

https://dspace.org/

A comparative study between pyrolytic oil obtained from used tyres and natural rubber

Osayi, Julius Ilawe

2016

http://hdl.handle.net/10539/22447

Osayi, Julius Ilawe (2016) Comparative study between pyrolytic oil obtained from used tyres and natural rubber, University of the Witwatersrand, Johannesburg, <http://hdl.handle.net/10539/22447>

Downloaded from a DSpace repository. https://dspace.org/

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

ACKNOWLEDGMENTS

Firstly, I would like to appreciate God Almighty who gave me the strength, knowledge and ability to do this research.

My appreciation goes to Professor Sunny E. Iyuke for his supervision, motivation and valuable support during the course of this research.

Professor Samuel E. Ogbeide my co-supervisor from the department of Chemical Engineering, University of Benin, Benin City, Edo State, Nigeria for his expertise and contribution to this study.

Dr Jaco Van Der Walt my co-supervisor from the South Africa Nuclear Energy Corporation (NECSA) is highly appreciated for the valuable comments and technical guidance he brought to this work.

Special thanks go to Dr Diakanua Bavon Nkazi my co-supervisor for his positive attitude, encouragement and willingness to offer technical assistance during this research.

Every member of the Nanotechnology and Petroleum Research Group of the University of the Witwatersrand is also acknowledged for their in-depth and knowledgeable contributions via our weekly research meetings.

I would also like to express my gratitude to the staff and students from the School of Chemical and Metallurgical Engineering, past and present, for the creation of an enjoyable and stimulating working environment. Special thank you regarding this goes to;

Mr. Bruce Mothibeli, Mr. Doctor Mbense and Mr. Xolani Mdletshe are also acknowledged for their laboratory assistance which contributed to the success of the laboratory experiments.

Rev (Mrs) Gina U. Oyakhilome and every member of All Souls for Christ Mission Int. Inc, Benin City, Edo State, Nigeria is also appreciated for their prayers which contributed to the success of this work. This is one of the fruit of your spiritual support.

My parents, Mr and Mrs Richard Ilawe Osayi (JP) are highly appreciated for their financial support and encouragement all through my academic pursuit, may you live long to eat the fruits of your labour.

The support of my wonderful wife, Nore Constance Osayi and my lovely children, Osanor, Emwonsa and Enioghogho contributed in no small measure to the completion of this work. Their prayer, patience and sacrifice strengthened me to weather the storm. Indeed you guys are my sure companions.

