

VARIATION IN GAS CHROMATOGRAPHY (GC) ANALYSIS IN SETTING UP LABORATORY PROTOCOLS FOR WASTE TO ENERGY NOVEL FIXED BED REACTOR SETUPS

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ABSTRACT

Gas Chromatography coupled with Mass Spectrometry (GC/MS) has been applied in various analytical chemistry works. However, to fine tune a system that can serve the purposes of pyrolysis oil identification has proven to be a laborious effort, especially when considering the fact that no standard protocol exists for such analysis. In addition, obtained products were yielded from a newly commissioned unit with a unique and novel design. In this study, a US patent office claimed reactor [SULTAN-1, Pyrolysis Reactor System for the Conversion and Analysis of Organic Solid Waste, Patent application number: 15,487,351] that degrades polyolefinic virgin and waste materials to obtain petroleum refinery and petrochemical feedstock, has been commissioned. The reactor produces three distinct physical states of matter products accumulated as testing specimens, i.e. solids, gaseous and oil. The samples analysed in this work were of the gas and oil produced by pyrolysis of end of life tyre (ELTs) shavings that required to have a special recipe to work with in the laboratory. Various MS cords were utilised and experimental setups to fine tune the process, and special emphasis was given on the gas samples variation in this communication. To reach the desired analysis results with high repeatability, a plethora of experiences of lab personnel and laboratory-based experimental work was accumulated. Laboratory protocols were also setup for this work. These will be detailed along the process execution which yielded a standard laboratory best practice analytical method as part of the State of Kuwait newly initiated Government Initiative project.

Keywords: analytical method, GC/MS, laboratory best practice, pyrolysis, rubber, tyres.

1 INTRODUCTION

1.1 ELTs in The Context of Solid Waste Management (SWM)

Solid waste (SW) comes from various sources. It is essential to understand the characteristics of the SW in question, in order to, be able to manage it in an optimal manner. Rubber and durable goods are typically considered as a debatable item, in terms of SW classification [1]. Namely, ELTs where globally some 1.5 billion tyres are produced annually and are presumed to be disposed of within the SW stream [2]. About 80% of new tyre sales are presumed to be discarded as ELTs in the 15 European Union (EU) member states, equivalent to a disposal rate of 2.5 million tonnes per annum [3].

In many countries, ELTs are not considered to be a municipal solid waste (MSW) *per se* but are rather categorised as ‘special waste’ or ‘durable products’. In 2010, about 3.3 million tonnes of ELTs were generated in the EU-27 member states and some 5.7 million ELTs were stockpiled throughout Europe [4]. ELTs accumulation in stockpiles is also considered as a serious fire hazard threat causing a near impossible situation to control which may produce large quantities of toxic compounds. Recently, such incidents occurred in Spain and Germany within Europe.

1.2 Origins and Chemical Recycling of ELTs

ELTs contain a high fraction of polymeric materials originating from petrochemical feedstock processed from petroleum-refining operations. These chemicals are high their calorific value (CV) and represent a good venture for recovery as a feedstock recycling process [5, 6]. The major chemical compounds typically found in ELTs are polyisoprene (PI), polybutadiene (PBD) and a significant proportion of styrene-butadiene-rubber (SBR) [3,7]. It should be kept in mind that both natural and synthetic rubbers are also main constituents of ELTs. This makes ELTs rich in synthetic polymers to be valorised for many industrial processes with the aim of SW recycling.

Pyrolysis is the thermal degradation of organic materials in the presence of heat surrounded by an inert atmosphere. Pyrolysis of ELTs is typically conducted at temperatures above 500°C in an open vent or atmospheric pressure. Pyrolysis yields three distinctive products, i.e. pyrolysis oil, gaseous fraction and solid char [8]. The recovery of steel from ELTs can be conducted either pre or post the process itself [1]. The oil resulting from the process can be used directly as a fuel similar to fuel oil or gas oil. It can also be added to refinery product cuts or upgraded using a catalyst [9]. Various studies were conducted in the past on ELTs utilising pyrolysis and where deemed successful [10–15].

