

BIOETHANOL PRODUCTION FROM SAGO PALM WASTE AS AN  
ALTERNATIVE FUEL FOR AUTOMOTIVE ENGINES

SARAVANA KANNAN THANGAVELU

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Doctor of Philosophy (Mechanical Engineering)

Faculty of Mechanical Engineering  
Universiti Teknologi Malaysia

JANUARY 2016

I dedicate this thesis to my beloved parents, brother, sister and parent-in-laws.  
Last but not least, to my beloved daughter and wife.

## ACKNOWLEDGEMENT

First of all, I would like to express my sincere appreciation and gratitude for my supervisor Prof. Dr. Farid Nasir Ani, Professor, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, for his guidance, encouragement, and valuable comments throughout the research work. He has provided great insights, feedback and motivation, in every step of the way, which has enabled me to learn and grow professionally.

I also would like to express my sincere gratitude towards my additional supervisor Assoc. Prof. Dr. Abu Saleh Ahmed, Associate Professor, Faculty of Engineering, Universiti Malaysia Sarawak, for his guidance, motivation and experimental support.

In addition to my supervisors, I would like to express my sincere appreciations to my brother Asst. Prof. Mr. T. Rajkumar, Assistant Professor, Department of Pharma-Chemistry, CES College of Pharmacy, India, for his help in analytical methods and experiments during the course of this research.

From my heart, I would like to thank my wife Mrs. Piraiarasi Chelladorai, Lecturer, Faculty of Engineering, Computing and Science, Swinburne University of Technology Sarawak, for her patience, encouragement and language proof reading supports. There have been many peaks and troughs along the way during my PhD study. She has been a pillar holding me up through all of the trails. I genuinely thank her for the role she has played in making this endeavor a success. I am also most grateful to my beloved parents and my sweet daughter Keerthana, for they were breath of fresh air during the moments of trails and tribulations.

I would like to extend my gratitude towards all my colleagues and student friends of Swinburne University of Technology, who were part of a knowledge community, and were directly or indirectly, helped me in my research work.

Finally, I would like to acknowledge the institutions, Swinburne University of Technology Sarawak, Malaysia; Universiti Malaysia Sarawak, Malaysia; Pondicherry Engineering College, India; Indian Institute of Petroleum, India; and STARTECH Labs Pvt. Ltd, India, for their continued support in experimental works. Research Management Centre, Universiti Teknologi Malaysia; Government of Sarawak, Malaysia; and Sarawak Biodiversity Centre, Malaysia is also kindly acknowledged.

## ABSTRACT

The increasing demands of petroleum fuels, together with the environmental pollution issues, have motivated the efforts on discovering new alternative fuels. Bioethanol produced from biomass is considered as one of the important alternatives for petroleum fuels. In Sarawak, wastes from sago factories are currently causing serious environment problems. These wastes can be used as favourable feedstock for bioethanol production. The purpose of this research is to produce bioethanol from sago palm waste, and study the effects of bioethanol on corrosion of materials, and performance and emissions of petrol engine. First, bioethanol was produced from sago pith waste (SPW) using microwave hydrothermal hydrolysis accelerated by CO<sub>2</sub> (MHH) and microwave assisted acid hydrolysis (MAH). Bioethanol was also produced from sago bark waste (SBW) using microwave aided acid treatment and enzymatic hydrolysis (MAEH). Second, effect of bioethanol and gasoline blends on corrosion of materials was studied using static immersion test. Furthermore, corrosion of materials in biodiesel–diesel–ethanol (BDE) fuel blends was also studied. Finally, the effect of bioethanol on performance and emissions of petrol engine was studied. A maximum of 15.6 g and 30.8 g ethanol per 100 g dry SPW was produced using MHH and MAH, respectively. In addition, a maximum of 30.67 g ethanol was produced from 100 g dry SBW using MAEH. Corrosion of materials and degradation of fuel properties were 2.4 times higher in higher ethanol blends (above E25) compared to lower ethanol blends (up to E25). Corrosion and degradation of materials in BDE fuel blends was 1.7 times higher than petro-diesel. Petrol engine results showed that use of sago waste bioethanol (E25) significantly increased the engine power, torque, brake thermal efficiency, and mean effective pressure by about 4.5%, 4.3%, 9% and 4.2% compared to gasoline (E0), respectively. Emissions results showed a significant reduction in CO, NO<sub>x</sub> and HC emissions by about 42%, 7% and 5.2%, respectively for E25 compared to E0. This study acclaims that sago bioethanol is a feasible alternative to reduce the dependence on fossil fuels for the automotive industry.

## ABSTRAK

Permintaan yang semakin meningkat untuk bahan api petroleum, bersama-sama dengan isu-isu pencemaran alam sekitar, telah mendorong usaha mencari bahan api alternatif baru. Bioetanol yang dihasilkan daripada biojisim dianggap sebagai salah satu alternatif penting untuk bahan api petroleum. Di Sarawak, sisa daripada kilang-kilang sagu kini mengakibatkan masalah alam sekitar yang serius. Bahan buangan ini boleh digunakan sebagai bahan mentah yang baik untuk pengeluaran bioetanol. Tujuan kajian ini adalah untuk menghasilkan bioetanol daripada sisa pokok sagu, dan mengkaji kesan bioetanol kepada kakisan bahan-bahan, dan prestasi dan pelepasan enjin petrol. Pertama, bioetanol dihasilkan daripada sisa empulur sagu (SPW) menggunakan ketuhar gelombang mikro hidroterma hidrolisis dipercepatkan oleh CO<sub>2</sub> (MHH) dan ketuhar gelombang mikro dibantu asid hidrolisis (MAH). Bioetanol juga dihasilkan daripada sagu sisa kulit (SBW) menggunakan ketuhar gelombang mikro dibantu rawatan asid dan hidrolisis enzim (MAEH). Kedua, kesan bioetanol dan petrol campuran ke atas kakisan bahan dikaji menggunakan ujian rendaman statik. Tambahan lagi, kakisan bahan-bahan dalam biodiesel-diesel-etanol (BDE) campuran bahan api juga telah dikaji. Akhir sekali, kesan bioetanol ke atas prestasi dan pelepasan enjin petrol telah dikaji. Setiap 100 g SPW kering menghasilkan sebanyak 15.6 g dan 30.8 g maksimum etanol menggunakan MHH dan MAH masing-masing. Di samping itu, 100 g SBW kering menghasilkan 30.67 g maksimum etanol menggunakan MAEH. Kakisan bahan dan degradasi bahan api adalah 2.4 kali tinggi dalam campuran etanol tinggi (melebihi E25) berbandingkan kepada campuran etanol rendah (sehingga E25). Kakisan dan degradasi bahan-bahan dalam campuran bahan api BDE adalah 1.7 kali lebih tinggi daripada petro-diesel. Keputusan enjin Petrol menunjukkan bahawa penggunaan bioetanol hampas sagu (E25) memberi peningkatan ketara untuk kuasa enjin, dayakilas, kecekapan brek haba dan tekanan berkesan min, masing-masing sebanyak kira-kira 4.5%, 4.3%, 9% dan 4.2% berbanding petrol (E0). Keputusan emisi menunjukkan pengurangan ketara dalam emisi CO, NO<sub>x</sub> dan HC dalam kira-kira 42%, 7% dan 5.2% masing-masing untuk E25 berbanding dengan E0. Kajian ini menunjukkan bahan api bioetanol sagu adalah alternatif yang boleh dilaksanakan untuk mengurangkan pergantungan kepada bahan api fosil bagi industri automotif.

## TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	<b>DECLARATION</b>	ii
	<b>DEDICATION</b>	iii
	<b>ACKNOWLEDGEMENT</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	xiii
	<b>LIST OF FIGURES</b>	xv
	<b>LIST OF ABBREVIATIONS</b>	xxi
	<b>LIST OF SYMBOLS</b>	xxiv
	<b>LIST OF APPENDICES</b>	xxv
<b>1</b>	<b>INTRODUCTION</b>	1
	1.1 Research Background	1
	1.2 Bioethanol as Alternative Fuel	4
	1.3 Research Problem Statement	7
	1.4 Hypothesis of Research Study	9
	1.5 Objectives	11
	1.6 Scope of the Research Study	12
	1.7 Significance of the Research	13
	1.8 Structure of the Thesis	14
<b>2</b>	<b>LITERATURE REVIEW</b>	16
	2.1 Introduction	16

2.2	Biomass and Bioethanol Production Technologies	16
2.2.1	Starchy Lignocellulosic Biomass	17
2.2.2	Sago Palm Waste	19
2.2.3	Pretreatments	20
2.2.3.1	Physical and Biological	21
2.2.3.2	Physico-chemical	22
2.2.3.3	Chemical	23
2.2.4	Hydrolysis	25
2.2.4.1	Enzymatic Hydrolysis	25
2.2.4.2	Acid Hydrolysis	27
2.2.4.3	Hydrothermal Hydrolysis	28
2.2.5	Fermentation	29
2.3	Bioethanol Production from SLC Biomass	32
2.3.1	Bioethanol Production from Sago Waste	39
2.4	Compatibility of Materials in Ethanol and Gasoline	42
2.5	Compatibility of Materials in Biodiesel and Diesel	47
2.6	Ethanol on Performance of SI Engines	58
2.6.1	Engine Torque	58
2.6.2	Brake Power	60
2.6.3	Brake Thermal Efficiency	62
2.6.4	Volumetric Efficiency	63
2.6.5	Brake Specific Fuel Consumption	64
2.6.6	Brake Mean Effective Pressure	66
2.7	Ethanol on Emissions from SI Engines	67
2.7.1	Carbon Monoxide	67
2.7.2	Carbon Dioxide	70
2.7.3	Oxides of Nitrogen	71
2.7.4	Unburned Hydrocarbon	72
2.8	Summary	73

<b>3</b>	<b>MATERIALS AND METHODOLOGY</b>	<b>74</b>
3.1	Bioethanol Production from SPW using Microwave Hydrothermal Hydrolysis	74
3.1.1	Biomass Preparation and Chemicals	74
3.1.2	Biomass Composition Analysis	76
3.1.3	Microwave Hydrothermal Hydrolysis	77
3.1.4	Fermentation and Distillation	78
3.1.5	Glucose, by-products and Ethanol Analysis	79
3.1.6	FTIR Spectroscopy Analysis	80
3.1.7	Gas Chromatography (GC) Analysis	80
3.1.8	Fermentation Kinetic Parameter Calculation	82
3.1.9	Energy Consumption	82
3.2	Bioethanol Production from SPW using Microwave Acid Hydrolysis	83
3.2.1	Biomass and Chemicals	84
3.2.2	Biomass Composition Analysis	84
3.2.3	Microwave Acid Hydrolysis	84
3.2.4	Ethanol Fermentation	86
3.2.5	Distillation and Dehydration	87
3.2.6	Analytical Methods	87
3.2.7	Glucose and Ethanol Yield	88
3.2.8	Energy Consumption Calculation	88
3.3	Bioethanol Production from SBW using Microwave Enzymatic Hydrolysis	90
3.3.1	Biomass and Chemicals	91
3.3.2	Biomass Composition Analysis	91
3.3.3	Microwave Pretreatment	92
3.3.4	Enzymatic Hydrolysis, Fermentation and Distillation	92
3.3.5	Sugar and Ethanol Analysis	92