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

Table of Contents

Page

DECLARATION…..i

ABSTRACT…….ii

DEDICATION.....v

ACKNOWLEDGMENTS…….vi

LIST OF REFEREED PUBLICATIONS…….viii

PRESENTATIONS AT CONFERENCES AND SEMINARS …….ix

CONTENTS.....x

LIST OF FIGURES.....xvii

LIST OF TABLES.....xxii

NOMENCLATURE……xxiv

CHAPTER 1: INTRODUCTION…….1

1.1Research Background and Motivation…..…….1

1.2 Hypothesis….4

1.3 Justification of Study……..…….4

1.4 Research Aims and Objectives……..…….5

1.5 Thesis Outline……...…….6

References.....8

CHAPTER 2: LITERATURE REVIEW…….15

2.1 Origin and General Concept of Natural Rubber…….15

2.1.1 Properties of rubber…….18

2.1.1.1 Elastomeric property…….18

2.1.1.2 Thermal property…….....19

2.1.1.3 The oxidation property…….....19

2.1.1.4 The elasticity property …….....20

2.1.2 Synthetic rubbers and natural rubber…….....21

2.1.3 Vulcanisation of rubber…….....22

2.1.4 Application of natural rubber…….....23

2.1.5 Natural rubber as liquid fuel…….....24

2.2 Used Tyres……..…….....24

2.2.1 Tyre production process and composition of used tyres…….....24

2.2.2 Proximate and ultimate analysis of used tyres…….....26

2.2.3 Thermogravimetric analysis of used tyres…….....28

2.3 Disposal Challenges of Used Tyres…….…….....29

2.3.1 Methods of recycling of used tyres…….....30

2.3.1.1 Retreading method…….....30

2.3.1.2 Mechanical or cryogenic method…….....31

2.3.1.3. Reclaiming rubber raw materials methods…….....31

2.4. Pyrolysis of Used Tyres ….....34

2.4.1 Pyrolysis description …….....34

2.4.2 Types of pyrolysis …….....35

2.4.2.1 Slow Pyrolysis …….....35

2.4.2.2. Fast Pyrolysis …….....36

2.4.2.3. Flash Pyrolysis …….....36

2.4.2.4. Catalytic Pyrolysis …….....36

2.4.3. Chemical Reaction of the Catalytic Pyrolysis…….....38

2.4.4 Mechanism of used tyre pyrolysis …….....39

2.4.5 Products obtained from used tyres pyrolysis and their compositions …….....43

2.4.5.1 Pyrolysis solid fraction ……43

2.4.5.2 Liquid fraction from pyrolysis ……...45

2.4.5.3 Pyrolysis gas fraction …….....46

2.4.6 Influence of pyrolysis process parameters on yield and properties of products….....47

2.4.7 Benefits and limitations of the pyrolysis process …….....53

2.5 Zeolite structures, Synthesis, Properties and Its Uses ……..…….....54

2.5.1 General overview of zeolites …….....54

2.5.2 Structures of Zeolites …….....55

2.5.3 Types of zeolites …….....57

2.5.3.1 Natural zeolites …….....58

2.5.3.2 Synthetic/Artificial zeolites …….....58

2.5.3.3 Properties and uses of zeolites ….....60

2.5.4 Zeolite synthesis techniques …….....61

2.5.4.1 Hydrothermal technique ……...61

2.6 Pyrolysed Tyre Oil as Fuel in Internal Combustion Engine …….....63

References.....68

CHAPTER 3: METHODOLOGY AND EXPERIMENTAL PROCEDURE.....84

3.1 Materials and Methods 84

3.2 Zeolite NaY Synthesis and Characterisation.....85

3.3 Physical Characterisation of the Raw Used Tyre and Natural Rubber Samples.....88

3.3.1 Thermogravimetric (TGA/DTG) analysis 89

3.3.2 Catalytic pyrolysis setup 90

3.3.3 Experimental procedure for pyrolytic oil production from used tyres and natural rubber.....92

3.4 Characterisation of Used Tyres and Natural Rubber Pyrolysis Products 94

3.4.1 Chemical characterisation of used tyres and natural rubber pyrolytic oil 94

3.4.1.1 Fourier transform infrared spectroscopy (FTIR) 94

3.4.1.2 GC-MS analysis 94

3.4.1.3 NMR analysis 95

3.4.2 Physical characterisation of used tyres and natural rubber pyrolytic oil 95

3.5 Characterisation of Used Tyres and Natural Rubber Pyrolytic Solid Residue.....96

3.5.1 Proximate and ultimate analysis of the used tyres and natural rubber pyrolytic solid residue

.....96

3.5.2 SEM analysis 97

3.6 Distillation of Used Tyres and Natural Rubber Pyrolytic Oil 97

3.6.1 Distillation set up 97

3.6.2 Distillation experimental procedure 100

3.7 Fuel blend Technique for Pyrolytic Oil Distillates and Petrol ……100

3.8 Combustion of Pyrolytic Oil Distillates and Petrol Blend in Internal Combustion Engine…..101

3.8.1 Experimental set up for fuel blend study …….....101

3.8.2 Experimental procedure for fuel blend test in the internal combustion engine…….....102

References.....104

CHAPTER 4: RESULTS AND DISCUSSION ……...…….……105

4.1 Zeolite NaY Synthesis and Characterisation.....105

4.1.1 XRF characterisation of calcined LBK ……105

4.1.2 SEM and XRD characterisation of refined and calcined LBK …….107

4.1.3 SEM and XRD characterisation of synthesised Zeolite NaY from LBK Metakaolin.....109

4.1.4 Summary of zeolite NaY synthesised from LBK Metakaolin …….....115