1.3 GC Analytical Methods of ELTs Products Identification

Analytical methods are typically used post treatment, or coupled with the instrument to conduct the pyrolytic reaction. To compare the analysis of the products between the pyrolysis and combustion of ELTs, Conesa *et al.* [16] used an experimental setup treating the feedstock and analysing the products with standard chemicals. Poly aromatics and other compounds were analysed using high resolution GC coupled to a high resolution mass spectrometer (MS) (HRGC/HRMS). Volatile organic compounds evolving from the various apparatus were analysed using GC and namely three different columns in Conesa *et al.* [17] work as per the following: Alumina-KCl with a flame ionisation detector (FID) for light hydrocarbons (CH_4 , C_2H_6 , $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$, C_3H_6 , C_4 and C_5 hydrocarbons), a Carbosieve SII column with a TCD for CO_2 analysis, and a Molecular Sieve 5 Plot column to separate nitrogen, oxygen, and CO .

Chang [18] utilised GC with dual TCD/FID to analyse the composition of oil produced from pyrolysis. Hence, variation exists in open literature regarding the use of appropriate equipment for product analysis. This is expected, since products have different compositions and both qualitative and quantitative analyses were conducted in the past. Therefore, to have a standard recipe or procedure for products analysis from pyrolysis is something that needs to be done for each equipment (or apparatus) depending on targeted compounds and what is expected to be gained from the analysis (and consequently the study).

1.4 Work Motivation

ELTs accumulation in stockpiles has been deemed as a serious environmental hazard. Moreover, it was announced in the near past that the State of Kuwait was the home of the largest ELTs disposal site, visible from space. The area of Sulaibya (Ruhayia) (see Fig. 1) hosts over 7 million tyres in one place [19]. There were also a number of reported incidents where ELTs caught fire. The Government of Kuwait is now taking an initiative to dispose and control the situation utilising technological means that can maximise the use of this SW.



Figure 1: Aerial (left) and top (right) view of the ELTs stockpile location in the State of Kuwait. Images source [19].

To this end, and given the rationale and reasons stated above; this work was initiated of dire necessity to the current situation in Kuwait when it comes to the management of ELTs. This study investigates a number of technical objectives and research statements and its specific objectives are as per the following:

- i. To utilise a novel bench scale reactor that conducts batch process pyrolysis on a local ELTs grade.
- ii. To determine major compounds obtained from the pyrolysis of local ELTs grade.
- iii. To study the variation from conducting various methods of analytical analysis on products obtained.
- iv. To develop and consequently come up with final recommendation, as to the best practice in handling ELTs pyrolysis and protocols that govern its execution.

The work presented in this study stems from an ongoing effort in executing a national government initiative project in establishing a waste management research unit (WMRU). The preliminary analysis conducted in this study is being accumulated with ongoing research efforts to establish the above-mentioned objectives and fine tune resulting efforts in the WMRU of the Kuwait Institute for Scientific Research (KISR).

2 EXPERIMENTAL

2.1 Materials

A locally sourced tyre grade deemed as scrap was secured from a local dealer in Kuwait in the amount of 10 kg. The ELTs were used in the form of shavings as received (Fig. 2). The average dimensions of the ELTs were 30×30 mm. Sample size was also verified using a JEOL-JSM-6010 LA SEM using a voltage of 3 kV resulting in various micrographs (Fig. 3).

2.2 Pyrolysis Bench Scale System

A total of 200 g of ELTs were charged into the fixed bed batch reactor system. The reactor system and configuration is of a novel design and recently patented (SULTAN 1-Pyrolysis Reactor System for the Conversion and Analysis of Organic Solid Waste, Patent application



Figure 2: End of life tyres (ELTs) shavings used in this study.

