LIQUEFACTION OF NATURAL RUBBER TO LIQUID FUEL USING WATER AND ALCOHOL SOLVENTS

NABEEL AHMAD

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2019

LIQUEFACTION OF NATURAL RUBBER TO LIQUID FUEL USING WATER AND ALCOHOL SOLVENTS

NABEEL AHMAD

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2019

UNIVERSITY OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

[redacted]

Name of Candidate : Nabeel Ahmad
Registration/Matric No : KHA150036
Name of Degree : Doctor of Philosophy
Title of Dissertation/Thesis ("this Work"):
LIQUEFACTION OF NATURAL RUBBER TO LIQUID FUEL USING WATER AND ALCOHOL SOLVENTS
Field of Study: Chemical Engineering

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;
(2) This Work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action a[redacted].

Candidate's Signatur[redacted] Date: 29 July 2019

Subscribed and solemnly declared before,

Witness's[redacted] Date: 29/7/2019

Name:
Designation:

UNIVERSITI MALAYA
PERAKUAN KEASLIAN PENULISAN

[redacted]

Nama : Nabeel Ahmad
No. Matrik : KHA150036
Nama Ijazah : Doktor Falsafah

Tajuk Kertas Projek/Laporan Penyelidikan/Disertasi/Tesis ("Hasil Kerja ini"):

Pencairan getah asli kepada cecair bahan api menggunakan air dan larutan alkohol

Bidang Penyelidikan: Kejuruteraan kimia

Saya dengan sesungguhnya dan sebenarnya mengaku bahawa:

(1) Saya adalah satu-satunya pengarang/penulis Hasil Kerja ini;
(2) Hasil Kerja ini adalah asli;
(3) Apa-apa penggunaan mana-mana hasil kerja yang mengandungi hakcipta telah dilakukan secara urusan yang wajar dan bagi maksud yang dibenarkan dan apa-apa petikan, ekstrak, rujukan atau pengeluaran semula daripada atau kepada mana-mana hasil kerja yang mengandungi hakcipta telah dinyatakan dengan sejelasnya dan secukupnya dan satu pengiktirafan tajuk hasil kerja tersebut dan pengarang/penulisnya telah dilakukan di dalam Hasil Kerja ini;
(4) Saya tidak mempunyai apa-apa pengetahuan sebenar atau patut semunasabahnya tahu bahawa penghasilan Hasil Kerja ini melanggar suatu hakcipta hasil kerja yang lain;
(5) Saya dengan ini menyerahkan kesemua dan tiap-tiap hak yang terkandung di dalam hakcipta Hasil Kerja ini kepada Universiti Malaya ("UM") yang seterusnya mula dari sekarang adalah tuan punya kepada hakcipta di dalam Hasil Kerja ini dan apa-apa pengeluaran semula atau penggunaan dalam apa jua bentuk atau dengan apa juga cara sekalipun adalah dilarang tanpa terlebih dahulu mendapat kebenaran bertulis dari UM;
(6) Saya sedar sepenuhnya sekiranya dalam masa penghasilan Hasil Kerja ini saya telah melanggar suatu hakcipta hasil kerja yang lain sama ada dengan niat atau sebaliknya, saya boleh dikenakan tindakan undang-undang atau apa-apa tindakan lain seba[redacted] UM.

Tandatangan Calo Tarikh: 29 July 2019

Diperbuat dan sesungguhnya diakui di hadapan,

Tand[redacted] Tarikh: 29/7/19

Nama:

Jawatan:

LIQUEFACTION OF NATURAL RUBBER TO LIQUID FUEL USING WATER AND ALCOHOL SOLVENTS

ABSTRACT

Natural rubber is a renewable resource that can potentially be used to produce liquid fuels via liquefaction process. Natural rubber is a rich biomass resource in Malaysia, and it is therefore very important that it could be utilized for more beneficial purposes, particularly in the context of development of biofuels. In this study, natural rubber was characterized using TGA and elemental analysis to understand its thermal and chemical properties, then it was liquefied at low temperature using hydrothermal liquefaction technique to produce liquid fuels. Furthermore, to improve the quality and quantity of the oil, the different types of alcohols were used as a solvent to replace the water. For all mentioned processes, the effect of different parameters such as temperature, material to solvent ratio and time were studied. All the obtained liquid products were analyzed by various methods such as pycnometer, viscometer, pH meter, FTIR, GCMS, and elemental analysis. Several important findings were also discussed in this study including potential energy recovery from natural rubber and energy consumption ratio study. In addition, the techno-economic study also provided in this thesis for feasibility assessment of the liquefaction of natural rubber using water and propanol as a solvent.

PENCAIRAN GETAH ASLI KEPADA CECAIR BAHAN API MENGGUNAKAN AIR DAN LARUTAN ALKOHOLS

ABSTRAK

Getah asli adalah sumber yang boleh diperbaharui yang berpotensi digunakan untuk menghasilkan bahan api cecair melalui proses pencairan hidroterma. Getah semulajadi adalah sumber biomas yang kaya di Malaysia, dan oleh itu sangat penting untuk digunakan bagi tujuan yang lebih bermanfaat, terutamanya dalam konteks pembangunan biofuel. Dalam kajian ini, getah asli dicirikan menggunakan analisis TGA dan elemen untuk memahami sifat haba dan kimianya, kemudian ia dicairkan pada suhu rendah menggunakan teknik pencairan hidroterma untuk menghasilkan bahan api cecair. Tambahan pula, untuk meningkatkan kualiti dan kuantiti minyak, pelbagai jenis alkohol telah digunakan sebagai pelarut untuk menggantikan air. Untuk semua proses yang disebutkan, kesan parameter yang berbeza seperti suhu, bahan kepada nisbah pelarut dan masa dikaji. Semua produk cecair yang diperolehi dianalisis dengan pelbagai kaedah seperti pycnometer, visketer, meter pH, FTIR, GCMS, dan analisis elemen. Beberapa penemuan penting juga dibincangkan dalam kajian ini termasuk pemulihan tenaga berpotensi dari kajian getah asli dan penggunaan tenaga. Di samping itu, kajian teknoekonomi juga disediakan dalam laporan ini untuk penilaian kebolehlaksanaan proses.

ACKNOWLEDGEMENTS

First of all and foremost, I thank to my ALLAH almighty for giving me strength, willpower, patience against many odds and fulfilling my prayers.

I would like to express my sincere gratitude to my supervisor Prof. Dr. Wan Mohd Ashri Bin Wan Daud and my co-supervisor Dr. Faisal Abnisa for the continuous support of my Ph.D. study and related research, for their patience, motivation, and immense knowledge. Their guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisors and mentors for my Ph.D study. I would like to thank them for their insightful comments and encouragement, but also for the hard question which incented me to widen my research from various perspectives. My sincere thanks also goes to all the staff members of University of Malaya, who provided me an opportunity to learn new things, and who gave access to the laboratory and research facilities. Without their precious support it would not be possible to conduct this research.

I would like to acknowledge financial funding support provided by University of Malaya through grant GSP-MOHE, project number MO008-2015 and through IPPP grant number PG074-2016A.

I thank my fellow lab mates in for the stimulating discussions, for the sleepless nights we were working together before deadlines, and for all the fun we have had in the last three and half years. Last but not the least, I would like to thank my family: my parents and to my brothers and sister for supporting me spiritually throughout writing this thesis and my life in general. I would like to thank my beloved fiancé Dr. Hira Abrar for being a great source of support and encouragement during hard and difficult times.

Nabeel Ahmad

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

NR : Natural rubber

SMR : Standard Malaysian rubber

HTL : Hydrothermal liquefaction

RES : Renewable Environment Solutions

TGA : Thermogravimetric analysis

FTIR : Fourier transform infrared radiation

GCMS Gas chromatograph–mass spectrometer

DI : Deionized

σ : Standard deviation

ρ : density

η : viscosity

HHV : High heating value

β : Beta

ST : Scrap tire

EP : Energy potential

G & A : General & Administrative

ROI : Return on investment

PI : Profitability index

LIST OF APPENDICES

Appendix A: List of publications and papers presented

CHAPTER 1: INTRODUCTION

1.1 Background

Natural rubber (NR) is an organic material obtained from *Hevea brasiliensis* tree and it is widely used to produce polymer products such as cloths, tires, and rubber bands. (Kohjiya & Ikeda, 2014). The utilization of NR in the making of various goods showed that this material play an important role in different manufacturing sectors. According to statistics, Malaysia produced 821.27 kilotonnes of NR in average annually from 2010 to 2016. However, the average utilization of NR was found to be low at about 55% only (Malaysian Rubber Research and Development Board, 2017). This situation caused decline in the price of NR in stated year period (Olaniyi, Abdullah, Ramli, & Sood, 2013). As a consequence, the fertile land for NR plantation were occupied for other commodities which is dominated by palm oil, and as a result it also affected the rubber cultivators and caused environmental issue (Hai, 2000; Saswattecha, Kroeze, Jawjit, & Hein, 2016).

Now, it is a challenge to ensure the maximum utilization of rubber and products produced and have high demand in the market. In this respect, the conversion of NR into the valuable commodities would be a viable option. Generally, NR is directly used for the production of end product without involving any chemical conversion process (Kohjiya & Ikeda, 2014). Surely, by the conversion of NR into the valuable commodities such as fuels and chemicals will open new opportunity to breakdown the problems of NR utilization.

Kawser and Farid (2000) initially carried out pyrolysis of natural rubber at high temperature of 500°C for the production of liquid fuels and subsequently liquefied the oil with the obtained yield of 72 wt.%. The oil obtained from this pyrolysis process was shown to have low oxygen content which would serve as better alternative fuel. This property makes NR-based oil to be more superior to the wood-biomass oil. The oil obtained from wood biomass contains a high level of oxygen which consequently lowers the calorific value and causes corrosiveness (Abnisa & Wan Daud, 2014). Other types of biomasses which have high calorific values such as scrap tire has also been utilized for the production of oil. Nevertheless, natural rubber is still considered the better alternative option because scrap tire contains higher sulfur contents.

At high temperature of 500^{o}C, natural rubber is converted to liquid fuel. The degradation of natural rubber at high temperature is an endothermic process. A lot of energy is required to reach this high temperature which in turn makes the process expensive. The temperature can be reduced by manipulating other process parameters such as increasing the pressure, introducing the hydrogen gas and use of solvent.

Hydrothermal liquefaction also known as hydrous pyrolysis is one of the most promising techniques in thermal conversion method that fulfills the criteria of reducing the temperature by increasing the corresponding pressure. This process is normally carried out in a closed vessel. The evolution of hot gaseous reaction products increases the internal pressure of the reactor. Consequently, this process is subjected to self-generated pressure in which its extent depends on the reaction temperature and the amount of solvent and material used. This technique was initially introduced by Berl in 1944 for the production of oil from plant materials (Berl, 1944). Currently, this process has been applied on various kinds of biomasses and organic materials for the production of bio-oil, char and gas. Many findings showed that this technique is a viable option for the production of high yield bio-oil at low temperature conditions.

The liquefaction technique was later improved by using different kinds of solvents. Recently, it has been reported that processing biomass with organic solvents can lead to better bio-oil quality and quantity. These solvents can be recycled by evaporation after liquefaction and can be reused. In this study, the use of liquefaction process was evaluated comprehensively in producing liquid fuel from natural rubber.

1.2 Problem statement

During the pyrolysis of natural rubber, high temperature of 500°C is required for the production of liquid fuels. High temperature process requires high energy consumption thereby increasing the budget of the process. According to Farret and Simões, all processes that consume high energy for making a commodity become less economical and attractive (Farret & Simões, 2006). Therefore, in this study, the main objective is to reduce the temperature through the optimization of pressure and solvent conditions.

Liquefaction is a process that can liquefy natural rubber to liquid fuel at low temperature by increasing the corresponding pressure. In this study, hydrothermal liquefaction process has been employed to convert natural rubber into liquid fuel at low temperature. Water is a common solvent used in hydrothermal liquefaction process since it is cheap, abundant, polar in nature, and non-hazardous. However, it has some flaws as it results in low liquid yield and the oil products tend to have high oxygen contents, high corrosivity and high viscosity (Yang, Gilbert, & Xu, 2009). Therefore, liquefaction process for natural rubber was also further improved by utilization of other solvents. Durak has enlisted the features required for the selection of good solvent: non-acidic, high proticity, low boiling point, easily separable from the product, and have low critical points (Durak, 2015). Hence, in this study, the same criteria has been adopted for the selection of solvents and three different organic solvents have been investigated and were compared with water. Organic solvents such as methanol, ethanol and propanol are usually considered to be the good solvents for the synthesis of bio oil from different biomasses.

According to Ravignani et al., when a new process is considered for replacing a current process or a sequence of processes, the economic viability of the new process should be evaluated (Ravignani, Tipnis, & Mantel, 1982). This process involves the utilizing of natural rubber as feedstock for the first time. Therefore, in order to assess the liability of a proposed process, the economic feasiblity of the process in term of investment and profits has also been investigated.

1.3 Objectives of research

At present, there is no information available on the liquefaction of natural rubber. The followings are the main objectives of the present study:

1. To study the effect of process parameters on the production of liquid fuel from natural rubber using hydrous pyrolysis process (Hydrothermal liquefaction).
2. To study the effect of different organic solvents on the liquid yield and process parameter behavior in natural rubber liquefaction.
3. To study the liquefaction of natural rubber and scrap tire to liquid fuel using water solvent for a comparative study.
4. To evaluate the economic feasibility of liquefaction process for the production of liquid from natural rubber at optimum conditions using water and organic solvent.

1.4 Flow of the research work

Figure 1.1 is showing the flow of the research work that has been explained in detail in the thesis. As natural rubber is tropical planation crop available in Malaysia in huge quantities, making it a potential alternative source to substitute fossil fuels. So the first investigation of this research is to characterize the natural rubber using elemental and proximate analysis and to study the hydrothermal liquefaction of natural rubber for the production of liquid fuels. The second investigation was aimed to enhance the quantity and quality of liquid fuels produced from natural rubber by employing different alcohols as a process solvents. Last study aimed to assess the economic viability of the process by estimation of process cost and return on investment.

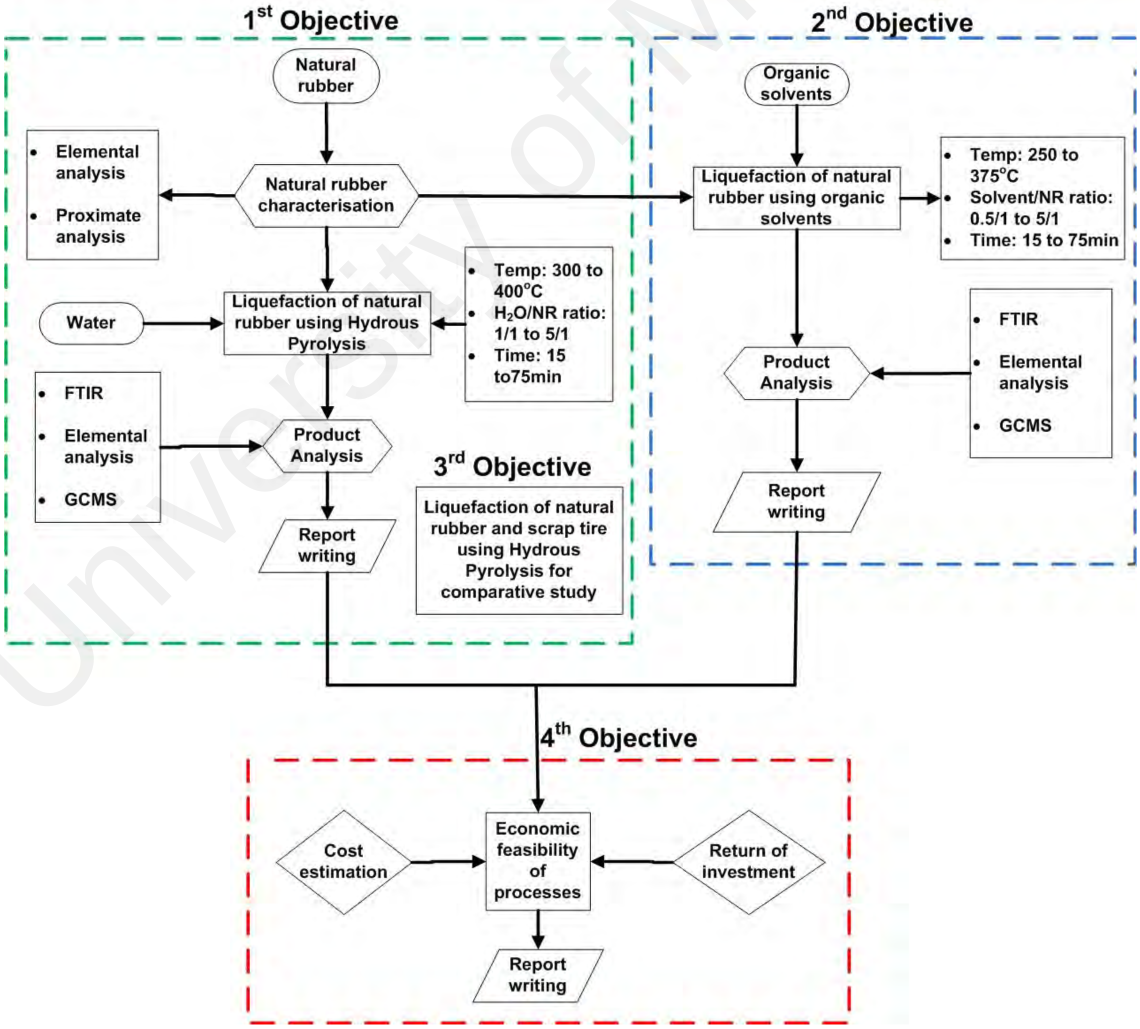


Figure 1-1: Flow of research work

1.5 Scope of study

In Malaysia, there are various grades of natural rubber available such as SMR L, SMR 5, SMR 10, SMR 20, and SMR 50. All of these grades can be utilized for the production of liquid fuel as they are polyisoprene based rubbers. In this study, natural rubber of grade SMR L was utilized in liquefaction process as it is rich in volatile matter and contains low dirt and ash contents. Three products namely liquid oil, char and gas were produced during the process. Since liquid is the main product, the product characterizations were done only for liquid.

