Recovery and Analysis of Oil from Used Rubber Tyre

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***Abstract*: Pyrolysis is the process of combustion of a certain material in the absence or with limited oxygen to obtain products. This process can be applied to waste tyre (tyre pyrolysis) to obtain solid product called char, liquid product called tyre pyrolysis oil and the gaseous product called pyro-gas. Research shows that tyre has different parts suited for its purpose, among which is the rubber tread. The rubber tread is found to have some essential components such as carbon and hydrogen which are essential components found in fuel. This part can then be used to produce some oil that is comparable to some conventional fuel. Tyre pyrolysis oil was produced in a simple distillation setup in a laboratory and was then analysed to ascertain its properties as compared to conventional fuel. About 55% of the product obtained from the pyrolysis is found to be tyre pyrolysis oil with the remaining 45% being char and pyro-gas. Analysis of the oil shows that tyre pyrolysis oil has lower pour point and gross calorific value which are -33^{o}C and 38.6MJ/kg respectively as compared to between -25^{o}C and -23^{o}C, and 43-46MJ/kg for diesel. This shows that tyre pyrolysis oil cannot be used in internal combustion engine as a replacement for diesel but can be blended with diesel of high heating value and pour point to be used in the engine. It was also discovered that the density of tyre pyrolysis oil is higher (925kg/m^3) as compared to that of diesel which is between 820 and 870kg/m^3 and high sulphur content which is about 3.8% as compared to 0.003-1.3% for diesel. It is recommended that the sulphur has to be reduced using desulphurisers if the oil is to be used as fuel in internal combustion engines. It was therefore concluded that tyre pyrolysis oil cannot be used alone as fuel in internal combustion engine but can be blended with diesel to obtain right quality of fuel for use in internal combustion engine.**

Index Terms: Pyrolysis, Diesel, Internal combustion, Fuel.

I INTRODUCTION

Automotive tyres are made up of synthetic rubber which is obtained from petroleum. Prior to the present day tyre, the development of tyre was based on improving the performance of natural rubber which is obtained from liquid latex secreted by some plants such as; guayule and spurge. Natural rubber was used to produce waterproof fabrics and in making balls, containers and shoes by pre-colonial people in south and central America [1].

Disposal of used tyre has become a major environmental concern globallymainly because they are not biodegradable and last for several decades if not properly handled. Since the number of automobile used in Nigeria is less than that obtained in developed countries the problem related to disposal of waste tyre is not seriously considered up till today, but it will be a serious problem in the near future. Hence, proper treatment methods for used tyre have to be devised in advance.This could be attributing to the increase in automobile usage as well as population especially in area of large population and highly industrialized nation [2], [3], [4].

Tyres are composed of chemical, rubber, steel and fabrics. Approximately 80% of the original constituents remain at the end of service [5]. Used tyres have a high content of volatile matter as well as fixed carbon that makes it an interesting solid as a fuel for production or hydrogenation process and in pyrolysis process to obtain different fraction of solid, liquid and gaseous products [6]. A car tyre has a mass of about 8.5 kg, whereas the mass of a tyre of a light duty vehicle is around 11 kg.

i Production of Tyre Pyrolysis Oil

The energy content of waste tyre can be exploited by thermo chemical process via pyrolysis into more valuable fuel and useful chemicals [7].Pyrolysis is a relatively new and potential process in recovery of value added product from solid or liquid waste substance. In the process thermal decomposition of a substance takes place in the absence of oxygen. The products of pyrolysis are liquid, gas, and solid containing carbon and ash. The raw material used in producing tyre include synthetic rubber and natural rubber, nylon, polyester cords carbon black, sulphur, oil resin and other chemical. The constituents provide the tyre with good strength and flexibility to ensure adequate road holding properties under all condition. The tread rubber portion of a tyre is primarily used for energy recovery to obtain tyre pyrolysis oil (TPO), pyro gas and carbon black.

Work done by [8] on the pyrolysis of scrap tyres shows that the pyrolysis oil is of high (42 MJ/kg) gross calorific value. About 30 wt% of the oil is an easily distillable fraction with a boiling point in the range of commercial petrol to diesel. It was found that, the density and the sulphur content of the tyre fuel were slightly higher than that of diesel fuel but other futures and distillation curve were very close to diesel fuel. In order to reduce the high sulphur content of the fuel, calcium oxide (CaO), calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH) were used [5]. Though this technology has been applied in developed countries, there is a need to indigenize the technology in under-developed countries such as Nigeria.

ii Composition of Tread Rubber

The elemental composition of tread rubber as analysed by [21] is given in Table 1. It contains hydrogen, carbon, sulphur, nitrogen and other element which makes it a suitable combination for production of pyrolysis products.

