A New Method for the Co-Liquefaction of Coal and Waste Tyre Rubber into Useful Products Using Microwave Metal Interaction Pyrolysis

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Summary: A mixture of waste rubber of tyre and Makarwal coal of Pakistan was converted into oil using microwave metal interaction pyrolysis. The reactions were carried out in reactor containing copper coil which supported in high temperature microwave-assisted pyrolysis. The high temperature is generated by the interaction of microwaves with copper coil, coal and the bake clay reactor. Copper is used as antenna for the microwaves and it is believed that this antenna may also catalyze the pyrolysis process and affect the nature of products. This faster method of liquefaction gives 12% aqueous liquid, 58% oily liquid, 3% benzene soluble tar, 2 % gases and 25% residues. The liquid products were collected using cold traps and the amount of gas was obtained by taking difference. The mixture of tarry and oily liquid product was analyzed using GC/MS and found that it contains aliphatic and aromatic compounds. It was investigated by the chemical tests that the gases contain hydrogen sulfide and acetylene in addition to other fuel gases. The range of products and product formation is also discussed in this communication.

Introduction

Waste tyres have significant contribution to the solid waste and their dumping in the landfill sites is not appreciated due to the resistance of this rubber to biodegradation. Their incineration is also wastage of useful carbon resource. The direct combustion of waste tyre is associated with serious environmental problems. Pyrolysis of waste tyres is considered as a useful practice which converts it into useful oil or chemical feed stock [1-8] or co-pyrolysis with coal and other wastes is also appreciated [9]. Rubber contains sulfur cross links and that cleaves during the pyrolysis and convert into active pyrites which facilitate the pyrolysis. It was also investigated that pyrites interact with the organic skeleton and facilitates liquefaction process [10, 11].

Besides conventional process, the microwave pyrolysis was also used for the liquefaction of coal and rubber [12-14]. This type of pyrolysis is carried out at high temperatures by the use of microwave absorbing species or by the use of plasma producing metal wires [15,16]. Microwave metal interaction pyrolysis is also important for the high temperature pyrolysis of the coal and waste plastics [17-21].

In the present study tyre rubber and Makarwal coal was co-pyrolysed by the microwave metal interaction process. The idea behind this work was to develop a product selective, yield effective and faster method for the useful disposal of tyre rubber and the conversion of coal into commercially valuable products.

Results and Discussion

Waste plastics and rubber are useful carbon resources, however, their waste are an environmental threat. The high temperature is obtained partially by the microwave copper interaction and microwave absorbing with matter of the coal. The high temperature is also due to the lower melting point of the waste rubber, which provides a fluidized medium to coal and facilitates the uniform and faster pyrolysis. This process is further facilitated by the active species produced during the de-polymerization reaction. It is believed that these active species are composed of alkyl radicals, sulfides of hydrogen and active hydrogen in addition to small quantities of gaseous oxides. The combine action of the microwave flux, high temperature and the catalysis of copper produce active chemical species. These active species are responsible for the nature of products and the facilitation of the cracking reaction. The products of the reaction were found to contain aqueous liquid, which was mainly composed of the sulfides which was due to sulfur present in coal and that in the rubber. The sulfide containing liquid was analyzed by its reaction with lead acetate solution. The same solution was also used for the detection of sulfide in the gaseous product too. The gases were found to give red copper acetylide on reaction with a solution of copper (I). This reaction is characteristic for the acetylene which is produced by the decomposition of coal and rubber at high temperature. The nature of products indicates that this reaction involves de-

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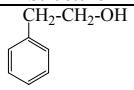
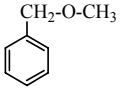
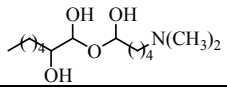
polymerization, de-sulfurization, dehydration and dehydrogenation by the primary reactions, however, secondary reactions are aromatization and substitution. The nature of products of the process mainly depends on these reactions. This process of the co-liquefaction has significant yield as can be seen from Table-1