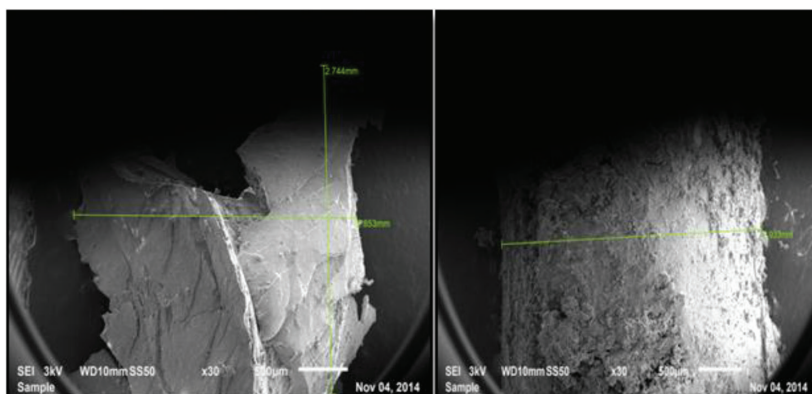


Figure 3: Scanning electron microscopy (SEM) images obtained for particle size dimension of ELTs.

number: 15,487,351). A minimum of two duplicate runs were conducted on the ELTs in the range between 500°C to 700°C (Figs. 4 & 5). Alumina packing of a 5-mm diameter (average bulk density- ρ -700 kg m⁻³) was used in the amount of 120 g. A cooling temperature of 20°C was used for the chilling unit. Gases evolved were collected in a Tedlar bag (5 L) over the course of the conducted run.

2.3 GC Analysis Laboratory Protocol

Two methods were used to establish the GC/MS protocol in this work for the gaseous and oil fraction obtained from the pyrolysis process. In the laboratory procedure, the gas and oil samples were received from the experiments that required a different analytical approach. Gas samples did not required any sample preparation step and were analysed as is. On the other hand, oil samples were not suitable for a direct injection and as a consequence a cleanup step was included in the analytical procedure. The GC-MS analysis was performed in an