To improve the quality and quantity of oil, many researchers have utilized different catalysts, solvents, and hydrogen gas atmospheres. However, there are some problems associated with the use of a catalyst in the process: the catalyst is a consumable and therefore adds to the running cost; the catalyst can have a short life-cycle due to deactivation; the catalyst leads to increased level of solid residue, thereby increasing the process cost in terms of its separation and disposal. Similarly, the use of hydrogen gas is expensive due to the need of a complicated equipment or reactor plugging in the proposed process. The use of solvent seems to be positive approach which was selected to be used in this research. The investigation on solvent effect is limited only to water and organic solvents in which different alcohol compounds were selected as organic solvent.

To assess the feasibility of the process, an investigation on economic aspects is also required. There are several methods that can be employed for the economic assessment of the process such as investment calculation, net future worth, pay-back time, net present worth, return on investment, and discounted cash-flow rate of return. Among these methods, the return on investment (ROI) was chosen to evaluate the economic feasibility. The advantage of ROI is that it could be used as a rough guide for judging projects and when decisions have to be made on whether to install additional equipment to reduce operating costs.

1.6 Importance of this research

a) This research will contribute to new insights on a new alternative energy source to substitute the depleting fossil fuel which is greener and renewable.
b) The study will provide the procedure for the production of liquid fuels from natural rubber via liquefaction process.
c) The success of this project could create a new field in the area of production of renewable fuels that could subsequently create employment opportunities and will help in the development of the nation economy and growth.

1.7 Outline of the thesis

The format of this thesis follows the article style format as stated in the University of Malaya guidelines. All of the work that was described in this thesis have been published in ISI journals. The complete framework as well as structural outline of this thesis are discussed in this section. The thesis comprises of six chapters, and each chapter is introduced as follows.

Chapter 1: This chapters discuss the background of research, statement of problem, research objectives, flow of work, scope of study, importance of this research, and outline of the thesis.

Chapter 2: This chapter discusses a broad literature review and the relevant discussions regarding the liquefaction from various points of view, including mechanism, feedstock production and statistics, exploration of different studies in liquefaction using different solvents and feedstocks, characteristics of products and by-products, and economic assessment. The content of this chapter has been published in the Journal of RSC Advances (Ahmad, N., F. Abnisa, and W.M.A.W. Daud, Potential use of natural rubber to produce liquid fuels using hydrous pyrolysis - A review. RSC Advances, 2016. 6: p. 68906-68921)

Chapter 3: Liquefaction of natural rubber to liquid fuels via hydrous pyrolysis. This chapter describes the work of objective 1. The scope of this chapter is limited only to investigation of water as a solvent for the production of liquid fuels from natural rubber. This work has been published in the journal of Fuel (Ahmad, N., F. Abnisa, and W.M.A. Wan Daud, Liquefaction of natural rubber to liquid fuels via hydrous pyrolysis. Fuel, 2018. 218: p. 227-235)

Chapter 4: Effect of alcohol solvents in the liquefaction process for liquid fuel production from natural rubber. This chapter describes the work of objective 2. The scope of this chapter is limited only to the investigation of different alcohol solvents on liquefaction process for the production of liquid fuels from natural rubber. The contents of this work has been published in the Journal of Analytical and Applied pyrolysis. (Ahmad, N., F. Abnisa, and W.M.A. Wan Daud, Synthesis of valuable intermediate products from natural rubber under supercritical alcohol conditions, Journal of Analytical and Applied pyrolysis. 2019) In Press, Accepted Manuscript.

Chapter 5: liquefaction of natural rubber and scrap tire to liquid fuels. This chapter is a comparative study of hydrothermal liquefaction of natural rubber and scrap tire.

Chapter 6: Techno-economic study of liquefaction of natural rubber. This chapter describes the work of objective 3. The scope of this chapter is limited only to the investigation of economic assessment of the liquefaction process using water and alcohol solvents for the production of liquid fuels. This work has been submitted for publication in the Chemical Engineering Journal.

Chapter 7: This chapter reviews the significant outcomes and core conclusions related to the research objectives.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

The depletion of fossil fuels and their impact on global warming has become a well-known and dominant issue over the past decades; consequently, this issue has motivated researchers to create alternatives for fossil fuels (AldoVieira et al., 2009; Dell, Moseley, & Rand, 2014). The reserves of fossil fuels, such as petroleum, gas and coal, are available up to 2044, 2046, and 2112, respectively (Shafiee & Topal, 2009). Natural gas and crude oil are consumed by around 9,413.69 million cubic meter per day and 77.83 million barrel per day worldwide ("The World Factbook 2013-14," 2013). The high consumption as well as depletion of fossil fuels are predicted to result in excessive increase in their prices in the next decades (Arapogianni, Moccia, Pineda, & Wilkes, 2014). To address this issue, scholars have developed alternative fuels that are efficient, environment friendly, and economical (Abnisa & Wan Daud, 2014; Dincer & Rosen, 2013).

Environmental aspect associated with using fossil fuels has been a major global issue for the past decades (Agarwal, 2007). Burning of fossil fuels has substantially increased environmental problems because of emission of harmful pollutants, such as SOx, NOx, CO_2, and hydrocarbons, which cause ozone depletion, acid rain, and global warming (Heidenreich & Foscolo, 2015; Hoel & Kverndokk, 1996; Kalogirou, 2004; Mohtasham, 2015; Rushdi, BaZeyad, Al-Awadi, Al-Mutlaq, & Simoneit, 2013). The use of fossil fuels contribute to 62% of global CO_2 emissions (Höök & Tang, 2013). China and the USA are the major emitters (about 44% of the global emission) of greenhouse gases from fossil fuels (Boden, Marland, & Andres, 2015; Doble, Rollins, & Kumar, 2010). According to the National Energy Information Center, the USA currently contributes approximately 19% of the worldwide CO_2 emissions (Energy; Leggett, 2011). By the year 2030, the CO_2

emission levels are estimated to increase to 40 billion Mg per year, which is an alarming situation (Zhen Fang, 2013). To combat these environmental issues, Barbose et al suggested that the use of fossil fuels should be reduced, and renewable fuels should be deployed as replacement for fossil fuels for environmental and social benefits (Ballester & Furió, 2015; Barbose, Bird, Heeter, Flores-Espino, & Wiser, 2015).

Many alternative energy resources for fossil fuels are available worldwide. Fuels are employed to produce heat, mechanical work, and power generation for subsequent use in people's daily lives (Gupta). An ideal fuel should possess the following properties: high hydrocarbon content, high calorific value, low cost, low moisture content, controllable combustion, harmless combustion products, easily transported at low cost, and low storage cost (R. V. Gadag, 2007; Sahgal); a suitable alternative fuel should also fulfill the criteria of ideal fuel (Dincer & Zamfirescu, 2014; Hua, Oliphant, & Hu, 2016). Various alternative renewable energy sources, such as biomass, bio-diesel, alcohol-fuels, ammonia, solar thermal power, hydropower, and wind power, can be used as substitute for fossil fuels (Abas, Kalair, & Khan, 2015; Mohtasham, 2015).

Biomass is one of the available potential alternative renewable sources of energy and can be used as substitute to fossil fuels (Abnisa, Wan Daud, Ramalingam, Azemi, & Sahu, 2013). Biomass is an organic material derived from living organisms, such as plants or animals (P. Basu, 2010). Biomass is available in bulk and can be found in agricultural residues (rice husk, pine cone, bagasse, wheat straw, etc (Aboyade, Carrier, Meyer, Knoetze, & Görgens, 2013; Ateş, 2011; Garcìa-Pèrez, Chaala, & Roy, 2002; Sánchez, Martínez, Gómez, & Morán, 2007; Ye, Cao, & Zhao, 2008)), wood residues (pine, weed, and fir sawdust (Sharypov et al., 2002)), and in industrial and municipal solid wastes (palm shell, wheat straw, legume straw, walnut shell, and so on (Abnisa et al., 2013; Haykiri-Acma & Yaman, 2010; Paradela, Pinto, Ramos, Gulyurtlu, & Cabrita, 2009;

Pinto, Paradela, Gulyurtlu, & Ramos, 2013; Samanya, Hornung, Apfelbacher, & Vale, 2012; Wei, Zhang, & Xu, 2011)). Natural rubber is a biomass usually obtained from the rubber tree, guayule plant, russian dandelion, and rubber rabbitbrush (Barlow, 1970; Mooibroek & Cornish, 2000; P.M. Priyadarshan, 2009; Ray, 2010; Rogers & Cornish, 2005; Simmonds, 1994; J. van Beilen, 2006; J. B. van Beilen & Poirier, 2007a, 2007b; Whaley & Bowen, 1947).

Natural rubber is one of the potential sources in meeting future energy needs. Natural rubber is a vital, strategic, and unique feedstock used in huge quantities worldwide (Rogers & Cornish, 2005). Natural rubber is an important plantation crop in tropical Asia and is abundant in Malaysia, Indonesia, Thailand, and various central African countries (Barlow, 1970). The rubber tree grows optimally in warm, humid climate (Rogers & Cornish, 2005). Natural rubber is a polymer of the organic compound isoprene (polyisoprene $(C_5H_8)n$) with minor amounts of impurities, including other organic compounds and water (Morton, 1999).

In 1997, the global production of natural rubber was estimated about 5 million metric tons, which increases gradually on account of its high usage (F. Chen & Qian, 2002). Due to its high availability, researchers utilize natural rubber as a useful feedstock for production of valuable chemical commodities (fuels, fertilizers, and chemicals) through depolymerisation (Niaounakis, 2013).

Depolymerization is the process of breaking down large organic polymeric molecules into small molecules or their respective monomers (Carraher & Seymour, 2007). Depolymerization processes include thermal degradation (pyrolysis, hydrogenation, and gasification), photo-induced degradation, chemical degradation (solvolysis, hydrolysis, ozonolysis, and oxidation), and biological degradation (Abbas, 2010; Aguado & Serrano, 2006). Hydrothermal liquefaction which is also known as a Hydrous pyrolysis, is an appropriate technique for conversion of natural rubber into liquid fuels (P. Basu, 2010; Scheirs & Kaminsky, 2006). In liquefaction process, materials, such as plastic, rubber, or biomass are heated using water to generate useful chemical commodities, such as liquid fuels. The use of water in hydrous pyrolysis presents an advantage over other depolymerization techniques because water is abundant, cheap, and environment friendly. Moreover, separation of the produced liquid fuels from water is easier and more economical compared with other techniques (Funazukuri, Takanashi, & Wakao, 1987; Savage, 1999; L. Zhang, Zhou, Duan, Wang, & Xu, 2016). Generally, the products of pyrolysis are char, oil, and gas. Liquefaction is a three step process: (i) the material is chopped into small pieces; (ii) the material is then heated at temperatures ranging from 200 °C to 300 °C using water at high pressure; and (iii) the produced hydrocarbons are broken down into light hydrocarbons at about 500 °C (P. Basu, 2010). This process is commercially employed to convert agricultural organic waste into valuable chemical commodities, such as fuels, fertilizers, and other chemicals (P. Basu, 2010). Changing World Technologies and the Renewable Environment Solutions LLC (RES) established the first commercial plant of hydrous pyrolysis in Carthage, Tunisia (T. N. Adams, Appel, Samson, & Roberts, 2004).

This chapter presents a review of the depolymerization of natural rubber through liquefaction. The influences of process parameters such as temperature, pressure, and water to material ratio on the product yield and composition are also discussed. Moreover, this chapter provides important information related to natural rubber statistics and alternative sources.

2.2 Natural Rubber and its sources

2.2.1 Natural rubber

Generally, natural rubber is produced from the rubber tree (*Hevea brasiliensis*), guayule plant, Russian dandelion, rubber rabbitbrush, fig tree, goldenrod, and sunflower. Natural rubber, also known as cis-1,4-polyisoprene and denoted as $(C_5H_8)n$, is a hydrocarbon with a molecular weight ranging from 1 to 2.5 e10^6 (Roberts, 1988; Vaysse, Bonfils, Sainte-Beuve, & Cartault, 2012). The structure of natural rubber and its monomer is shown in Figure 2.1.

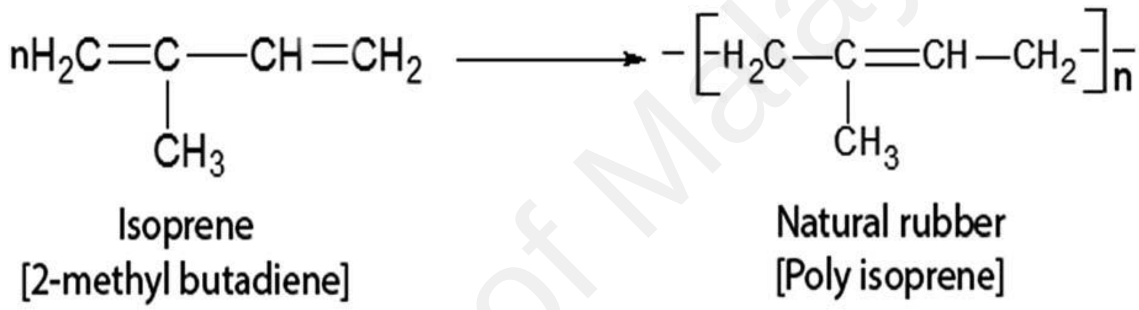


Figure 2-1: Structure of natural rubber and its monomer isoprene

Rubber is recovered from liquid latex through coagulation and addition of acids, such as formic acid. The coagulum, a soft solid slab, is squeezed through a series of rollers to remove excess water and increase surface area. The obtained rubber sheets are dried using smoke ovens (Blackley, 2012; Groover, 2010).

2.2.2 Production of natural rubber

According to 2015 statistics, the global production of natural rubber almost doubled from 2000 to 2014. The amount of rubber produced was 6.8 million metric tons in 2000 and 12 million metric tons in 2014 ("Natural Rubber Statistics," 2015). The global consumption of natural rubber was about 7 million metric tons in 2000 (FAO., 1992; Inc., 2015); consumption increased to 12.1 million metric tons in 2014 ("Natural Rubber Statistics," 2015). The world production and consumption of natural rubber are shown in Figure 2.1

Figure 2-2: Global natural rubber production and consumption trends from 2000 to 2014

Thailand, Indonesia, and Malaysia are the major producers of natural rubber. The amount of natural rubber produced in Malaysia was 927,608 tons in 2000 and 668,613 tons in 2014 ("Natural Rubber Statistics," 2015). Moreover, the amounts of natural rubber consumed in in China, India, the United States, Thailand, and Malaysia were 864, 900, 380, 3863, and 826 thousand tons, respectively, in 2013 ("Top consumers of natural rubber worldwide in 2013 and 2014 (in 1,000 metric tons)," 2015). According to the statistics of the Food and Agriculture Organization, the natural rubber production in Indonesia increased from 1,792 to 3,108 thousand tons from 2003 to 2013 (FAO.).

