

Production of Liquid Oil by Pyrolysis of Natural Rubber

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Abstract

The importance of energy as a vital commodity to support the economic and social needs of man is indisputable. Present world consensus is on rapid introduction of environmental compatible energy and technology systems. The increasing energy consumption continues to outstrip energy supply from the fast diminishing conventional energy reserves and necessitates an intensified search for viable alternative renewable sources of energy. Thus, an intensive search for new sources of energy has become imperative. The ASEAN countries, especially Malaysia and Indonesia are producing a huge amount of natural rubber. Considering this availability of natural rubber and its favourable elemental and thermal characteristics, an attempt has been made to produce liquid oil from natural rubber by fixed-bed pyrolysis technique. The liquid oil may be used as an alternative fuel in diesel engines and in industrial gas turbines. The oil was characterized by FT-ir and GC-MS techniques for its detailed chemical compositions. The fuel properties of the derived oil were also analysed and compared to the values for petroleum products.

Introduction

Energy is indestructible that can neither be created nor destroyed. This can only be transformed from one form to another. The transformation of energy into useful and suitable forms aims to fulfill and suit the needs and requirements of human being in the best possible way. Actually energy propels the society. The standard of living is correlated with per capita energy consumption. The more the energy is consumed, the higher the standard of living is considered. It is not out of place to mention that the world population is increasing at an average rate of 1.5-2.5% per annum. By the year 2100 the world population is expected to be in excess of 12 billion and it is estimated that the demand for energy will be increasing by five times from what it is now [1]. Thus, the demand of energy will be continuing to outstrip its supply. As a result engineers, scientists and technologists are searching for new, alternative and promising sources of energy. Natural rubber represents an important source of alternative potential energy, fuel and value-added chemicals. The fascination of natural rubber is its easy availability in Malaysia, high carbon content, low moisture and ash content and renewability.

Malaysia is the world's leading producer of natural rubber, a commodity produced from the rubber tree (*Hevea brasiliensis*). In 1988, Malaysia's natural rubber export accounted for 33.1% of the total world natural rubber production [2]. However, Malaysia's natural rubber production continued declining due to the conversion of uneconomic rubber holdings to the cultivation of oil palm and cocoa. In order to find an alternative use for natural rubber an endeavour from the point view of energy recovery from it by the thermo-chemical pyrolysis may be worthwhile.

Pyrolysis is considered to be an emerging, new and potential technology to recover value-added energy, fuel and chemicals from natural rubber. Pyrolysis may be described as the thermal degradation of materials in complete absence or inadequate presence of oxygen [3]. More recently pyrolysis is meant for liquid production although solid char and gas are also obtained as by-products. Considering the availability of natural rubber in

Malaysia and Indonesia in a significant amount and its favourable elemental and thermal composition, an attempt has been made to produce liquid oil from natural rubber using fixed-bed pyrolysis technique. Three main products formed in the pyrolysis process are liquid oil, solid char and gas. The liquid oil and solid char were collected separately while the gas was flared. This liquid oil can be used as a potential fuel in diesel engines and industrial gas turbines. The solid char can be used for making activated carbon. The gas has its potential use as a fuel gas. Finally, the liquid products were analysed for some of their physical properties and compared to petroleum fuels.

Experimental set-up and procedure

Materials

The natural rubber (SMR 20) was obtained from Dunlop Malaysia Industries Berhad, Kuala Lumpur, Malaysia. It was then shredded and sieved to the size of 1-2 cm and finally dried for 24 hours at 105°C prior to pyrolysis.

Characterization of solid rubber for pyrolysis process

For the purpose of investigating the suitability of natural rubber locally available in significant amount as feedstock for pyrolysis so as to obtain value-added liquid product, the following analysis has been considered:

- Proximate and ultimate analysis
- Thermo gravimetric analysis (TGA)

Important parameters like volatile matter, fixed carbon, ash content and moisture content of the natural rubber feedstock essential to know in order to examine its suitability for pyrolysis process, can be obtained from the proximate analysis of the feedstock. ASTM (American Society for Testing and Materials) Standard D3172-73 (1984) test procedures for solid fuel, titled "Standard Method for Proximate Analysis of Coal and Coke" was used for the proximate analysis [4]. The ultimate analysis for the elemental composition in terms of carbon, hydrogen, nitrogen, oxygen, and sulphur (CHNOS) content is also important in order to make necessary material balance of each component. The ultimate analysis was conducted in a C-H-N-S analyser, according to the ASTM D3176-84 standard test procedures. Oxygen content was determined by difference, knowing the ash content. It has been seen that the percentage of carbon in the solid natural rubber is very high. The proximate and ultimate analysis of solid natural rubber are presented in Table 1.