3.3.6	Yield and Energy Consumption	93
3.4	Corrosion of Metals in Bioethanol and Gasoline Blends	94
3.5	Compatibility of Materials in Biodiesel–Diesel–Ethanol (BDE)	98
3.5.1	Corrosion of Metals in BDE blends	99
3.5.2	Compatibility of NBR and PTFE in BDE Blend	101
3.6	Performance and Emissions of Petrol Engine using Bioethanol Fuel	103
3.6.1	Engine Specifications and Setup	103
3.6.2	Experimental Procedure	106
<b>4</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>108</b>
4.1	Bioethanol Production from SPW using Microwave Hydrothermal Hydrolysis	108
4.1.1	Biomass Composition Analysis	108
4.1.2	Microwave Hydrothermal Hydrolysis	109
4.1.3	Ethanol Fermentation and Distillation	111
4.1.4	GC Analysis	112
4.1.5	Energy Consumption	113
4.1.6	FTIR Analysis	115
4.1.7	Overall Mass Balance	115
4.2	Bioethanol Production from SPW using Microwave Acid Hydrolysis	119
4.2.1	Biomass Composition	119
4.2.2	Microwave Acid Hydrolysis	119
4.2.3	By-products and Degradation	121
4.2.4	Ethanol Fermentation	122
4.2.5	Distillation and Dehydration	124
4.2.6	Energy Consumption for Microwave Hydrolysis	125
4.2.7	Overall Energy Consumption	126

4.2.8	Overall Mass Balance	127
4.3	Bioethanol Production from SBW using Microwave Enzymatic Hydrolysis	129
4.3.1	Biomass Composition	129
4.3.2	Enzymatic Hydrolysis	129
4.3.3	Ethanol Fermentation	130
4.3.4	Energy Consumption	132
4.3.5	Comparison of Bioethanol Production from Sago Waste	133
4.4	Corrosion of Metals in Bioethanol and Gasoline Blends	135
4.4.1	Corrosive Rate	135
4.4.2	pHe	137
4.4.3	Total Acid Number	138
4.4.4	Density and Viscosity	139
4.4.5	Water Content	141
4.4.6	Oxidation Products	142
4.4.7	Calorific Value	144
4.4.8	Chemical Structure of Metals	144
4.5	Corrosion of Metals in BDE Blends	145
4.5.1	Corrosion Rate	145
4.5.2	Total Acid Number	148
4.5.3	Density and Viscosity	151
4.5.4	Calorific Value and Flash Point	152
4.5.5	Oxidation Products	154
4.5.6	Water Content	155
4.5.7	Color Changes	156
4.5.8	Surface Morphology	156
4.5.9	Chemical Structure of Metals	157
4.6	Compatibility of NBR & PTFE in BDE	160

4.7	Performance of Bioethanol in Petrol Engine	164
4.7.1	Air-Fuel ratio and Air Mass Flow rate	164
4.7.2	Engine Power	166
4.7.3	Engine Torque	167
4.7.4	Fuel Consumption	168
4.7.5	Exhaust Gas Temperature	170
4.7.6	Brake Thermal Efficiency	171
4.7.7	Mean Effective Pressure	172
4.8	Exhaust Emissions from Bioethanol in Petrol Engine	174
4.8.1	Carbon Monoxide	174
4.8.2	Oxides of Nitrogen	175
4.8.3	Unburned Hydrocarbon	176
<b>5</b>	<b>CONCLUSIONS AND FUTURE RECOMMENDATIONS</b>	<b>178</b>
5.1	Conclusions	178
5.2	Future Recommendations	180
	<b>REFERENCES</b>	<b>182</b>
	Appendices A - L	195 - 208

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
1.1	Classification of biofuels (Demirbas, 2011)	3
1.2	Conversion of biomass into biofuels (IEA Bioenergy, 2005)	4
1.3	Fuel properties of ethanol and gasoline (Kumar <i>et al.</i> , 2010)	5
2.1	World bioethanol production (Lichts, 2015)	17
2.2	Chemical composition of SLC biomass (%)	18
2.3	Physical and biological pretreatment	22
2.4	Physico-chemical pretreatments	23
2.5	Chemical pretreatments	24
2.6	Acid and enzymatic hydrolysis (Taherzadeh and Karimi, 2007a)	27
2.7	Comparison of different fermentation methods	30
2.8	Biocatalyst for ethanol fermentation	31
2.9	Bioethanol production from SLC biomass	33
2.10	Bioethanol yield from SLC biomass	38
2.11	Corrosion rate (mpy) of metals in biodiesel	48
2.12	Studies on ethanol fuel in SI engines	59
2.13	Effect of ethanol on performance of SI engines	61
2.14	Effect of ethanol on emission from SI engines	68

3.1	Equipment and bioethanol processing details	89
3.2	The properties of diesel and palm biodiesel	100
3.3	Engine specifications	103
3.4	Measurement Specification of Emission Analyzer	104
3.5	Accuracy and uncertainty	106
4.1	Glucose yield in microwave hydrothermal hydrolysis (%)	109
4.2	Comparison of glucose yield obtained from SPW	110
4.3	Fermentation kinetic parameters for different microwave hydrolysates	112
4.4	Energy consumption for different microwave hydrolysis condition	114
4.5	Glucose yield in microwave treatment and hydrolysis (%)	120
4.6	By-products in microwave acid hydrolysis (g/L)	122
4.7	Fermentation kinetic parameters for microwave SPW hydrolysates	124
4.8	Energy consumption for microwave assisted acid hydrolysis	125
4.9	Total energy consumption to produce bioethanol from SPW	127
4.10	Glucose yield (%) in enzymatic hydrolysis	130
4.11	Energy consumption at various pretreatment conditions	132
4.12	Comparison of bioethanol production from Sago Palm Waste	133
4.13	Comparison of energy consumption of Sago Palm Waste	134
4.14	Metal elements in fuel blends	140
4.15	Corrosion rate (mpy) of metals in biodiesel	146
4.16	TAN value (mg KOH/g) of fuels exposed to metals	149
4.17	Metal elements (ppm) in B20D70E10	149
4.18	Properties of test fuels	166

## LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Share of biomass in world total primary energy supply (IEA, 2014)	2
1.2	Ethanol fermentation from biomass	6
1.3	Overall organisation of research study	17
1.4	Research work flow of bioethanol production	18
1.5	Research work flow of material compatibility	19
2.1	Conversion of SLC biomass into ethanol	18
2.2	Schematic flow diagram of sago processing (Awg-Adeni <i>et al.</i> , 2010)	19
2.3	Schematic pretreatment of lignocellulosic biomass (Mood <i>et al.</i> , 2013)	20
2.4	Overall mass balance of okara (Choi <i>et al.</i> , 2015)	26
2.5	Monosaccharides or glucose yield under hydrothermal condition (Miyazawa and Funazukuri, 2005)	28
2.6	Glucose fermentation	29
2.7	Ethanol production from acid hydrolysate of potato peel waste (Adopted from: Arapoglou <i>et al.</i> , 2010)	32
2.8	Ethanol production from hydrolysed potato peel waste (Adopted from: Khawla <i>et al.</i> , 2014)	34
2.9	Ethanol yield obtained from banana peel waste (Adopted from: Oberoi <i>et al.</i> , 2011)	35

2.10	Ethanol yield obtained from food waste (Kim <i>et al.</i> , 2011)	36
2.11	Ethanol production yield from cassava pulp (Adopted from: Kosugi <i>et al.</i> , 2008)	37
2.12	Ethanol production from sago hampas (Adopted from Awg-Adeni <i>et al.</i> , 2013)	39
2.13	Glucose production from sago waste (Adopted from Kumoro <i>et al.</i> , 2008)	40
2.14	Reducing sugar obtained from sago pith residue (Adopted from: Linggang <i>et al.</i> , 2012)	41
2.15	Carbon steel exposed to fuel at 45 °C for 90 days (a) gasoline (b) E20 (Baena <i>et al.</i> , 2012)	43
2.16	Corrosion rate of metals in ethanol fuel (Jafari <i>et al.</i> , 2011)	43
2.17	SEM image of aluminum alloy exposed to ethanol (E100) at 78 °C for a time period of (a) 3 h, (b) 4 h, (c) 12 h, and (d) 24 h (Thomson <i>et al.</i> , 2013)	44
2.18	Corrosiveness of ethanol fuel in Al alloy (Yoo <i>et al.</i> , 2011)	45
2.19	Weight losses of Al alloy in oxygen free E20 for 12 h (Yoo <i>et al.</i> , 2011)	45
2.20	Optical photograph (100 x) of copper after immersion at room temperature in (a) B0, (b) B50 and (c) B100 and; at 60 °C in (d) B0 (e) B50 and (f) B100 (Haseeb <i>et al.</i> , 2010a)	49
2.21	Corrosion rate of copper in palm biodiesel (Fazal <i>et al.</i> , 2013)	50
2.22	Change of TAN number of biodiesel exposed to metals at room temperature for 2880 h (Fazal <i>et al.</i> , 2012)	50
2.23	The color change of fuel exposed to different metals at room temperature for 2880 h (Fazal <i>et al.</i> , 2012)	51
2.24	Corrosion rate of metals in palm biodiesel at room temperature (Fazal <i>et al.</i> , 2014b)	52
2.25	Water content absorbed in biodiesel exposed to metals at room temperature (Fazal <i>et al.</i> , 2014b)	52
2.26	Variation of (a) density and (b) viscosity of fuel exposed to metals at 80 °C for 1200 h (Fazal <i>et al.</i> , 2010)	54

2.27	Oxidation products exposed to metals at 80 °C (Fazal <i>et al.</i> , 2010)	55
2.28	Changes in (a) weight and (b) volume in B100 (Haseeb <i>et al.</i> , 2010b)	55
2.29	Changes in hardness of elastomers in different blends at different condition for 500 h (Haseeb <i>et al.</i> , 2010b)	56
2.30	Mass changes of nitrile rubber hose at 25 °C and 70 °C according to fuel type (Coronado <i>et al.</i> , 2014)	56
2.31	Loss of properties of NBR after immersion in (a) castor bean oil biodiesel (b) coconut oil biodiesel (Linhares <i>et al.</i> , 2013)	57
2.32	Effect of various fuels on power and specific fuel consumption (Celik, 2008)	62
2.33	Effect of ethanol addition on brake thermal efficiency (Al-Hasan, 2003)	63
2.34	Effect of ethanol addition on volumetric efficiency (Al-Hasan, 2003)	64
2.35	Effect of ethanol addition on brake specific fuel consumption (Al-Hasan, 2003)	65
2.36	Effect of various fuels on CO and CO <sub>2</sub> emissions (Celik, 2008)	67
2.37	Effect of various fuels on HC and NO <sub>x</sub> emissions (Celik, 2008)	71
3.1	The process flow of bioethanol fuel preparation from SPW using MHH	75
3.2	SPW (a) wet residue (b) after drying and milling (c) in powder form	76
3.3	The microwave hydrothermal hydrolysis with CO <sub>2</sub> (a) before treatment (b) after treatment (9MH2)	77
3.4	Fermentation in an incubator shaker at 35 °C and 200 rpm	79
3.5	Glass alcohol distillation units	79
3.6	High Pressure Liquid Chromatography (HPLC)	80
3.7	Fourier Transform Infrared (FTIR) Spectrometer	81