2.2.3 Sources of natural rubber

Natural rubber is a bio-polymer obtained as latex from different plants; *H. brasiliensis*, commonly known as the Hevea rubber tree, is the most significant commercial source of natural rubber (P.M. Priyadarshan, 2009; Whalen, McMahan, & Shintani, 2013). The rubber tree grows optimally in warm, humid, even climate at 24 °C–28 °C throughout the year, with humidity above 70%, and scattered well-distributed rainfall of 1800–2000 mm/year on well-drained soils (Rogers & Cornish, 2005). Several years are needed for a rubber tree fully mature and to be ready for extraction of natural rubber latex.(Groover, 2010; Priyadarshan, 2011) The *H. brasiliensis* is shown in Figure 2.3.

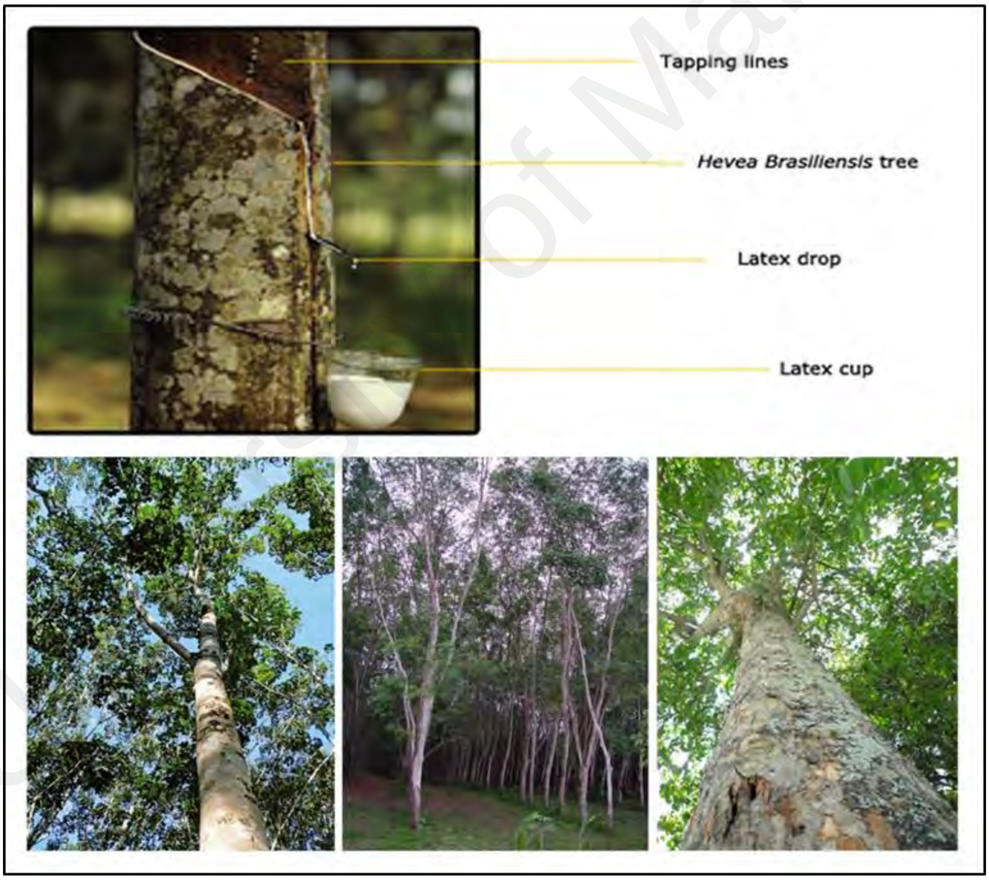
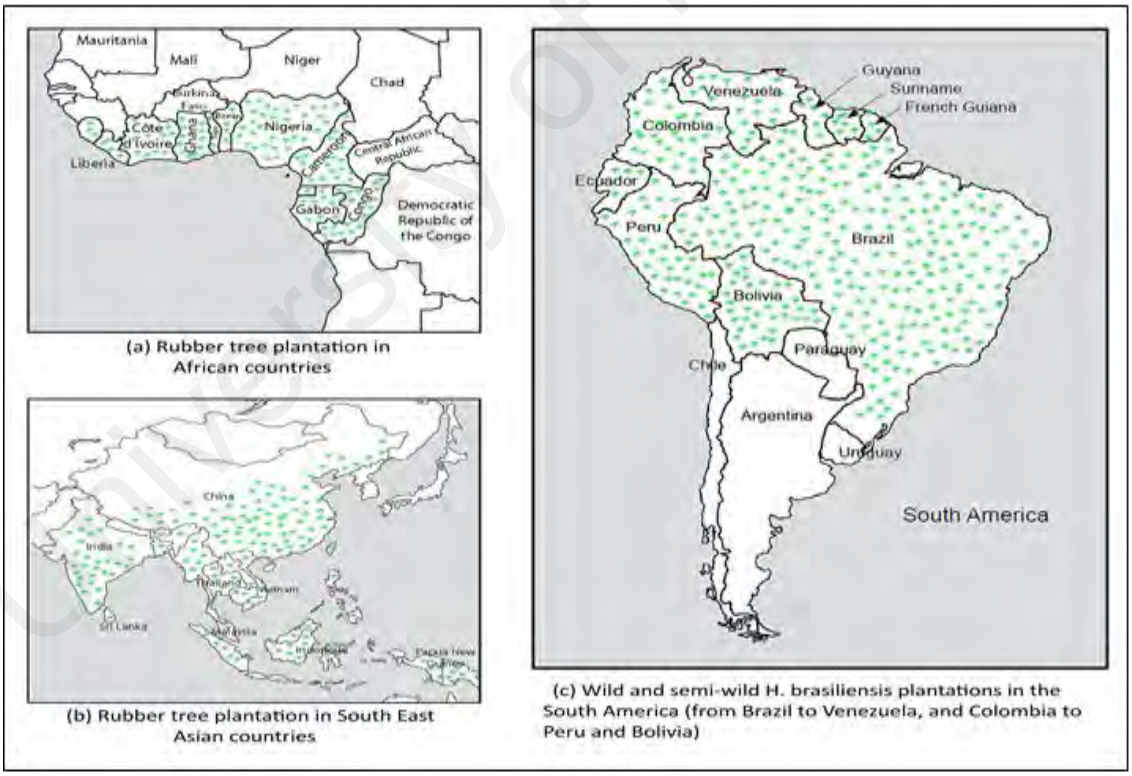


Figure 2-3: Natural rubber latex collected in a mug after skillful tapping of the bark of a H. brasiliensis tree

In the wild, *Hevea* rubber tree can grow to a height of 100–130 ft and can live up to 100 years. However, in the semi-wild environment, the tree can only live up to 30 years because tapping decreases its productivity. Wild and semi-wild *H. brasiliensis* plantations are commonly found in South America (Brazil, Guiana francesa, Suriname, Guiana, Venezuela, Colombia, Equador, Peru, and Bolivia, as shown in Figure 2.4c), followed by South East Asian countries (Malaysia, Indonesia, Thailand, Vietnam, Sri Lanka, China, India, and Papua New Guinea, as shown in Figure 2.4a) and African countries (Nigeria, Côte d'Ivoire, Cameroon, Liberia, Ghana, Republic of Congo, and Gabon, as shown in Figure 2.4b) (Mooibroek & Cornish, 2000; P.M. Priyadarshan, 2009; Simmonds, 1994; J. van Beilen, 2006). Approximately 90% of the total natural rubber worldwide is obtained from *H. brasiliensis* (Verheye, 2010).



(a) Rubber tree plantation in African countries

(b) Rubber tree plantation in South East Asian countries

(c) Wild and semi-wild H. brasiliensis plantations in the South America (from Brazil to Venezuela, and Colombia to Peru and Bolivia)

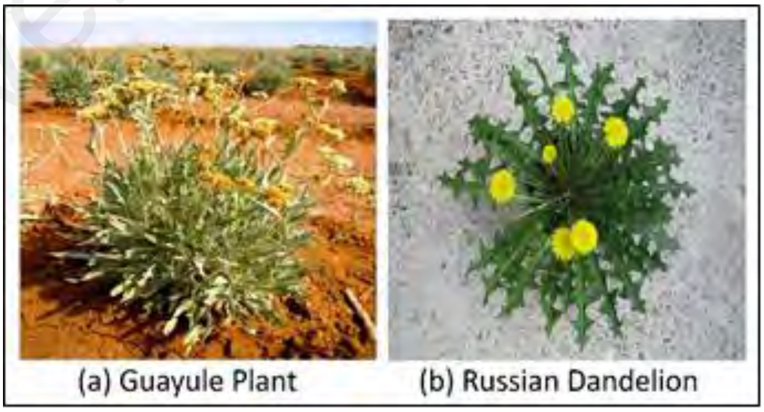
Figure 2-4: Natural rubber Plantation in African, South East Asian and in South American countries

Table 2-1: Literature in available sources of natural rubber globally

Rubber Source	Rubber MW (KDa)	Production (Tons/Yr)	Rubber Content (%)	Yield (kg ha^{-1} year^{-1})	Comments	Ref
Rubber tree *H. Brasiliensis*	1,310	9,000,000 (2005)	30 to 50 in latex, 2% of tree dry weight	500 to 3000	The usual maturity duration of the rubber tree is 6 years. The tree can live up to 100 years but is usually cut after 30 years because tapping decreases the productivity of latex. Latex re-growth takes a couple of days depending on the condition of the tree.	(Blanc, Baptiste, Oliver, Martin, & Montoro, 2006; Han et al., 2000; Priya, Venkatachalam, & Thulaseedharan, 2006; Venkatachalam, Geetha, Sangeetha, & Thulaseedharan, 2013)
Guayule shrub *P. argentatum* Gray	1,280	10,000 (1910)	3 to 12 of plant	300 to 1000	Production time usually takes 2–5 years, and re-growth time is 12 to 18 months.	(Coates, Ayerza, & Ravetta, 2001; Kim, Ryu, Kwak, & Kang, 2004; Mooibroek & Cornish, 2000; Polhamus, 1962; Swanson, Buchanan, & Otey, 1979; Venkatachalam et al., 2013)
Russian dandelion *T. kok-saghyz*	2,180	3000 (1943)	0 to 15 of root	150 to 500	Russian dandelion is usually planted in the early spring And takes 85 to 95 days to fully mature.	(Hallahan & Keiper-Hrynko, 2004; Venkatachalam et al., 2013; Whaley & Bowen, 1947)
Rubber Rabbitbrush *C. nauseous*	585	n.a	less than 7 of plant	n.a	Rubber rabbit brush reaches maturity within 2 to 4 years and has a lifetime of 5 to 20 years. This plant produces seed	(Polhamus, 1962; Scheinost, 2010; Swanson et al., 1979; J.

					at the age of 2 years or more.	van Beilen, 2006)
Goldenrod *S. virgaureaeminuta*	160-240	n.a	5 to 12 of root dry weight	110 to 155	A Low-quality rubber producer reported in a Demonstration Project in 1931.	(Polhamus, 1962; Swanson et al., 1979; J. van Beilen, 2006)
Sunflower *Helianthus sp.*	279, 69	Research stage	0.1 to 1 of plant	n.a	This plant yields rubber with a low molecular weight.	(Hussin Mohd Nor & Ebdon, 1998; Polhamus, 1962; Swanson et al., 1979)
Fig tree *Ficuscarica*	190	n.a	4 in latex	n.a	The research and development of this plant is related to biochemistry.	(Hunseung Kang, Min Young Kang, & Kyung-Hwan Han, 2000; J. B. van Beilen & Poirier, 2007a; Venkatachalam et al., 2013)
Lettuce *Lactuca serriola*	1,380	Research stage	1.6 to 2.2 in latex	n.a	The research and development of this plant is related to genetic engineering and characterization.	(Bushman et al., 2006; J. van Beilen, 2006; J. B. van Beilen & Poirier, 2007a)

The other crops that produce natural rubber include guayule plant, Russian dandelion, rubber rabbitbrush, fig tree, goldenrod, and sun flower. Rasutis et al (Rasutis, Soratana, McMahan, & Landis, 2015) reported that guayule (*Parthenium argentatum* Gray) is a dry, non-tropical, and low-input perennial plant native to Mexico and southern Texas; this plant has received significant research attention because of its potential as a substitute source of natural rubber. Natural rubber is harvested in parenchyma cells in the bark of guayule plant (Figure 2.5a) (Rasutis et al., 2015). Guayule plant is a feasible alternative source to *Hevea* rubber tree because of the high quantity and quality of the produced natural rubber, which exhibits the same molecular weight as that of natural rubber from the *Hevea* rubber tree (J. B. van Beilen & Poirier, 2007a). Guayule plant is the only non-tropical plantation crop used commercially to produce natural rubber in the early 20th century (J. B. van Beilen & Poirier, 2007a). Guayule requires fewer nutrients and pesticides compared with other plantation crops (Kroschwitz & Mark, 2004; Mark, 2013; Ray, 2010). In addition, the residual, non-latex guayule exhibits a potential to produce useful chemical commodities, such as bio-fuels, insulations, and paper pulps (Boateng, Elkasabi, & Mullen, 2016; Rasutis et al., 2015).



(a) Guayule Plant (b) Russian Dandelion

Figure 2-5: (a) Guayule Plant and (b) Russian Dandelion

Russian dandelion is another alternative source of natural rubber discovered in Kazakhstan, Soviet Union in 1932 (J. B. van Beilen & Poirier, 2007b; Whalen et al., 2013). Russian dandelion fully matures within 85 to 95 days. Rubber is collected in the roots and leaves of Russian dandelion (J. B. van Beilen & Poirier, 2012). Van Beilen and Poirier reported that Russian dandelion produced 150–500 kg/ha/year natural rubber during World War II to fabricate make tires for the Soviet Union and Germany (J. B. van Beilen & Poirier, 2007b; Whaley & Bowen, 1947). Russian dandelion is shown in Figure 2.5(b).

The other plant species used as a source of natural rubber include rubber rabbitbrush, fig tree, goldenrod, and sunflower. The available sources of natural rubber are shown in Table 2.1.

2.2.4 Uses of Natural rubber

Currently, thousands of commodities, such as tires, balloons, and boots, are fabricated using latex obtained from rubber trees (Alkhatib, Loubar, Awad, Mounif, & Tazerout, 2015). Natural rubber exhibits distinct physical properties and function as a perfect insulator (Engineers, 2010); hence, natural rubber is used or cable insulation and production of scrap tires, automotive parts, and galoshes (Alkhatib et al., 2015; F. Chen & Qian, 2002; Martínez et al., 2013; Rodgers & Abdullahi, 2016; Williams, 2013). Natural rubber is also used to develop heavy mega structures and vibration insulators (Fukahori, 2014). Evans and Evans reported that scrap tire contains 45–47 wt% of natural rubber along with carbon black filler, styrene-butadiene rubber, butadiene rubber, and other commodities (F. Chen & Qian, 2002; Evans & Evans, 2006). Natural rubber is also applied in the food, cosmetics, packaging, paper, clothing, wall covering, and medical industries (Kohjiya & Ikeda, 2014). Moreover, natural rubber is used extensively for preparation of adhesives, thermoplastic polymers, binders, resins, paints, and varnishes (Abdullah, 1994). The uses of natural rubber in various sectors are summarized in Figure 2.6.

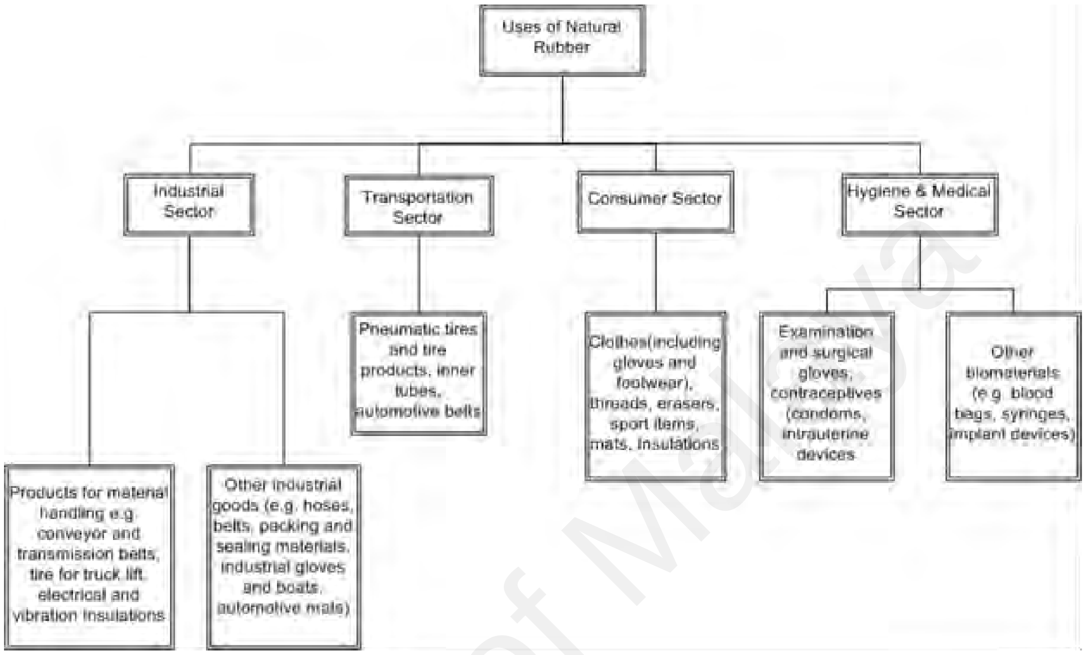


Figure 2-6 Uses of Natural rubber

2.3 Methods for conversion of natural rubber to fuel

Various techniques, such as pyrolysis, gasification, chemical degradation, catalytic cracking, and hydrogenation, are used to convert natural rubber to fuels and valuable chemicals.