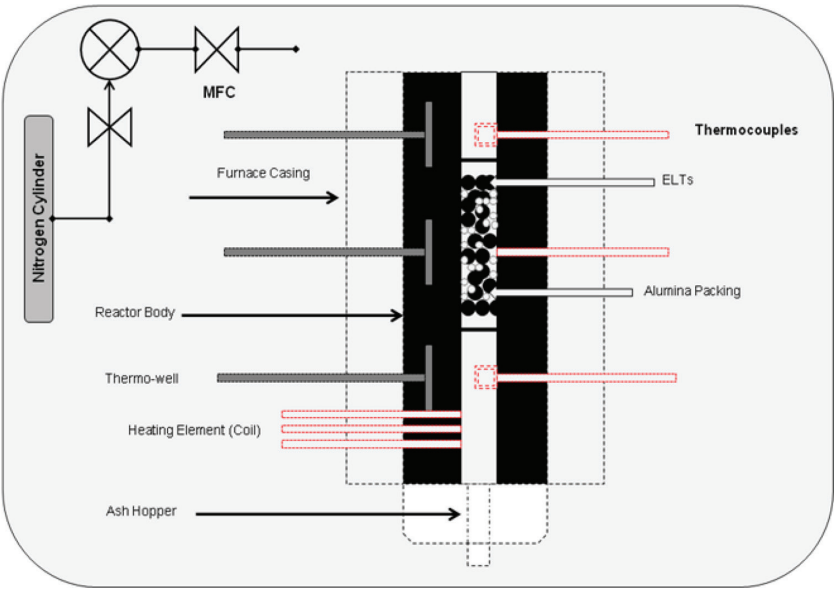


Figure 4: Schematic Flow Diagram of the Reactor Configuration

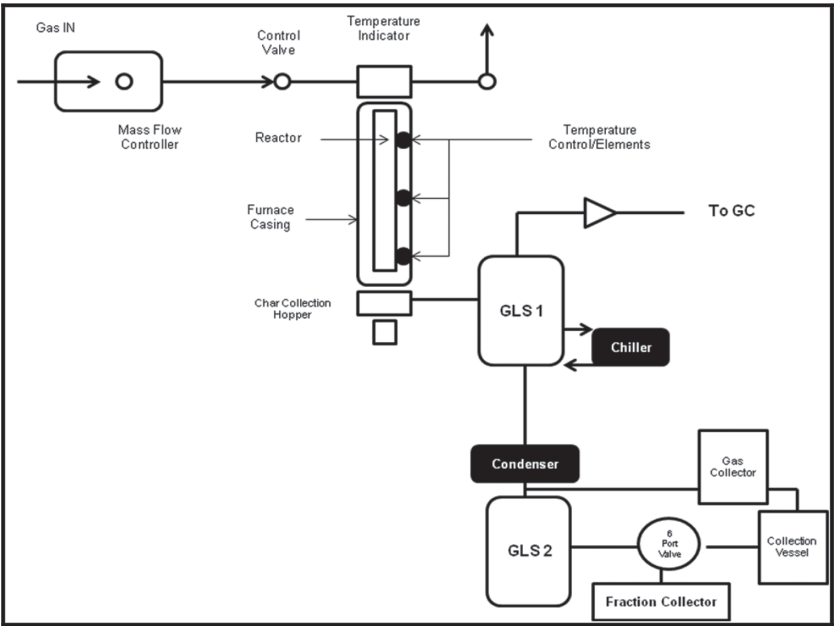


Figure 5: Pyrolytic system configuration and setup used in the waste management research unit (WMRU).

Agilent 5977A GC/MSD system. The initial tests were carried out in a 15-m column (Restek-5MS 15m, 0.25mm, 0.25 μ m). A 30-m column was also installed (Restek-5MS 30m, 0.25mm, 0.25 μ m) and experimented with. Mass detector was operated in EI and Scan mode (50-550 m/z). The qualitative analysis was performed with MassHunter using a deconvolution algorithm to find the compounds in the chromatogram and the identification of the potential compounds were carried out comparing their spectra with the ones included in the NIST 2014 Library. Adsorption chromatography was used to clean-up the oil samples. A glass column containing 5 g silica and 5 g alumina was prepared and conditioned with hexane. An amount of 2 ml of the sample was introduced on the top of the column and allowed to pass through it. The elution was carried out with 100 ml of hexane. Gas samples were manually injected (10 μ l) in splitless mode. That is why the system was reconfigured by removing the auto-sampler and the sample tray. In contrast, oil samples were injected (1 μ l) in split mode (ratio: 300:1) using the auto-sampler.

Procedures for the detection and identification of compounds in pyrolysis oils for the second set of experiments, are described based on two different clean-up approaches prior to injections of samples. The first procedure was the solid phase extraction (SPE), which is one of the most popular sample preparation techniques used as an alternative to liquid-liquid extraction (LLE). SPE is an extremely versatile technique for the extraction of a wide range of compounds. SPE is performed in cartridges packed with various packing materials ranging from polar to non-polar ones; typically similar phases as used in liquid chromatography. The stationary phase is conditioned prior to loading of the sample. Conditioning is performed using different solvents to remove any impurities and to 'wet' the stationary phase.

After conditioning the silica cartridge (1.0 g/6 ml) with hexane the sample (0.2 ml in 1 ml hexane) was loaded and the cartridge was rinsed with a weak eluent to remove sample impurities which are not of interest. Subsequently, the analytes of interest are eluted by a 6-ml dichloromethane with a polarity similar to target compounds. Solvent was evaporated under nitrogen for GC/MS injection. In order to improve the flow of the sample and solvents, vacuum was used. The choice of the stationary phase depends on the nature of the analytes. The second procedure to be experimented with was the back extraction of semi-polar and polar organic volatile compound, which was performed by mixing 5 ml of deionised water with 2 ml of TDO. The mixture was shaken vigorously and then centrifuged for 10 min at 3,000 rpm to allow separation of the aqueous and organic layer. The aqueous layer was removed and back extracted with DCM using 4 ml aqueous layer and 2 ml of DCM. The DCM was removed and dried on anhydrous Na₂SO₄. The extract was injected by auto-sampler for GC/MS analysis.