Table 1: Proximate and ultimate analysis of natural rubber (SMR 20)

Ultimate analysis (wt %)			Proximate analysis (air dry wt %)	
Carbon (C)	79.431		Volatile matter	95.40
Hydrogen (H)	12.36		Fixed carbon	3.8
Oxygen (O)	4.967		Moisture content	0.5
Nitrogen (N)	-		Ash content	0.3
Sulphur (S)	-			

The thermal characteristics of natural rubber was analysed by thermogravimetric analyser (TGA). The experiment was conducted at the Polymer Engineering Laboratory, Faculty of Chemical Engineering, UTM. A Perkin Elmer model TGA 7-series, thermogravimetric analyser was used for the analysis. Natural rubber samples were pyrolysed in an inert atmosphere of nitrogen gas over a temperature range from ambient to 900°C

at various heating rates. The loss in weight of the sample was continuously recorded as a function of temperature and time. TGA gives information about the temperature at which pyrolysis is initiated, when the rate of devolatilisation is at its maximum and finally the temperature at which the process is completed. They also give an indication of the fractional weight of the volatile in the sample. Fig.1 shows the thermogram from the TGA produced when the natural rubber sample was subjected to a heating rate of 25°C/min. At this heating rate, the devolatilisation was initiated at about 258°C and nearly completed at 490°C. From the DTG curve, the maximum rate of the devolatilisation occurred at 422°C at a rate of 0.123% wt loss/°C.

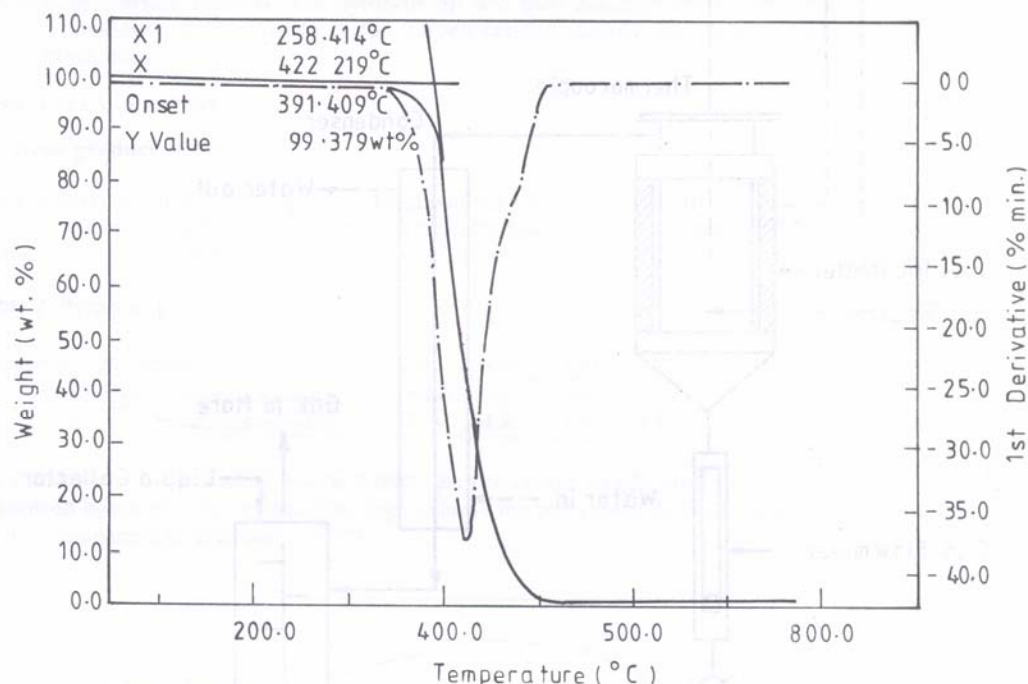


Fig.1. TG and DTG curves for solid natural rubber at a heating rate of 25°C/min.