3.8	Gas Chromatography (GC) analyzers	81
3.9	The process flow of bioethanol fuel production from SPW using MAH	83
3.10	Microwave acid hydrolysis (a) biomass loading (b) adding acid (c) microwave treatment (d) SPW hydrolysate	85
3.11	SPW hydrolysate MH1 (a) before fermentation (b) after fermentation	86
3.12	Ethanol separation (a) distillation (b) dehydration using NaCl	87
3.13	The process flow of bioethanol production from SBW using MAEH	90
3.14	(a) SBW obtained from factory (b) SBW after milling	91
3.15	(a) Adding enzymes in the microwave treated SBW for hydrolysis (b) Bioethanol produced after fermentation of SBW hydrolysate	93
3.16	Long flat plate (a) mild steel (b) copper (c) aluminum	94
3.17	The work flow of corrosion testing in bioethanol and gasoline blends	95
3.18	The work flow of corrosion testing in BDE fuels	98
3.19	Micro Hardness Testers	102
3.20	Experimental engine setup (a) schematic diagram; (b) actual	105
4.1	Ethanol yield obtained from SPW using MHH	111
4.2	Ethanol peaks obtained in GC analysis	113
4.3	FTIR spectra of (A) untreated SPW, (B) 9MH1 and (C) 9MH2	116
4.4	FTIR spectra of distilled ethanol	117
4.5	Overall mass balance of SPW	118
4.6	Ethanol yield from SPW using MAH	123
4.7	Overall mass balance for bioethanol fuel production from SPW	128

4.8	Ethanol produced under various pretreatment conditions at 10% SBW loadings	130
4.9	Ethanol produced at different SBW loadings at 1100 W for 30 s	131
4.10	Corrosion rates of metals in bioethanol and gasoline blends for (a) 700 h and (b) 1400 h	136
4.11	Total acid number (TAN) of the bioethanol fuel blends before and after exposure to metals	138
4.12	Density of the fuel exposed to metals at room temperature for 1400 h	140
4.13	Viscosity of the fuel blends exposed to metals at room temperature for 1400 h	141
4.14	Water content in the fuel blends exposed to metals at room temperature for 1400 h	142
4.15	Oxidation product level of fuel exposed to metals at room temperature for 1400 h	143
4.16	Corrosion rates of metals exposed to fuel blends (a) at room temperature (b) at 60 °C	147
4.17	Total acid number (TAN) of fuel blends upon exposure to metals (a) at room temperature (b) at 60 °C	150
4.18	Density of fuels exposed to metals at room temperature for 800 h	151
4.19	Kinematic viscosity of fuels exposed to metals at room temperature for 800 h	152
4.20	Calorific value of fuels exposed to metals at room temperature	153
4.21	Flash points of fuels exposed to metals at room temperature	153
4.22	Oxidation products in the fuel blends before and after the immersion tests at room temperature	154
4.23	Water content in the fuel blends before and after immersion tests at room temperature	155
4.24	FTIR spectra of copper upon exposure to B20D70E10 fuel blend (A) before exposure (B) after exposure at room temperature (C) exposure at 60 °C	158

4.25	FTIR spectra of mild steel upon exposure to B20D70E10 fuel blend (A) before exposure (B) after exposure at room temperature (C) exposure at 60 °C	159
4.26	Change of weight after immersion test at 50 °C for 200 h	160
4.27	Change of volume after immersion test at 50 °C for 200 h	161
4.28	Surface of the specimens (250x) before and after static immersion test at 50 °C for 200 h in B20D75E5	162
4.29	Effect of fuel blends on (a) actual air-fuel ratio; (b) air mass flow rate	165
4.30	Effect of fuel blends on engine power	167
4.31	Effect of fuel blends on engine torque	168
4.32	Effect of fuel blends on fuel consumption	169
4.33	Effect of fuel blends on exhaust temperature	170
4.34	Effect of fuel blends on brake thermal efficiency	171
4.35	Effect of fuel blends on mean effective pressure	173
4.36	Effect of fuel blends on CO emission	174
4.37	Effect of fuel blends on NO <sub>x</sub> emission	176
4.38	Effect of fuel blends on HC emission	177

## LIST OF ABBREVIATIONS

1C	-	Single Cylinder
4C	-	Four Cylinders
4S	-	Four Strokes
AC	-	Air Cooled
ASTM	-	American Society for Testing and Materials
B0	-	100% Diesel
B100	-	100% Biodiesel
B20D70E10	-	20% Biodiesel, 70% Diesel & 10% Ethanol
B20D75E5	-	20% Biodiesel, 75% Diesel & 5% Ethanol
B50	-	50% Biodiesel & 50% Diesel
BDE	-	Biodiesel–Diesel–Ethanol or Bioethanol
BMEP	-	Brake Mean Effective Pressure
BP	-	Brake Power
BSFC	-	Brake Specific Fuel Consumption
BSHC	-	Brake Specific Heat Consumption
BTE	-	Brake Thermal Efficiency
CO	-	Carbon Monoxide
CO <sub>2</sub>	-	Carbon Dioxide
CR	-	Compression Ratio
CV	-	Calorific Value
DE	-	Diesel–Ethanol or Bioethanol
DMC	-	Direct Microbial Conversion
DMF	-	Bio-Dimethyl Furan
DOHC	-	Double Overhead Camshaft
DVVT	-	Dynamic Variable Valve Timing
E0	-	0% Ethanol & 100% Gasoline

E100	-	100% Ethanol & 0% Gasoline
E25	-	25% Bioethanol & 75% Gasoline
E50	-	50% Bioethanol & 50% Gasoline
EDS	-	Energy Dispersion Spectroscopy
EFI	-	Electronic Fuel Injection
EIS	-	Electrochemical Impedance Spectroscopy
EN	-	European Standard
ET	-	Engine Torque
EtOH	-	Ethanol
FC	-	Fuel Consumption
FFV	-	Flexi Fuel Vehicle
FI	-	Fuel Injection
FTIR	-	Fourier Transform Infrared
GC	-	Gas Chromatography
GHG	-	Greenhouse Gas
HC	-	unburned Hydrocarbon
HE or Eh	-	Hydrous Ethanol
HMF	-	Hydroxymethyl Furfural
HPLC	-	High Pressure Liquid Chromatography
ICP	-	Inductively Coupled Plasma
ICP-MS	-	Inductively Coupled Plasma Mass Spectrometry
ITE	-	Indicated Thermal Efficiency
LHV	-	Lower Heating Value
MOA	-	Multi Element Analyser
MPFI	-	Multi-Port Fuel Injection
MS	-	Mild Steel
NBR	-	Nitrile Butadiene Rubber
NO <sub>x</sub>	-	Oxides of Nitrogen
NREL	-	National Renewable Energy Laboratory
OM	-	Optical Microscope
PFI	-	Port Fuel Injection
PTFE	-	Polytetrafluoroethylene
RE	-	Renewable Energy
SBW	-	Sago Bark Waste

SEM	-	Scanning Electron Microscope
SHF	-	Separate Hydrolysis and Fermentation
SI	-	Spark Ignition
SLC	-	Starchy Lignocellulosic
SOHC	-	Single Overhead Camshaft
SPORL	-	Sulfite Pretreatment Top Overcome Recalcitrance
SPW	-	Sago Pith Waste
SSF	-	Simultaneous Saccharification and Fermentation
TAN	-	Total Acid Number
VE	-	Volumetric Efficiency
WC	-	Water Cooled
WOT	-	Wide Open Throttle
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	X-ray Diffraction

**LIST OF SYMBOLS**

$A$	-	Surface area
$Abs.$	-	Absorbance
$\rho$	-	Density
$l$	-	Length
$t$	-	Time
$W$	-	Weight
$N$	-	Speed
$\phi$	-	Equivalent air-fuel ratio
$\lambda$	-	Relative air-fuel ratio

**LIST OF APPENDICES**

<b>APPENDIX</b>	<b>TITLE</b>	<b>PAGE</b>
A	GC purification of fuel grade bioethanol (MH1)	195
B	GC purification of fuel grade bioethanol (MH2)	196
C	Materials used in the manufacture of diesel fuel system	197
D	Optical photographs (100×) of corrosion products after immersion in bioethanol and gasoline blends	198
E	FTIR spectra of copper exposed to E50 (a) before exposure (b) after exposure	199
F	FTIR spectra of mild steel exposed to E50 (a) before exposure (b) after exposure	200
G	FTIR spectra of (a) mild steel and (b) copper in E85	201
H	Color changes of B20D70E10 (a) as- received (b) in MS (c) in Cu (d) in Al	202
I	Optical photograph (100×) of metal (a) as-received; (b) in B20D75E5 at 30 °C; (c) in B20D70E10 at 30 °C; (d) in B20D75E5 at 60 °C and (e) in B20D70E10 at 60 °C	203
J	FTIR spectra of NBR (a) before; after immersion at 50 °C for 200 h	204
K	FTIR spectra of PTFE (a) before; (b) after immersion at 50 °C for 200 h	205
L	List of Publications	206



## **CHAPTER 1**

### **INTRODUCTION**

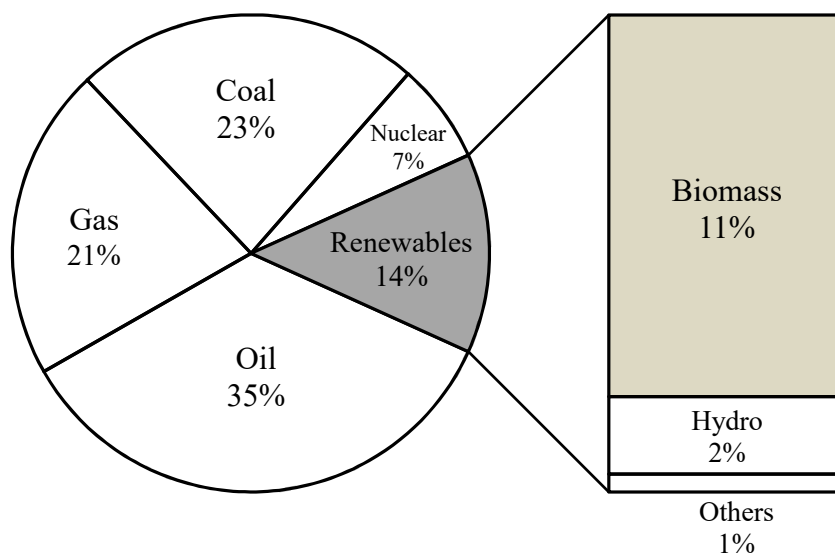
#### **1.1 Research Background**

Worldwide increment in population growth rate, economic interdependencies between nations and the rapid developments in industries and automotive society have created several impeding issues around the world. These issues comprises of, but not limited to: uncompensated demands of petroleum based fuels that causes increasing fuel prices; environmental pollution problems; climate changes; energy crisis; and waste management. There is now global insistence to manage the above listed issues.

One of the promising solutions to address the above listed issues is renewable energy (RE) technology. RE sources, such as solar, wind, biomass, hydro, nuclear, geothermal, and tidal are most commonly utilized in different tropical location for power generation. RE sources have number of benefits, such as being sustainable having environmental and economic benefits; and pricing flexibility. However, the main drawbacks of most of the RE sources are reliability of supply due to unpredictable weathers, high capital cost and large land requirement. However, the biomass energy, which is among the RE family, can overcome the above mentioned drawbacks. There are many environmental benefits of using biomass energy as described below (IEA Bioenergy, 2005):

- reduced the reliance on limited natural resources
- reduced greenhouse gas (GHG) emission through fossil fuel replacement
- reduced landfill waste
- enhanced biodiversity
- protection of ground water supplies
- reduced dry land salinity and erosion

Currently, about 10 to 15% of world energy demand is supplied by bioenergy in developed countries, and the same is up to 3% in developing countries (Hosseini and Wahid, 2014). Figure 1.1 shows the share of biomass in world total primary energy supply. Most of the RE sources are utilized for electrical power generation globally. However, the global automotive and industry sectors are completely dependent on petroleum-based fuels as main energy source, which cannot be easily met by RE sources such as solar and wind other than bioenergy.