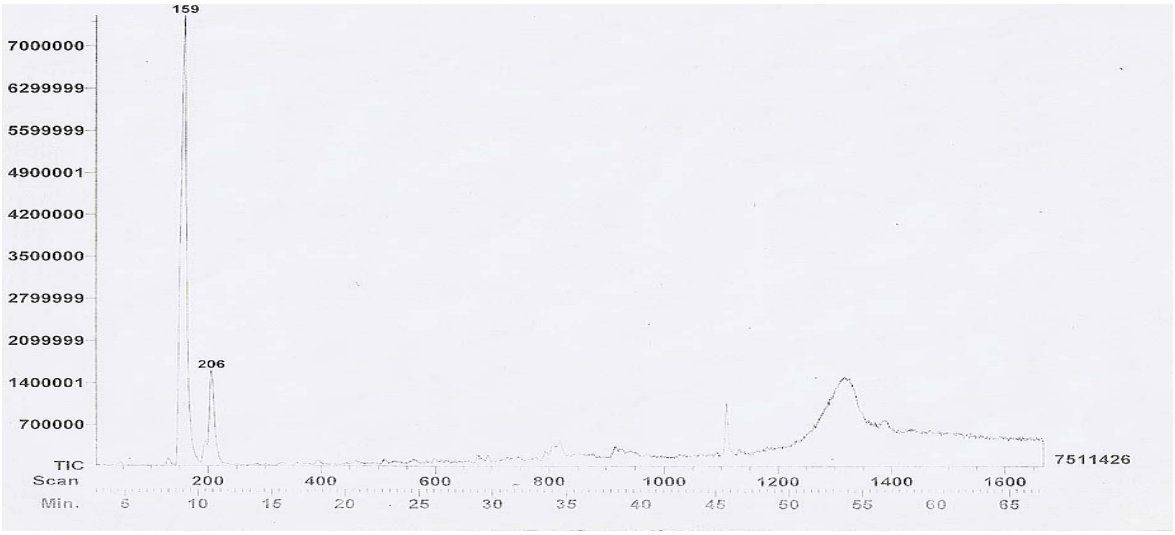
Table-1: Investigation of the products / yield of co-pyrolysis of Makarwal coal and tyre rubber in copper coil reactor

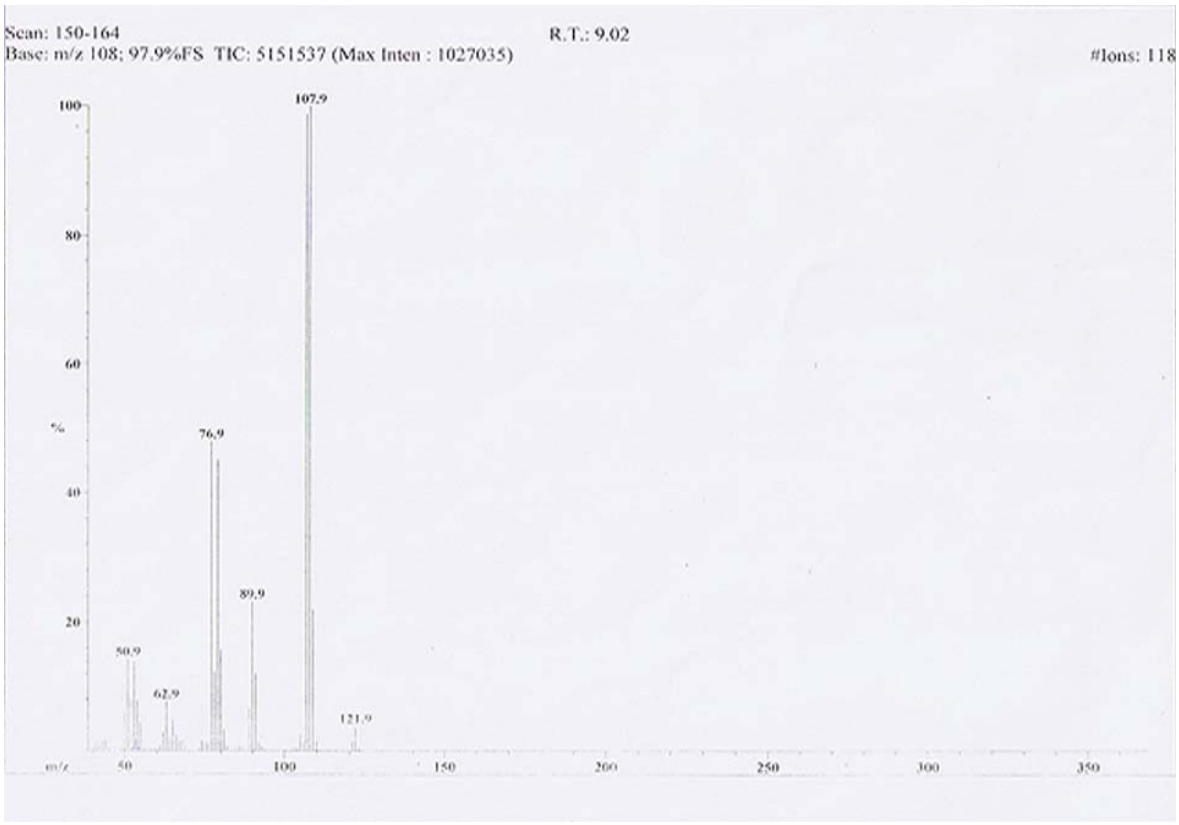
Specifications	% Aqueous Liquid	% Oily Liquid	% Sticky Liquid	% Gases	% Residue
Copyrolysis	12.00 ± 0.01	58.00± .01	3.00 ± 0.01	2.00 ± 0.01	25.0 ± 0.01
Coal	25.00 ± 0.01	24.00 ± .01	15.00 ± 0.01	20.00± 0.01	16.00 ± 0.01
Rubber	6.00 ± 0.01	67.00 ± .01	5.00 ± 0.01	2.00 ± 0.01	20.00 ± 0.01

