fundamental step for all coal conversion processes, yet it exhibits a wide variation. The origins of these variations are for a given set of experimental conditions, both structural and compositional in nature. Because of its thermochemical and catalytic properties, mineral matter plays an important role in both the thermodynamics and kinetics of coal pyrolysis [1-4]. It is therefore essential to ascertain the role of these mineral present in coal matrix on the volatilization behavior of a given coal samples before it can be used for any commercial process.

In continuation of our work on pyrolysis studies of Pakistani coals [5-8], the work reported in this manuscript was aimed to investigate the effect of inherent mineral matter and inorganic solid additives on the yield of tar, liquid and gaseous fractions from the pyrolysis of Makerwal coals at 690 °C. The production of char, tar, liquid and gas from coal pyrolysis gives a wide range of chemicals.

In the present study two coal sample codes named MC-1 and MC-3 were obtained from Makerwal coalfields, District Mianwali in Punjab, Pakistan. Pyrolysis products were divided into three fractions tar, liquid and gas. Tar and liquid were collected in two traps while the gaseous fraction leaving the traps was directly injected to gas chromatograph equipped with flame ionization.

Results and Discussion

To study the effect of inorganic solid additives on the yield of volatiles, obtained after pyrolysis at 690 °C, solid additives (Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, Fe_2O_3 and $CaSO_4$) were mechanically mixed with de-mineralized form coal at the ratio of 1:9. The results obtained from the pyrolysis of MC-1 and MC-3 de-mineralized, and salt treated samples, are discussed below:

(a). MC-1 Coal

The salt form coals were pyrolyzed under the same set of experimental conditions as employed for raw and de-mineralized form coal samples. The quantitative results are reported in Table-1 and the results of compositional analyses of gaseous fraction from GC-FID are reported in Table-2. In the case of MC-1 de-mineralized coal and de-mineralized + Na_2CO_3 coal samples it was observed that the yield of pyrolysate decreased by 9.65 % after the addition

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Table-1: Comparison of pyrolysate yield from pyrolysis of MC-1 raw, demineralized and salt additives form coals at 690 °C.

Coal Type	Char wt %	Tar wt %	Liquid wt %	Gas wt %
MC-1 Raw	55.50	15.45	15.65	13.40
MC-1 DM	58.65	11.55	14.85	14.95
Na_2CO_3	63.30	12.15	13.25	11.30
K_2CO_3	62.50	8.70	13.30	15.50
$CaCO_3$	63.50	10.85	9.85	18.45
$MgCO_3$	58.90	10.15	12.50	18.45
Fe_2O_3	65.80	9.75	11.30	13.15
$CaSO_4$	63.70	11.75	12.15	12.40

Table-2: Comparison of hydrocarbon yields from the pyrolysis of MC-1 raw, demineralized and salt additive form coal samples at 690 °C.

Coal Type	Peak Area x E5 (μV. S)					
	Methane	Ethylene	Ethane	Propene/ Propane	1-Butene/ *n*-Butane	1-Pentene/ *n*-Pentane
MC-1Raw	45.35	15.47	30.13	31.65	19.18	1.70
MC-1DM	32.49	10.22	14.10	16.05	8.41	0.90
$MgCO_3$	21.13	7.06	7.18	10.76	7.16	2.73
$CaCO_3$	20.77	7.37	7.32	10.04	7.24	0.75
Na_2CO_3	20.33	7.32	7.90	11.85	9.03	2.43
Fe_2O_3	20.31	7.59	6.18	9.29	6.56	2.55
K_2CO_3	21.69	7.05	7.60	10.29	8.14	2.87
$CaSO_4$	21.33	7.90	11.48	10.21	6.37	-

of Na_2CO_3. The decrease in yield of tar and liquid was 6.85 and 8.2 %, respectively, while the gas fraction was increased by 5.4 %. The gaseous analysis carried out by GC-FID, and it was observed that the yield of methane, ethylene and propane + propene decreased, whereas the yield of *n*-butane + 1-butene and *n*-pentane + 1-pentene increased. However, there was a decrease of 16.52 % in the total yield of hydrocarbons.

The results obtained from the pyrolysis of MC-1 de-mineralized and de-mineralized + K_2CO_3 coal samples showed that the yield of pyrolysate decreased by 7 % after the addition of K_2CO_3. The decrease in yield of tar and liquid was 6.55 % and 5 %, respectively, while the gas fraction was increased by 4.55 %. It was also observed that the yield of methane, ethylene, propane + propene and *n*-butane + 1-butene decreased whereas the yield of *n*-pentane + 1-pentene increased. The total hydrocarbons yield was observed to be decreased by 17.54 %.