3 RESULTS AND DISCUSSION

The results of the GC analysis will be detailed in this section, with respect to each analytical method used. The first set of gas samples were analysed in a 15-m column. Unfortunately, those samples were not reanalysed in the 30-m columns because only five sampling bags were available and they were required for new sampling episodes. To avoid cross-contamination among samples, the sampling bags were cleaned and purged with nitrogen gas. This gives one of the main indicators in running this experiments laboratory protocols where sufficient personnel is needed for the change in shift within the GC lab. A sample of the results from gas samples is shown in Table 1 and a sample of the absolute abundance (peak area) of the compound detected is shown in Figure 6. Silicone Contaminants, aliphatic compounds (long-chain alkane hydrocarbon) and sulphur compounds were detected in all of them. A combination of low temperature in the pyrolysis experiment and a 15-m column could justify

Table 1: Gas chromatography results using 15-m column on the gas product from ELTs at 500°C (operating temperature).

Compound detected in exp. run #1	Amount (%)	Compound detected in exp. run #2	Amount (%)
Sulfur (S8)	40	Sulfur (S8)	33
Homosalate	16	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-ethyl-	29
Hexathiane	16	Hexathiane	29
Hexadecanoic acid, methyl ester	11	D-Limonene	6
Cyclopentasiloxane, decamethyl-	11	Cyclohexasiloxane, dodecamethyl-	2
Cyclooctasiloxane, hexadecamethyl-	2	Cycloheptasiloxane, tetradecamethyl-	1
Cyclohexasiloxane, dodecamethyl-	1	3H-1,2-Dithiole-3-thione, 4-methyl-	1
Cycloheptasiloxane, tetradecamethyl-	1		
2-Ethylhexyl trans-4-methoxycinnamate	1		
13-Octadecenoic acid, methyl ester	0.2		

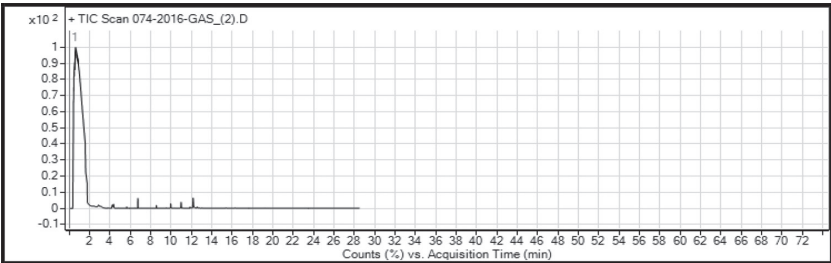


Figure 6: GC scan of Run no. 1 (500°C) gas product showing count (%) vs. acquisition time (min) on the 15-m column.

the fact that in the first set of samples the number of compounds detected were lower than in the second set of gas samples on the 30- m column. Detection for larger amount of compounds was conducted later on at retention times below 5 min. By comparison to 30-m column, detection was higher for the 700°C gas product (Fig. 7).