4.2 Proximate and Ultimate Analysis and GCV of Used Tyres and Natural Rubber …….....115

4.3 Degradation of Used Tyres and Natural Rubber …….....117

4.4 Thermal Pyrolysis of Used Tyres and Natural Rubber …….....120

4.4.1 Determination of feed material optimum particle sizes on thermal pyrolysis of used tyres……120

4.4.2 Temperature effect on the product yield of used tyres thermal pyrolysis.....123

4.4.3 Temperature effect on the product yield of natural rubber thermal pyrolysis.....127

4.4.4 Catalyst concentration effect on the pyrolysis of used tyres and natural rubber…….....130

4.4.5 Zeolite NaY particle sizes effect on biogasoline yield from produced pyrolytic oil.....136

4.5 Characterisation of Produced Pyrolytic Oil ……...……...138

4.5.1 Physical properties of produced pyrolytic oil …….....139

4.5.2 Chemical properties of produced pyrolytic oil …….....143

4.5.2.1 FT-IR analysis of UT and NR pyrolytic oil…….....144

4.5.2.2 NMR analysis of UT and NR pyrolytic oil …….....149

4.5.2.3 GC-MS analysis of UT and NR pyrolytic oil …….....157

4.6 Batch Distillation of UT and NR Pyrolytic Oil …….....166

4.7 Characterisation of UT and NR Solid Residue ……..…….....173

4.7.1 Proximate and ultimate analysis of UT and NR solid residue.....173

4.7.2 SEM. analysis of UT and NR solid residue …….....174

4.8 Kinetic Study of Thermal Degradation …….....177

4.8.1 Kinetics of thermal degradation.....177

4.8.2 Mechanism and determination of kinetic parameters …….....178

4.9 Testing of Pyrolytic Oil Distillates and Petrol Blends …….....189

4.9.1 Fuel consumption over time as a function of fuel blend composition …….....189

4.9.2 Fuel power as a function of PD composition in the fuel blend …….....196

4.10 Mathematical Modeling and Simulation of Pyrolysis of the Rubber…….....200

References.....216

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS…….....224

5.1 Conclusion …….....224

5.2 Recommendations.…….....228

APPENDIX A…….....229

APPENDIX B.....233

APPENDIX C.....238

APPENDIX D.....244

APPENDIX E.....270

LIST OF FIGURES

Page

1.1 Work flowchart of objectives/activities of the study …….....6

2.1 World top 10 countries in natural rubber production (in tons) as at 2013…….....16

2.2(a) Natural rubber tree latex being tapped …….....17

2.2(b) Collection of natural rubber latex after tapping……...…….....17

2.3 Cis-polyisoprene structure (the key component of natural rubber)…….....18

2.4 A typical Ozonolysis reaction equation…….....20

2.5 Production process of Natural rubber…….....21

2.6 Production process of Synthetic rubbers…….....22

2.7 Vulcanization of Natural rubber…….....23

2.8 Tyre rubber monomers…….....26

2.9 Flowchart of organic material catalytic pyrolysis ……..38

2.10 Limonene formation from dimeric species through pyrolytic Isomerization…….....40

2.11 Examples of heterocyclic hydrocarbons formed from gas phase reaction in UT pyrolysis…..41

2.12 Diels–Alder reaction pathway for PAH formation in used tyre pyrolysis…….....41

2.13 Reaction scheme of PAH formation from thermal degradation of Limonene…….....42

2.14 Scheme of pyrolysis according to weight percent and products fraction……..47

2.15 The primary building unit TO4 of Zeolites…….....56

2.16 Secondary Building Units (SBUs) that describe known Zeolite framework…….....57

2.17 Structure of Zeolite A…….....59

2.18 (a): Zeolite ZSM-5 structure (b): Zeolite structure type FAU…….....60

2.19 Pictorial scheme of hydrothermal synthesis……..62

2.20 Reaction schemes for gel formation and zeolite crystallization……..……..63

3.1Process description of the refinement of raw LBK to particle size reduction before calcination…….....86

3.2 Autoclave used for Zeolite NaY synthesis in this study…….88

3.3 Experimental setup for pyrolytic oil production from used tyres and natural rubber.....90

3.4 (a) Schematic set-up for the UT and NR pyrolytic oil batch distillation…….....98

3.4 (b) Pictorial scheme of batch distillation of pyrolytic oil from used tyres and natural rubber set up……..…….99

3.5 Setup for blending of pyrolytic oil distillates and petrol.....100

3.6 (a) A Sinemaster IG2600 BUNDU POWER (AC Generator) (b) Bench Grinder powered during the combustion study.....101

4.1 SEM image of LBK Metakaolin used in this study. Scale bar = 2µm.....107

4.2(a) XRD pattern of the LBK Metakaolin used in this study for zeolite NaY synthesis.....107

4.2(b) XRD pattern of reference commercial zeolite NaY showing its composition.....108

4.3SEM image of zeolite NaY from LBK Metakaolin (Effect of Ageing time A= 0, B= 0.5, C=1, D=3, E=6, F=9, G=12, H=24 h) and I is commercial zeolite NaY.....110