Fixed-bed pyrolysis reactor system

Rubber particles were pyrolysed in an externally heated stainless steel fixed bed reactor system with nitrogen as the carrier gas. The system consists of fixed bed reactor, gas preheater, condenser and liquid collector. The pyrolysis reactor is 300 mm long and 50 mm in diameter. Schematic diagram of the fixed-bed pyrolysis reactor is presented in Fig. 2. Two electric tube heaters each of 1 kW power supplied the heat to the pyrolysis reactor and the gas pre-heat chamber. The temperature of the reactor was controlled by means of a temperature controller and measured by a thermocouple within the reactor bed. Carrier gas nitrogen was supplied at a constant rate to drive the pyrolysis product out of the reactor. The pyrolysis reactor bed was maintained at 480°C to get the maximum amount of liquid product. The product vapors and gases passed through the water-cooled condenser and the condensed liquid was collected in two ice-cooled liquid collectors in series. The uncondensed gas from the liquid collector was released to atmosphere. A fumed cupboard and piping system were used for the gases to flare to atmosphere by means of a motor driven exhaust blower. The entire experimental set-up was closed by transparent perspex sheet so that the pyrolysis product gases could not spread in the laboratory atmosphere.

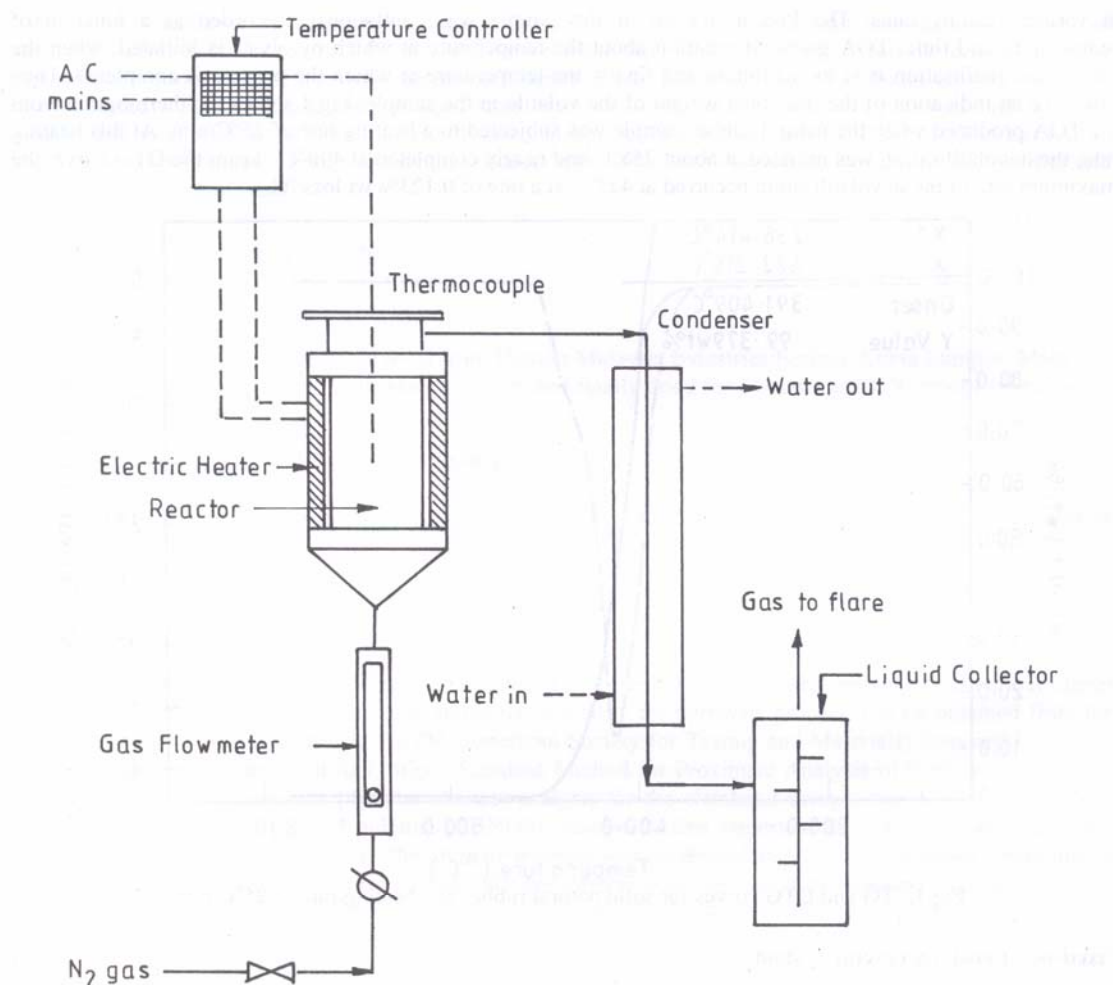


Fig. 2. Schematic diagram of fixed-bed pyrolysis reactor system

Oil product analysis

FT-ir analysis: The pyrolysis oil was analysed for its compositional groups identification by Fourier Transform infra-red spectroscopy (FT-ir). The FT-ir instrument of type Perkin-Elmer 7 series with an on-line pen plotter was used to produce the ir-spectra of the derived liquid. A thin uniform layer of the liquid was placed between two salt cells and was exposed to infra-red beam. The absorption frequency spectra were recorded and plotted. It had provided the absorption spectrum in percentage incident intensity, along the wave numbers 4400 to 370 per unit centimetre (cm^{-1}). The standard ir-spectra of hydrocarbons were used to identify the functional groups of the components of the derived liquid.

