Gas chromatographic-Mass Spectrometric Analysis of the Products Obtained by Microwave-Metal Interaction Pyrolysis of Coal

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Summary: A novel method for the liquefaction of coal has been investigated. It is a microwave assessed thermal cracking of coal in the presence of iron mesh. The iron mesh acts as antenna for the microwaves. This microwave metal interaction generates large quantities of heat which was used for the pyrolysis of coal. The cracking products were condensed outside the microwave using cold traps. The products were characterized by their physical state, chemical tests and GC-MS. The products include H_2S containing gases, hydrocarbon gases, aqueous liquids, oil, tar, and char like residue. The dependence of the rate of reaction on the form and shape of the antenna and the relative amount of the products as well as nature of the products is discussed in this paper.

Introduction

Microwaves are electromagnetic radiations in the frequency range of 300 MHz.-300 GHz. Microwaves generate heat on interaction with dielectric materials [1]. It is used for heating, and processing of food. Now it is widely used both at home and industry. Microwave energy is also used for the synthesis of compounds since 1986 [2]. Microwaves ensure uniform heating with effective heating efficiencies. The reaction carried out by the use of microwave energy are faster and product selective. The selectivity of products is due to kinetic reasons. Microwaves produce heat with in the material therefore the chance of heat loss is less as compared to the conventional heating [3, 4]. That is why microwaves can also be used for high temperature reactions like Pyrolysis. Using microwave energy, materials like Biomass, Coal, Oil Shale, and waste organic compounds has been converted into useful products [5-7]. Some workers used it for the Pyrolysis of polymeric materials like tyres, rubbers and polyethylene [1,8]. Some of these materials are not microwaves absorbing. That is why these are mixed with microwave absorbing materials for reaction [9, 10]. Absorption of microwaves by these materials raises the temperature up to 1000 °C. The use of copper wire for the generation of plasma in the reaction medium is also reported [11].

In the present work coal was pyrolyzed into oil and gas using microwave energy. Microwave energy is used for the generation of heat and high temperature. In this work an iron mesh was used instead of microwave absorbing materials. Iron is a reflecting antenna for the microwaves. It also interacts with the microwaves and generates heat and high temperature. The temperature range for this interaction is from 1000 °C up to the melting point of the metal. This interaction depends upon the shape of interacting object, mass and surface area. The mechanism of pyrolysis is also described. The products of Pyrolysis were analyzed using GC-MS.

Results and Discussion

Makarwal coal was converted into oil and wax using microwave energy. The dose of microwave was applied in 2-minute pulses. The microwave was focused on the sample using iron mesh as reflecting antenna. This antenna interacts with the microwaves and generates heat in addition to focusing the microwave energy on the coal. This interaction raises the temperature in the range of 1000-1200 °C. The range of temperature was investigated from the partial melting of the copper wire placed near the iron mesh antenna. This high temperature and microwave flux cracks coal compounds into low molecular weight compounds. In addition to microwave focusing and heat generation the metal also catalyses the chemical reactions of the coal. The presence of inorganics is another factor

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which catalyse the reaction and generate heat. The cracking is a combine action of high temperature, catalysis and the chemical reaction of the chemicals other than coal. The presence of H_2S in the product gases was confirmed by its reaction with lead acetate. This gas indicates the presence of sulfur and sulfur containing chemicals. Where sulfur is highly reactive at this high temperature and can crack hydrocarbons [12].The presence of acetylene in the gaseous products indicates the high temperature pyrolysis of coal. This was confirmed by the reaction of the gases with the copper-(I)-chloride.

This is a complex process of the decomposition, which completes in various steps. This involves the drying and dehydration, desulphurization and dehydrogenation. It was observed that in first four minutes there was dehydration along with the emission of water soluble and insoluble volatiles. The color of the obtained water was brownish with foul sulphide smell. The % mass of aqueous phase and oil like liquid is given in Table-1. It was observed that the wall of the receiving flask and the tube through which the products distils away from the reactor contains a sticky wax like product. This product is soluble in benzene and the oily fraction obtained during this reaction. The residue was a mixture of two types of solids, the light porous material and the black shiny material. The amount of black material is greater than the porous. The mass of total residue was found in the range of 5-6 g for 20 g of coal. The porous material is believed as mainly composed of inorganic salts and the black shiny material is carbon black. In addition to solids and liquids gases were also produced during the process. These gases were allowed to escape. The % mass of the gases was determined by difference. The efficiency of the process and the rate of reaction were also found to depend upon the shape of the iron antenna as well as the number of layers and mass. It was observed that when the iron mesh was used the reaction completed in twenty minutes. In case of a coil of the same dimensions the time for reaction was found 12 -13 minutes. It was also observed that when a cylindrical strip was used as antenna the time of reaction was increased to 35 minutes. However, the nature and number of the various fractions remained the same. When the same was converted into strips the reaction was completed in 25 minutes. This is because of the change in the reflecting and interacting area and mass of the metal. In addition to the change in reaction time, change in the relative mass of the product was also found as can be seen from the table.