Table 1: Elemental Composition of Tread Rubber

Element	Percentage (%)
Carbon	73.8-88.50
Hydrogen	5.80-8.10
Oxygen	1.30-8.92
Nitrogen	0.21-0.50
Sulphur	0.92-1.71

iii Pyrolysis processes and Conditions

Thereare different pyrolysis processes which are either based on the nature of pyrolysis or based on residence time.

These include vacuum pyrolysis, flash pyrolysis and fluidized bed pyrolysis based on nature of pyrolysis, and slow pyrolysis and fast pyrolysis based on residence time.

The conditions of pyrolysis are temperature, heating rate, and particle size. The product of pyrolysis is obtained between the temperature of 450°C and 700°C.High yield of liquid product is at a temperature of around 450°C which increases with increase in temperature to a maximum at 600°C which then starts decreasing as temperature gets to 700°C [10]. Heating rate and particle size has little effect on the product yield with heating rate having effect on the surface area of solid product. A higher heating rate (>20°C) decreases liquid rate unlike moderate heating rate [11], while high particle size increases liquid yield at higher temperature [12].

iv Tyre Pyrolysis Oil as a Fuel

Direct injection into diesel engine of tyre pyrolysis oil (TPO) blended with the diesel fuel was carried out and combustion parameter such as; heat release rate, cylinder peak pressure were analysed [10], [13]. The result showed that nitrogen oxide (NO_x), carbon monoxide CO, hydrocarbon HC, and smoke emission were found to be higher at higher blend concentration due to the high aromatic content and longer ignition delay [10], diesel engine can run with tyre pyrolysis fuel blends up to 90% TPO [13]. They concluded that it's possible to use tyre pyrolysis oil in diesel engine as an alternative fuel in the future. Meanwhile, further studies by[14] on the suitability of tyre pyrolysis oil (TPO) as an alternative fuel for industrial furnaces, foundries and boilers in power plant shows that further improvement in fuel quality in terms of desulphurization, reduction in viscosity and aromatic contents and increase in cetane number is required if tyre oil is to be used as fuel in internal combustion engine [16].

II EQUIPMENT AND EXPERIMENTAL PROCEDURE

In this experiment, vacuum pyrolysis will be applied where the material is heated in a vacuum to obtain the pyrolysis product. The following equipment/apparatuses are used;

Condenser, Bomb calorimeter, GC-MS spectrometer, jar, Freezer, Thermometer, Meter ruler, Electric hot plate, Test tube, Beaker, Heating mantle,Round bottom flask, Retort stand, Holder, Distillation flask, Clamp, Temperature read out, Thermocouple, Reagent bottle and Receiver flask.

The reagents used include; Acetone, Cooling water and Ice block.

i Sample collection and Preparation

The raw material (used automobile tyre) used for pyrolysis process was collected from nearby vulcanizer workshop.
All the steel wires and fibre cords were separated from the tyre tread to be used for the pyrolysis process.
The tread was then cut into small pieces to reduce the surface area of the material for proper reaction.

ii Experimental Procedure

(a) Distillation Setup

The lab distillation setup is shown in Figure 1

Figure 1: Distillation Setup for the Experiment

The equipment was setup as shown in Figure 1

The tread part of the tyre prepared was placed in a round bottom flask which was connected to a distillation flask and placed in a heating mantle that was connected to an electric source.

The heating mantle which has a control knob for controlling the rate of heating, was switched on and the rate of heating was set at 20^{o}C/min.

A thermocouple was slot into the flask and connected to a temperature read out which has a range between -200^{o}C and 1300^{o}C.

The water tap was switched on to allow water flow through the condenser for condensing the gas coming from the flask while the uncondensed gas was absorbed in an acetone solvent.

The tyre pyrolysis oil was then collected in a flask placed in a beaker filled with ice block to avoid evaporation of the liquid.

The heating mantle was manually manipulated such that the temperature did not rise above 600^{o}C.

(b) Analysis of Tyre Pyrolysis Oil (TPO)

The various analysis carried out on the tyre pyrolysis oil were the absolute viscosity, density, heating value, pour point and flash point.

The absolute viscosity was measured using a falling sphere method where the oil was placed in a cylinder and a spherical object was allowed to fall freely in the oil and the time of fall was used to calculate the absolute viscosity.

The density of the oil was measured by placing it in a container with a known mass and weighed to calculate. The weight and the volume were then used to calculate the density of the oil.

The heating value was determined by placing a certain volume of the fuel in heating equipment and it was used to heat a certain quantity of water. The initial and final temperatures and the mass of the water heated and mass of fuel used were used to determine the heating rate.

The pour point of the oil was determined by keeping the oil in a freezer and then pouring it on a white flat tile to determine the temperature at which it lost its flow characteristics.

The oil was heated for sometimes using electric plate and was then exposed to a bare flame to determine the temperature at which the oil ignited (Flash point).