The complexity of the oil sample chromatograms were higher as expected. The number of compounds that could be identified were also higher than in gas product samples. A considerable number of aromatic compounds appeared in the chromatogram such as benzene derivatives, polycyclic aromatic hydrocarbons (PAHs) hydro and methyl derivatives. The Total Ion Chromatogram (TIC) were also analysed for the samples. Internal standards are

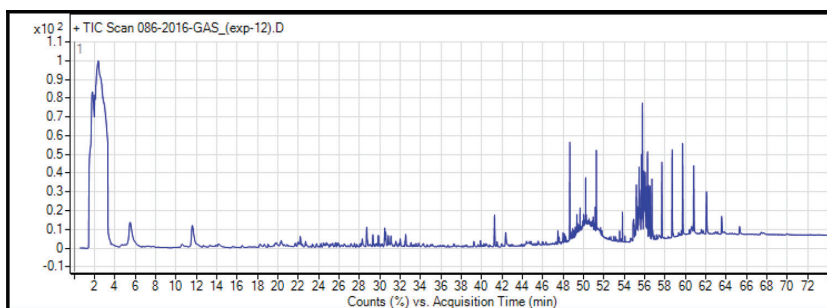


Figure 7: GC scan of Run no. 2 (700°C) gas product showing count (%) vs. acquisition time (min) on the 30-m column.

advised to be added to the oil extracts before injection to have a more accurate semi-quantitative analysis. Space limitation in this correspondence has limited showing all results obtained (gas and liquid). However, Figure 8 shows samples of the derived results from the oil analysed. Al-Salem *et al.* [5] pyrolysed 15 mg of tyre scrap in a micro setup (thermo-gravimetry) and analysed the products using the means of a chromatograph provided with a thermal conductivity (TCD) and FID connected to the micro balance using a thermostated

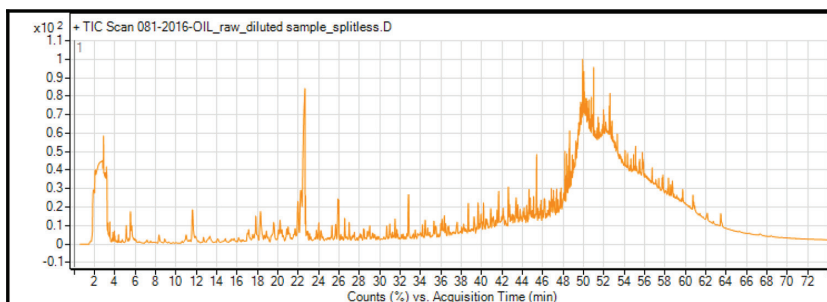


Figure 8: GC scan of Run no. 2 (550°C) oil product showing count (%) vs. acquisition time (min) on the 30-m column.

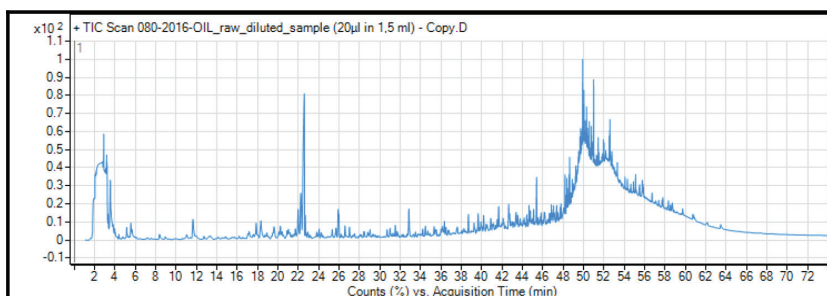


Figure 9: GC scan of Run no. 1 (550°C) oil product showing count (%) vs. acquisition time (min) on the 30-m column.

line. The identification of the products was conducted in a lump product fashion categorising the evolved compounds from pyrolysis as per the following: gases (C_1-C_4), liquids (non-aromatic C_5-C_{10}), single ring aromatics (C_5-C_{10}), and char.