Table-1: Investigation of the form of Antenna on the product distribution.

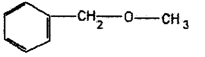
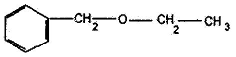
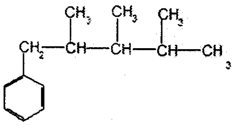
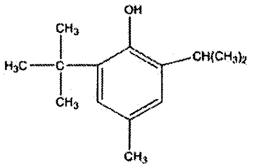
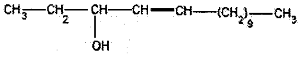
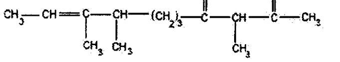
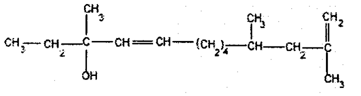
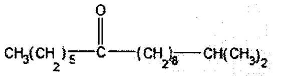
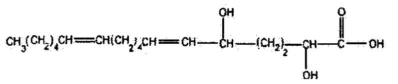
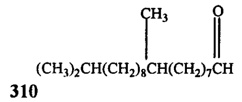
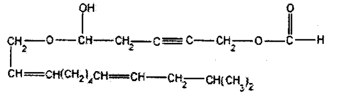
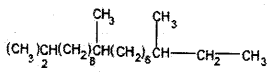
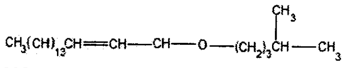
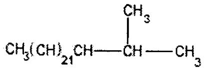
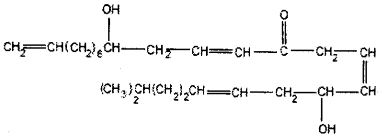
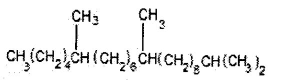
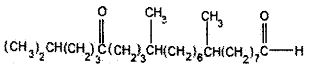
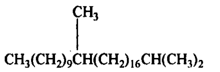
Antenna	% Aqueous Liquid	% Oily Liquid	%Sticky Liquid	% Gases	% Residue
Mesh	25.0 ± 0.01	15.0 ± 0.007	13.0 ± 0.006	22.0 ± 0.01	25.0 ± 0.01
Coil	25.0 ± 0.01	24.0 ± 0.007	15.0 ± 0.006	20.0 ± 0.01	16.0 ± 0.01
Solid cylinder	25.0 ± 0.01	13.0 ± 0.007	10.0 ± 0.006	23.0 ± 0.01	30.0 ± 0.01
Strip cylinder	25.0 ± 0.01	15.0 ± 0.007	13.0 ± 0.006	22.0 ± 0.01	25.0 ± 0.01

Despite of changes in the relative concentration of various fractions the chemical nature was found the same. The list of compounds investigated by the GC-MS analysis in the benzene soluble fraction of the products is given in Table-2. It can be seen from the table that the compounds are mainly hydrocarbons which indicates its usefulness as fuel. It contains both aromatic and aliphatic compounds. The presence of these compounds is important for understanding the mechanism of the reaction. The product was found to contain oxygen containing compounds. This oxygen is believed to be coal based in addition to the entrapped oxygen.

Experimental

Crude coal of the Makrwal range of Pakistan was used as the raw material. It was pyrolyzed in a medium sized 2450 MHz on/off domestic microwave oven of the Sharp Corporation. The reactor for the Pyrolysis was a cylindrical container made of baked clay. The lid for this reactor was of the pyrex. This was made leak proof using teflon tape. The internal diameter of the reactor was 70 mm and its length was 10.5 cm. the lid has a side tube of 60 cm. A wire-gauze made of the commercial grade iron having 1mm mesh size and made of the wires of 0.1 mm gauge was used as antenna and heat generation media. The gauze was rolled in the shape of cylinders. The length of which was 4.5 cm and its external diameter was kept 60mm to avoid the breakage of reactor by high temperature. The wire gauze was placed on a clay disc to protect the bottom of the reactor from high temperature. The side wall of the oven has a window through which the side tubes come out. The reaction was started just at room temperature and under atmospheric pressure. However, the pressure and temperature changed during the reaction. 20 gram of the finely powdered coal was placed in the iron mesh reactor which was

Table-2: List of the compounds on the basis of GC/MS.