2.3.1 Pyrolysis

Pyrolysis, also known as thermolysis, is the process of thermally breaking down organic materials into relatively smaller molecules at high temperatures of 400°C–600°C. Pyrolysis is classified as a slow or a fast process based on heating rate. If the time required to heat the raw material to the pyrolysis temperature is longer than the characteristic pyrolysis reaction time, then the process is considered slow; otherwise, the process is considered fast (P. Basu, 2010). Pyrolysis can also be classified into hydropyrolysis, hydrous-pyrolysis, oxidative-pyrolysis, vacuum pyrolysis, and catalytic pyrolysis based on the type of the environment where the process is employed (Martínez et al., 2013). Pyrolysis is characterized based on operating parameters, such as reaction period, heating rate, temperature, pressure, and the nature of agents and catalyst used (Abnisa et al., 2013; Andresen & Lim, 2011; Scheirs & Kaminsky, 2006). The products of pyrolysis are solid (char or carbon), liquid (tar, hydrocarbons, and water) and gas (CO_2, CO, H_2O, C_2H_2, C_2H_4, and C_2H_6) (P. Basu, 2010).

Various investigations were conducted on the pyrolysis of natural rubber. Chen and Qian performed pyrolysis of natural rubber (cis-1,4-polyisoprene) in an inert atmosphere to determine the effect of temperature on the composition and yield of the pyrolysis product, such as pyrolytic oil, residues, and gases; however, only the yield of the main component from pyrolytic oil has been reported. Studies also revealed that di-pentene is a main component of pyrolytic oil at temperatures below 431° C,. At ambient temperatures of -330°C, 331°C–390°C, and 391°C–430 °C, the di-pentene yields were 53.57%, 29.03%, and 11.89%, respectively (F. Chen & Qian, 2002). Cataldo reported the detailed pyrolysis of synthetic and natural rubber (cis-1,4-polyisoprene) in a heated flask under direct flame at low pressure; the produced oil presented a yield of 44.5% and mainly consists of 90% di-pentene with small amount of isoprene (3.5%) and other commodities (Cataldo, 1998). Munger outlined the production of gaseous and liquid fuels from small tire pieces at temperatures below 482°C. The yields of products, such as gas, oil, and carbon black were 5% to 50%, 20% to 50%, and 30% to 50%, respectively. The gross calorific value of the oil product was estimated as 18,000 Btu per pound (Munger, 1992). Groves et al studied the thermal degradation of natural rubber through pyrolysis to investigate the oil product obtained at 500 °C; the major products obtained include monomer, isoprene, dimmer, and di-pentene with other commodities in substantial concentrations (Groves, Lehrle, Blazsó, & Székely, 1991). Similar investigations on pyrolysis showed that di-pentene and isoprene are the major products of natural rubber pyrolysis (Bhowmick, Rampalli, Gallagher, Seeger, & McIntyre, 1987; Chien & Kiang, 1979). The pyrolysis of natural rubber can be carried out at 330°C–400°C to obtain liquid fuels. Heating rate is an important factor that should be considered because it positively influences the yield of the pyrolysis product. Heating rate can be determined by the type of pyrolysis process used (P. Basu, 2010).

2.3.2 Gasification

Gasification is a thermal process that converts organic- or fossil-based carbonaceous materials into carbon monoxide, hydrogen, carbon dioxide, and methane (Luque & Speight, 2014). This process is achieved by subjecting the material to high temperatures (> 700°C) by using a controlled amount of oxygen and/or steam without peforming combustion (Higman & van der Burgt, 2011; Luque & Speight, 2014). The resulting gas product is called syngas (synthesis gas or synthetic gas) or producer gas, which is a fuel with a heating value (Engineers, 2015; Higman & van der Burgt, 2011; Luque & Speight, 2014). Furthermore, gasification stores energy into a chemical bond (Engineers, 2015). Gasification is carried out in three types of reactors: (i) fixed-bed gasification, (ii) fluidized-bed gasification, and (iii) entrained-flow gasification. When choosing the appropriate gasification process, the different factors that should be considered include fuel reactivity, plant size, raw material used, and oxidant type (air, steam, or air/steam) (P. Basu, 2010; Higman & van der Burgt, 2011; Luque & Speight, 2014).

Thus far, gasification of 100% pure natural rubber has not been investigated. However, various studies reported that the gasification of tire rubber (consists of 40%–52.2% natural rubber (A. K. Basu, 2009; Evans & Evans, 2006; Funazukuri et al., 1987)) in an oxidizing medium under low-temperature conditions produced gaseous products, oil, and solid residues (Manuel, Dierkes, & Limited, 1997). Ahmed and Gupta performed pyrolysis and steam gasification of rubber tires at 800°C and 900°C to produce syngas (Ahmed & Gupta, 2011). A comparative study of gasification and pyrolysis was also conducted to determine the effect of temperature on gaseous product yield. Furthermore, the characteristics of syngas were investigated. At 800°C–900°C, the yield of hydrogen from gasification is higher than that from pyrolysis (Ahmed & Gupta, 2011). Rubber can be used as an additive for coal gasification. Straka et al used a moving bed gasifier for co-gasification of rubber with brown coal on laboratory and industrial scales at 850°C (Straka, KŘÍŽ, & BUČKO, 2008). The use of rubber particles (10–20 wt%) improved the calorific value of the final product (10.67–11.78 MJ/m3) (Straka et al., 2008). Straka and Bučko performed oxygen-steam co-gasification of lignite with tire rubber through lurgi gasification (Straka & Bučko, 2009). The net heating value of the final gas product is higher for the mixture of lignite and rubber tyre 10–20 wt% compared with that obtained through gasification of lignite alone. The gross calorific values of the final product obtained through co-gasification of lignite/waste-tire and gasification of lignite alone were calculated as 12.77 and 12.40 MJ/m3, respectively. Moreover, the sulfur contents in the gas product are lower in co-gasification than those in gasification of lignite alone (Straka & Bučko, 2009).

Gasification of natural rubber can be conducted at 800°C to 900°C. Rubber can also be employed for coal co-gasification because it reduces sulfur content in the gas product and improves the calorific value.

2.3.3 Chemical degradation

Chemical degradation is the decomposition of polymeric materials into useful chemical commodities by using chemicals, such as acids, bases, and solvents.(Allen & Edge, 1992) This process is due to many types of chemical reactions, which mostly result in the breakage of double bonds (International & Lampman, 2003). Chemical degradation processes include hydrolysis, ozonolysis, and solvolysis (Peacock & Calhoun, 2006).

Campistron et al performed chemical degradation of natural rubber in a controlled manner by using m-chloroperbenzoic acid; the results showed that reaction time and periodic amount of acid can be used to control the degree of breakdown (Sadaka, Campistron, Laguerre, & Pilard, 2012). Chaikumpollert et al (Chaikumpollert et al., 2011) examined the chemical degradation of natural rubber with potassium persulfate at 30°C; the viscosity of natural rubber was observed to be a function of the amount of potassium persulfate used. FT-IR and 1H NMR analyses were then performed to study the structure of natural rubber; the products obtained from oxidation degradation included carbonyl and formyl groups (Chaikumpollert et al., 2011). Nor and Ebdon studied the chemical degradation of natural rubber in chloroform solution through ozonolysis. The molecular weight of natural rubber rapidly decreased upon addition of various oxygenated functional groups (H. M. Nor & Ebdon, 2000). Similarly, Anachkov et al investigated the ozonolysis of cis-1,4-polyisoprene and trans-1,4-polyisoprene by using carbon tetrachloride solution (Anachkov, Rakovski, & Stefanova, 2000). Analysis using IR-spectroscopy and 1H NMR spectroscopy showed that the products included ozonides, aldehydes, and ketones (Anachkov et al., 2000).

2.3.4 Catalytic cracking

Catalytic cracking process is the process of breaking down polymeric organic materials by using a catalyst (Aguado & Serrano, 2006). This process is faster than thermal degradation (Aguado & Serrano, 2006). A wide range of catalysts (Friedel–Crafts catalyst, basic and acidic solids, and bifunctional solids) can be employed to promote the catalytic cracking of rubber and plastics materials (Aguado & Serrano, 2006). Depending on the types of catalysts and operational conditions used, different mechanisms and approaches have been observed during the process. The product of catalytic cracking is of higher quality compared with those of thermal degradation (Aguado & Serrano, 2006; P. Basu, 2010; Scheirs & Kaminsky, 2006).

Catalytic cracking exhibits potential in the preparation of high-value commodities from organic materials. Many studies were conducted to depolymerize rubber through pyrolysis, co-gasification, and hydrogenation; however, limited information is available regarding the depolymerization of rubber through catalytic cracking. Larsen investigated the catalytic cracking of waste rubber (scrap tire) by using molten salts, which exhibit the properties of Lewis acids, such as ZnCl2, SnCl2, and SbI3, at 380°C–500°C (J.W. Larsen, 1976). The yields of oil (38–78 wt%), gas (10–17 wt%), and solid residues (45–49 wt%) are similar to the product yield obtained from thermal decomposition (J.W. Larsen, 1976). Wingfield et al. (1984 & 1985) developed a catalytic cracking process for decomposition of plastic and rubber waste by using zinc and copper salts. The use of these salts as catalysts could decrease sulfur and nitrogen contents (Wingfield, Braslaw, & Gealer, 1984). The use of a basic salt catalyst can also improve the yield of oil and gas products (Wingfield, Braslaw, & Gealer, 1985). Hall et al performed the pyrolysis of latex gloves by using Y-zeolite as catalyst at 380°C and 480°C; the experiment resulted in high yields of valuable aromatic hydrocarbon compounds (Hall, Zakaria, & Williams, 2009). The use of catalyst also increased the overall product yield. In the absence of a catalyst, the yield of pyrolytic oil increased from 57.9 wt% to 79.8 wt% at 380°C to 480°C. However, the use of catalyst reduced the oil yield but increased the yield of the gaseous product from 7.4% to 11.7%. High product yields were observed at high temperatures in the presence and absence of a catalyst (Hall et al., 2009).

2.3.5 Hydrogenation

Hydrogenation is a potential alternative for depolymerization of rubber and plastic polymeric materials. This process uses hydrogen mixed with a typical catalyst, such as Ni, Mo, Fe, and Pt, for breaking down double and triple bonds (Albert, 1939). Hydrogenation reduces the numeber of saturated hydrocarbon compounds and promotes the removal of sulfur, chlorides, and nitrogen (Scheirs & Kaminsky, 2006).

Several studies were conducted on the hydrogenation of natural rubber. Bhattacharjee et al studied the depolymerization of epoxidized natural rubber by using $C_4H_6O_4Pd$ as catalyst (Bhattacharjee, Bhowmick, & Avasthi, 1993). Combined with epoxy groups, the catalyst played a remarkable role in the breakage of carbon double bonds. Infrared and nuclear magnetic spectroscopy techniques were used to analyze the products (Bhattacharjee et al., 1993). Mahittikul et al examined the hydrogenation of natural rubber latex by using using iridium catalyst ($[Ir(cod)(PCy_3)(py)]PF_6$)). In mono-chlorobenzene, $[Ir(cod)(PCy_3)(py)]PF_6$ was found to be an effective catalyst for hydrogenation of natural rubber latex. Observations also showed that the use of sulfonic acid retarded the poisoning of the catalyst during hydrogenation of natural rubber latex (Mahittikul, Prasassarakich, & Rempel, 2009).

2.4 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is also known as hydrous pyrolysis (Gollakota, Kishore, & Gu, 2018). Hydrous pyrolysis is a technique that converts organic materials (rubber, biomass, plastics, etc.) into liquid fuel. This process is conducted using water at high temperatures and high pressure conditions and induces the decomposition of long-chain polymers of carbon, hydrogen, and oxygen into small-chain petrochemicals (monomers) (P. Basu, 2010; John W. Larsen & Hu, 2006). Hydrous pyrolysis is performed in water at high temperatures (250°C–400°C) and pressures (4–22 MPa). This process can also be conducted under self-generated pressure. This process is similar to other processes that uses hot water such as hydrothermal liquefaction, thermochemical conversion, and hydrothermal processing (Crocker, 2010; Muraza, 2015; Obeid, Salmon, Lewan, & Hatcher, 2015; Strande & Brdjanovic, 2014). One of the most important advantages of this technique is that it can use a raw material with high moisture content without the need for pre-drying. The products of hydrous pyrolysis are oil, solid residue, and gases. The amount of liquid oil obtained is higher than that of solid residue and gaseous products. In addition, the oil obtained through hydrous pyrolysis exhibits similar properties to those of naturally occurring crude oil (Lewan, Winters, & Mcdonald, 1979).

Various studies were conducted on the depolymerization of kraft lignin, polystyrene, polytrimethylene terephthalate, nylon-6, circuit board waste, shale, kerogen, and coal through hydrous pyrolysis (Beltrame et al., 1997; Gao, Jin, & Pan, 2012; Kidena, Adachi, Murata, & Nomura, 2008; Liang et al., 2015; Michels, Landis, Philp, & Torkelson, 1995; Miknis, Netzel, & Surdam, 1996; Nguyen et al., 2014; Yildirir, Onwudili, & Williams, 2015). Chen et al performed hydrous pyrolysis of nylon-6 using phosphotungstic heteropoly acid as catalyst at 280°C–330°C (J. Chen et al., 2010). Under the optimum conditions, the main product of hydrous pyrolysis was found to be caprolactum, with a yield of 77.96 wt.%, and a small amount of 6-aminocaproic acid and oligomers (J. Chen et al., 2010). Miknis et al conducted hydrous pyrolysis of sub-bituminous rank coal in helium atmosphere at 290°C–360°C and 20 psi (Miknis et al., 1996). The liquid products were obtained in two separate phases, namely, oil and solid residues. Oil was obtained as floating liquid on the water surface and as absorbed oil on the coal surface. The floating material contained more than 75% expelled oil (Miknis et al., 1996). Similarly, Beltrame et al examined the hydrous pyrolysis of polystyrene (Beltrame et al., 1997). The process was carried out under in argon atmosphere at 300°C–350°C and 18 MPa. Liquid oil was obtained as the main product, with an overall amount of 95%, and mainly consisted of toluene, cumene, and ethylbenzene (Beltrame et al., 1997).

Nguyen et al reported that the yield of char obtained from hydrous pyrolysis of kraft lignin at 350°C and 25 MPa ranged from 17% to 20% (Nguyen et al., 2014). The gaseous products were not collected because no significant amount of gas was obtained in the sampling bags. Similarly, Li et al reported the production of gaseous products through hydrous pyrolysis of brown coal at 320°C (Li, Jin, & Lehrmann, 2008). The yield of the gaseous product was estimated to be 54.8 kg/ton coal, which tends to increase with increasing temperature (Li et al., 2008).

The first full-scale commercial plant of hydrous pyrolysis was established by the Changing World Technologies and the Renewable Environment Solutions LLC (RES) in Carthage, Missouri for conversion of waste into useful chemical commodities (fertilizers, fuels, etc.). RES reported that any type of waste materials, such as plastic waste, sewage waste, and rubbers could be used as feedstock. This plant converts 200 tons of waste into 500 barrels of oil per day. RES also claimed the energy efficiency of the process to be as much as 85%, depending on the heating value of the product and the dry feedstock (T. N. Adams et al., 2004).