**Figure 1.1** Share of biomass in world total primary energy supply (IEA, 2014)

Presently, petroleum-based fuels are obtained from limited reserves, so there is a greater anxiety about the shortage of petroleum fuels due to finite reserves; moreover, environmental pollutions problem have been emphasized around the

world in recent days. Similar to the global situation, Malaysian automotive society is also more dependent on petroleum based fuels. The transportation sector of Malaysia has been the largest consumer of petroleum fuels and the largest contributor of GHG emission accounting more than 40% of the total GHG emission (Abdul-Manan *et al.*, 2014). Thus, it is of urgency to find a suitable alternative fuels for automotive engines. The most preferred choice for replacing petroleum-based fuels as the main energy in automotive sector is biofuels (Demirbas, 2011).

Biofuels are produced from biomass and bioenergy crops through different conversion process, which are generally thermochemical or biochemical. Biofuels have gained progressive importance as alternative fuels for automotive engines. Biofuels have shared 10% in the world primary energy supply of  $1.56 \times 10^{11}$  MWh by fuels in the year 2012 (IEA, 2014). Biofuels are classified based on the production technologies, namely, first, second, third and fourth generation biofuels (Demirbas, 2011). Table 1.1 shows the classification of biofuels based on different feedstock.

**Table 1.1:** Classification of biofuels (Demirbas, 2011)

<b>Generation</b>	<b>Feedstock</b>	<b>Biofuels examples</b>
First Generation	Sugar, starch grains, vegetable oils and animal fats	Bio-alcohols such as ethanol, propanol and butanol, vegetable oils, biodiesel, green diesel, bio-syngas and biogas
Second Generation	Non-food crops, agriculture residues, woody biomass and municipal solid wastes	Bio-alcohols such as bioethanol and methanol, bio-oil, bio-dimethyl Furan (DMF), bio-hydrogen, bio-char and bio-Fischer–Tropsch diesel
Third Generation	Algae based	Vegetable oils, biodiesel and bioethanol, methanol, butanol
Fourth Generation	Vegetable oils and biodiesels	Bio-gasoline and jet fuel

First generation biofuels are mainly produced from the food based feedstock, such as sugar, starch, vegetable oils and animal fats. Second generation biofuels are produced from the feedstock, such as non-food crops, agricultural residues, wood and municipal solid wastes. Algae based biofuel production is named as third generation biofuels. Among the various classifications of biofuels, liquid biofuels,

namely, biodiesel and bioethanol offer promising alternatives for petroleum based fuels in automotive engines. Biodiesel is produced from vegetable oils or animal fats through transesterification process, and bioethanol is produced from biomass and bioenergy crops using biochemical conversion. Table 1.2 shows the processes of converting biomass into biofuels and corresponding energy services.

**Table 1.2:** Conversion of biomass into biofuels (IEA Bioenergy, 2005)

<b>Biomass resources</b>	<b>Processes</b>	<b>Biofuels</b>	<b>Energy services</b>
Agriculture and forestry residues	Densification	Wood pellets Briquettes	Heat Electricity
Energy crops: Biomass, sugar, oil	Combustion Gasification Pyrolysis Esterification Fermentation	Char/charcoal Fuel gas Bio-oil Biodiesel Bioethanol	Heat Electricity Electricity Transportation Transportation
Biomass processing wastes	Digestion Hydrolysis/ fermentation	Biogas Bioethanol	Transportation
Municipal solid wastes	Digestion Combustion Gasification	Refuse-derived fuels (RDF) Biogas	Heat Electricity

## 1.2 Bioethanol as Alternative Fuel

Bioethanol (ethanol, fuel ethanol, ethyl alcohol, grain alcohol, EtOH or CH<sub>3</sub>-CH<sub>2</sub>-OH) is one of the liquid biofuel, which is considered as a clean, renewable and green combustible fuel, alternative to petroleum fuels in internal combustion engines. The ethanol fuel has the properties of higher octane number, higher flammability limit, similar or lower flame speeds, and higher heats of vaporization than gasoline fuel (as in Table 1.3). These fuel properties allow for a higher compression ratio, shorter burn time and leaner burn engine, which leads to better performance over gasoline in internal combustion engines (Balat and Balat, 2009). The higher octane helps to run the vehicles more smooth, and keeps the vehicle's fuel system clean for optimal performance (Kumar *et al.*, 2010).

**Table 1.3:** Fuel properties of ethanol and gasoline (Kumar *et al.*, 2010)

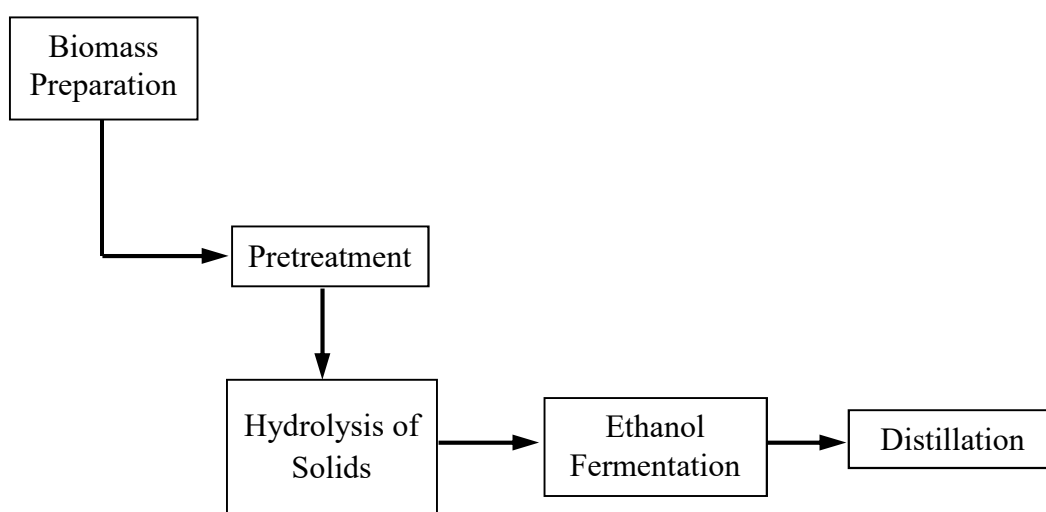
Property	Ethanol	Gasoline
Formula	C <sub>2</sub> H <sub>5</sub> OH	C <sub>5</sub> to C <sub>12</sub>
Specific gravity at 15.55 °C	0.79	0.72-0.75
Distillation temperature (°C)	78.4	32-210
Flash point (°C)	12	13
Kinematic viscosity (mm <sup>2</sup> /s)	1.5	0.6
Reid vapour pressure at 37.8 °C (kPa)	17	35-60
Octane number		
(i) Research	111	91-100
(ii) Motor	92	82-92
Oxygen content (wt.%)	34.7	0
Stoichiometric air/fuel ratio (w/w)	8.97	14.6
Net heat of combustion (MJ/kg)	27	43.5
Heat of vaporization (kJ/kg)	900	400
Water solubility	∞	0
Vapour flammability limit (vol.%)	3.5-15	0.6-8
Maximum flame speed (m/s)	0.33	0.40
Flame temperature at 101.325 kPa (°C)	478	392
Color	Colorless	Colorless to light amber glass

The anti-knock characteristics of ethanol allow for a high compression ratio, and therefore, produce higher engine power output. In addition, higher heat of vaporization of ethanol and faster flame speed permit for increased fuel conversion efficiency compared to gasoline (Costa and Sodre, 2011). Ethanol acts as oxygenate in gasoline engines, elevating its oxygen content, allowing a best oxidation of hydrocarbon, reducing the amount of aromatic compounds and carbon monoxide released to atmosphere (Balat *et al.*, 2008).

Globally, bioethanol production reached 24.6 billion gallons in 2014, up from 22.4 billion gallons in 2011. Bioethanol presently accounts for more than 95% of the global biofuel production, with the majority coming from first generation food based feedstock, such as sugarcane, corn, wheat and cassava (Lichts, 2015). Due to the ethical concern about the food being used as fuel raw material, researches have re-

directed their work on the second generation lignocellulosic feedstock (Balat and Balat, 2009).

Extensive research has been carried out on bioethanol production from lignocellulosic biomass in the past two decades. Rice straw, wheat straw, corn straw, and sugarcane and sorghum bagasse are the major agricultural wastes which are suitable for large scale bioethanol production in terms of quantity of biomass available. Moreover, the starchy lignocellulosic biomasses, such as waste from starch processing and potato food factories, beverage and brewery factories are promising feedstock for bioethanol production in the tropical locations. A short process chart for bioethanol production from lignocellulosic feedstock is shown in Figure 1.2.



**Figure 1.2** Ethanol fermentation from biomass

The second generation of bioethanol fuel production from lignocellulosic biomass involves four different steps, such as pretreatment, hydrolysis, fermentation and ethanol recovery (as in Figure 1.2). Different pretreatments, such as physical, chemical, physico-chemical and biological have been studied in the past decade to alter structural characteristics of lignocellulosic biomass. Hydrolysis is an essential step to produce fermentable sugars which are then fermented into ethanol by microbial biocatalyst.

### 1.3 Research Problem Statement

Bioethanol fuel has the potential to replace petroleum fuels in internal combustion engines. However, the cost of bioethanol production (0.97 USD/litre) is high compared to petroleum-based fossil fuels (0.22 USD/litre) (Banerjee *et al.*, 2010; Macrelli *et al.*, 2012). Currently, large scale bioethanol production is mainly based on sugar containing raw materials (e.g. sugar cane) and starch grains (e.g. corn, wheat and cassava), which is not appropriate due to their feed value. The lignocellulosic biomass, such as agriculture waste, woody biomass, algae, and municipal solid waste is not only a sustainable feedstock, as it incurs low cost and is abundantly available (Limayem and Ricke, 2012).

Although lignocellulosic biomass is sustainable and abundant; the bioethanol fuel production from lignocellulosic biomass is not commercialized in many countries including Malaysia. The main obstacles in bioethanol production are high production cost and energy requirements. The conversion of biomass into bioethanol using energy efficient, economic and faster technique is the greatest concern for commercial bioethanol production. Currently, acid and enzymatic hydrolysis is widely employed to breakdown the starch, cellulose and hemicellulose of biomass into fermentable sugar. These existing approaches tend to be slow, expensive and of high dilutions that give poor yields of glucose (Fan *et al.*, 2013).

In Malaysia, the availability of lignocellulosic biomass, such as waste from wood industry, agriculture residues, oil palm waste and sago palm waste is abundant. The sago palm wastes, namely, sago pith waste, sago bark waste and sago effluent are the starchy lignocellulosic by-product generated from *Metroxylon sagu* (sago palm) after extraction of starch. Sago bark, which is peelings from initial process, is generated in sago starch processing factories. It is estimated that about 5 to 15 tons of sago bark waste and about 50 to 110 tons of sago pith waste are produced daily from starch processing factories in Sarawak, Malaysia, which are currently washed off into the nearby stream together with waste water (Awg-Adeni *et al.*, 2010). This can cause serious environmental problems in Sarawak, Malaysia.