4.4 Effect of ageing on zeolite NaY particle size.....111

4.5 SEM image of 0 h aging at room temperature of 25 ^{o}C…….....112

4.6 TEM image of synthesised zeolite NaY with particles nanoscale sizes.....113

4.7 XRD pattern for the synthesised Zeolite NaY from LBK produced at different ageing time at constant crystallisation time and temperature.....114

4.8 TGA/DTG curve of UT at 15^{o}C/min heating rate…..117

4.9 TGA/DTG curve of NR at 15^{o}C/min heating rate.....117

4.10 (a) Particle size effect on UT pyrolysis yield (b) Experimental and theoretical plot of size effect on UT pyrolytic oil production.....121

4.11 (a) Effect of Temperature on UT pyrolysis product yield. (b) Experimental and theoretical plot of temperature effect on UT pyrolytic oil production.....124

4.12 (a) Effect of Temperature on NR pyrolysis products yield (b) Experimental and theoretical plot of temperature effect on NR pyrolytic oil production…….…….....128

4.13 (a) Catalyst concentration effect on UT pyrolysis at 600 ^{o}C (b) Experimental and theoretical plot of catalyst effect on UT pyrolytic oil production.....132

4.14 (a) Catalyst concentration effect on natural rubber pyrolysis at 600 ^{o}C and (b) Experimental and theoretical plot of catalyst effect on NR pyrolytic oil production.....133

4.15 Effect of zeolite NaY catalysts particle sizes on Pyrolytic oil composition.....136

4.16 Pyrolytic oil from (a) Used tyres and (b) Natural rubber.....139

4.17 FTIR transmittance spectrum for used tyres Pyrolytic oil….....146

4.18 FTIR transmittance spectrum for catalysed used tyres pyrolytic oil.....146

4.19 FTIR transmittance spectrum for natural rubber pyrolytic oil …….....147

4.20 FTIR transmittance spectrum for catalysed natural rubber pyrolytic oil.....147

4.21 (a-b) ^{1}H (a) and ^{13}C (b) NMR spectra of NR pyrolytic oil……..…….....151

4.22 (a-b) ^{1}H (a) and ^{13}C (b) NMR spectra of NRZ pyrolytic oil ……..…….....152

4.23 (a-b) ^{1}H (a) and ^{13}C (b) NMR spectra of UT pyrolytic oil……..153

4.24 (a-b) ^{1}H (a) and ^{13}C (b) NMR spectra of UTZ pyrolytic oil…….……..154

4.25 GC-MS total compound chromatogram for NR pyrolytic oil obtained at 600 ^{o}C ……..158

4.26 GC-MS total compound chromatogram for NRZ pyrolytic oil obtained at 600 ^{o}C.....158

4.27 GC-MS total compound chromatogram for UT pyrolytic oil obtained at 600 ^{o}C ….....161

4.28 GC-MS total compound chromatogram for UTZ pyrolytic oil obtained at 600 ^{o}C.....161

4.29 Different distillates obtained from distillation of NR and UT pyrolytic oil…….…....168

4.30 Hydrocarbon group present in distillates obtained from the various pyrolytic oil….....169

4.31 GC-MS total compound chromatogram for NR pyrolytic oil distillates…….....170

4.32 GC-MS total compound chromatogram for NRZ pyrolytic oil distillates…… …170

4.33 GC-MS total compound chromatogram for UT pyrolytic oil distillates …….....171

4.34 GC-MS total compound chromatogram for UTZ pyrolytic oil distillates …….....171

4.35 (a) SEM image of UT solid residue at 150X…….....175

4.35 (b) SEM image of Catalysed UT solid residue at 150X…….....176

4.35 (c) SEM image of NR solid residue at 150X……...……...176

4.35 (d) SEM image of NRZ solid residue at 150X …….....177

4.36 Kinetic plots of different phases of NR at 15^{o}C/min heating rate…….....180

4.37 Kinetic plots of different phases of NR at 20^{o}C/min heating rate…….…….....181

4.38 Kinetic plots of different phases of NR at 30^{o}C/min heating rate…….……...…….....181

4.39 Kinetic plots of different phases of UT at 15^{o}C/min heating rate……...……...182

4.40 Kinetic plots of different phases of UT at 20^{o}C/min heating rate……...……...182

4.41Kinetic plots of different phases of UT at 30^{o}C/min heating rate…...…….....183