The advantage of this process as compared to other above mentioned processes is that it produce high liquid product at low temperature. Whereas, other process like gasification is good for high gas yields, pyrolysis is good for liquid product but it requires high temperature. Similarly, torrefaction is used for the production of solid fuels. Hydrogenation and catalytic cracking are low temperature processes but the use of hydrogen and catalyst would increase the process cost.

2.4.1 Use of natural rubber in hydrothermal liquefaction

Few studies utilized 100% pure natural rubber for degradation. However, information is available regarding depolymerization of rubber tire containing 40–52.2 wt.% of rubber through hydrothermal liquefaction (A. K. Basu, 2009; Evans & Evans, 2006; Funazukuri et al., 1987). Furthermore, various investigations were conducted on hydrous pyrolysis of rubber tire to assess the effect of different parameters for production of useful liquid products (D. T. Chen, Perman, Riechert, & Hoven, 1995; Funazukuri et al., 1987; S. Park & Gloyna, 1997; Rushdi et al., 2013; L. Zhang et al., 2016).

Many parameters affect hydrothermal liquefaction process; these parameters include particle size, reaction time, water to material ratio, heating rate, and operating atmosphere. Raw material quality also significantly influences the final product, overall temperature was found to be the most effective parameter that significantly affects product quantity and quality. Studies on hydrous pyrolysis of rubber are shown in Table 2.2.

Table 2-2: Various reported investigations on hydrous pyrolysis of rubber

Ref	Materials	Process parameters					Product analysis		Comments
		Type of reactor	T (°C)	P (MPa)	Water as an agent	time	Quantitative analysis	Qualitative analysis	
(D. T. Chen et al., 1995)	• Rubber tire • Natural rubber	All experiments were conducted in a 180 mL Hastelloy autoclave.	380	27.6	Water at the super-critical condition	0.5–3 h	Oil was obtained as the main pyrolysis product. Gases were not collected. Solid residues were also obtained and identified as carbon black (about 30 wt.%).	• The NMR analysis of the products showed the presence of aromatic, olefinic, and aliphatic groups. • Natural rubber produces homogeneous organic liquid. The carbon content of natural rubber is low (<1 wt.%); consequently, Consequently, no solid is produced. • Tire rubber product fraction includes the aqueous phase; if SCF water is used, organic fraction is present as a free layer or absorbed on carbon black (around 70 wt.%).	In this work, super-critical H_2O and CO_2 were used to depolymerize tire and natural rubber in a controllable manner. Molecular weight analysis of the degraded material indicates that reaction time can be used to control the degree of breakdown; materials in the molecular weight range of 10^{-3}–10^{-4} were obtained. In addition, both material composition and super-critical fluid affect the rate at which the material is depolymerized. Functional analysis of the processed material shows carbonyl and aromatic groups.

(L. Zhang et al., 2016)	Rubber tire	Hydrous pyrolysis was conducted using a batch reactor. The reactor was heated using a molten salt bath. The temperature was controlled using a thermocouple.	200–430	0–28	• Water at a sub-critical and super-critical condition • H_2O/rubber tire mass ratio is 0/3 to 12/3.	20–120 min	• Maximum liquid product yield was 52.7 wt.% at 370°C. • At 390°C, the lowest yield of char was achieved (about 38 wt.%).	Under the optimum conditions, the calorific value of oil, energy recovery efficiency, carbon content, and hydrogen content were reported to be 44.09–45.09 MJ/kg, 62.49%, 86.66 wt.%, and 10.99 wt%, respectively.	Hydrous pyrolysis of rubber tire was performed to produce liquid fuels. The effect of different parameters, such as temperature (200°C to 430°C), corresponding pressure (0 to 28 MPa), water to rubber tire ratio (0/3 to 12/3), time (20 to 120 min), and environment (air, CO_2, CO, H_2, and N_2) was studied. Temperature significantly influenced the yield and characteristics of the end product.
(Yi, Ma, Chen, & Chen, 2009)	Rubber tire	Rubber tires and water were placed into a batch reactor and heated with the inlet opening. After water boiling and vapor was used, 30 min was needed to exclude air in the reactor. The reactor was sealed and heated electrically. After residence time, the reaction products were drained when the temperature and pressure reached the requirement.	350–550	13.9–25	Water at sub-critical and super-critical conditions	30 min	• Oil, gas, and solid residues were obtained as the main products. • Oil was not collected because of some limitations. • Gas products consist of CO_2, CO, H_2, CH_4, and other low-molecular-weight hydrocarbons. The amounts of CH_4 and H_2 are comparatively higher than the other components of the gas.	• Carbon contents were high in solid residues. The average value of carbon contents was estimated to be higher than 80 wt.%. • The hydrogen content was estimated to be 0.58–4.76 wt.%. • At 500°C and 22.2 MPa, the percentages of CH_4, H_2, and CO_2 were approximately 38%, 38%, and 16%.	Pyrolysis efficiency of used rubber tires and the effect of temperature and pressure on sub-critical/super-critical water were studied. Products were analyzed by GS-Mass, FTIR, and elementary analyzer.
(S. Park & Gloyna, 1997)	Rubber tire	Thermal depolymerization was conducted using a U-shaped stainless steel batch reactor consisting of electrically heated fluidized sand bath, cold water bath, and thermocouple. The working volume of the reactor was 35.2 mL. About 1 g of the rubber sample was used with 0.1 g of catalyst and 6.5 mL of water. The experiment was conducted under different atmospheres, such as air and helium.	400–450	22.7–31.1	• Water at super-critical conditions • 1 g of rubber:6.5 mL of water	15–30 min	• The maximum oil yield and conversion of rubber tire were reported to be 44 wt.% and 58%, respectively at 400°C in helium atmosphere.	–	Thermal degradation of rubber tire in a batch reactor using super-critical water was performed to investigate the effect of process variables on product yield and conversion. The temperature and gas atmosphere were the most significant factors affecting oil yield and conversion.

(Funazukuri et al., 1987)	Rubber tire	An autoclave with a capacity of 0.7 L was used to conduct hydrous pyrolysis of rubber tire. About 1 g of the sample was loaded in an autoclave.	330–450	5.2–23	Water at a sub-critical and super-critical conditions	5.5 h	The yield of the oil product and solid residues was estimated to be 47.6 and 42.9 wt.%, respectively, at 380°C and 22 MPa.	• Oil product consisting of about 85 wt.% and 10 wt.% of carbon and hydrogen, respectively. Solid residues consisted of 91.6 and 1.48 wt.% carbon and hydrogen, respectively.	Autoclave as a batch reactor was used to perform the thermal degradation of rubber tire (containing 52.2 wt.% natural rubber) by using super-critical water and n-pentane. Although the magnitude of pressure of super-critical water is higher than the super-critical pentane (critical pressure is 3.37 MPa), water at super-critical condition was as effective as super-critical pentane.
(Rushdi et al., 2013)	Rubber tire	Hydrous pyrolysis experiments were conducted using 316 stainless steel vessels as a batch reactor. The reactor was capable of handling 4137 MPa pressure. The volume of the reactor is 480 ± 20μL.	150–400	–	Exp Set 1: • Double distilled water • 30 mg of rubber tire and 480 mg of water	48 h	The product yields obtained in the presence and absence of oxalic acid were reported to be 47.53 wt.%. and 41.95 wt.%, respectively, at 350 °C.	Alkanes, methyl n-alkanoates, plasticizers, n-alkanoic acids, phenols, and polycyclic aromatic hydrocarbons were found to be the major products of hydrous pyrolysis.	This research mainly aimed to study the effect of temperature and different experimental conditions in hydrous pyrolysis on the chemical composition of products from scrap tire.
					Exp Set 2: • Double distilled water and oxalic acid • 30 mg of rubber tire and 480 mg of water with 4 mg of oxalic acid				

2.4.1.1 Effect of water

In hydrothermal liquefaction of rubber tire, water is used in sub-critical and super-critical conditions for degradation various materials (L. Zhang et al., 2016). If the temperature of the water is above the atmospheric boiling point (100°C) but below it's the critical temperature (374°C), the water is said to be in sub-critical condition. However, if the temperature and pressure of water is equal to or above 374°C and 22.1 MPa, respectively, the water is said to be in super-critical condition (Anne Loppinet-Serani, 2014; Brunner, 2014). Water under the sub-critical condition is used as solvent for polar and ionic compounds; conversely, water under super-critical condition exhibits the properties of non-polar solvents and is thus used to dissolve and degrade various non-polar compounds (Vladimir Anikeev & Fan, 2013). Super-critical water is more aggressive than sub-critical water because the water changes its structure and most of hydrogen bonds are broken under super-critical condition; this phenomenon shift the polar forces of attractions to dipole–dipole attractions, which subsequently decreases the dielectric constant of water (Z. Fang & Xu, 2014; García, Pérez, Fdez-Polanco, & Cocero, 2003). Degradation of rubber tire can also be carried out using various compounds, such as pentane, carbon dioxide, and toluene. However, toluene and pentane are hazardous to the environment and can cause water pollution, landfill contamination, and serious harm to human life (Kumar, 2001; "Public Health Statement for Toluene," 2015). Hence, water is the most suitable solvent for degradation because it is not only environment friendly but also cheap and easily available.

Various investigations were conducted on the use of water under sub-critical and super-critical conditions for degradation of rubber tire (D. T. Chen et al., 1995; Funazukuri et al., 1987; Leung & Wang, 1998; Y. Park, Hool, Curtis, & Roberts, 2001; Yi et al., 2009). Under super-critical condition, water is miscible with non-polar rubber, provides the thermal energy for bond breaking, and acts as a source of heat transfer agent and hydrogen provider (L. Zhang et al., 2016). Rubber is decomposed almost completely in super-critical water compared with that in sub-critical water, thereby suppressing the formation of char (Yi et al., 2009).

The amount of water influences the yield of the liquid product. Zhang et al reported that the amount of liquid products increased with increasing water to rubber tire ratio during hydrous pyrolysis of rubber tire (L. Zhang et al., 2016). The yield of the liquid products also increased from 46 to 53 wt.% when water/rubber tire ratio was increased from 3/3 to 12/3 at 390°C. Furthermore, the high amount of water increased water density and nucleophile concentration, thereby increasing the pressure of the reactor. This condition is unfavorable for gas formation (L. Zhang et al., 2016).

Chen et al examined the thermal depolymerization of rubber tire and natural rubber at 380°C and 27.6 MPa by using carbon dioxide and water under super-critical conditions (D. T. Chen et al., 1995). During thermal degradation using super-critical water and carbon dioxide, natural rubber yielded products with lower molecular weight than those obtained using rubber tire. These results showed that super-critical water renders a more aggressive environment for degradation of materials compared with super-critical carbon dioxide. The discrepancy in the results is due to the fact that water is a stronger nucleophilic compound than carbon dioxide (D. T. Chen et al., 1995).

Similarly, Funazukuri et al reported the liquefaction of rubber tire using super-critical water and n-pentane, with a super-critical point of 196.7°C and 3.37 MPa (Funazukuri et al., 1987). Although the level of pressure of super-critical water is higher than that of super-critical pentane, both solvents were considered effective. The yields of liquid products obtained using super-critical water and pentane were found to be 47.6 and 48 wt.%, respectively (Funazukuri et al., 1987).

From all above studies it can be concluded that for the degradation of scrap tire, water under supercritical conditions should be employed in liquefaction process.

2.4.1.2 Effect of temperature

Various investigations were conducted to study the effect of temperature on hydrothermal liquefaction products. Zhang et al performed hydrothermal liquefaction of rubber tire at 200°C to 430°C (L. Zhang et al., 2016). The temperature highly influenced the yield of the product. The yield of the liquid product increased from 13.5 to 52.7 wt.% as the temperature was increased from 200°C to 370°C. A further increase in temperature at 400°C did not significantly increase the liquid product yield. However, in the yield of the liquid product decreased at temperatures higher than 400°C. This decrease in yield could be attributed to the degradation of oil into lighter fractions and volatiles (L. Zhang et al., 2016).

Park and Gloyna performed thermal degradation of rubber tire in a batch reactor using super-critical water (S. Park & Gloyna, 1997). The experimental results showed that the maximum yield of oil was attained at 400°C. However, the oil yield decreased at 400°C to 450°C because of the conversion of oil into lighter hydrocarbons and volatiles during thermal degradation. At 450°C, the conversion of rubber was found to be 5% to 6% higher than that achieved at 400°C. The maximum oil yield and conversion of rubber tire were reported to be 44 wt.% and 58%, respectively, at 400°C (S. Park & Gloyna, 1997).

Funazukuri et al used autoclave as a batch reactor for thermal degradation of rubber tire (containing 52.2 wt.% natural rubber) using super-critical water (Funazukuri et al., 1987). At 380°C and 22 MPa, the yields of oil and solid products were 47.6 and 42.9 wt.%, respectively (Funazukuri et al., 1987). Similarly, Rushdi et al conducted hydrous pyrolysis of rubber tire using stainless steel batch reactor at 150°C to 400°C (Rushdi et al., 2013). Two sets of experiments were conducted. One experiment set was conducted using rubber tire and water, whereas the other experiment used the same materials and oxalic acid. The product yield increased with increasing temperature for both experimental sets. The concentration of hydrocarbons also increased as the temperature was increased to 250°C in the presence and absence of oxalic acid. At 350°C, the yields of the liquid product in the presence and absence of oxalic acid were reported to be 47.53

wt.% and 41.95 wt.%, respectively. Furthemore, the oil product yield decreased at temperatures higher than 400°C. This decrease could be due to the decomposition of oil products into lighter hydrocarbons and volatiles. However, the oil yield was high in the presence of oxalic acid (Figure 2.7). The presence of oxalic acid provided excess hydrogen, which can enhance the reduction of rubber (Rushdi et al., 2013).

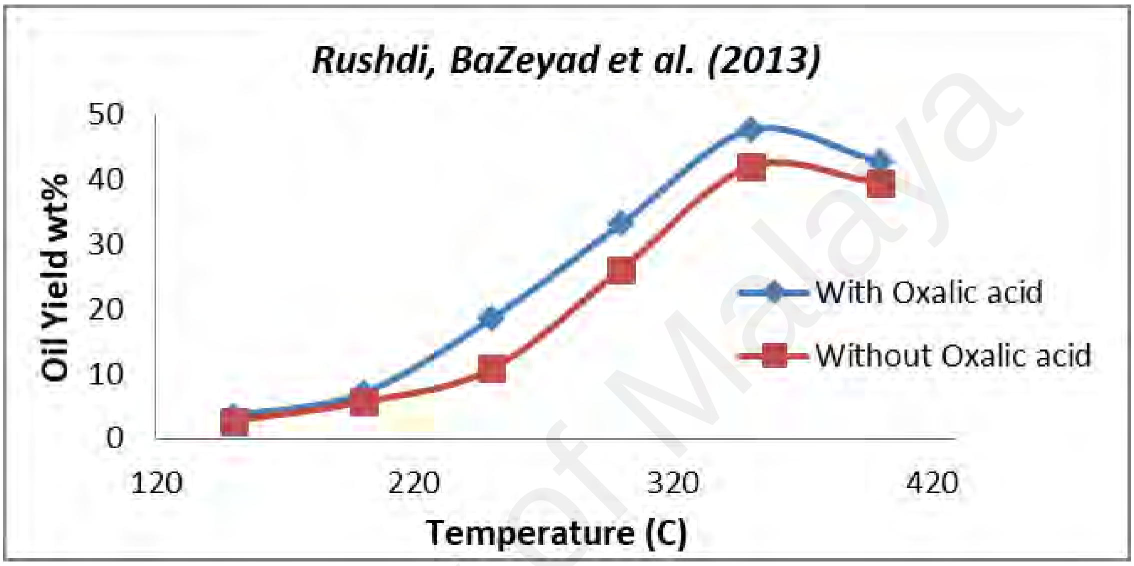


Figure 2-7: Effect of temperature on the yield of oil produced from rubber tire

Similarly, Yi et al conducted hydrothermal liquefaction of rubber tire in a batch reactor at 350°C–550°C and 13.9–25 MPa. Oil, gas, and solid residues were obtained as the main products (Yi et al., 2009). However, oil was not collected because of limitations in the system. Pyrolysis efficiency increased with increasing temperature and pressure. The pyrolysis efficiencies were 40% at 350°C and 13.9 MPa and 71% at 550°C and 25 MPa. The reaction completed at 550°C and 25 MPa because of the super-critical nature of water (Yi et al., 2009).

Similarly, Zhang et al also reported that the lowest yield of char (40 wt.%) was obtained at 370°C (L. Zhang et al., 2016). The yield of gaseous products was low at temperatures above 300°C. The energy recovery of the process increased with increasing temperature (L. Zhang et al., 2016). Funazukuri et al reported that the yield of the solid product was 42.9 wt.% at 380 °C and 22 MPa (Funazukuri et al., 1987).