In addition to the above problems in bioethanol production, material compatibility of bioethanol fuels in automotive engines is another issue, for which the engineers and manufactures are working to find a suitable solution. The addition of bioethanol to gasoline in petrol engines normally creates corrosion in fuel system materials. In petrol engines, fuel gets in contact with various parts contributing to corrosion. The blends of diesel and ethanol could be used in existing diesel engines without engine modification. In addition, the biodiesel–diesel–ethanol (BDE) blend represents an important alternative fuel for diesel engines; however, changes in the fuel composition and the introduction of new alternative fuel often results corrosion in fuel system metals, and degradation in fuel system elastomers and polymers.

Most of the spark ignition (SI) engine studies discovered a significant improvement in engine performance and emission reductions, such as carbon monoxide (CO) and unburned hydrocarbon (HC) for ethanol fuel compared to gasoline. However, carbon dioxide (CO<sub>2</sub>) and oxides of nitrogen (NO<sub>x</sub>) emissions were not significant (increased or decreased), and moreover, the brake specific fuel consumption (BSFC) also increased or decreased due to low calorific value of bioethanol fuel (27 MJ/kg) compared to gasoline (43.5 MJ/kg). There are contradictory results attained for CO<sub>2</sub> and NO<sub>x</sub> emission and BSFC (Masum *et al.*, 2013), motivating for further investigations using lignocellulosic bioethanol, such as sago bioethanol.



#### 1.4 Hypothesis of Research Study

Currently, acid and enzyme hydrolysis are generally employed to breakdown the starch, cellulose and hemicellulose of sago pith waste into fermentable sugar, however, little information is only available in bioethanol production from sago pith waste using economic, environmental friendly and energy efficient method. Further experimentation required for sago pith waste to produce bioethanol using alternative hydrolysis. Hydrothermal hydrolysis offers an alternative way to hydrolyze starchy and cellulosic biomass into fermentable sugars. Bioethanol fuel production from sago pith waste using microwave assisted hydrothermal hydrolysis and microwave hydrothermal hydrolysis accelerated by CO<sub>2</sub> is required to be further experimented.

The acid hydrolysis aided with microwave irradiation offers an economical and energy efficient alternative method for bioethanol production from sago pith waste. The microwave assisted acid hydrolysis was widely used to produce glucose but with no emphasis on energy consumption to produce fermentable sugars. Moreover, a low concentration of acid (< 0.5 mol/L) was commonly used with long irradiation time (5 min to 30 min) to achieve maximum fermentable sugars. However, no information on the microwave assisted acid hydrolysis (both H<sub>2</sub>SO<sub>4</sub> and HCl with  $\geq 0.5$  mol/L) for sago pith waste with an aim to develop energy efficient approach. In addition, microwave aided acid treatment followed with enzyme hydrolysis was used for bioethanol production from sorghum bagasse, wheat straw, and rape straw. However, no research is found on bioethanol production from sago bark waste using microwave aided acid treatment, which necessitates further investigation.

The corrosion behavior of metals in ethanol and gasoline blends was studied through electrochemical properties. However, little information is available on change of bioethanol fuel properties after exposure to metals and the corrosive nature of bioethanol fuel for metallic materials. In addition, the effect of sago waste bioethanol on corrosion and degradation of materials requires further investigation.

The corrosion behavior of materials (metals, polymers and elastomers) in different biodiesel, such as palm oil, rapeseed oil and sunflower oil was widely studied. Literatures show a gap that no study has reported on corrosion and degradation behavior of materials in biodiesel–diesel–ethanol (BDE) fuel blend. Moreover, none of the study investigated the change of BDE fuel properties after exposure to materials, and the corrosive nature of BDE fuels. Further experimentation is required to analyze the corrosive behavior of BDE fuel blend on engine fuel system materials.

Investigations on the effect of ethanol and gasoline on performance and emissions of SI engine were carried out in past decade. Hydrous ethanol was found to be suitable to reduce  $\text{NO}_x$  and  $\text{CO}_2$  emissions compared to anhydrous ethanol. Hydrous ethanol reduces the  $\text{NO}_x$  and  $\text{CO}_2$  emission, however, engine performance decreased. Thus, further experimentation is required for achieving significant reduction in  $\text{NO}_x$  and  $\text{CO}_2$  emissions, without affecting the engine performance. Literatures show a gap that the effect of sago waste ethanol on the performance and emissions of petrol engine need to be further investigated.

## 1.5 Objectives

The main objectives of this study are:

- a) To produce bioethanol fuel from sago palm wastes using economic and energy efficient approach.
- b) To evaluate the corrosion of fuel system materials in bioethanol and gasoline fuel blends.
- c) To examine the compatibility of fuel system materials in biodiesel–diesel–ethanol (BDE) fuel blends.
- d) To assess the effect of sago bioethanol fuel on performance and emissions of petrol engine.

## 1.6 Scope of the Research Study

The scope of this research is to achieve the objectives described below:

- a) Bioethanol fuel was produced from sago pith waste (SPW) using microwave hydrothermal hydrolysis accelerated with CO<sub>2</sub> (MHH) and without CO<sub>2</sub>. MHH was carried out for different microwave power rating (550, 700 and 900 W) and heating time (1, 2, 3 and 5 min).
- b) Bioethanol fuel was also produced from SPW using microwave acid hydrolysis (MAH) using both H<sub>2</sub>SO<sub>4</sub> and HCl (0.5, 1.0 and 1.5 mol/L concentration only used to avoid decomposition of sugar). MAH was carried out for different microwave power (550, 700 and 900 W) and heating time (1, 2 and 3 min).
- c) Bioethanol was produced from sago bark waste (SBW) using microwave aided acid pretreatment followed with enzymatic hydrolysis (MAEH) and fermentation. MAEH was carried for different microwave power (700, 900 and 1100 W), heating time (30 s, 1, 2 and 3 min), and biomass liquid loading (10, 20, 30, 40 and 50%).
- d) Corrosive behaviors of bioethanol fuel (E10, E25, E50 and E85) and gasoline (E0) on metals (mild steel, copper and aluminum) were examined at room temperature (25 to 30 °C). Corrosion immersion testing was carried for 700 and 1400 h.
- e) Corrosive behaviors of biodiesel–diesel–ethanol (BDE) blends (B20D75E5 and B20D70E10) on metals (mild steel, copper and aluminum) were studied at room temperature and 60 °C.
- f) The impact of B20D75E5 fuel on degradation of elastomer, namely nitrile rubber (NBR) and polymer, namely polytetrafluoroethylene (PTFE) at 50 °C was studied.
- g) The performance and emission characteristics of a 1.3 litre 4-stroke 4-cylinder petrol engine using three different fuel blends, such as E0 (100%

gasoline), E25 (25% sago waste ethanol and 75% gasoline) and E25C (25% commercial anhydrous ethanol and 75% gasoline) were studied.

- h) The properties of fuel blends (E0, E25 and E25C) were determined according to the American Society for Testing and Materials standards (ASTM D1298, ASTM D2699 & ASTM D240).

## **1.7 Significance of the Research**

The importance of this study is to implement the economic and energy saving technology to produce bioethanol commercially in Malaysia, from the resources available locally within the country. The use of bioethanol fuel in transportation sector save significant amount of fossil fuels and reduce greenhouse gas emission in Malaysia. This research developed a novel technique (MHH) to produce bioethanol fuel from sago pith waste, which is suitable for any kind of starchy lignocellulosic biomass. Moreover, this research developed an economic, environmental friendly and energy efficient methods to produce bioethanol fuel from sago palm waste (pith and bark waste). An alternative waste management for sago factories in Malaysia to convert all the sago waste into a renewable fuel is also proposed in this research. Another importance of this research is to identify the suitable materials to make engine fuel system parts that can perform effectively with alternative fuels such as bioethanol. Investigation of corrosion behavior of materials in bioethanol fuel proposes proper materials to manufacture engine fuel system parts. Sago waste bioethanol produced in this research is suitable for petrol engine compared to gasoline for better engine performance and low engine out emissions.

## 1.8 Structure of the Thesis

This thesis reports the results of the research work carried out by the author during the years 2012 – 2015. The research focused on bioethanol fuel production from sago palm waste as an alternative fuel for automotive engines including material compatibility, and engine performance and emissions. The outline of the thesis is as follows:

In Chapter 1, the background of the research along with the importance of bioenergy and biofuels are discussed in the beginning. Then, the research problem is pointed out towards the essentials of bioethanol fuel production, and its effects on engine materials, engine performance and emissions. The hypothesis of the research is discussed through the literatures. Then, the objectives of this thesis are reported, followed with the scope and significance of this research. Finally, the structure of the thesis is presented in the end of the chapter.

In Chapter 2, a detailed literature review is presented about the existing bioethanol production technologies including the comprehensive review of various pretreatment techniques, hydrolysis and fermentation methods. In addition, types of lignocellulosic biomass, existing bioethanol production techniques from various starchy lignocellulosic biomasses, and its potential ethanol yields are reported. The importance of sago palm waste as a potential substrate for bioethanol production in Malaysia is also discussed. Moreover, existing studies in bioethanol production from sago palm waste is described. In addition, existing studies in corrosion behavior of metals in ethanol and gasoline blends are presented. Furthermore, existing studies in the corrosion behavior of various biodiesel and diesel blends are also discussed. Finally, a comprehensive review on effects of ethanol blended gasoline on SI engine performance and emission characteristics are described.

In Chapter 3, materials and experimental methodology utilized for bioethanol production from sago pith waste (SPW) and sago palm waste (SBW) are described (Sections 3.1 to 3.3). The materials and experimental methodology utilized to study

the corrosion of fuel system metals in bioethanol and gasoline blends are described in Section 3.4, additionally, the materials and experiments used to study the compatibility of automotive fuel system materials in biodiesel-diesel-ethanol (BDE) blend is presented in Section 3.5. Finally, the engine setup and experimental procedure used to investigate the effect of bioethanol fuel blend on performance and emissions of petrol engine are described in Section 3.6.

Chapter 4 describes the results and discussion of different methods (MHH, MAH and MAEH) used for bioethanol production from sago pith waste (Section 4.1 and 4.2) and sago bark waste (Section 4.3). Results and discussion for the methods used in the Sections 3.4 about the corrosion of metals in bioethanol and gasoline blends is described in Sections 4.4. In addition, results and discussion for the methods used in Section 3.5 about the compatibility of materials in in biodiesel-diesel-ethanol (BDE) blend are presented in Sections 4.5 and 4.6. Finally, the results and discussion for engine study is presented in Sections 4.7 and 4.8.

Chapter 5 provides the conclusions and findings of the thesis, highlighting the most important findings of each section. The suggestions for the future work are also provided at the end of the thesis.