A more detailed spectra was detected using the second method applied for the GC ELT oil samples, explained in the previous section. This can be attributed to the retention time increase in GC and the SSE (preparation method). Hence, SSE is more appropriate for ELTs and can be highly recommended for future works. The library matching procedure using the Nist 02 (National Institute of Standards and Technology, Gaithersburg, MD, USA) was also conducted. As criterion, a minimum spectral match factor of 70% was used. The major compounds identified were as follows: Cyclohexane, 2,2,4-Trimethyl Petane, Heptane, 4,4-dimethy cyclopentane, 2,4- dimethyl 1,3 Pentene, 2,4,4-trimethyl 1-Pentadiene, 3,5-Dimethyl cyclopentene, Methyl cyclohexane, 3,4,4 trimethyl 2-Pentene, 3, methyl cyclohexene and Styrene. Other compounds are reported in Table 2 and scans are shown in Figs 10 and 11. It can be noted that more PAHs are detected with the SLE method due to the contact with the pre-treatment cartridge allowing for developing a better separation phase for analysis.

Table 2: Main compounds detected with the SLE method for GC oil analysis.

Compound	Compound
Methyl Iso butyl Ketone	3,5 dimethyl cyclopentene
Toluene	2,2,4,4 tetramethyl Pentane
3,5-dimethyl cyclohexene	Ethyl benzene
P-xylene	3-1 methyl cyclohexane
O-Xylene	Styrene
1,5,5-Trimethyl 6- methylene Cyclohexene	m- Cymene
D-Limonene	
1,3,5-trimethyl benzene	Naphthalene

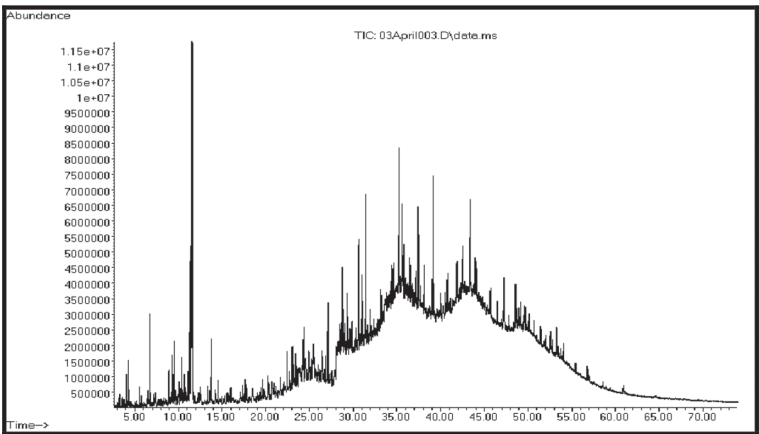


Figure 10: GC scan pyrolysis oil using SLE method.

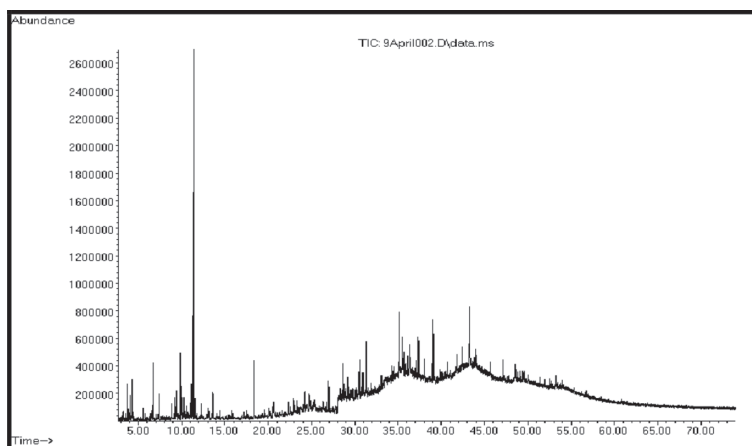


Figure 11: GC scan pyrolysis oil using LLE method.

CONCLUSIONS

The variation in chord (column) length and the detection time interpretation of the GC results contribute considerably in the analysis of the pyrolysis gas and oil samples. The preliminary work conducted in this study indicates so far that the GC protocol ideal for analysis in these cases is noted as the protocol shown for SPE. For higher detection scan and limit in retention time compounds, results are ideal to be analysed from start of scan rather than after 4 to 6 min of retention time in columns. This was noted for gaseous samples, since past works have not indicated a clear protocol for such analysis.

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