Apart from the above analysis, the compositions of the oil can also be analysed using gas chromatography/mass spectrometer (GC/MS). The elements identified are carbon, hydrogen, nitrogen and sulphur which are the components as reviewed in the literature [21].

III RESULTS AND DISCUSSION

Upon analysis of the tyre pyrolysis oil using the simple approaches described above, the following results were obtained as shown in Table 2.

Table 2: Properties of Tyre Pyrolysis Oil

Description	Value
Density at 30^{o}C (kg/m^3)	925
Viscosity at 30^{o}C (cp)	2.8
Gross Calorific Value (Mj/kg)	38.6
Pour Point (^{o}C)	-33
Flash Point (^{o}C)	43
Carbon (%)	84.6
Hydrogen (%)	10.3
Sulphur (%)	3.8
Nitrogen (%)	1.3

Properties of tyre pyrolysis oil and that of diesel fuel obtained from [17], [18] and [20]are compared to see the suitability of tyre pyrolysis oil replacement for a diesel fuel. The result is as shown in Table 3.

Table 3: Comparison of the Properties of TPO from this work to that from [18] and Diesel Fuel

Description	Diesel Fuel	TPO (from [18])	Tyre Pyrolysis Oil
Density at 30^{o}C (kg/m^3)	820-870	957	925
Viscosity at 30^{o}C (cp)	1.60-5.50	4.75	2.8
Gross Calorific Value (MJ/kg)	43-46	42	38.6
Pour Point (^{o}C)	-25-(-23)	-	-33
Flash Point (^{o}C)	40-65	32	43
Carbon (%)	85.31-86.98	85.86	84.6
Hydrogen (%)	13.15-14.32	9.15	10.3
Sulphur (%)	0.003-1.30	1.25	3.8
Nitrogen (%)	Trace	0.65	1.3

i Discussion of Results

At the end of the pyrolysis process, three products were obtained called the pyrolysis products. These include the tyre pyrolysis oil (TPO), the pyro-gas and the solid char. On weighing the TPO and the solid gas, the distribution of the product was found to be 55% TPO, 35% solid char and 10% pyro-gas. The tyre pyrolysis oil was dark brown oil, highly viscous with a sharp and irritating smell which may be due to the high percentage of sulphur as shown by the measurement.

Table 2 shows that there is high percentage of sulphur contained in the oil which is in agreement with[14]. This means there is a need to reduce the sulphur to an acceptable level if it is to be used in combustion engines. The density of TPO was found to be far above the density of diesel which shows that TPO cannot be used in internal combustion engine if not blended with diesel but the viscosity is within the limit as shown on the table. The gross calorific value of TPO is below the value specified for diesel fuel but can be improved when blended with diesel fuel of high calorific value. Therefore if TPO is to be blended with diesel, diesel of high calorific value should be used. The value is approximately same with that of fuel oil as reported by [18] which shows that TPO if considered in term of energy value can be used in furnaces and boilers as fuel. The elemental analysis shows that there are slight differences between the components in TPO and that in diesel owing to the fact that the two oils are from different sources but the composition shows that both of them can be used as fuel. The only important problem from the composition of TPO is the sulphur which can have significant effect on its use as a fuel since high sulphur in a fuel can lead to emission of high sulphur oxideleading to major environmental pollution.

The above discussion is based on the use of TPO as a fuel or as a substitute for diesel fuel meanwhile the result can be validated by comparing the TPO produced in this work with that produced by [18]. The result shows that most of the properties have similar values with little disparities which may be due to the differences in the production processes or in the equipment used. The major differences are in the viscosities and the flash points with that of [18] havingviscosity and flash point of 4.75 and 32^{o}C respectively compared to 2.8 and 43^{o}Cin this work for viscosity and flash point, respectively. This can be due to the source of the tyre shown in Table 1; it shows that the tyre.are from different sources with range of properties as reported by [17].

IV CONCLUSION

From the results obtained and the discussion made, the following conclusions were drawn;

Pyrolysis of used rubber tyre produces tyre pyrolysis oil (TPO) that can be used as liquid fuel in industrial furnaces and boilers due to their equivalent calorific values compared to fuel oil and also composition.

It was discovered that TPO cannot be used directly in internal combustion engine in its pure form due to its higher sulphur content, low calorific value and flash points compared to other conventional fuel used for the same purpose.

A blend of TPO and diesel can be considered in such a way that the calorific value is increased to the required value and the density reduced to the desired value suitable for use in internal combustion engine.

GC-MS analysis shows that TPO has major components such as carbon and hydrogen which makes it suitable for use as a fuel. Tyre pyrolysis to obtain useful products such as tyre pyrolysis oil can be applied to reduce the environmental effect caused by disposal of used tyre.

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