## REFERENCES

- Abdul-Manan, A. F. N., Baharuddin, A., and Chang, L. W. (2014). A detailed survey of the Palm and Biodiesel Industry Landscape in Malaysia. *Energy*. 76, 931–941.
- Al-Hasan, M. (2003). Effect of Ethanol–Unleaded Gasoline Blends on Engine Performance and Exhaust Emission. *Energ. Convers. Manage.* 44, 1547–1561.
- Alvira, P., Tomas-Pejo, E., Ballesteros, M., and Negro, M. J. (2010). Pretreatment Technologies for an Efficient Bioethanol Production Process based on Enzymatic Hydrolysis: A Review. *Bioresour. Technol.* 101, 4851–61.
- Arapoglou, D., Varzakas, T., Vlyssides, A., and Israilides, C. (2010). Ethanol Production from Potato Peel Waste. *Waste Manage.* 30, 1898–1902.
- Awg-Adeni, D. S., Abd-Aziz, S., Bujang, K., and Hassan, M.A. (2010). Review: Bioconversion of Sago Residue into Value Added Products. *Afr. J. Biotechnol.* 14, 2016–2021.
- Awg-Adeni, D. S., Bujang, K. B., Hassan, M. A., and Abd-Aziz, S. (2013). Recovery of Glucose from Residual Starch of Sago Hampas for Bioethanol Production. *BioMed Res. Int.* Article ID: 935852, 8 pages.
- Baena, L. M., Gómez, M., and Calderón, J. A. (2012). Aggressiveness of a 20% Bioethanol–80% Gasoline Mixture on Autoparts: I Behavior of Metallic Materials and Evaluation of their Electrochemical Properties. *Fuel*. 95, 320–328.
- Balat, M., and Balat, H. (2009). Recent trends in Global Production and Utilization of Bio-ethanol fuel. *Appl. Energ.* 86, 2273–82.
- Balat, M., Balat, H., and Oz, C. (2008). Progress in Bioethanol Processing. *Prog. Energ. Combust. Sci.* 34, 551–573.
- Banerjee, N., Bhatnagar, R., and Viswanathan, L. (1981). Inhibition of Glycolysis by Furfural in *Saccharomyces cerevisiae*. *Eur. J. Appl. Microbiol. Biotechnol.* 11, 226–228.



- Banerjee, S., Mudliar, S., Sen, R., Giri, B., Satpute, D., and Chakrabarti, T., *et al.* (2010). Commercializing Lignocellulosic Bioethanol: Technology Bottlenecks and Possible Remedies. *Biofuels, Bioprod. Biorefin.* 4, 77–93.
- Bian, J., Peng, P., Peng, F., Xiao, X., Xu, F., and Sun, R. (2014). Microwave-Assisted Acid Hydrolysis to produce Xylooligosaccharides from Sugarcane Bagasse Hemicelluloses. *Food Chem.* 156, 7–13.
- Bielaczyc, P., Woodburn, J., Klimkiewicz, D., Pajdowski, P., and Szczotka, A. (2013). An Examination of the Effect of Ethanol–Gasoline Blends' Physicochemical Properties on Emissions from a Light-Duty Spark Ignition Engine. *Fuel Process. Technol.* 107, 50–63.
- Boonmanumsin, P., Treeboobpha, S., Jeamjumnunja, K., Luengnaruemitchai, L., Chaisuwan, T., and Wongkasemjit, S. (2012). Release of Monomeric Sugars from *Miscanthus Sinensis* by Microwave-Assisted Ammonia and Phosphoric Acid Treatments. *Bioresour. Technol.* 103, 425–431.
- Bujang, K.B. (2006). Potentials of Bioenergy from the Sago Industries in Malaysia. *EOLSS - Encyclopedia of Life Support Systems*. UNESCO - IOBB, Brisbane, Australia.
- Canakci, M., Ozsezen, A. N., Alptekin, E., and Eyidogan, M. (2013). Impact of Alcohol Gasoline Fuel Blends on the Exhaust Emission of an SI Engine. *Renew. Energ.* 52, 111–117.
- Cardona, G. A., and Sanchez, O. J. (2006). Energy Consumption Analysis of Integrated Flow Sheets for Production of Fuel Ethanol from Lignocellulosic Biomass. *Energy.* 31, 2447–59.
- Celik, M. B. (2008). Experimental Determination of Suitable Ethanol–Gasoline Blend rate at High Compression Ratio for Gasoline Engine. *Appl. Therm. Eng.* 28, 396–404.
- Ceviz, M. A., and Yuksel, F. (2005). Effects of Ethanol–Unleaded Gasoline Blends on Cyclic Variability and Emissions in an SI Engine. *Appl. Therm. Eng.* 25, 917–925.
- Chandel, A. K., Es, C., Rudravaram, R., Narasu, M. L., Rao, L. V., and Ravindra, P. (2007). Economics and Environmental Impact of Bioethanol Production Technologies: An Appraisal. *Biotechnol. Molec. Biol. Rev.* 2, 14–32.

- Chaudhary, G., Singh, L. K., and Ghosh, S. (2012). Alkaline Pretreatment Methods followed by Acid Hydrolysis of Saccharum Spontaneum for Bioethanol Production. *Bioresour. Technol.* 124, 111–118.
- Chen, C., Boldor, D., Aita, G., and Walker, M. (2012). Ethanol Production from Sorghum by Microwave-Assisted Dilute Ammonia Pretreatment. *Bioresour. Technol.* 110, 190–197.
- Chen, R. H., Chiang, L. B., Chen, C. N., and Lin, T. H. (2011a). Cold-Start Emissions of an SI Engine using Ethanol Gasoline Blended Fuel. *Appl. Therm. Eng.* 31, 1463–1467.
- Chen, R. H., Chiang, L. B., Wu, M. H., and Lin, T. H. (2010). Gasoline Displacement and NOx reduction in an SI Engine by Aqueous Alcohol Injection. *Fuel.* 89, 604–610.
- Chen, W. H., Tu, Y. J., and Sheen, H. K. (2011b). Disruption of Sugarcane Bagasse Lignocellulosic Structure by Means of Dilute Sulfuric Acid Pretreatment with Microwave-Assisted Heating. *Appl. Energ.* 88, 2726–2734.
- Chew, K. V., Haseeb, A. S. M. A., Masjuki, H. H., Fazal, M. A., and Gupta, M. (2013). Corrosion of Magnesium and Aluminum in Palm Biodiesel: A Comparative Evaluation. *Energy.* 57, 478–483.
- Choi, I. S., Kim, Y. G., Jung, J. K., and Bae, H. J. (2015) Soybean waste (okara) as a valorization biomass for the bioethanol production. *Energy* 93, 1742–1747.
- Conde-Mejia, C., Jimenez-Gutierrez, A., and El-Halwagi, M. (2012). Comparison of Pretreatment Methods for Bioethanol Production from Lignocellulosic Materials. *Process Saf. Environ.* 90, 189–202.
- Coronado, M., Montero, G., Valdez, B., Stoytcheva, M., Eliezer, A., García, C., Campbell, H., and Pérez, A. (2014). Degradation of Nitrile Rubber Fuel Hose by Biodiesel use. *Energy.* 68, 364–369.
- Costa, R. C., and Sodre, J. R. (2010). Hydrous ethanol vs. Gasoline-ethanol Blend: Engine Performance and Emissions. *Fuel.* 89, 287–293.
- Costa, R. C., and Sodre, J. R. (2011). Compression ratio Effects on an Ethanol/Gasoline Fuelled Engine Performance. *Appl. Therm. Eng.* 31, 278–283.
- Cursaru, D. L., Branoiu, G., Ramada, I., and Miculescu, F. (2014). Degradation of Automotive Materials upon exposure to Sunflower Biodiesel. *Ind. Crop. Prod.* 54, 149–158.

- De Sanctis, M., Dimatteo, A., Lovicu, G. F., Marc, D., and Valentini, R. (2010). Metallic Materials Compatibility in E22 and M15 Motor Fuel Blends. *La Metallurgia Italiana*. 7-8, 33–39.
- Deh Kiani, M. K., Ghobadian, B., Tavakoli, T., Nikbakht, A. M., and Najafi, G. (2010). Application of Artificial Neural Networks for the Prediction of Performance and Exhaust Emissions in SI Engine using Ethanol- Gasoline Blends. *Energy*. 35, 65–69.
- Demirbas, A. (2011). Competitive Liquid Biofuels from Biomass. *Appl. Energ.* 88, 17–28.
- Elfasakhany, A. (2015). Investigations on the Effects of Ethanol-Methanol-Gasoline Blends in a Spark-Ignition Engine: Performance and Emissions Analysis. *Engineering Science and Technology, an International Journal*. <http://dx.doi.org/10.1016/j.jestch.2015.05.003>
- Eyidogan, M., Ozsezen, A. N., Canakci, M., and Turkcan, A. (2010). Impact of Alcohol–Gasoline Fuel Blends on the Performance and Combustion Characteristics of an SI Engine. *Fuel*. 89, 2713–2720.
- Fan, J., Zhu, Z., Budarin, V., Gronnow, M., Gomez, J. D., Macquarrie, D., and Clark, J. (2013). Microwave-enhanced Formation of Glucose from Cellulosic Waste. *Chem. Eng. Process.* 71, 37–42.
- Fan, S. P., Jiang, L. Q., Chia, C. H., Fang, Z., Zakaria, S., and Chee, K. L. (2014). High yield Production of Sugars from Deproteinized Palm Kernel Cake under Microwave Irradiation via Dilute Sulfuric Acid hydrolysis. *Bioresour. Technol.* 153, 69–78.
- Fazal, M. A., Haseeb, A. S. M. A., and Masjuki, H. H. (2010). Comparative Corrosive Characteristics of Petroleum Diesel and Palm Biodiesel for Automotive Materials. *Fuel Process. Technol.* 91, 1308–1315.
- Fazal, M. A., Haseeb, A. S. M. A., and Masjuki, H. H. (2011). Effect of Temperature on the Corrosion Behavior of Mild Steel upon exposure to Palm Biodiesel. *Energy*. 36, 3328–3334.
- Fazal, M. A., Haseeb, A. S. M. A., and Masjuki, H. H. (2012). Degradation of Automotive Materials in Palm Biodiesel. *Energy*. 40, 76–83.
- Fazal, M. A., Haseeb, A. S. M. A., and Masjuki, H. H. (2013). Corrosion Mechanism of Copper in Palm Biodiesel. *Corro. Sci.* 67, 50–59.

- Fazal, M. A., Haseeb, A. S. M. A., and Masjuki, H. H. (2014a). A Critical Review on the Tribological Compatibility of Automotive Materials in Palm Biodiesel. *Energ. Convers. Manage.* 79, 180–186.
- Fazal, M. A., Jakeria, M. R., and Haseeb, A.S.M.A. (2014b). Effect of Copper and Mild Steel on the Stability of Palm Biodiesel Properties: A comparative study. *Ind. Crop. Prod.* 58, 8–14.
- Ferrari, M. D., Guigou, M., and Lareo, C. (2013). Energy Consumption Evaluation of Fuel Bioethanol Production from Sweet Potato. *Bioresour. Technol.* 136, 377–384.
- Ghazikhani, M., Hatami, M., Safari, B., and Ganji, D. D. (2013). Experimental investigation of Performance Improving and Emissions Reducing in a Two Stroke SI engine by using Ethanol Additives. *Propulsion and Power Research.* 2, 276–283.
- Haseeb, A. S. M. A., Fazal, M. A., Jahirul, M. I., and Masjuki, H. H. (2011a). Compatibility of Automotive Materials in Biodiesel: A review. *Fuel.* 90, 922–931.
- Haseeb, A. S. M. A., Jun, T. S., Fazal, M.A., and Masjuki, H. H. (2011b). Degradation of Physical Properties of Different Elastomers upon exposure to Palm Biodiesel. *Energy.* 36, 1814–1819.
- Haseeb, A. S. M. A., Masjuki, H. H., Ann, L. J., and Fazal, M. A. (2010a). Corrosion Characteristics of Copper and Leaded Bronze in Palm Biodiesel. *Fuel Process. Technol.* 91, 329–334.
- Haseeb, A. S. M. A., Masjuki, H.H., Siang, C.T., and Fazal, M. A. (2010b). Compatibility of Elastomers in Palm Biodiesel. *Renew. Energ.* 35, 2356–2361.
- Hashem, M., and Darwish, S. M. I. (2010). Production of Bioethanol and Associated By-products from Potato Starch Residue Stream by *Saccharomyces Cerevisiae*. *Biomass Bioenerg.* 34, 953–59.
- He, B. Q., Wang, J. X., Hao, J. M., Yan, X.G., and Xiao, J. H. (2003). A study on Emission Characteristics of an EFI Engine with Ethanol Blended Gasoline Fuels. *Atmos. Environ.* 37, 949–957.
- Hermiati, E., Mangunwidjaja, D., Sunarti, T. C., Suparno, O., and Prasetya, B. (2012a). Microwave-assisted Acid Hydrolysis of Starch Polymer in Cassava Pulp in The Presence of Activated Carbon. *Procedia Chemistry.* 4, 238–244.