4.42 Effect of heating rate on Temperature degradation of UT……..187

4.43 Effect of heating rates on temperature degradation of NR.....188

4.44 Fuel consumption rate as a function of NRPD-Petrol fuel composition…….....191

4.45 Contour plot of consumption time vs. 20 % NRPD-Petrol, Commercial Petrol (ml)…….....191

4.46 Fuel consumption rate as a function of NZPD-Petrol fuel composition…….....192

4.47 Contour Plot of Consumption time vs. 10 % NZPD-Petrol, Commercial Petrol (ml)…….....192

4.48 Fuel consumption rate as a function of UTPD-Petrol fuel composition…….....193

4.49 Contour Plot of Consumption time vs. 15 % UTPD-Petrol, Commercial Petrol (ml).....194

4.50 Fuel consumption rate as a function of UZPD-Petrol fuel composition…….…….... ..195

4.51 Fuel consumption rate for observed optimum PD-Petrol blend fuel…….....195

4.52 Curve showing the fuel power as a function of NRPD concentration in the fuel blend…….196

4.53 Curve showing the fuel power as a function of NZPD concentration in the fuel blend.....197

4.54 Curve showing the fuel power as a function of UTPD concentration in the fuel blend…….197

4.55 Curve showing the fuel power as a function of UZPD concentration in the fuel blend……..198

4.56 TGA curve of UT weight loss versus temperature at 15^{o}C/min heating rate (where (A) is experimental data of this work, while (B) is data from literature……..…….201

4.57 Three phase thermal degradation of weight change with time mathematical derivation..... 202

4.58 First, second and third phase weight loss versus time at different fixed temperature…….210

4.59 First, second and third phase weight loss versus time at different fixed temperature with the experimental TGA……...212

4.60 UT Weight against temperature for the model fixed operating time and the experimental in a fixed bed reactor……..214

List of Tables

Page

2.1 Composition of a tyre …….....25

2.2 Proximate analysis of used tyre rubber…….…….....27

2.3 Used tyre rubber ultimate analysis …..…….....28

2.4 Commencement and end temperatures of pyrolysis of used tyre…….....28

2.5 Tyre pyrolysis processes used within the past three decades…….....33

2.6 Elemental and proximate analysis of used tyre pyrolysis solid residue reported in literature…….....44

2.7 Elemental and calorific value of liquid fraction reported in literature…….....46

2.8 Composition and calorific value of pyrogas reported in literature……..46

2.9 Reactors and their heating methods…….....49

2.10 TPO and diesel blend fuel properties…….....64

3.1Standard methods for physical property analysis…….....96

3.2 Specification and characteristics of the internal combustion engine……...……..102

4.1 XRF chemical constituent present in LBK Metakaolin……106

4.2 Proximate and ultimate analysis of natural rubber and used tyres…….....116

4.3 Fuel properties of natural rubber pyrolytic oil in comparison to used tyre pyrolytic oil and commercial diesel…….....143

4.4 The FTIR functional groups and the indicated compounds of this study pyrolytic oil with other pyrolysis liquids……...…….....148

4.5 ^{1}H and ^{13}C NMR results for NR and NRZ pyrolytic oil obtained at 600 ^{o}C…….....155

4.6 ^{1}H and ^{13}C NMR results for UT and UTZ pyrolytic oil obtained 600^{o}C.....156

4.7(a) Some of the compounds identified by GC-MS characterisation of NR pyrolytic oil.....159

4.7(b) Some of the compounds identified by GC-MS characterisation of NRZ pyrolytic oil.....160

4.8(a) Some of the compounds identified by GC-MS characterisation of UT pyrolytic oil.....162

4.8(b) Some of the compounds identified by GC-MS characterisation of UTZ pyrolytic oil.....163

4.9 Temperature range and distillate volume% obtained for the batch distillation of the different pyrolytic oil produced…….....172

4.10 HHV, proximate and ultimate analysis of UT and NR…….....174

4.11 Trend line equations and Regression coefficients for UT and NR……..184

4.12 Activation energy and pre-exponential factor of used tyres sample.....185

4.13 Activation energy and Pre-exponential factor of natural rubber sample…….……185

4.14 Average Activation energy and Pre-exponential factor for UT and NR…….186

4.15 First and second phase total degradation time for model different fixed temperature……211

4.16 Standard deviation of models from experimental data at different operating time…….....215

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*