GC-MS analysis: In order to identify the individual compounds in the pyrolysis oil, it was analysed by gas

chromatography-mass spectrometry (GC-MS) technique. The GC-MS system was an HP5989x Hewlett Packard unit with J & W Scientific DB-1701 capillary column. Methanol was used as the standard solution. The following conditions were used for this DB-1701:

Column dimensions: 60 m x 0.25 mm, film thickness: 0.25 μ m,
GC condition: Inlet system: split-injector, He, 250°C, Oven temperature: 40°C isotherm for 4 min, 5 K/min to 280°C, Detection: FID/MS, 280°C.

Physical properties analysis: The pyrolysis oil was then characterized for its physical properties including kinematic viscosity, gross calorific value, carbon residue, density, moisture content, etc by standard ASTM testing procedures.

Results and discussions

Pyrolysis product yields

The pyrolysis of natural rubber produced a maximum yield of 72 wt% oil, 3.2 wt% solid char and 24.8% gas at bed temperature of about 480°C from the pre-pilot scale fixed-bed reactor. The pyrolysis product yields at various operating temperatures are presented in Table 2.

Table 2: Pyrolysis product yields at various operating temperatures.

Operating temperature °C	440	450	460	480	490	500	510	520
Liquid oil yield (% of feed weight)	64.4	68.2	70.1	72	71.3	71	70.6	69.8
Solid char yield (% of feed weight)	5.2	4.8	3.9	3.2	3.6	3.8	3.9	4.3

For the fixed-bed pyrolysis of natural rubber, the percentage weight yield of liquid and solid char products are influenced by the process temperature. Fig. 3 shows the percentage yield of liquid products and char at various pyrolysis temperatures from 440 to 520°C.