Scane No	M/Z	Structure Name Molecular weight
164	107	 122 **(Methoxymethyl)benzene**
223	121	 150 **(Ethoxymethyl)benzene**
373	173	 188 **2,3,4-Dimethyl-5-phenylpentane**
414	170	 205 **2-*Tert*-butyl-6-isopropyl-4-methylphenol**
423	57	 $CH_3-CH_2-\underset{OH}{CH}-CH=CH-(CH_2)_9-CH_3$ 226 ***Z*-Pentadec-4-en-3-ol**
418	83	 $CH_3-CH=\underset{CH_3}{C}-\underset{CH_3}{CH}-(CH_2)_3-\overset{O}{\overset{\parallel}{C}}-\underset{CH_3}{CH}-\overset{O}{\overset{\parallel}{C}}-CH_3$ 224 **3,8,9-Trimethylundec-9-ene-2,4-dione**
477	83	 $CH_3-CH_2-\overset{CH_3}{\underset{OH}{C}}-CH=CH-(CH_2)_4-\overset{CH_3}{CH}-CH_2-\overset{CH_2}{\overset{\parallel}{\underset{CH_3}{C}}}$ 238 **3,10,12-Trimethyltrideca-4,12-dien-3-ol**
590	57	 $CH_3(CH_2)_5-\overset{O}{\overset{\parallel}{C}}-(CH_2)_8-CH(CH_3)_2$ 268 **16-Methylheptadecan-7-one**
637	93	**AMBIGOUS SPECTRA** **280**
733	97	 $CH_3(CH_2)_4CH=CH(CH_2)_4CH=CH-\overset{OH}{CH}-(CH_2)_2-\underset{OH}{CH}-\overset{O}{\overset{\parallel}{C}}-OH$ 313 **(6*E*,12*E*)-2,5-Dihydroxyoctadeca-6,12-dienoic acid**
736	57	 $(CH_3)_2CH(CH_2)_8\overset{CH_3}{CH}(CH_2)_7\overset{O}{\overset{\parallel}{CH}}$ 310 **9,18-Dimethylnonadecanal**
777	97	 322 **(*S*)-5-Hydroxy-5-((2*Z*,8*E*)-11-methyldodeca-2,8-dienyloxy)pent-2-ynyl formate**
780	57	 $(CH_3)_2CH(CH_2)_8\overset{CH_3}{CH}(CH_2)_6\overset{CH_3}{CH}-CH_2-CH_3$ 324 **2,11,18-Trimethylicosane**
823	57	 $CH_3(CH)_{13}CH=CH-CH-O-(CH_2)_3\overset{CH_3}{CH}-CH_3$ 338 **1-[(4-Methylpentyl)oxy]-2-heptadecene $C_{23}H_{46}O$**
864	57	 $CH_3(CH)_{21}CH-\overset{CH_3}{CH}-CH_3$ 352 **2- Methyl pentacosane**
884	279	 390 **(5*E*,9*E*,13*E*)-8,16-Dihydroxy-2-methyltetracosa-5,9,13,23-tetraen-12-one**
906	71	 $CH_3(CH_2)_4\overset{CH_3}{CH}(CH_2)_6\overset{CH_3}{CH}(CH_2)_8CH(CH_3)_2$ 366 **2,11,18-Trimethyltricosane**
943	71	$(CH_3)_2CH(CH_2)_{21}CH(CH_3)_2$ 380 **2,24-Dimethylpentacosane**
980	71	$CH_3(CH_2)_{24}CH(CH_3)_2$ 394 **2-Methylheptacosane**
1019	57	$CH_3(CH_2)_{25}CH(CH_3)_2$ 408 **2-Methyloctacosane**
1065	57	 $(CH_3)_2CH(CH_2)_3\overset{O}{\overset{\parallel}{C}}(CH_2)_3\overset{CH_3}{CH}(CH_2)_6\overset{CH_3}{CH}(CH_2)_7\overset{O}{\overset{\parallel}{C}}-H$ 422 **9,16,24-Trimethyl-20-oxopentacosanal**
1081	191	**412** **Ambigous spectra**
1122	57	 $CH_3(CH_2)_9\overset{CH_3}{CH}(CH_2)_{16}CH(CH_3)_2$ 436 **2,17-Dimethylheptacosane**

closed with Pyrex lid. The reactor was placed in the microwave oven while connected with the cold traps through Teflon tubes. The microwaves were applied in pulses.

GC- MS Analysis

General profile for the product of pyrolysis was obtained using EI-MS. Analysis of the product were conducted on a mass spectrometer GC-MS 600 H Jeol and the product was separated into its components using Agilent 6890 N gas chromatograph equipped with a fused capillary column (HP.5 L = 30 meter I.d.; 0.32mm film thickness 0.25 µm) with poly dimethylsiloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/minute. Condition for analysis: Injection mode was split at split rate 35. The column was held at 60 °C for 2 min and then heated to 260 °C at the rate of 5 °C per minute while injector temperature was 260 °C. The identification of the components of the products was confirmed using total ion chromatograms as well as fragmentation pattern.

Conclusion

Microwave iron interaction was found to generate heat and high temperature. This heat was used for the rapid pyrolysis of coal. This converted coal into liquid and gaseous fuel products. The yield of the reaction and nature of product was found improved than the conventional pyrolsis reactions of coal. In addition to this the amount of the benzene soluble liquid fraction was found greater than the conventional methods. This liquid fuel fraction was found cleaner form the sulphur and other pollution causing elements.

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