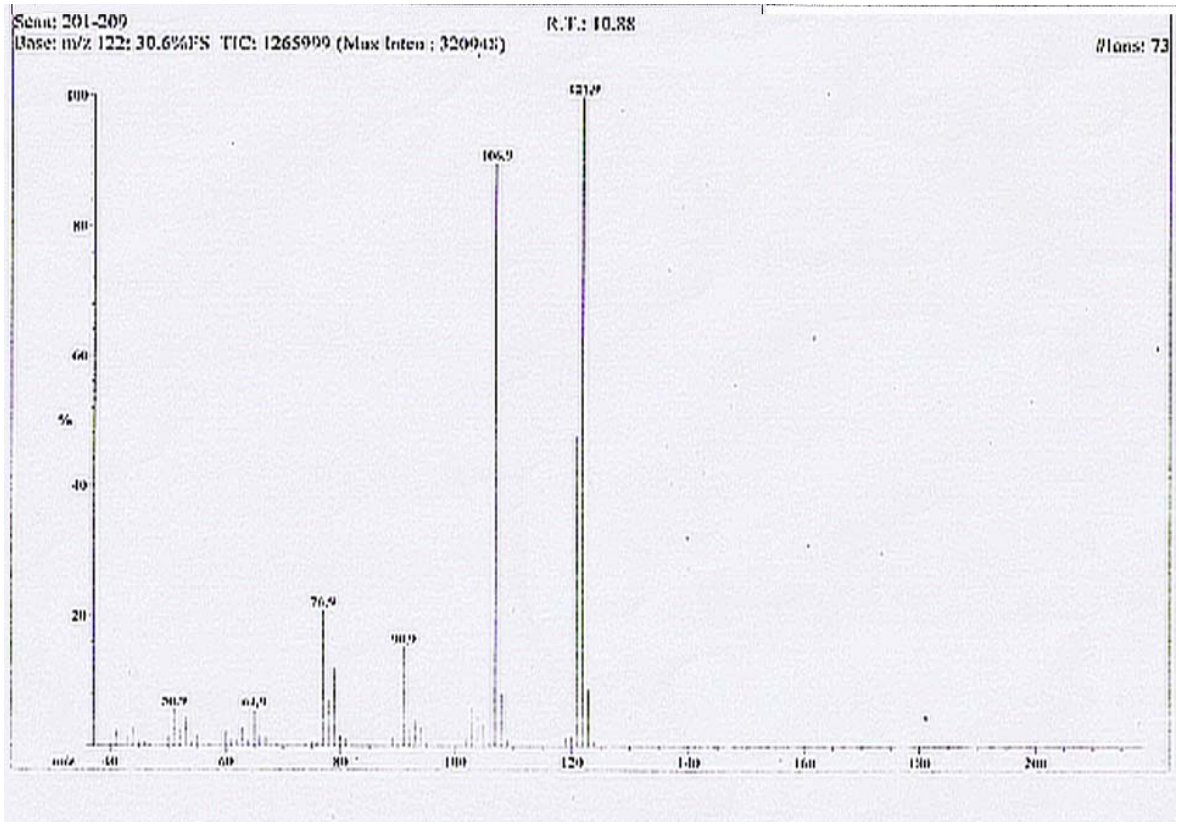
It can be seen from the Table-1 that the mass of aqueous liquid is 12%, unlike 25% for the pyrolysis of coal by this method. This indicates the reaction of oxygenated sites of the coal with species other than active hydrogen and the larger quantity of residue has mechanistic significance. It is mainly composed of the char and the char formation is believed to be due to sulfur contents of both the coal and rubber. The sulfur contents are responsible for the removal of hydrogen as sulfide of hydrogen. This can be confirmed from the relatively less amount of the gases and larger sulfur contents of the aqueous fraction of the liquid. This rapid dehydrogenation is responsible for the greater char and residue. The organic fraction was found of two types: the oil and tar viscous fraction. The tar was found soluble in the oily fraction and benzene therefore, both the oil and tar was dissolved in benzene and was analyzed by the GC-MS. The spectra and chromatogram are given in Fig. 1. It can be seen from the chromatogram that the product contains limited number of compounds. This is due to the uniformity of the composition of the active species and might be due to the sulfur containing compounds and Table-2 contains the list of these compounds. The names and structures of the three compounds are given while the fourth one was difficult to be named due to peaks of very haphazard nature. It can be seen from the table that the compounds are oxygenated aromatics with side chains. It is believed that the aromatics are produced both, from the coal and the aromatization of the moieties resulted from the pyrolysis of rubber. The oxygen contents of these compounds are from the coal based oxygen and partially from the trace quantities of the air present in the reactor. The presence of nitrogenous compound may be due to the same reasons. Total ion chromatogram indicates that the peak for volatile compound which is 2-phenylethanol is greater indicating its high concentration.