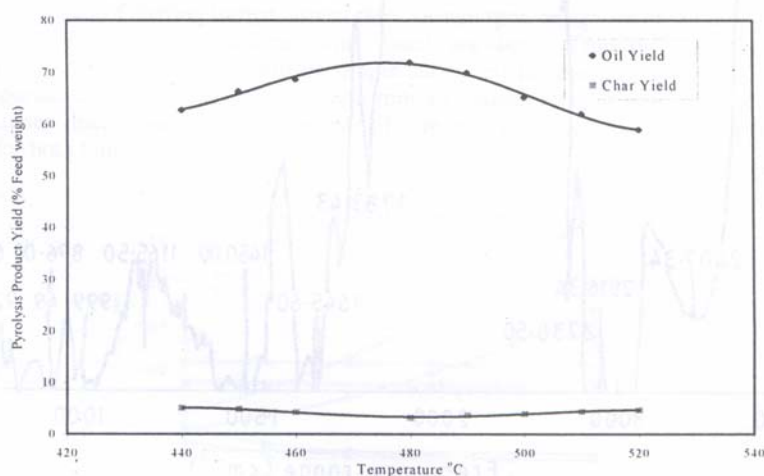


Fig. 3. Effect of pyrolysis temperature on oil and char yield

This figure shows that the maximum liquid yield of around 72 wt% occurs at temperature 480°C. As the temperature is raised, the oil yield decreases to 59 wt% at a temperature 520°C. The decrease in oil yield at higher temperature can be postulated due to the rapid increase of the gas yield. The high char yield, around 5.2 wt%, at the lowest temperature of 440°C is suggested to be due to the incomplete devolatilisation during the pyrolysis process.

Oil product analysis

FT-ir analysis: From the Fourier transform infra-red spectroscopy of the derived pyrolysis oil (Fig.-4), the functional groups were identified using the standard ir-spectra of hydrocarbons. The results are summarized in Table 3. The presence of polymeric O-H in the oil was indicated by the broad absorbance peak of O-H stretching vibration between 3600 and 3200 cm^{-1} . The strong absorbance peaks of C-H vibrations between 3000 and 2800 cm^{-1} indicated the presence of alkanes and the C-H and deformation vibrations between 1475 and 1350 cm^{-1} indicate the presence of alkanes. The absorption peaks between 1780 and 1640 cm^{-1} represented the C=O stretching vibration indicating the presence of ketones and aldehydes. The possible presence of alkenes were indicated by the absorbance peaks between 1650 and 1580 cm^{-1} .

