DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

(Signature of candidate)

---------- Day of----------2016

ABSTRACT

Thermal pyrolysis is one of the viable technologies suitable for the management of organic solid waste, which has become a global challenge over the years. This is due to the non-biodegradability of these materials and their continuous usage across all segments of man's daily activities. Effectiveness of the method is in converting these materials under controlled process conditions, that enable the optimization of the fraction of interest, such as the liquid fraction also referred to as pyrolytic oil with a near zero pollution effect on the environment.

The main setback in the production of the liquid fraction include low yield, presence of sulphur and other aromatic compounds which have been linked to environmental pollution and health complications. This study focuses on improving the liquid fraction yield and composition obtainable from pyrolysis process. Latex natural rubber (obtained from Hevea Brasiliensis) was pyrolysed and its products compared with that of the used tyres.

The production of pyrolytic oil from used tyres and natural rubber was performed using thermal and catalytic pyrolysis processes. The operating temperature range of 375 to 750 ^{o}C (at an interval of 75 ^{o}C) at a heating rate of 15^{o}C/min and feed material particle sizes of 2, 4, 6, 8 and 10 mm were used. In addition, Zeolite NaY was synthesized from Lawani Benin River Kaolin (LBK) at a synthesis time and temperature of 9 h and 100 ^{o}C respectively, using hydrothermal synthesis method, and used for catalytic pyrolysis.

The chemical characterisation revealed pyrolytic oil composition to be a complex mixture of aliphatic, aromatics, polycyclic aromatic hydrocarbons and other oxygen, nitrogen, sulphur and

chlorinated compounds in small proportions. The non-catalysed and catalysed pyrolysis using natural rubber resulted in pyrolytic oil with 80 and 66% of aliphatic, 12 and 15% aromatic (with polycyclic aromatic hydrocarbons concentration of 2 and 1%). The non-catalysed and catalysed pyrolysis using used tyres yielded pyrolytic oil with 42 and 32% of aliphatic, 34 and 39% aromatic (with polycyclic aromatic hydrocarbons concentrations of 18 and 23%).

The kinetics of the thermal degradation with the aid of a thermogravimetry and differential thermogravimetry analyzer was performed over a temperature range of 30 to 800 ^{o}C at a heating rate of 15, 20 and 30^{o}C/min. Results showed that natural rubber displayed higher activation energy than used tyres, with respect to the heating rates. This is an indication that natural rubber is more difficult to thermally decompose than used tyres.

The distillation temperature of the distillates was within the temperature range of the conventional petrol and diesel. The composition of the distillates revealed carbon chain length of C_5-C_{30} with majority being $C_8 - C_{10.}$ A spark ignition generator engine was used to perform the combustion tests for the various pyrolytic oil distillates and petrol blended in the ratio 0, 5, 10, 15 and 20% successfully without engine modification. For the fuel consumption with respect to generator run time, it was observed that an optimum of 20% natural rubber pyrolytic oil distillates (NRPD)-Petrol blend gave comparative fuel consumption behavior with that of commercial petrol. Furthermore, the 20% NRPD distillates gave optimum fuel consumption and power. Hence, a significant yield improvement and combustion performance were observed for the pyrolytic oil derived from natural rubber than that of used tyres. Further treatment of the

pyrolytic oil distillates could pave the way for effective use of the oil as chemical feedstock for industries, or as substitutes for fossil fuel.

It was also requisite to develop a mathematical model which adopts thermogravimetry analyser (TGA) as a dynamic apparatus to predict weight change of a material as it degrades with time at a fixed temperature. The proposed models were in three consecutive phases which were classified into three time zones $0 \leq t \leq t_1$, $t_1 \leq t \leq t_2$ and $t \leq t_2$.