Table-2: List of the compounds obtained during the co-pyrolysis of rubber and coal.

Scan No.	Base Peak	Structure	Name	Molecular ion Peak
150-164	108		2-Phenylethanol	122
201-209	122		Methoxymethyl benzene	122
1109	148		1-(5-(Dimethylamino)-1-hydroxypentayloxy)heptane-1,2-diol	277




Scan: 150-164
Base: m/z 108; 97.9%FS TIC: 5151537 (Max Inten : 1027035)
R.T.: 9.02
#Ions: 118
107.9
76.9
89.9
50.9
62.9
121.9
%
m/z


Scan: 201-209
Base: m/z 122; 30.6%FS TIC: 1265999 (Max Inten : 320943)
R.T.: 10.88
#Ions: 73
121.9
106.9
76.9
89.9
%
m/z

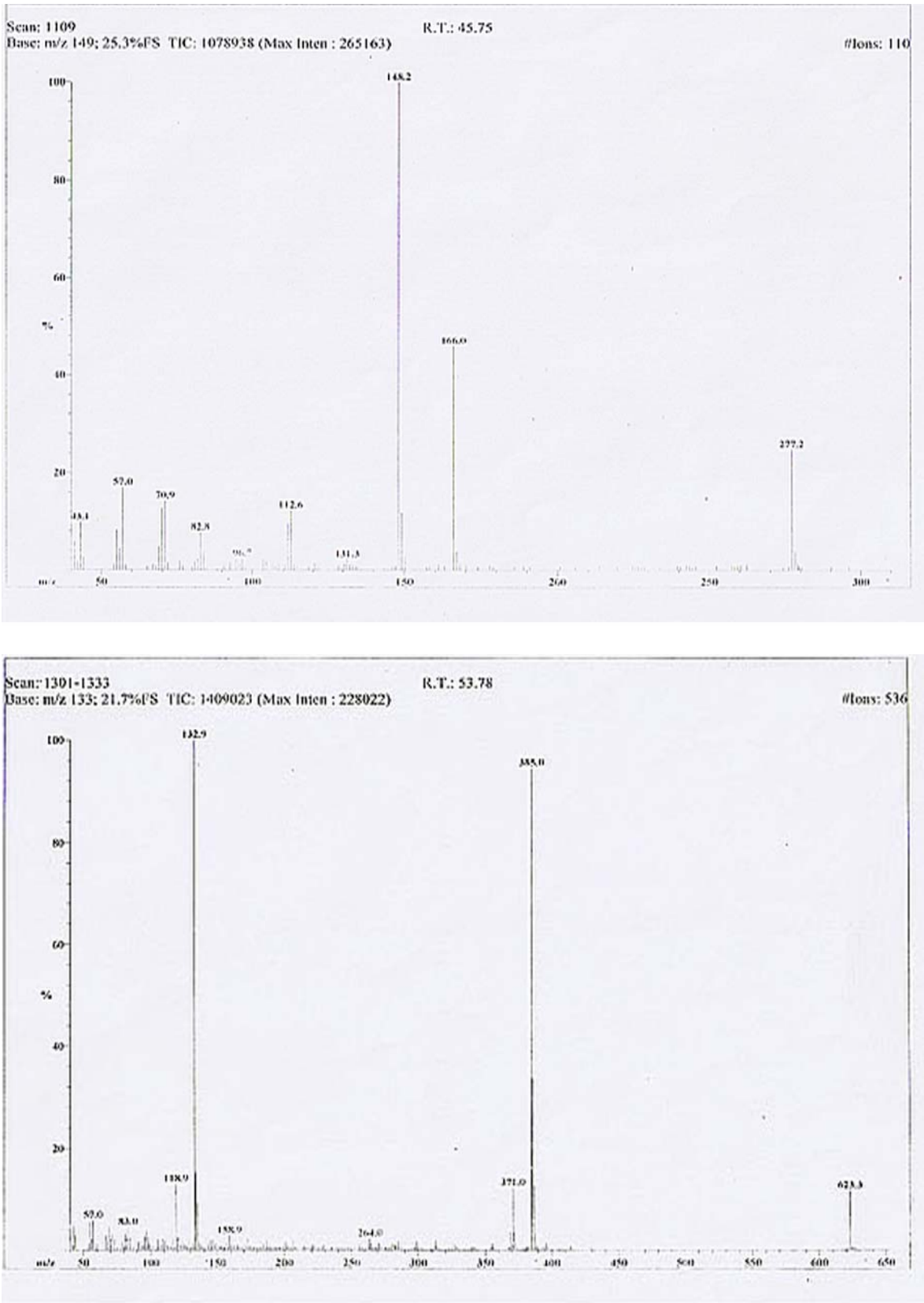


Fig. 1: Total ion Chromatogram for the copyrolysis oil of rubber and coal.

Experimental

Suzuki 800 cc car tyres were employed for this work, the tyre was MA 701 of the tubeless type and manufactured by the MAXIS (Thailand). It was thoroughly cleaned using various types of the cleaners and then it was cut into fine pieces using a sharp cutter. It was mixed with fine powder of the Makarwal coal of Pakistan in 1:1 weight ratio. This mixture was placed in and around a tightly coiled wire of copper in a baked clay reactor. The coil was placed on a clay disc in the reactor for avoiding the overheating of the clay reactor. The internal diameter of the coil was 60 mm and the height was 4.5 cm while the gauge of wire was 3 mm. The internal diameter of the reactor was 70 mm and its length was 10.5 cm. The shape of this reactor was cylindrical with a lid of Pyrex® and was made leak proof using Teflon® tape. On charging, the reactor was closed with the Pyrex® lid having a side tube for the delivery of products. Each experiment was carried out in triplicate. The pyrolysis experiments were carried out in medium sized domestic microwave of 2450 MHz frequency. A