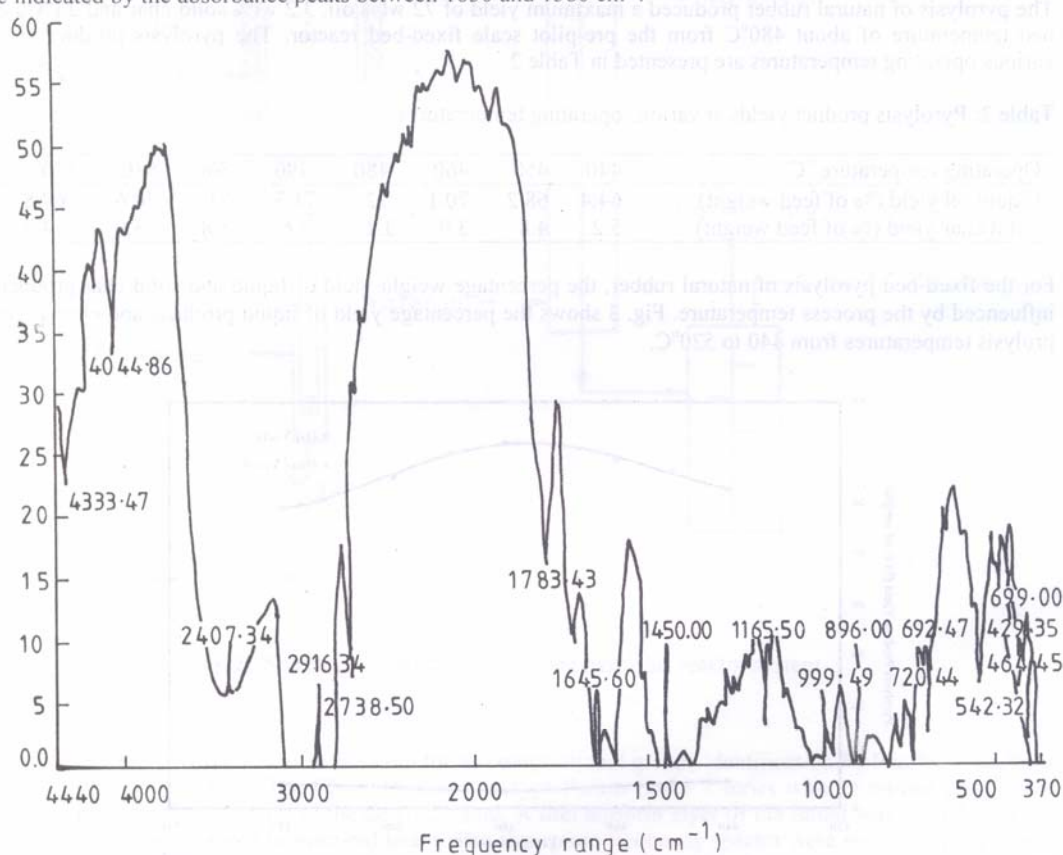


Fig. 4. FT-ir spectra of natural rubber pyrolysis liquid oil

The absorbance peaks between 1550 and 1490 cm^{-1} represented the $-\text{NO}_2$ stretching vibration indicating the presence of nitrogenous compounds. The overlapping peaks between 1300 and 950 cm^{-1} were due to the presence of alcohols, ethers and esters showing the C-O stretching. The presence of alkane, alkene, aldehyde, alcohol groups indicated the fact that the liquid has the potential to be considered as fuel.

Table 3: The FT-ir functional groups and the indicated compositions of pyrolysis oil

Frequency range (cm^{-1})	Group	Class of compound
3600-3200	O-H stretching	Polymeric O-H, water impurities
3000-2800	C-H stretching	Alkanes
1780-1640	C=O stretching	Ketones, aldehydes, carboxylic acids
1650-1580	C=C stretching	Alkenes
1550-1490	$-\text{NO}_2$ stretching	Nitrogenous compounds
1475-1350	C-H bending	Alkanes
1300-950	C-O stretching	Primary, secondary & tertiary alcohols, phenol, esters, ethers

GC-MS analysis: The identification and quantification of the individual compound present in the pyrolysis liquid oil were carried out with GC-MS techniques. Results are presented in Table 4. The chemical compounds present in the pyrolysis oil were grouped according to their carbon numbers and are presented in Table 5.

Table 4: Chemical compounds identified and quantified in the pyrolysis oil

Chemical compounds	Chemical formula	Wt% of pyrolysis oil
1-Limonene	$\text{C}_{10}\text{H}_{16}$	51.2
Camphene	$\text{C}_{10}\text{H}_{16}$	3.5
Pentasiloxane, dodecamethyl	$\text{C}_{12}\text{H}_{36}\text{O}_4\text{Si}_5$	10.7
Benzoic acid	$\text{C}_{16}\text{H}_{30}\text{O}_4\text{Si}_3$	4.8
1,3-diphenyl-1,3,5,5-tetramethyl	$\text{C}_{12}\text{H}_{22}\text{O}_3\text{Si}_5$	12.91
Octadecan-1-ol trimethylsilyl ether	$\text{C}_{12}\text{H}_{46}\text{Osi}$	8.21
Benzothiazole	$\text{C}_7\text{H}_5\text{NS}$	2.66

Table 5: Group of chemical compounds identified in natural rubber pyrolysis oil

Chemical compounds	Weight percent of pyrolysis oil
Hydrocarbons	54.7
Acids	4.8
Silicon-oxygenated hydrocarbons	31.82
Aldehydes	2.66
Others	6.02

The oil was mostly found to be in C_{10} group and represent the hydrocarbon groups. It is observed that in the oil derived by pyrolysis of natural rubber the percentage of hydrocarbons very high indicating the suitability of the oil as a liquid fuel. The oil also contains acids, aldehydes and aromatic compounds. It is interesting to note the

fact that unlike other biomass-derived pyrolysis oil, the polycyclic aromatic hydrocarbon (PAH) compounds those are known to be responsible for carcinogenic action were not found in the oil [5]. The chromatogram obtained from GC-MS analysis of natural rubber pyrolysis oil is presented in Fig. 5.