When MC-1 demineralized coal and demineralized + $CaCO_3$ coal samples were pyrolysed, it was observed that the yield of pyrolysate decreased by 9.15 % after the addition of $CaCO_3$. The decrease in yield of tar and liquid was 2.45 and 3.9 %, respectively, while the gas fraction was increased by 2.8 %. The yield of gaseous hydrocarbons *i.e.* methane, ethylene, propane + propene, *n*-butane + 1-butene and *n*-pentane + 1-pentene was observed to decrease. The total hydrocarbons yield was decreased by 21.14 %.

In the case of MC-1 de-mineralized and de-mineralized + $MgCO_3$ coal samples it was observed that the yield of pyrolysate decreased by 6.15 % after the addition of $MgCO_3$. The decrease in yield of tar and liquid was 2.1 and 6.15 %, respectively, while the gas fraction was increased by 2.1 %. It was also observed that the yield of methane, ethylene, propane + propene & *n*-butane + 1-butene decreased whereas the yield of *n*-pentane + 1-pentene increased. The total hydrocarbons yield was decreased by 18.89 %.

From the pyrolysis of MC-1 de-mineralized coal and de-mineralized + Fe_2CO_3 coal samples it was observed that the yield of pyrolysate decreased by 12.25 % after the addition of Fe_2CO_3. The decrease in yield of tar, liquid and gas fractions was 3.15, 8.5 and 0.6 %, respectively. It was observed that the yield of methane, ethylene, propane + propene and *n*-butane + 1-butene decreased whereas the yield of *n*-pentane + 1-pentene increased in case of Fe_2O_3 treated coal samples. The total hydrocarbons yield was decreased by 22.04 %.

The results obtained from the pyrolysis of MC-1 de-mineralized coal and de-mineralized + $CaSO_4$ coal samples exhibited that the yield of pyrolysate decreased by 9.05 % after the addition of $CaSO_4$. The decrease in yield of tar and liquid was 4.85 and 5.6 %, respectively, while the gas fraction was increased by 1.4 %. It was observed that the yield of methane, ethylene, propane + propene and n-butane + 1-butene decreased whereas *n*-pentane + 1-pentene was not detected. The total hydrocarbons yield was decreased by 17.84 %.

(b). MC-3 Coal

In the case of MC-3, the solid additive form coal samples were also pyrolyzed under the same experimental conditions as used for raw and de-mineralized coal samples. The results are presented in Tables-3 and 4. For MC-3 de-mineralized coal, the addition of these salts showed dissimilar effect on pyrolysate as observed in the case of MC-1. The addition of $MgCO_3$, $CaCO_3$ and Fe_2O_3 increased the amount of tar, while $MgCO_3$, $CaCO_3$, K_2CO_3 and $CaSO_4$ increased liquid yield, whereas Na_2CO_3, K_2CO_3 and $CaSO_4$ increased the yield of gaseous fraction.

Table-3: Comparison of pyrolysate yield from *pyrolysis of MC-3* raw, demineralized and salt additives form coals at 690°C.

Coal Type	Char wt %	Tar wt %	Liquid wt %	Gas wt %
MC-3 Raw	61.80	11.75	13.35	13.10
MC-3 DM	65.60	7.60	8.60	18.20
Na_2CO_3	68.30	4.70	6.65	20.35
K_2CO_3	65.65	5.00	9.85	19.50
$CaCO_3$	67.80	9.10	10.95	12.15
$MgCO_3$	64.80	9.45	8.70	17.05
Fe_2O_3	70.90	8.40	6.35	14.35
$CaSO_4$	65.65	5.00	9.85	19.50

Table-4: *Comparison of hydrocarbon yields from the* pyrolysis of MC-3 raw, demineralized and salt additive form coal samples at 690 °C.

Coal Type	Peak Area x E5 (μV. s)					
	Methane	Ethylene	Ethane	Propene/ Propane	I-Butene/ n-Butane	I-Pentene/ n-Pentane
MC-3 Raw	24.39	7.32	15.07	11.18	5.66	1.37
MC-3 DM	16.74	4.66	6.63	6.19	4.86	1.49
$MgCO_3$	17.14	4.78	5.29	6.95	4.72	-
$CaCO_3$	17.44	4.54	5.37	6.25	3.75	-
Na_2CO_3	10.69	2.82	3.42	4.9	2.89	-
Fe_2O_3	19.56	5.79	10.29	7.39	6.15	-
K_2CO_3	18.53	6.13	12.29	10.88	2.49	-
$CaSO_4$	21.35	6.75	7.94	10.52	7.94	-