In hydrothermal liquefaction of rubber tire, temperature is reported to be the most significant variable. At 370°C–400°C, the yield of the liquid products was 44–53 wt.%. However, the degradation of the liquid products was observed as the temperature exceeded 400 C, thereby decreasing the product yield. The complete decomposition of rubber tire occurred at around 500°C during hydrous pyrolysis.

2.4.1.3 Effect of gas atmosphere

Various gas atmospheres or environments could be used to carry out hydrothermal liquefaction of rubber; these gas environments include helium, nitrogen, carbon monoxide, carbon dioxide, hydrogen, and air. Gas atmosphere minimally affect the yield of the final product (L. Zhang et al., 2016). Zhang et al conducted hydrous pyrolysis under different atmospheres, such as air, CO_2, CO, H_2, and N_2 (L. Zhang et al., 2016). The results showed that gas atmosphere did not affect or enhance the product yield. The liquid products obtained under CO and H_2 showed a higher proportion of light fractions compared with those produced under CO_2 or N_2 (L. Zhang et al., 2016).

Similarly, Park and Gloyna performed hydrothermal liquefaction of rubber tire in air and helium atmospheres (S. Park & Gloyna, 1997). The gas atmosphere is the second most important parameter after temperature that affects the liquid product yield. However, the atmosphere showed minimal effect on oil yield. The use of helium, instead of air, was more effective for oil recovery. The maximum yield of the oil product was 44 wt.% at 400°C in helium atmosphere (inert atmosphere). The use of air as the atmosphere results in oxidative reaction, which increased the volume of effluent gas (S. Park & Gloyna, 1997).

2.4.1.4 Effect of time

Various studies were conducted to determine the effect of reaction time on product quality during hydrothermal liquefaction. Zhang et al studied the effect of reaction time from 20–120 min at 390°C (L. Zhang et al., 2016). At 390°C, the reaction time of 20 min was sufficient for degradation of rubber tire and the yield of the liquid product was 40 wt.%. The liquid product yield increased to a maximum of 53 wt.% when the reaction time was further increased to 60 min with slight increase in temperature (L. Zhang et al., 2016). Chen et al observed that the degree of depolymerization can be controlled using reaction time and can be employed to control the molecular weight for formation of chemicals (D. T. Chen et al., 1995). The molecular weight decreased during time interval of 30–180 min (D. T. Chen et al., 1995). Similarly, Funazukuri et al reported that the molecular weight decreased as a function of time at 380°C and 22 MPa (Funazukuri et al., 1987). Zhang et al also reported that prolonged reaction led to low nitrogen and sulfur contents in the liquid product (L. Zhang et al., 2016).

2.4.2 Characteristics of products

Various investigations were conducted to characterize products obtained during pyrolysis and hydrothermal liquefaction of rubber. Zhou et al reported that the calorific value of oil obtained under the optimum conditions is a 44.09–45.09 MJ/kg (L. Zhang et al., 2016). The calorific value obtained is close to that of petroleum derived from crude oil, such as diesel (44.8 MJ/kg) (Sinha, Agarwal, & Garg, 2008). The properties of liquid oil obtained from hydrothermal liquefaction of rubber tire are comparable with other crude-oil-derived fractions, such as gasoline and diesel, as well as other solid and gaseous fuels (Table 2.3).

Table 2-3: Calorific value of various fuels

Fuel	Calorific value	Ref
Oil from rubber tire	**45.09 MJ/kg**	**(L. Zhang et al., 2016)**
High rank coal	36.0 MJ/kg	(Demirbas, 2007)
Biomass	17.072 MJ/kg	(Everard, McDonnell, & Fagan, 2012)
Diesel	44.5 MJ/kg	(Sinha et al., 2008)
Natural gas	54 MJ/kg	(Chandra, 2006)
Gasoline	46 MJ/kg	(Dias De Oliveira, Vaughan, & Rykiel, 2005)

According to Zhou et al, elemental analysis of oil product obtained under optimum conditions contained carbon and hydrogen contents of 86.66 wt% and 10.99 wt%, respectively (L. Zhang et al., 2016). Similarly, Funazukuri et al reported that oil products contained 85 wt.% and 10 wt.% carbon and hydrogen, respectively, at 380°C and 22 MPa (Funazukuri et al., 1987).

Funazukuri et al performed elemental analysis of solid residues; the results showed that the residues contained 91.8 wt.% and 1.48 wt.% carbon and hydrogen, respectively, at 380°C and 22 MPa (Funazukuri et al., 1987). Moreover, Yi et al reported the presence of high carbon contents in solid residues. The average value of carbon contents was estimated to be higher than 80 wt.% (Yi et al., 2009).

Yi et al reported that the gas product mostly consisted of CH_4, H_2, CO, CO_2, and hydrocarbons with low molecular mass (Yi et al., 2009). The concentrations of CH_4 and H_2 were high in the product. The yield of CH_4 increased at 400°C to 550°C. Furthermore, the yields of CH_4, H_4, and CO_2 were approximately 38%, 38%, and 16%, respectively, at 500°C and 22.2 MPa; meanwhile, NOx and SOx were not detected in the gas products (Yi et al., 2009).

Cataldo reported a detailed pyrolysis of synthetic and natural rubber (cis-1,4 polyisoprene) (Cataldo, 1998). The yield of the oil product was 44.5%. The pyrolytic oil mainly consisted of 90% di-pentene with low amounts of isoprene (3.5%) and other commodities (Cataldo, 1998). Groves et al studied the thermal degradation of natural rubber through pyrolysis to investigate the oil product derived at 500°C (Groves et al., 1991). The major products obtained were monomer, isoprene, dimmer, and di-pentene with other commodities in substantial concentrations (Groves et al., 1991). In a similar investigation on pyrolysis, di-pentene and isoprene were found to be the major products of natural rubber pyrolysis (Bhowmick et al., 1987; Chien & Kiang, 1979). According to Chen and Qian, the pyrolytic oil obtained from natural rubber (cis-1,4-polyisoprene) at temperatures below 431°C mainly consisted of di-pentene (F. Chen & Qian, 2002). The yields of di-pentene at temperature ranges of ambient–330°C, 331°C–390°C, and 391°C–430°C were 53.57%, 29.03%, and 11.89% respectively. Roy et al performed pyrolysis of pure natural rubber and commercial rubber (consisting of 52% polyisoprene) at 500°C with varying pressures from 8 kPa to 28 kPa (Christian Roy, Darmstadt, Benallal, & Amen-Chen, 1997). The oil yield for pure natural rubber was estimated to be 97.3 and 90.3 wt.% at 0.8 and 28 kPa, respectively. For commercial rubber, the yields of pyrolytic oil were 62.6 and 61.7 wt.% at 0.8 and 28 kPa, respectively. Characterization of naphtha obtained from pyrolysis showed high amounts of dl-limonene. The yield of dl-limonene from naptha obtained from pure natural rubber was estimated to be 54.64 wt.% at 0.8 kPa. For commercial rubber, the yield of dl-limonene was reported to be 31.40 and 31.22 wt.% at 0.8 and 28 kPa, respectively. The total amounts of aromatics, olefins, and alkanes obtained from pure natural rubber were reported to be 4.24, 70.35, and 3.89 wt.%, respectively at 0.8 kPa. Chen et al performed NMR analysis of liquid products and reported the presence of aromatic, olefinic, and aliphatic groups (D. T. Chen et al., 1995). Products with a molecular mass of 10^3 to 10^4 were obtained. The reported compositions of hydrocarbons, aromatic rings, and olefinic groups in the products were 81 wt.%, 19 wt.%, and 0.4 wt.%, respectively, at 380 °C and 27.6 MPa (D. T. Chen et al., 1995). Zhang et al reported the composition of oil products at 250°C, 350°C, and 430°C (L. Zhang et al., 2016). Aromatics, saturated, and unsaturated hydrocarbons were 15.97 wt.%, 14.08 wt.%, and 7.10 wt.%, respectively, at 350°C. This difference in composition is due to changes in temperature. According to Zhang et al, the composition of aromatics and unsaturated hydrocarbons increased to 50.49 and 45.68 wt.%, respectively, at 430°C (L. Zhang et al., 2016). Rushdi et al reported that alkanes, methyl n-alkanoates, plasticizers, n-alkanoic acids, phenols, and polycyclic aromatic hydrocarbons were found to be the major products of hydrous pyrolysis (Rushdi et al., 2013). According to Rushdi et al, the polycyclic aromatic hydrocarbons in the absence of oxalic acid was 25.78% at 350°C (Rushdi et al., 2013). The concentration of cyclic aromatic hydrocarbon increased with increasing temperature. In the presence of oxalic acid, the concentration increased from 0.001 mg/g at 150°C to 5.15 mg/g at 400°C; by contrast, in the absence of oxalic acid, the concentration increased from 0.002 mg/g at 150 °C to 5.21 mg/g at 400°C.

2.5 Liquefaction using organic solvents

Now a days, in liquefaction process, the use of organic solvents has gained much more consideration than former methods as it is environmental friendly and can be conducted at comparatively lower temperatures (ranging between 250ºC and 400ºC) (Mazaheri, Lee, Bhatia, & Mohamed, 2010). The liquefaction process has positive benefits over pyrolysis process such as the presence of solvent avoids the cross-linking and reverse reactions in final product (Durak & Aysu, 2014). Water is a common medium in the liquefaction process, many scientists have conducted various studies on the liquefaction of numerous biomass for the production liquid fuels using water as a solvent. (Chandra, 2006; Dias De Oliveira et al., 2005; Sinha et al., 2008; Toor, Rosendahl, & Rudolf, 2011). The high critical values (374 °C and 22 MPa) of water need severe operating conditions. therefore, many efforts were made to investigate low critical value organic solvents, such as methanol, ethanol, and propanol (Yan et al., 2015). The low critical points of organic solvents offer milder conditions for liquefaction, which can make up the shortcoming of water (Yan et al., 2015). Alcohols are considered as an alternative solvent in liquefaction process of the biomass because of their features. Alcohol solvent are better solvent because they have fewer corrosion effects, good hydrogen donor, can be separated easily, low critical points and high product efficiency. Due to these remarkable feastures of alcohols,they are preferred more (Durak, 2015). The properties of different supercritical solvents are shown in table 2.4. Among all the properties shown in table 2.4, low critical points of alcohols are most attractive feature.

Table 2-4: Properties of different supercritical solvents

Solvent	**Formula**	**Boiling point (ºC)**	**Molar mass (g/mol)**	**Tc (ºC)**	**Pc (Mpa)**	**density (g/cm^3)**	**polarity**	**Dielectric constant @20ºC**
Water	H_2O	100	18.01	374	22.06	1	100	80.1
Methanol	CH_3OH	64.7	32.04	240	7.95	0.79	76.2	32.6
Ethanol	C_2H_5OH	78.24	46.07	241	6.3	0.78	65.4	22.4
Propanol	C_3H_7OH	97	60.1	263.8	5.2	0.8	—	20.18

2.5.1 Utilization of biomass in liquefaction process using alcohols

Currently, there is no information available on the liquefaction of scrap tire/ natural rubber using alcohol. However, information on the liquefaction of various biomasses are available. There are many parameters that affect in liquefaction process using alcohols such as size of particle, residence time, alcohol to biomass mass ratio, heating rate, and reaction atmosphere. In addition, the quality of raw material also has a significant influence on the final product, however, the temperature and solvent is found to be the most effective parameter that has an influence on the product quantity and quality. Few studies on the liquefaction of different biomass using different alcohols are shown in Table 2.5.

Table 2-5: Few studies on the liquefaction of different biomass using different alcohols

Ref	Materials	Process parameters					Product analysis	
		Type of reactor	**T (°C)**	**P (MPa)**	**Solvent**	**time**	**Quantitative analysis**	**Qualitative analysis**
(Aysu & Küçük, 2013)	Giant fennel (Ferula orientalis L.)	75mL capacity cylindrical autoclave	240 – 360	30	Methanol, ethanol and propanol	75mins	Maximum oil yield of 36.33 wt. %, 43.91 wt. % and 37.57 wt. % was obtained using methanol. Ethanol and propanol respectively.	Aromatics, aliphatic, oxygenated and nitrogenated compounds were detected from GCMS analysis
(Huang et al., 2013)	Rice husk	500ml autoclave	240 – 361	4.1 - 9.7	Ethanol (5 - 15%). Lower material to ethanol ratio had positive impacts on the bio-oil yield. As the material to ethanol ratio increased from 5% to 15%, the corresponding bio-oil yield decreased from 24.24% to 19.06%.	50 - 60mins	The highest yield of bio-oil, gas and solid was 24 wt.%, 37 wt.% and 44 wt.% respectively was obtained at temperature of 320ºC	Bio-oil obtained have 20.845MJ/kg of HHV. The C and H contents were estimated to be 52.59% and 6.63% respectively. The GCMS study of bio oil obtained from rice husk showing that phenolic compounds (18%) were the major compounds identified in the bio-oil, followed by esters (15%), long-chain alkanes (11%), benzene ramifications (3.2%) and furan derivatives (2.7%).

(Mohamad, Mohamad Yusof, & Yong, 2017)	Oil palm fronds	30ml mini batch reactor	100 – 230	9	Methanol and Ethanol	0.5 - 30mins	The maximum yield of 41wt. % was achieved at temperature of 230ºC using ethanol with time of 20mins	—
(Yan et al., 2017)	Sweet sorghum stalk	100mL stainless-steel magnetically stirred autoclave	240 – 320	—	Methanol	0 - 60mins	At optimal condition of 300 °C and 30 min, the maximum yield of BO is 40.5 wt%	Bio oil have HHV of 25.1 kJ g^{-1}. From GCMS analysis, the compounds detected in bio oil were grouped into hydrocarbons, alcohols, phenolic compounds, methoxybenzenes, ketones, esters, and others.

(Brand & Kim, 2015)	Red pine sawdust	160ml batch autoclave	260 – 360	—	material to Ethanol ratio = 1/10	30mins	The yield of bio crude increased from 32.1 to 42.0 wt. % with an increase in temperature from 265 to 350°C.	The C and H contents of bio crude increase as the temperature increases from 265 to 360°C. At 360°C, the HHV of bio crude was 31.28MJ/kg. Most of the product gas produced from the liquefaction of red pine sawdust were comprised of CH_4, C_2H_4, C_2H_6, H_2, CO, CO_2
(Durak, 2015)	Phellinus pomaceus	75mL cylindrical autoclave reactor	250 – 300	4 – 5	Ethanol	75mins	At 290°C, the maximum liquid yield of 29wt % was achieved.	At 290°C, the C and H contents in bio oil were 52.83 and 7.79%. The HHV of oil was 22.23 MJ/kg. Also, bio-oils from liquefaction were composed of various organics including aromatics, nitrogenated and oxygenated compounds
(Mazaheri et al., 2010)	Oil palm fruit press fiber	450ml High-pressure autoclave reactor	210 - 330	—	Methanol and Ethanol were used. Material to solvent ratio = 1/10	45mins	At temperature of 210 – 330^{a}C, with methanol and ethanol, the highest liquid product yield obtained were 38.0% and 36.9% respectively.	—

2.5.1.1 Effect of temperature

Various investigation have been made to study the effect of process temperature on liquefaction of biomass using alcohols. Aysu and Küçük performed the liquefaction of giant fennel (Ferula orientalis L.) using different organic solvents such as methanol, ethanol and propanol (Aysu & Küçük, 2013). The effects of different parameters such as temperature and solvent on product yields were investigated. The results showed that conversion highly depends on the temperature. The yield of bio-oil increases with the increase in the temperature from 240°C to 320°C. However, opposite trend was observed for the solid product yield. The highest bio-oil yield (43.91%) was obtained using ethanol at 360°C.

Similarly, Huang et al. conducted the liquefaction of rice husk for the production of bio oil using ethanol (Huang et al., 2013). The Liquefaction experiments were performed at various reaction temperatures ranging from 240°C to 360°C. The highest bio-oil yield of 24 wt.% was obtained at temperature of 320°C. Further increase in temperature to 360°C resulted in the reduction of bio-oil yield.

Mohammad et al. carried the liquefaction of oil palm fronds for the production of furfural using methanol and ethanol as a solvents (Mohamad et al., 2017). The effect of process temperature was studied from 100°C to 230°C. The furfural yield increased as the temperature increased. The maximum yield of 41wt. % was achieved at temperature of 230°C using ethanol with reaction time of 20mins (Mohamad et al., 2017). Same investigations that have been made are shown in Table 2.5.