The general model equation for the first phase of degradation was $w(t) = w_0 e^{-\sigma_1 \frac{t^2 T_0}{2}}$, while the second phase model was $w(t) = \frac{\beta_1 w_0 k}{\beta_1 w_0 + (k - \beta_1 w_0) e^{-\sigma_2 T_0 (t - t_1)}}$ and at the third phase, it is assumed that the limit of weight loss (in the second phase equation) as t tends to ∞ gives a value k, at which change in weight loss with time is negligible. The proposed model was used to plot graph of weight loss versus time at different fixed temperature which fitted well with the experimental TGA and had a characteristic pattern fitted closely to the second phase degradation of the fixed bed reactor.

DEDICATION

My lovely wife, Nore Constance Osayi, my children, Osanor, Emwonsa and Enioghogho for their inestimable support and being my source of strength

My parents, Mr and Mrs Richard Ilawe Osayi, for their confidence in me and encouragement throughout my years of study

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LIST OF REFEREED PUBLICATIONS

Julius I. Osayi, Sunny Iyuke, and Samuel E. Ogbeide. Biopyrolytic oil Production through Pyrolysis of Used Tyres -Review Article. *Journal of Catalysts*, Volume 2014, Article ID 386371, 9 pages

Julius I. Osayi, Sunny Iyuke, Diakanua N. Bavon, Jaco Van Der Walt and Samuel E. Ogbeide. Liquid Fuels Production from Natural Rubber. *Journal of oilflow assurance and chemistry* Submitted. 2015

Julius I Osayi, S Iyuke, and S.E. Ogbeide, "Pyrolysis of used tyres for valuable products -A review", *Journal of Natural sciences,* ID JNS-1035, Accepted. 2015

PRESENTATIONS AT CONFERENCES AND SEMINARS

Date	Name	Venue	Type
July 27th - August 1st 2014	International Conference of Chemical Thermodynamics(ICCT) and South African Institute of Chemical Engineers (SAIChE)	Durban International Conference centre, Durban, South Africa	Oral
September 11th – 14th 2014	IAFOR The north American Conference on Sustainability, Energy & the Environment	The Providence Marriott Downtown, Providence, RI, USA	Oral
October 27th-28th 2014	6th Cross Faculty Post Graduate Symposium	University of the Witwatersrand, Johannesburg	N/A
June 22nd -24th 2015	Oilflow Conference	Institute of Petroleum studies, University of Port Harcourt, Nigeria	Oral

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Nomenclature

Description	Symbol
Calorific Value	CV
Degree centigrade	^{o}C
Differential thermogravimetric	DTG
Diesel fuel	DF
Distillated tyre pyrolytic oil	DTPO
Elongation or compression (offset) of the object	*dL*
Energy dispersive X-ray analysis	EDAX
Ethene	C_2H_4
Ethyne	C_2H_2
Fixed carbon	FC
Force	F
Fourier transform infrared spectroscopy	FTIR
Heat	ΔH
Higher heating value	HHV
Internal combustion engine	ICT
Lawani Benin River Nigeria Kaolin	LBK
Mega Joule	MJ
Micrometer	µm
Millimetre	mm

Mole	mol
Natural rubber pyrolytic oil distillate	NRPD
Natural rubber zeolite pyrolytic oil distillate	NZPD
Natural rubber Zeolite	NRZ
Natural rubber	NR
Nitrogen oxides	NO_x
not reported	n.r
Nuclear magnetic resonance	NMR
Percent	%
Polybutadiene rubber	BR
Polycyclic aromatic hydrocarbons	PAH
Polystyrene-butadiene rubber	SBR
Scanning electron microscope	SEM
Sodium hydroxide	NaOH
Sodium carbonate	Na_2CO_3
Synthetic rubbers	SR
Thermogravimetric analysis	TGA
Transmission electron microscope	TEM
Tyre pyrolytic oil	TPO
Used tyres	UT
Used tyres pyrolytic oil distillate	UTPD

Used tyres zeolite pyrolytic oil distillate	UZPD
Used tyres Zeolite	UTZ
Volatile material	VM
Volatile organic Compounds	VoCs
Waste tyre	WT
Weight	wt.
X-ray fluorescence	XRF
X-ray diffraction	XRD
Young's modulus of elasticity	*E*