Mineral matter plays an important role in both the thermodynamics and kinetics of coal pyrolysis. The addition of various salts to coal matrix showed variable effects. The decrease in the yield of tar and liquid indicates that Na_2CO_3 as a catalyst can affect the tar fragmentation reactions leading to an increase in the yields of H_2, CH_4 and C_2-C_5 hydrocarbons and as result of this the tar yield is decreased. Yeboah *et al.* [9] studied the yield of volatile tar and gas obtained during rapid pyrolysis of bituminous coal and lignite in the presence of dolomite particles. Results showed that the presence of dolomite decreased tar yield and increased gas yield. These changes were presumed to occur due to secondary tar cracking reactions on the surface of dolomite particles. In a related study Liu *et al.* [10] reported that CaO, K_2CO_3 and Al_2O_3 all had a catalytic effect on the reactivity of coal pyrolysis, their effects were closely related to temperature region and coal types. Addition of inorganic matter decreased the activation energy and the characteristic temperature of coal was changed. Franklin *et al.* [11] demineralized a Pittsburgh No. 8 bituminous coal with HF-HCl solution and co-slurred in water for 24 hours with extremely fine particles (0.1 μm) of calcium carbonate. They carried out rapid pyrolysis of both demineralized and calcium treated samples. Addition of calcium resulted in substantially lower tar yield. The decreased yield of tar was attributed to secondary cracking and re-polymerization catalyzed by calcium additive. Such reactions would normally increase the yield of light hydrocarbons. The increase in the yield of carbon dioxide was shown to result from the decomposition of calcium carbonate to calcium oxide, a reaction catalyzed by the carbon surface. On the other hand the increased yield of carbon monoxide was attributed to the decomposition of phenolic groups in the coal structure. The catalytic effect of other salts almost shows the same trend.

From GC analyses it was observed that in case of MC-1 coal samples the yield of gaseous hydrocarbons (C_1-C_5) decreased, while in case of MC-3 coal samples, an increase in the yield of gaseous hydrocarbons was observed when the coal is treated with K_2CO_3, Fe_2O_3 and $CaSO_4$. The comparison of both coals in de-mineralized and de-mineralized + salt additives is shown in Fig. 1. The variations in the yield of both coal samples were due to heterogeneous nature of coal and carbon content. This indicates that coal rank also plays an important role in the distribution and temperature dependence of various products. Other researchers reported similar results [12-14]. The observed higher yield of gaseous hydrocarbons show that these salts on addition remain as discrete particle external to coal organic matter which act as catalysts for secondary decomposition of tar molecule to lower molecular weight hydrocarbon gases.

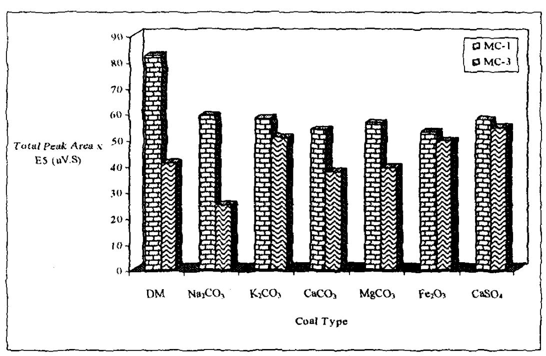

Fig. 1: Comparison of the yield of total gaseous hydrocarbons released from MC-1 and MC-3 in DM and DM + Additive form coals at 690 °C.

Experimental

Two Representative coal samples, code names MC-1 and MC-3 were collected from Makerwal coalfields, District Mianwali, Pakistan.

Acid-form coals were prepared from raw coal by a method as described earlier [15]. The salt form coal samples were prepared as; salt: sample mixture (1:9, w/w) was added with an appropriate amount of distilled water and mechanically mixed to form a slurry and then left it for 24 hours. These samples were then dried in electric oven at 105 °C for 8 hours, cooled to room temperature in a desiccator and used for pyrolysis studies.

For the quantitative determination of pyrolysis fragments; char, tar, liquid and gas, an off-line procedure was adopted. There were two traps between pyrolyzer and GC *i.e.,* trap-1 (U-shaped) Pyrex glass tube containing quartz wool and placed in cold water (~20 °C), while trap-2 was placed in methanol-liquid nitrogen slush bath (-93.9 °C). The quartz pyrolysis tubes, trap-1 and trap-2 were weighed before and after pyrolysis. The whole assembly is shown in Fig. 2. The quartz pyrolysis tube was cleaned by soaking it overnight in chromic acid cleansing solution and rinsing in distilled water. The tube was dried at 150°C for one hour.