window of 50 X 50 mm was made in the side wall of this oven. The reactor was placed in the microwave oven after charging with coal and tyre rubber mixture and connected to the cold traps through the side tube coming out of the side window of the microwave oven. The microwaves were applied in 2 minute pulses to avoid the over fast reaction. The pressure and temperature changed during the reaction. A schematic diagram of the process is given in Fig. 2.

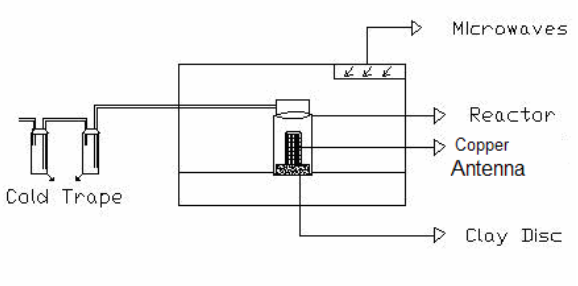


Fig. 2: Schematic diagram of the microwave metal interaction co-liquefaction of coal and waste tyre rubber

GC-MS Analysis

General profile for the product of pyrolysis was obtained using EI-MS. Analysis of the products was conducted on a mass spectrometer GC-MS 600 H Jeol and the products were separated into their components using an Agilent 6890 N gas chromatograph equipped with a fused capillary column (HP.5 L = 30 m, I.d.; 0.32 mm film thickness 0.25 μm) with polydimethylsiloxane as the stationary phase. The carrier gas was helium at a flow rate of 1.8 mL/min.

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/min 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 metal interaction pyrolysis was found an effective method for the conversion of rubber and coal into useful products. It was observed that the process is product selective and yields limited number of compounds and achieved in short time. It was also found that this process is effective for de-sulfurization which results in the formation of clean fuel. The process scrubs the sulfur containing gases by dissolution in aqueous phase. The nature of product is helpful in the description of the mechanism of the process.

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