2.5.1.2 Effect of solvent

Aysu and Küçük conducted the liquefaction of giant fennel (Ferula orientalis L.) using different organic solvents such as methanol, ethanol and propanol (Aysu & Küçük, 2013). At optimum condition of 320ºC, the use of methanol, ethanol and propanol produced 36.33 wt.%, 43.91 wt.%, and 9.91 wt.% of liquid oil yield. Whereas, for by-products, the use of ethanol at 320ºC, produced 53.76 wt.%, and 12.36 wt.% of solid and gas yield respectively.

Similarly, Huang et al. studied the effect of material to solvent ratio on product yield during the liquefaction of rice husk using ethanol (Huang et al., 2013). AT 200ºC, the ratio of material to solvent was varied from 5 to 15%. Lower material to ethanol ratio had positive impacts on the bio-oil yield. As the material to ethanol ratio increased from 5% to 15%, the corresponding bio-oil yield decreased from 24.24% to 19.06%. At high biomass to solvent ratios, the relative interactions among molecules of biomass and that of solvent become less influential, which can suppress the dissolution of biomass components.

Mohammad et al. also studied the effect of type of solvent used for liquefaction of oil palm fronds (Mohamad et al., 2017). Methanol and ethanol were as a solvents. The highest oil yield of 36 wt. % and 25 wt. % was achieved using ethanol and methanol respectively at 230ºC. Similar investigations that have been made are shown in Table 2.5.

2.5.1.3 Effect of time

Various studies also have been made on the effect of reaction time on product yield and composition in liquefaction process using alcohols. Mohammad et al. studied the influence of reaction time (0.5 to 30mins) on liquid yield during the liquefaction of oil palm fronds using methanol and ethanol as a solvents (Mohamad et al., 2017). At temperature of 230ºC, longer reaction time significantly increased the furfural yield for the first 20 min but subsequently decreased at longer reaction time (30 min). The increase in furfural formation initially can be attributed to the high accessibility of xylose in the biomass. On the other hand, the subsequent decrease in furfural yield at 30 min can be attributed to side reactions i.e. condensation and resinification. At 230 ºC and 20mins, the maxium liquid yield of 43 wt.% and 34 wt.% was obtained using ethanol and methanol as a solvent respectivety.

Similarly, Zong et al. studied the effect of reaction time during the liquefaction of sweet sorghum stalk using methanol (Yan et al., 2017). According to Zong et al. at constant temperature of 300ºC and material to solvent ratio of 1:15, the yield of bio oil increase from 30 wt. % to 40 wt. % as the time increases from 0 to 30mins. Further, prolonging in time reduced the bio oil yield. It was reported that at optimal reaction time for the liquefaction of sweet sorghum stalk is 30 min. The reduction in the bio oil yield with increase in reaction time from 30 min could be attributed to condensation, cyclization, and polymerization of some species in the bio oil into residue or deep degradation of some species in the bio oil into gaseous products (Yan et al., 2017). Similar investigations that have been made are shown in Table 2.5.

2.5.2 Characteristics of liquid products obtained by liquefaction using alcohols

Various investigations have been made on the characteristics of liquid products obtained by liquefaction using different alcohols. Huang et al. reported that at optimum conditions the maximum HHV of oil obtained was 20.84 MJ/kg by the liquefaction of rice husk using ethanol as a solvent (Huang et al., 2013). Similarly, Zong et al. reported that maximum HHV of 25.1 kJ/g was obtained by the liquefaction of sweet sorghum stalk using methanol as a solvent (Yan et al., 2017). Also, Kim and Brand conducted that liquefaction of red pine sawdust using ethanol and at optimum condition the maximum HHV of bio crude obtained was 31.28MJ/kg (Brand & Kim, 2015). According to Durak, at optimum condition, the maximum HHV of oil obtained was 22.23 MJ/kg by the liquefaction of Phellinus pomaceus using ethanol (Durak, 2015).

Huang et al. reported, the ultimate analysis of oil product obtained from rice husk at optimum conditions contained C and H contents of 52.59 wt.% and 6.63 wt.% correspondingly (Huang et al., 2013). Also, Kim and Brand performed the elemental analysis of oil products obtained from red pine sawdust consisting about 74.6 wt. % and 6.44 wt.% of carbon and hydrogen contents at 360°C (Brand & Kim, 2015). The C and H contents of bio crude increase as the temperature increases from 265 to 360°C (Brand & Kim, 2015). Similarly, Durak showed that the results of elemental analysis of bio-oils obtained from liquefaction of phellinus pomaceus in ethanol at 290°C consisting about 52.83 wt.% and 7.79 wt.% of C and H contents respectively (Durak, 2015). For solid products, Durak reported the elemental analysis of solid residue consisting about 60.20 wt.% and 4.61 wt.% of C and H contents at 290°C (Durak, 2015).

Kim and Brand studied that most of the product gas produced from the liquefaction of red pine sawdust were comprised of CH_4, C_2H_4, C_2H_6, H_2, CO, CO_2 (Brand & Kim, 2015). The yield of gases increased as the temperature increased from 265°C to 250°C. The concentration of CO_2 and CO was high in the product gas (Brand & Kim, 2015). Aysu and Küçük conducted the GCMS study of the oil products obtained from giant fennel, which showed the presence of Aromatics, aliphatic, oxygenated and nitrogenated compounds (Aysu & Küçük, 2013). Huang et al. performed the GCMS study of bio oil obtained from rice husk showing that phenolic compounds (18%) were the major compounds identified in the bio-oil, followed by esters (15%), long-chain alkanes (11%), benzene ramifications (3.2%) and furan derivatives (2.7%) (Huang et al., 2013). Similar investigations made on the characteristic of products obtained by the liquefaction can be seen in Table 2.5.

2.6 Environmental and economic feasibility

Liquefaction is a viable and environment friendly technique for conversion of wastes (such as scrap tires and organic wastes) into liquid fuels. Liquefaction of rubber tire yields three main products, namely, liquid oil, gas, and solid residues. During liquefaction of rubber tire, most sulfur and nitrogen contents are retained in the solid residue, thereby substantially reducing the emission of SOx and NOx in the gas products (D. T. Chen et al., 1995; S. Park & Gloyna, 1997; Yi et al., 2009). However, reduction of nitrogen and sulfur contents in solid residues must be further improved. Similarly for liquid products, minimal improvements are required for reduction of nitrogen and sulfur contents (L. Zhang et al., 2016). Zhou et al. reported the sulfur contents in oil obtained were 1.07 to 2.28%. Similarly, Chen et al and Funazukuri et al reported 1 wt.% and 2 wt.% sulfur in the oil obtained from the liquefaction of scrap tire respectively (D. T. Chen et al., 1995; Funazukuri et al., 1987). For greenhouse gas emissions, Pilusa et al reported quantitative analysis of the flue gas produced by the combustion of tire derived oil (J. Pilusa, Shukla, & Muzenda, 2014). According to their studies, the burning of tire oil generated 0.23, 12.5, 0.003, and 0.01 (vol. %) of SOx, CO_2, NOx and CO respectively (J. Pilusa et al., 2014; T. Pilusa, Shukla, & Muzenda, 2013). Table 2.6 shows the greenhouse gases emissions from tire oil.

Table 2-6: Greenhouse gases emissions from tire derived oil

Gas components	Concentration (Vol. %)	Emission level (g/KWh)
Sulfur dioxide (SO_2)	0.23	8
Nitrogen Oxide (NOx)	0.003	0.08
Carbon dioxide (CO_2)	12.5	296
Carbon monoxide (CO)	0.01	0.15
Hydrocarbons (HC)	0.02	0.18
Nitrogen (N_2)	73.6	1110
Oxygen (O_2)	3.5	60
Moisture (H_2O)	10.1	98

(J. Pilusa et al., 2014)

Liquefaction of rubber tire produces high quality and quantity of oil products. Thus, this technique exhibits a potential for developments in the energy industry. Hydrous pyrolysis of rubber tire is a cost-effective technique used to convert rubber tire into fuel (Rushdi et al., 2013). Generally, pyrolysis of rubber tire is conducted at temperatures higher than 400°C, thereby increasing the operational cost of the process ("Daily Prices of Natural Rubber (US dollar per 100 kg)," 2015). Therefore, studies have focused on optimizing pyrolysis by using water below 400°C. Rushdi et al presented the economic viability of liquefaction of rubber tire (Rushdi et al., 2013). According to their report, a yearly profit of $1.18–1.78M can be obtained through liquefaction of 30 MT rubber tire per day. The process could be more profitable using solid residues as a fuel and product gases for waste heat recovery through process upgrading.

Another study conducted by California Integrated Waste Management Board reported that the gross revenue of $1.45 per tire rubber could be made through this process. This study also estimated the capital cost and operational cost for the plant. According to this report, capital cost of \$257 per tons per annum and \$238 per kilowatt were required for the plant, whereas the operational cost of the plant was calculated 4.5% of capital cost with heat recovery system (BOARD, 2006).

Similarly, Huffman and Shah (1997) reported that 8.4 million barrel of oil per year could be produced by using the rubber tire of 2.8 million tons/year, generating the revenue of \$168 million/year (including the revenue from by-products) (Huffman & Shah, 1997).

A techno-economic study conducted by Shelley and El-Halwagi showed the promising economic feasibility of pyrolysis for economic assessment of liquefaction of rubber tire (Shelley & El-Halwagi, 1999). According to their study, investment decisions were made using return on investment (ROI) approach. ROI is defined as, a profitability measure that evaluates the performance of investment or a business by dividing the net profit by net worth (Ichsani & Suhardi, 2015; Menezes, Kim, & Huang, 2015). ROI is one of the important tools used to measure the efficiency or consequences of investment. In many cases, it is also used to compare the efficiency of a number of different investments. In this approach, the investment was considered positive if the ROI was positive. The results showed the promising and advantageous economic feasibility with ROI of approximately 12%. In addition, the tipping fee obtained for raw material was found to play a key role in overall profitability. The high tipping fees received will be linearly subsidized to increase in ROI.

2.7 Conclusions

Natural rubber is one of the promising sources of alternative energy and can be employed to solve the problem of energy crisis. Studies in the literature showed numerous techniques are available for depolymerization of natural rubber; these techniques include pyrolysis, gasification, chemical degradation, catalytic cracking, hydrogenation, and hydrous pyrolysis. Liquefaction of natural rubber is the most cost-effective process because it produces high liquid yield under low-temperature conditions. Most studies also focused on using rubber tires. A maximum liquid yield of approximately 44% was obtained under the optimum conditions of 400°C, water/rubber ratio of 2:1, and reaction time of 60 min. The advantage of this process is that it can also use raw materials with high moisture contents without requiring a pre-drying process. Moreover, the use of water as a reaction medium in liquefaction has gained considerable attention because it can easily separate water from oil products and is more economical compared with other organic solvents, such as pentane and toluene. Other solvents, such as alcohols can also be employed in the process due to their low critical points as compared to water. The use of alcohols not only provide the milder conditions for the process but they will also improve the quantity and quality of the liquid products. For environmental concerns, during liquefaction of rubber tire, NOx and SOx were not produced in the gas product. The use of pure natural rubber as a feedstock in liquefaction is environment friendly because pure natural rubber does not contain sulfur. Moreover, the advantage of using natural rubber is that it would required low degradation conditions as compared to scrap tire. Furthermore, this process is an optional solution to contribute to fulfillment of energy requirements and reduce dependence on fossil fuels. Liquefaction process seems to be one of the promising techniques for production of alternative fuels and chemicals. However, limited information is available regarding liquefaction of natural rubber. Therefore, further research is needed on liquefaction of natural rubber to assess the effect of different parameters on product quality and quantity and determine environmental and economic feasibility.

CHAPTER 3: LIQUEFACTION OF NATURAL RUBBER TO LIQUID FUELS VIA HYDROUS PYROLYSIS

3.1 Introduction

Nowadays, researchers are using many different techniques to convert biomass into liquid fuels. Pyrolysis, chemical degradation, hydrothermal liquefaction, and hydrogenation are well known techniques used for this purpose. Among these processes, hydrothermal liquefaction process is promising technique for the production of liquid fuels. It is also known as Hydrous pyrolysis. One of the most important advantages of this technique is that it can be used on raw material with high moisture content without the need for pre-drying. This process is conducted using water at high temperatures and high pressure conditions and induces the decomposition of long-chain polymers of carbon, hydrogen, and oxygen into small-chain petrochemicals (monomers) (P. Basu, 2010; John W. Larsen & Hu, 2006). The products of hydrous pyrolysis are oil, solid residue, and gases. The amount of liquid oil obtained is higher than that of solid residue and gaseous products. The typical yield of oil, solid and gas obtained by this process is ranging from 21 to 77 wt.%, 12 to 60 wt.% and 0 to 63.4 wt.% respectively. Usually the properties of oil obtained through hydrous pyrolysis depend upon the type and composition of biomass (Jahirul, Rasul, Chowdhury, & Ashwath, 2012).

Many researchers have carried out studies on the hydrous pyrolysis of various biomass to produce liquid fuels. In general, it is observed that the oil obtained from biomass have lower calorific value within the range of 30 to 36 MJ/kg compared to petroleum based fuels (Chandra, 2006; Dias De Oliveira et al., 2005; Sinha et al., 2008; Toor et al., 2011). Zhang et al. (He, Zhang, Funk, Riskowski, & Yin, 2000) converted the swine manure into liquid fuel at the temperature of 275 to 350^{o}C and at pressure of 5.5 to 18 MPa. The oil obtained had calorific value of 35 MJ/kg. The elemental analysis of oil showed that the oil contained 71% carbon and 0.21 ppm of sulfur in it (He et al., 2000). Minowa et al. (Minowa, Murakami, Dote, Ogi, & Yokoyama, 1995) reported the conversion of synthetic garbage (consisting of mixture of rice, vegetables, butter and bread) into oil. The maximum oil yield obtained was 21 wt.%. The reported operating parameters were: 350^{o}C temperature, 18 MPa pressure and 30 min reaction time. The calorific value of oil was 36 MJ/kg and the reported oil composition consisted of 73.6 % of carbon, 9.1% of hydrogen, 4.6 % of nitrogen and 12.7 % of oxygen (Minowa et al., 1995). Minowa et al. (Minowa, Kondo, & Sudirjo, 1998) studied the conversion of Indonesian biomass residual to liquid oil using hydrous pyrolysis technique at 300^{o}C temperature, 10 MPa pressure and 0.5 hour. The reported yield was 21 to 36 wt.%. At optimum conditions the oil produced was having a calorific value of 30 MJ/kg. The reported elemental composition was C: 67 to 80 %, H: 6 to 8%, N: 0 to 2 % and O: 11 to 23 % (Minowa et al., 1998).

As an optional technique, researchers have utilized scrap tire to obtain the oil which has high heating value. Zhou et al. (L. Zhang et al., 2016) conducted the hydrous pyrolysis of scrap tire and reported that the calorific value of oil obtained under the optimum conditions was 44.09–45.09 MJ/kg. The calorific value obtained was close to that of petroleum derived from crude oil, such as diesel (44.8 MJ/kg) (Sinha et al., 2008). However, the oil obtained from the scrap tire contained high sulfur contents. Generally, tire contains around 1 to 4 wt.% of sulfur contents (Martínez et al., 2013; S. Park & Gloyna, 1997; Williams, 2013). The presence of sulfur in a tire is generated from the vulcanization process (S. Park & Gloyna, 1997). When tire is subjected to hydrous pyrolysis, as consequence, high amount of sulfur also will be detected in the oil yield. Zhou et al. reported the sulfur contents in oil obtained were 1.07 to 2.28%. Similarly, Chen et al. (D. T. Chen et al., 1995) and Funazukuri et al. (Funazukuri et al., 1987) reported 1 wt.% and 2 wt.% sulfur in the oil obtained from the hydrous pyrolysis of scrap tire respectively. The presence of sulfur in fuel oil is able to decrease the ambient air quality by generating the SOx when it is burnt (Schmidt, 1985; Totten, 2003). This SOx subsequently causes contamination and pollution in environment.