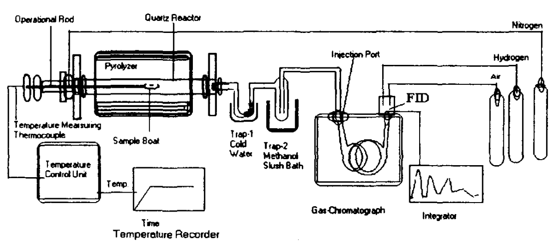

Fig. 2: Experimental setup for the quantitative determination of pyrolysates into fractions from the flash pyrolysis of coal.

Analytical System and Conditions

In all the pyrolysis studies, the analyses of the products were carried out by using Shimadzu GC-7AG Gas chromatograph coupled with flame ionization detector (FID). The analyses of the products were carried out on a spiral, stainless steel column (1828.8 mm x 3.175 mm ID) and packed with Porapak Q (100-120 mesh). For all the pyrolytic studies column temperature was programmed from 60-150 °C at the rate of 32 °C/min with initial time 2 min. The nitrogen gas was used, as a carrier at a flow rate of 40 mL/min. Analysis detector was FID with range 10^3 and attenuation 64. Air pressure was 0.5 Kg/cm^2 and hydrogen pressure was 1.0 Kg/cm^2. The injector and detector temperatures were kept at 170 and 150 °C, respectively. Pyrolysis of each coal sample was carried out at the temperature of 690 °C. The pyrolysis products were identified by comparison of the retention times of the unknown peaks in the pyrogram with those of pure compounds. The standards used were of Matheson Company.

Conclusions

This study suggested a novel approach for the characterization of coal based on accurate and reliable analyses of the pyrolysate. The quantitative information obtained through this technique is helpful for the effective use of coal and its fragments. As the pyrolysis products (char, tar, liquid and gas) were collected separately so these can be used separately. The general conclusions, which can be drawn from these results, are:

1. The major hydrocarbon products identified by GC were methane, ethane, ethylene, propane, propene, *n*-butane, 1-butene, *n*-pentane and 1-pentene.
2. The demineralization decreased the total pyrolysates, the yield of tar and liquid decreased, while the gas yield increased.
3. The inorganic solid additives (Na_2CO_3, K_2CO_3, $CaCO_3$, $MgCO_3$, Fe_2O_3 and $CaSO_4$) had varied effect on the yield of pyrolysates. It was observed that all these salts reduced the total pyrolysates yield.

References

1. G. R. Gavalas, *Coal Science and Technology 4 Coal Pyrolysis*, Elsevier, New York, 1982.
2. K. J. Voorhees, *Anal. Pyr. Tech. and Appl.,* Butterworth, London, 1984.
3. F. J. Tian, B. Q. Li, Y. Chen, and C. Z. Li, *Fuel,* **81**, 2203 (2002).
4. N. D. Marsh, D. Zhu, and M. J. Wornat, Proceeding of Twenty Seventh Symposium (International) on Combustion Pittsburgh, The Combustion Institute, 1897 (1998).
5. I. A. Awan, T. Mahmood and J. Nisar, *J. Chi. Chem. Soc.,* **51**, 291 (2004).
6. I. A. Awan, J. Nisar, A. Yamin and T. Mahmood, *J. Chem. Soc. Pak.,* **25**, 88 (2003).
7. J. Nisar, I. A. Awan, T. Ahmad and G. Naz, *J. Chem. Soc. Pak.,* **29**, 247 (2007).
8. I. A. Awan and Ikramullah, *J. Chem. Soc. Pak.,* **18**, 64 (1996).

9. Y. D. Yeboah, J. P. Longwell, J. B. Howard and W. A. Peters, *Ind. Eng. Chem. Process Des. Dev.,* **19**, 646 (1980).
10. Q. Liu, H. Hu, Q. Zhou, S. Zhu and G. Chen, *Fuel,* **83**, 713 (2004).
11. H. D. Franklin, W. A. Peters and J. P. Howard, *Prepr. Div., Fuel Chem. Am. Chem. Soc.*, **26**, 121 (1981).
12. X. Li and C. Z. Li, *Fuel*, **85,** 1518 (2006).
13. C. Z. Li, *Fuel,* **86,** 1664 (2007).
14. D. M. Keown, J. I. Hayashi and C. Z. Li, *Fuel,* **87**, 1187 (2008).
15. R. J. Tyler and H. N. S. Schafer, *Fuel,* **59**, 487 (1980).