- Hermiati, E., Mangunwidjaja, D., Sunarti, T. C., Suparno, O., Prasetya, B., Anita, S. H., and Risanto, L. (2012b). Ethanol Fermentation of Microwave-assisted Acid Hydrolysate of Cassava Pulp with *Saccharomyces cerevisiae* in the Presence of Activated Carbon. *International Journal of Environment and Bioenergy*. 3(1), 12–24.
- Hong, Y. S., and Yoon, H. H. (2011). Ethanol Production from Food Residues. *Biomass Bioenerg.* 35, 3271–75.
- Hosseini, S. E., and Wahid, M. A. (2014). Utilization of Palm Solid Residue as a Source of Renewable and Sustainable Energy in Malaysia. *Renew. Sustain. Energ. Rev.* 40, 621–632.
- Hsieh, W. D., Chen, R. H., Wu, T. L., and Lin, T. H. (2002). Engine Performance and Pollutant Emission of an SI Engine using Ethanol–Gasoline Blended Fuels. *Atmos. Environ.* 36, 403–410.
- Hu, E., Xu, Y., Hu, X., Pan, L., and Jiang, S. (2012). Corrosion Behaviors of Metals in Biodiesel from Rapeseed oil and Methanol. *Renew. Energ.* 37, 371–378.
- IEA Bioenergy. (2005). *Benefits of bioenergy*. Retrieved on June 15, 2015, from [http://www.seai.ie/Renewables/Bioenergy/Benefits\\_of\\_bioenergy.pdf](http://www.seai.ie/Renewables/Bioenergy/Benefits_of_bioenergy.pdf)
- IEA. (2014). Key World Energy Statistics. *International Energy Agency*. Retrived on June 15, from <http://www.iea.org/publications/freepublications/publication/key-world-energy-statistics-2014.html>
- Izmirliglu, G., and Demirci, A. (2012). Ethanol Production from Waste Potato Mash by Using *Saccharomyces Cerevisiae*. *Appl. Sci.* 2, 738–753.
- Jafari, H., Idris, M. H., Ourdjini, A., Rahimi, H., and Ghobadian, B. (2011). EIS Study of Corrosion Behavior of Metallic Materials in Ethanol Blended Gasoline Containing Water as a Contaminant. *Fuel*. 90, 1181–1187.
- Jia, L. W., Shen, M. Q., Wang, J., and Lin, M. Q. (2005). Influence of Ethanol–Gasoline Blended Fuel on Emission Characteristics from a Four-Stroke Motorcycle Engine. *J. Hazard. Mater.* A123, 29–34.
- Karagoz, P., Rocha, I. V., Ozkan, M. and Angelidaki, I. (2012). Alkaline Peroxide Pretreatment of Rapeseed Straw for Enhancing Bioethanol Production by Same Vessel Saccharification and Co-Fermentation. *Bioresour. Technol.* 104, 349–357.
- Karavalakis, G., Short, D., Vu, D., Villela, M., Asa-Awuku, A., and Durbin, T. D. (2014). Evaluating the Regulated Emissions, Air toxics, Ultrafine Particles, and

- Black Carbon from SI-PFI and SI-DI Vehicles Operating on Different Ethanol and Iso-butanol Blends. *Fuel*. 128, 410–421.
- Khawla, B. J., Sameh, M., Imen, G., Donyes, F., Dhouha, G., and Raoudha, E. G. *et al.* (2014). Potato Peel as Feedstock for Bioethanol Production: A Comparison of Acidic and Enzymatic Hydrolysis. *Ind. Crop. Prod.* 52, 144–149.
- Kim, J. H., Lee, J. C., and Pak, D. (2011). Feasibility of Producing Ethanol from Food Waste. *Waste Manage.* 31, 2121–25.
- Kosugi, A., Kondo, A., Ueda, M., Murata, Y., Vaithanomsat, P., and Thanapase, W. *et al.* (2009). Production of Ethanol from Cassava Pulp via Fermentation with a Surface Engineered Yeast Strain Displaying Glucoamylase. *Renew. Energy*. 34, 1354–58.
- Kruger, L., Tuchscheerer, F., Mandel, M., Muller, S., and Liebsch, S. (2012). Corrosion Behavior of Aluminum Alloys in Ethanol Fuels. *J. Mater. Sci.* 47, 2798–806.
- Kumar, S., Singh, N., and Prasad, R. (2010). Anhydrous Ethanol: A Renewable Source of Energy. *Renew. Sust. Energ. Rev.* 14, 1830–1844.
- Kumoro, A. C., Ngoh, G. C., Hasan, M., Ong, C. H., and Teoh, E. C. (2008). Conversion of Fibrous Sago (Metroxylon sago) Waste into Fermentable Sugar via Acid and Enzymatic Hydrolysis. *Asian J. Sci. Res.* 1, 412–420.
- Kwanchareon, P., Luengnaruemitchai, A., and Jai-In, S. (2007). Solubility of a Diesel– Biodiesel–Ethanol Blend, its Fuel Properties, and its Emission Characteristics from Diesel Engine. *Fuel*. 86,1053–61.
- Kyriakides, A., Dimas, V., Lympelopoulou, E., Karonis, D., and Lois, E. (2013). Evaluation of Gasoline Ethanol–Water Ternary Mixtures used as a Fuel for an Otto Engine. *Fuel*. 108, 208–215.
- Lai, J. C., Rahman, W. A. W. A., and Toh, W. Y. (2013). Characterisation of Sago Pith Waste and its Composites. *Ind. Crop. Prod.*, 45, 319–326.
- Lee, K. M., Ngoh, G. C., and Chua, A. S. M. (2013). Process Optimization and Performance Evaluation on Sequential Ionic Liquid Dissolution–Solid Acid Saccharification of Sago Waste. *Bioresour. Technol.* 130, 1–7.
- Lee, W. S., Chen, I. C., Chang, C. H., and Yang, S. S. (2012). Bioethanol Production from Sweet Potato by Co-Immobilization of Saccharolytic Molds and *Saccharomyces Cerevisiae*. *Renew. Energ.* 39, 216–222.

- Lichts, F. O. (2015). RFA, *World Fuel Ethanol Production*, Washington, Renewable Fuels association. Retrieved on May 12, 2015, from: <http://ethanolrfa.org/pages/World-Fuel-Ethanol-Production>
- Limayem, A., and Ricke, S. C. (2012). Lignocellulosic Biomass for Bioethanol Production: Current Perspectives, Potential Issues and Future Prospects. *Prog. Energy Combust. Sci.* 38, 449–467.
- Linggang, S., Phang, Y., Wasoh, M. H., and Abd-Aziz, S. (2012). Sago Pith Residue as an Alternative Cheap Substrate for Fermentable Sugars Production. *Appl. Biochem. Biotechnol.* 167, 122–31.
- Linhares, F.N., Corrêa, H. L., Khalil, C. N., Leite, M. C. A. M., and Furtado, C. R. G. (2013). Study of the Compatibility of Nitrile Rubber with Brazilian Biodiesel. *Energ.* 49, 102–106.
- Lu, X., Xi, B., Zhang, Y., and Angelidaki, I. (2011). Microwave Pretreatment of Rape Straw for Bioethanol Production: Focus on Energy Efficiency. *Bioresour. Technol.* 102, 7937–7940.
- Macrelli, S., Mogensen, J., and Zacchi, G. (2012) Techno-economic evaluation of 2<sup>nd</sup> generation bioethanol production from sugar cane bagasse and leaves integrated with the sugar-based ethanol process. *Biotechnology for Biofuels* 5, p. 22.
- Maldonado, J. G., and Kane, R. D. (2008). Stress Corrosion Cracking of Carbon Steel in Fuel Ethanol Service. *Environmental induced cracking of materials.* 2, 337–347.
- Masum, B. M., Masjuki, H. H., Kalam, M. A., Fattah, I. M. R., Palash, S. M., and Abedin, M. J. (2013). Effect of Ethanol–Gasoline Blend on NO<sub>x</sub> Emission in SI engine. *Renew. Sust. Energ. Rev.* 24, 209–222.
- Melo, T. C., Machado, G. B., Belchior, C. R. P., Colaço, M. J., Barros, J. E. M., and Oliveira, E. J *et al.* (2012). Hydrous Ethanol–Gasoline Blends – Combustion and Emission Investigation on a Flex-Fuel Engine. *Fuel.* 97, 796–804.
- Miyazawa, T., and Funazukuri, T. (2005). Polysaccharide Hydrolysis Accelerated by Adding Carbon Dioxide under Hydrothermal Conditions. *Biotechnol. Progr.* 21, 1782–1785.
- Mood, S. H., Golfeshan, A. H., Tabatabaei, M., Jouzani, G. S., Najafi, G. H., Gholami, M., and Ardjmand, M. (2013). Lignocellulosic Biomass to Bioethanol, A Comprehensive Review with a Focus on Pretreatment. *Renew. Sust. Energ. Rev.* 27, 77–93.

- Nagamori, M., and Funazukuri, T. (2004). Glucose Production by Hydrolysis of Starch under Hydrothermal Conditions. *J. Chem. Technol. Biotechnol.* 79, 229–233.
- Najafi, G., Ghobadian, B., Tavakoli, T., Buttsworth, D. R., Yusaf, T. F., and Faizollahnejad, M. (2009). Performance and Exhaust Emissions of a Gasoline Engine with Ethanol Blended Gasoline Fuels using Artificial Neural Network. *Appl. Energ.* 86, 630–639.
- Ni, J., Wang, H., Chen, Y., She, Z., Na, H., and Zhu, J. (2013). A Novel Facile Two-Step Method for Producing Glucose from Cellulose. *Bioresour. Technol.* 137, 106–110.
- Norouzi, S., Eslami, F., Wysynski, M. L., and Tsolakis, A. (2012). Corrosion Effects of RME in Blends with ULSD on Aluminium and Copper. *Fuel Process. Technol.* 104, 204–210.
- Noureddini, H., and Byun, J. (2010). Dilute-acid pretreatment of distillers' grains and corn fiber. *Bioresour. Technol.* 101, 1060–1067.
- Oberoi, H. S., Vadlani, P.V., Saida, L., Bansal, S., and Hughes, J. D. (2011). Ethanol Production from Banana Peels using Statistically Optimized Simultaneous Saccharification and Fermentation Process. *Waste Manage.* 31, 1576–84.
- Okamoto, K., Nitta, Y., Maekawa, N., and Yanase, H. (2011). Direct Ethanol Production from Starch, Wheat Bran and Rice Straw by the White Rot Fungus *Trametes Hirsute*. *Enzyme Microb. Technol.* 48, 273–277.
- Ozsezen, A. N., and Canakci, M. (2011). Performance and Combustion Characteristics of Alcohol– Gasoline Blends at Wide-Open Throttle. *Energy.* 36, 2747–2752.
- Panga, X., Mu, Y., Yuan, J., and He, H. (2008). Carbonyls Emission from Ethanol-Blended Gasoline and Biodiesel-Ethanol-Diesel used in Engines. *Atmos. Environ.* 42, 1349–1358.
- Park, I. J., Yoo, Y. H., Kim, J. G., Kwak, D. H., and Ji, W. S. (2011). Corrosion Characteristics of Aluminum Alloy in Bio-ethanol Blended Gasoline Fuel: Part 2. The effects of Dissolved Oxygen in the Fuel. *Fuel.* 90, 633–639.
- Parmar, I., and Rupasinghe, H. P. V. (2013). Bio-Conversion of Apple Pomace into Ethanol and Acetic Acid: Enzymatic Hydrolysis and Fermentation. *Bioresour. Technol.* 130, 613–620.