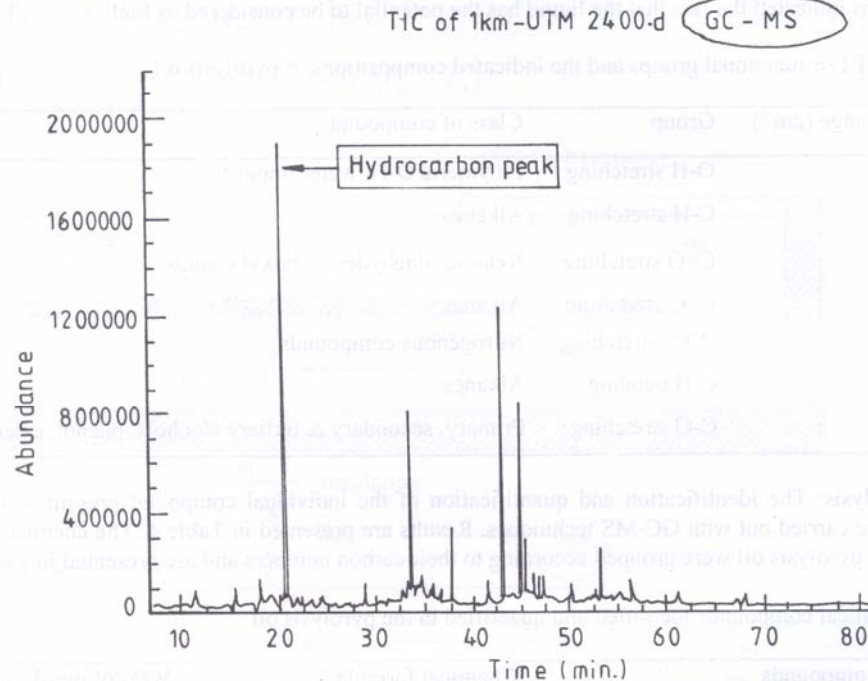


Fig. 5. Gas chromatogram of pyrolysis liquid oil from natural rubber

Physical properties analysis and its comparison: The pyrolysis oil was analysed for some physical properties. Table 6 shows the characteristics of the rubber pyrolysis oil in comparison to petroleum fuels such as diesel and heavy fuel oil. The elemental analyses show that the carbon and hydrogen content of the derived oil is close to that of petroleum fuels. The ash content in the oil is very low which is 0.053% and no sulphur in the oil, suggesting it will not produce hazardous sulphuric emission after combustion. The low viscosity of the oil around 1.377 cST at 60°C is a favourable feature in the handling and transportation of the liquid. The density of the derived oil is between that of diesel fuel and heavy fuel oil. The most significant property is that the calorific value of the oil is high 42.75 MJ/kg, reflecting the high potential of the oil for utilization as a fuel.

Table 6: Characteristics of the rubber pyrolysis oil compared to petroleum fuels

	Rubber Pyrolysis oil	Diesel Fuel	Heavy fuel Oil
Elemental Analysis (% wt.)			
Carbon (C)	84.705	86.1	85-86
Hydrogen (H)	12.191	13.2	11-11.5
Nitrogen (N)	0.602	-	0.3-0.5
Oxygen (O)	-	-	1.0-2.6
Sulphur (S)	-	0.7	-
C/H	6.95	6.7	7.6-7.8
Ash	0.053	0.01	0.1

Physical Property			
Gross calorific value, MJ/kg	42.750	45-46	42-43
K. viscosity at 60°C, Cst	1.377	1.3-3.3	200
Density at 15°C, kg/L	0.92	0.780	0.980
Carbon residue, %	0.58	0.35	-
Moisture content, % wt.	-	-	0.1

Conclusions

Pyrolysis of natural rubber in a fixed-bed reactor has successfully produced oil with gross calorific value comparable to that of petroleum products, suggesting that the oil may be used as a fuel. The kinematic viscosity of rubber pyrolysis oil is almost similar to that of diesel fuel. The density of the rubber pyrolysis oil is between that of diesel and heavy fuel oils. FT-ir analysis of the natural rubber pyrolysis oil indicates the presence of alkenes, alkanes, ketones/aldehydes, aromatic and substituted aromatic groups.

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