- Perez, J. A., Ballesteros, I., Ballesteros, M., Saez, F., Negro, M. J., and Manzanares, P. (2008). Optimizing Liquid Hot Water pretreatment conditions to enhance Sugar Recovery from Wheat Straw for Fuel-Ethanol Production. *Fuel*. 87, 3640–3647.
- Qi, D. H., and Lee, C.F. (2014). Combustion and Emissions Behaviour for Ethanol–Gasoline-Blended Fuels in a Multipoint Electronic Fuel Injection Engine, *International Journal of Sustainable Energy*, DOI: 10.1080/14786451.2014.895004
- Rao, K., Chaudhari, V., Varanasi, S., and Kim, D. S. (2007). Enhanced Ethanol Fermentation of Brewery Waste Water using the Genetically Modified Strain *E. coli* KO11. *Appl. Microbiol. Biotechnol.* 74, 5–60.
- Rose, D. J., and Inglett, G. E. (2010). Production of Feruloylated Arabinoxylo-Oligosaccharides from Maize (*Zea mays*) Bran by Microwave-Assisted Autohydrolysis. *Food Chem.* 119, 1613–1618.
- Sales, L. C. M., and Sodre, J. R. (2012). Cold Start Emissions of an Ethanol-Fuelled Engine with Heated Intake Air and Fuel. *Fuel*. 95, 122–125.
- Sanchez, O. J., and Cardona, C. A. (2008). Review: Trends in Biotechnological Production of Fuel Ethanol from different Feedstocks. *Bioresour. Technol.* 99, 5270–95.
- Sanchez, R., Sanchez, C., Lienemann, C. P., and Todoli, J. L. (2015). Metal and Metalloid determination in Biodiesel and Bioethanol. *J. Anal. At. Spectrom.* 30, 64–101.
- Sarkar, N., Ghosh, S. K., Bannerjee, S., and Aikat, K. (2012). Bioethanol Production from Agricultural Wastes: An overview. *Renew. Energ.* 37, 19–27.
- Sasaki, M., Kabyemela, M., Malaluan, R., Hirose, S., Takeda, N., and Adschiri, T. (1998). Cellulose Hydrolysis in Subcritical and Supercritical Water. *J. Supercrit. Fluids.* 13, 261–268.
- Schifter, I., Diaz, L., Gomez, J., and Gonzalez, U. (2013). Combustion Characterization in a Single Cylinder Engine with Mid-Levels Hydrated Ethanol–Gasoline Blended Fuels. *Fuel*. 103, 292–298.
- Schifter, I., Diaz, L., Rodriguez, R., Gomez, J. P., and Gonzalez, U. (2011). Combustion and Emissions Behavior for Ethanol–Gasoline Blends in a Single Cylinder Engine. *Fuel*. 90, 3586–3592.

- Shahir, S. A., Masjuki, H. H., Kalam, M. A., Imran, A., and Ashraful, A. M. (2015). Performance and Emission Assessment of Diesel–Biodiesel–Ethanol/Bioethanol Blend as a Fuel in Diesel Engines: A review. *Renew. Sust. Energ. Rev.* 48, 62–78.
- Shahir, S. A., Masjuki, H. H., Kalam, M. A., Imran, A., Rizwanul Fattah, I. M., and Sanjid, A. (2014). Feasibility of Diesel–Biodiesel–Ethanol/Bioethanol Blend as Existing CI Engine Fuel: An Assessment of Properties, Material Compatibility, Safety and Combustion. *Renew. Sust. Energ. Rev.* 32, 379–395.
- Sileghem, L., Coppens, A., Casier, B., Vancoillie, J., and Verhelst, S. (2014). Performance and Emissions of Iso-stoichiometric Ternary GEM Blends on a Production SI Engine. *Fuel*. 117, 286–293.
- Singh, B., Korstad, J., and Sharma, Y.C. (2012). A Critical Review on Corrosion of Compression Ignition (CI) Engine Parts by Biodiesel and Biodiesel blends and its Inhibition. *Renew. Sustain. Energ. Rev.* 16, 3401–3408.
- Singhal, R. S., Kennedy, J. F., Gopalakrishnan, S. M., Kaczmarek, A., Knill, C.J., and Akmar, P. F. (2008). Review: Industrial Production, Processing, and Utilization of Sago Palm-derived Products. *Carbohydr. Polym.* 72, 1–20.
- Sluiter, A., and Sluiter, J. (2008). Determination of Starch in Solid Biomass Samples by HPLC. *NREL Chemical Analysis and Testing Laboratory Analytical Procedures*, NREL/TP-510-42624.
- Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2011). Determination of Structural Carbohydrates and Lignin in Biomass. *NREL Chemical Analysis and Testing Laboratory Analytical Procedures*, NREL/TP-510-42618.
- Su, M. Y., Tzeng, W.S., and Shyu, Y.T. (2010). An Analysis of Feasibility of Bioethanol Production from Taiwan Sorghum Liquor Waste. *Bioresour. Technol.* 101, 6669–75.
- Sun, Y., and Cheng, J. (2002). Hydrolysis of Lignocellulosic Materials for Ethanol Production: a review. *Bioresour. Technol.* 83, 1–11.
- Sunarti, T. C., Dwiko, M., Derosya, V., and Meryandini, A. (2012). Effect of Microwave Treatment on Acid and Enzymes Susceptibilities of Sago Pith. *Procedia Chemistry*. 4, 301–307.
- Taherzadeh, M. J., and Karimi, K. (2007a). Enzyme-based hydrolysis processes for ethanol from lignocellulosic materials: a review. *Bioresources*. 2(4), 707–738.

- Taherzadeh, M. J., and Karimi, K. (2007b). Acid-based Hydrolysis Processes for Ethanol from Lignocellulosic Materials: A review. *BioResources*. 2, 472–499.
- Taherzadeh, M. J., and Karimi, K. (2008). Pretreatment of Lignocellulosic Wastes to Improve Ethanol and Biogas production: a review. *Int. J. Mol. Sci.* 9, 1621–1651.
- Tasic, M. B., Konstantinovic, B. V., Lazic, M. L., and Veljkovic, V. B. (2009). The Acid Hydrolysis of Potato Tuber Mash in Bioethanol Production. *Biochem. Eng. J.* 43, 208–211.
- Thomson, J. K., Pawel, S. J., and Wilson, D. F. (2013). Susceptibility of Aluminum Alloys to Corrosion in Simulated Fuel Blends Containing Ethanol. *Fuel*. 111, 592–597.
- Topgul, T., Yucesu, H. S., Cinar, C., and Koca, A. (2006). The Effects of Ethanol–Unleaded Gasoline Blends and Ignition Timing on Engine Performance and Exhaust emissions. *Renew. Energ.* 31, 2534–2542.
- Tsubaki, S., Oono, K., Onda, A., Yanagisawa, K., and Azuma, J. I. (2012). Microwave-assisted Hydrothermal Hydrolysis of Cellobiose and effects of Additions of Halide Salts. *Bioresour. Technol.* 123, 703–706.
- Turner, J. W. G., Pearson, R. J., Dekker, E., Iosefa, B., Johansson, K., and Bergström K. (2013). Extending the Role of Alcohols as Transport Fuels Using Iso-Stoichiometric Ternary Blends of Gasoline, Ethanol and Methanol. *Appl. Energ.* 102, 72–86.
- Umoren, S. A., Eduok, U. M., Solomon, M. M., and Udoh, A. P. (2011). Corrosion Inhibition by Leaves and Stem Extracts of *Sida acuta* for Mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> solutions investigated by Chemical and Spectroscopic Techniques. *Arab. J. Chem.* doi:10.1016/j.arabjc.2011.03.008
- Vavouraki, A. I., Angelis, E. M., and Kornaros, M. (2013). Optimization of Thermo-Chemical Hydrolysis of Kitchen Wastes. *Waste Manage.* 33, 740–745.
- Wu, C. W., Chen, R. H., Pu, J. Y., and Lin, T. H. (2004). The influence of Air–fuel ratio on Engine Performance and Pollutant Emission of an SI Engine using Ethanol–Gasoline-Blended Fuels. *Atmos. Environ.* 38, 7093–7100.
- Yan, S., Li, J., Chen, X., Wu, J., Wang, P., Ye, J., and Yao, J. (2011). Enzymatical Hydrolysis of Food Waste and Ethanol Production from the Hydrolysate. *Renew. Energ.* 36, 1259–65.

- Yang, H. H., Liu, T.C., Chang, C. F., and Lee, E. (2012). Effects of Ethanol-Blended Gasoline on Emissions of Regulated Air Pollutants and Carbonyls from Motorcycles. *Appl. Energ.* 89, 281–286.
- Yao, Y. C., Tsai, J. H., and Wang, I. T. (2013). Emissions of Gaseous Pollutant from Motorcycle Powered by Ethanol–Gasoline Blend. *Appl. Energ.* 102, 93–100.
- Yemis, O., and Mazza, G. (2011). Acid-catalyzed Conversion of Xylose, Xylan and Straw into Furfural by Microwave-Assisted Reaction. *Bioresour. Technol.* 102, 7371–7378.
- Yoo, Y. H., Park, I. J., Kim, J. G., Kwak, D. H., and Ji, W. S. (2011). Corrosion Characteristics of Aluminum Alloy in Bio-ethanol Blended Gasoline Fuel: Part 1. The Corrosion Properties of Aluminum Alloy in High Temperature Fuels. *Fuel.* 90, 1208–1214.
- Yucesu, H. S., Sozen, A., Topgul, T., and Arcaklioglu, E. (2007). Comparative Study of Mathematical and Experimental Analysis of Spark Ignition Engine Performance used Ethanol–Gasoline Blend Fuel. *Appl. Therm. Eng.* 27, 358–368.
- Yucesu, H. S., Topgu, T., Cinar, C., and Okur, M. (2006). Effect of Ethanol–Gasoline Blends on Engine Performance and Exhaust Emissions in different Compression ratios. *Appl. Therm. Eng.* 26, 2272–2278.
- Zhu, S., Wu, Y., Yu, Z., Zhang, X., Wang, C., and Yu, F. *et al.* (2006). Production of Ethanol from Microwave Assisted Alkali Pretreated Wheat Straw. *Process Biochem.* 41, 869–873.
- Zhuang, Y., and Hong, G. (2013). Primary investigation to Leveraging Effect of using Ethanol Fuel on Reducing Gasoline Fuel Consumption. *Fuel.* 105, 425–431.