Tire usually consists 40-52.2% of natural rubber (NR) and other components of tire are carbon black, metal, textile, sulfur and additives (A. K. Basu, 2009; Evans & Evans, 2006; Funazukuri et al., 1987). From those compositions shows that the natural rubber is found to be a dominant compound in tire. In this regard, it will be an interesting study to use the natural rubber alone in the hydrous pyrolysis process in order to understand the characteristic of the product yields. Currently, no literature is avalaible on the depolymerization of pure natural rubber through hydrous pyrolysis process. Natural rubber is an organic matter obtained from plants and typically obtained from the rubber tree, guayule plant, russian dandelion and rubber rabbitbrush (Barlow, 1970; Mooibroek & Cornish, 2000; P.M. Priyadarshan, 2009; Ray, 2010; Rogers & Cornish, 2005; Simmonds, 1994; J. van Beilen, 2006; J. B. van Beilen & Poirier, 2007a, 2007b; Whaley & Bowen, 1947). It is a tropical plantation crop usually found in Malaysia, Indonesia, Thailand and various central African countries (Barlow, 1970).The rubber tree cultivates best in a warm humid climate (Rogers & Cornish, 2005). According to Morton (1999), natural rubber is an organic polymeric compound of Isoprene, i.e. Poly Isoprene $(C_5H_8)n$ with minor amounts of impurities like other organic compounds and water (Morton, 1999).

In 2014, the worldwide production of natural rubber is estimated about 12.2 million metric tons which is increasing gradually on account of its high usage (Ahmad, Abnisa, & Daud, 2016; Inc., 2015). The high availability of natural rubber has attracted the industries to utilize the natural rubber as raw material for the preparation of valuable items such as gloves, tires, automotive parts, footwear, clothes, medical equipment, wall covering, paper, and cosmetics etc. (Abdullah, 1994; Alkhatib et al., 2015; F. Chen & Qian, 2002; Kohjiya & Ikeda, 2014; Martínez et al., 2013; Niaounakis, 2013; Rodgers & Abdullahi, 2016; Rogers & Cornish, 2005; Williams, 2013). According to 2013 statistics, the global consumption of natural rubber is calculated to be 11.3 million metric tons ("Natural Rubber Statistics," 2015; Statista, 2015), where around 7.4% of natural rubber remains un-utilized. This potential amount of natural rubber along with waste/discarded natural rubber can be used for the synthesis of liquid fuels.

In this study, the main objective was to conduct the hydrous pyrolysis of natural rubber for the production of sulfur free liquid fuel having a high heating value. The effect of different parameters such as temperature, pressure, water to material ratio, and reaction time on product yield obtained from the hydrous pyrolysis of natural rubber were also studied. Furthermore, the liquid product was characterized by several analysis devices to observe its quality. The energy potential from natural rubber based oil was calculated and presented in this paper.

3.2 Experimental

3.2.1 Materials

The natural rubber (NR) with SMR L grade (Malaysian Standard Rubber) was obtained from Malaysian Rubber Board. The NR used was chopped to particle size of approximately 3-5 mm. The NR was characterized using Thermogravimetric analysis (TGA). The proximate and ultimate analyses of NR were also performed. Distilled water that used as a reaction medium in this study was produced from Auxilab S.L, QUARTZ. Moreover, the inert nitrogen gas with 99 % purity was used to create a non-oxidative environment inside the reactor.

3.2.2 Experimental Procedure

The experimental setup was designed and fabricated by Amar Equipment Private Limited, Mumbai, India. The stainless steel autoclave (SS 316) was used as a batch reactor to carry out hydrous pyrolysis experiment with total capacity of batch reactor was 1 liter. The reactor consisted of furnace for heating. The reactor than was heated electrically to desired temperatures. It was also equipped by thermocouple, pressure gauge, safety valve, stirrer, and vent valve. Distilled (DI) water was used as a reaction medium in this study. The complete experimental system was shown in Figure 3.1.

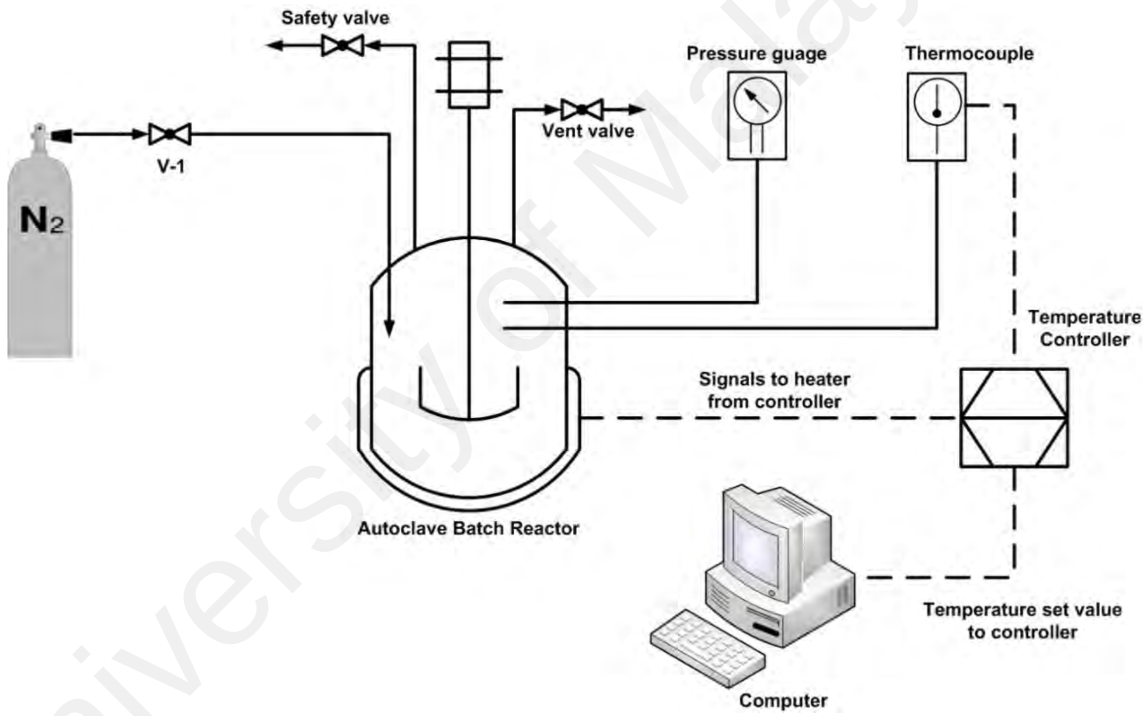


Figure 3-1: Schematic of experimental set up for the production of liquid fuels from natural rub

In this study, the experiment was performed by loading the NR and water into autoclave, then closed and purged with nitrogen to create the non-oxidative environment at 2 bar. The reactor was heated electrically to desired temperature and the temperature was monitored using K-type thermocouple. The heating rate of reactor was set to

10^{o}C/min and the stirrer rate was set to 10 rpm. Since experimental work was carried out in a closed system, the evolution of hot gas reaction products increased the internal pressure of the reactor during experimental runs. Consequently, the hydrous pyrolysis experiments were subjected to self-generated pressure whose extent depended on reaction temperature and the amount of water to NR mass ratio used. Three different sets of experiments were performed in this study. In the first set, the experiment was conducted at different temperature conditions within the range of 300 to 400^{o}C with the increment of 25^{o}C at different corresponding pressures of 54, 62, 70, 92, and 95 bar by keeping constant the H_2O/NR mass ratio and time at 3:1 (54g: 18g) and 30 mins respectively. In the second set, the experiment was performed by using different H_2O/NR mass ratio (g/g) [H_2O/NR=1:1 (18g:18g), 2:1 (36g:18g), 3:1 (54g:18g), 4:1 (72g:18g), and 5:1 (90g:18g)] with the corresponding pressures of 52, 61, 70, 93, and 97 bar at temperature and time of 375^{o}C and 30 mins respectively. For the last set, the experiment was conducted by varying the reaction time from 15 to 75 mins with the increment of 15 mins at 375^{o}C, 92 bar and H_2O/NR mass ratio of 3:1 (54g: 18g). After the process was done, the heater was switched off and the reactor was cool down to room temperature by cooling coils system. Three products were obtained liquid, tar, and gas products, where the liquid was considered to be the main product. The gas product was not collected due to limitations in reactor design. The liquid products and tar were collected and weighted. The gas product was calculated by the material balance. The yields of products were calculated by dividing its mass by the mass of NR loaded into the autoclave batch reactor, equation (3.1) was used for that purpose.

$$\text{Product Yield}(\%) = \frac{\text{wt. of product}}{\text{wt. of NR}} \times 100 \tag{3.1}$$

The yield of product gas was estimated by the subtraction: 100-(Oil yield + tar yield + water soluble). All experiments were repeated three times under the identical conditions to validate the experimental outcomes.

3.2.3 Raw material and Product analysis

The elemental analysis of raw material was performed using CHNS/O analyzer model 2400, whereas, the proximate analysis of raw material was conducted using ASTM standard (ASTMD 3173 and ASTMD3175) methods. The TGA analysis was performed using model NETZSCH STA 449F3. The TGA study of NR was conducted with 10 C^o/min heating rate to investigate their thermal characteristics. The analysis was carried out within the temperature range of 28^oC to 800^oC in the presence of nitrogen atmosphere. The flowrate of nitrogen purge gas was 20 mL/min. 11.58 mg of NR sample was used to carry the analysis.

After the completion of reaction time, the whole mixture inside the reactor was transferred in a 50 mL conical centrifuge tubes and subjected to centrifugation process at 3200 RPMs for 20 mins. As a result, three separate layers were obtained, consisted of oil layer at the top, water in the middle and solid at the bottom. The oil sample was collected by using micropipette, while the remaining portion in funnel was filtered out using whatman filter papers. The residue obtained on filter paper was dried in an over at 110^oC and weighted. The filtrate left was considered as water (aqueous phase). Using solvent extraction technique, water soluble fractions were extracted. The quantitative analysis of water soluble fraction was provided in this study. However, the main focus of this study was on liquid oil. Hence, the product characterizations were done only for liquid oil.

The physical analysis of liquid includes the viscosity (η) and density (ρ). The viscosity (η) of the liquid was estimated by using a rotational viscometer equipped with an SC4-18 spindle (Brookfield Viscometer made in USA, model DV-II+Pro EXTRA). All the measurements were taken at room temperature with sample amount about 7 mL. A 25 mL pycnometer was used to determine the density (ρ) of the liquid product. Liquid oil was filled in the pycnometer and weight of liquid oil was calculated by subtracting the weight of pycnometer. Density (ρ) was estimated by dividing this weight by the volume. Several chemical analysis were performed using pH meter, CHNS/O analyzer, Fourier transform infrared (FTIR), and gas chromatograph–mass spectrometer (GCMS). METTLER Toledo pH meter was used for the determination of pH values for liquid product at room temperature. FTIR spectroscopy analysis was conducted with a PerkinElmer Frontier FT-IR spectrometer. The samples were scanned within the range of 450–4000 cm^{-1} with a resolution of 4 cm^{-1}. The elemental analyses of all the oil samples were performed using CHNS/O analyzer model 2400 Perkin Elmer Series. The high heating value (HHV) was calculated by using the data obtained from the ultimate analysis. The Dulong formula (equation 2) was used for the estimation of the HHV of the liquid product based on the result of ultimate analysis (L. Zhang et al., 2016).

$$\mathrm{HHV}\left({}^{\mathrm{MJ}}/_{\mathrm{kg}}\right) = 0.338\mathrm{C} + 1.428\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) + 0.095\,\mathrm{S} \tag{3.2}$$

In equation (3.2), C, H, O and S stand for carbon, hydrogen, oxygen, and sulfur respectively.

For the calculation of energy balance, the energy input to the system was calculated based on the NR calorific value. Energy output is the total energy from liquefaction products based on HHV. The amount of energy recovery in the product was calculated in terms of percentage using Equation (3.3) (Hanif, Capareda, Iqbal, Arazo, & Baig, 2016).

$$\text{Energy recovery (\%)} = \frac{\mathrm{m}_{\mathrm{oil}} \times \mathrm{HHV}_{\mathrm{oil}}}{\mathrm{m}_{\mathrm{NR}} \times \mathrm{HHV}_{\mathrm{NR}}} \times 100 \tag{3.3}$$

Where, m_{oil} is the mass of product oil (kg), m_{NR} is the mass of raw material NR (kg), HHV_{oil} is the heating value of product oil (MJ/kg), HHV_{NR} is the heating value of raw material NR (MJ/kg). However, this relationship only describes the conversion of energy from the starting material to bio-crude and does not take into account the energy required for the liquefaction process. So as to compare the energy content of the resultant products (bio-crude) with the energy required to bring the reactants to the desired temperature the energy consumption ratio (ECR) was introduced (Minowa et al., 1998), (Yokoyama et al., 1987) and (Biller & Ross, 2011). ECR is defined as:

$$ECR = \frac{E_L}{E_P} \tag{3.4}$$

Where, E_L the energy required for the hydrothermal liquefaction and E_P is the energy of the products (bio-crude). If ECR<1 then the energy required for the process is favorable as the products have higher energy content as compared to that required for the reaction. If ECR>1 more energy is required for the process to happen as compared to the energy content of the products. E_L is calculated according to following procedure:

$$E_L = \frac{(Wf_{\cdot water} C_{p,water} \times \Delta T + (1 - Wf_{\cdot water}) C_{p,NR}\, \Delta T)(1 - R_h)}{R_C} \tag{3.5}$$

Substituting equation (3.5) in equation (3.4):

$$ECR = \frac{(Wf_{\cdot water} C_{p,water} \times \Delta T + (\, Wf_{\cdot NR}) C_{p,NR}\, \Delta T)(1 - R_h)}{(X_{oil} \times \mathrm{HHV}_{\mathrm{oil}}) R_C} \tag{3.6}$$

Where $Wf._{water}$ is initial fraction of water. R_h and R_c are the efficiencies of heat recovery and combustion energy assumed to be 0.5 and 0.7 respectively, X_{oil} is the bio crude oil yield.

The compound identification in the oil products were performed by GCMS (Shimadzu GC-2010 plus) equipped with a capillary column (RTX-5MS, 60 m length, 0.25 mm i.d., 0.25 μm film thickness). The samples were prepared as 50 ppm solution in cyclohexane. The injector temperature was set at 300°C. The oil products sample was injected with a split ratio of 3:1. A two-minute solvent delay was set to protect the filament. The column was firstly held at 40°C for 4 min. The temperature was increased to 300°C at 4°C min^{-1} and held isothermally for 4 min, giving a total runtime of approximately 73 min. Helium flowing at 3 mL min^{-1} served as the carrier gas.

Furthermore, in order to minimize the margin of mistake and to generate more reliable data, the analysis of every product from all experimentations were repeated three times, and the averaged results were reported here. Moreover, the standard deviation (SD) was calculated for the replicated experimental runs for oil and tar yield. The values of gas yield which were obtained by the difference were also used for the calculation of SD using SD correlation. This data describes the error analysis, originality and reproducibility of results. However, for the analysis, the accuracy and uncertainty of analyzers were improved by using standards. Therefore, to reduce the chances of error and to generate more accurate and precise results, every instrument employed for the analysis was calibrated and verified by using standards.

3.3 Results and discussion

3.3.1 Characterization of raw material

Ultimate and proximate analyses of any materials are very important since they provide information about the chemical and elemental composition of materials. The ultimate and proximate analyses of raw material are shown in Table 3.1. The proximate analysis consists volatile matter, fixed carbon, ash, and moisture. The volatile matter is the condensable and non-condensable vapors released when organic material is heated, whereas the fixed carbon is the solid combustible residue that remains after a precursor particle is heated and volatile matter is driven off. In determining the total volatile matter, the samples were heated and annealed at 900°C (Telmo, Lousada, & Moreira, 2010). The fixed carbon content was calculated by subtracting from 100% the sum of moisture, volatile matter and ash contents in percentage. From Table 3.1, it can be seen that the volatile matter in NR is 89.98 %, while the fixed carbon and ash contents in NR are 4.71 % and 3.60 % respectively. It is reported that high volatile contents in organic material provides high volatility and reactivity, which subsequently favors the production high quantity of liquid and gas products, whereas the presence of fixed carbon leads to the formation of char (Jahirul et al., 2012). Moreover, it can also be seen that NR consists of high hydrocarbons as it is pure poly-isoprene. The carbon and hydrogen contents in NR were estimated to be 83.63 % and 11.97 % respectively. Furthermore, the Table 3.1 is also showing that the NR is sulfur free material with low oxygen contents. The high amount of carbon and hydrogen contents have positive effect on the HHV, whereas, high oxygen contents reduces the HHV (Abnisa & Wan Daud, 2015). Therefore, the presence of high hydrocarbons, high HHV, volatile matter and less sulfur clearly showed that the properties of NR is reliable and suitable alternative material to produce liquid fuels.

Table 3-1: Characteristics of natural rubber

Characteristics	Natural rubber
Proximate Analysis (wt.%)	
Volatile matter	89.98
Fixed carbon	4.71
Ash	3.60
Moisture	1.71
Ultimate Analysis (wt.%)	
Carbon	83.63
Hydrogen	11.97
Nitrogen	1.58
Oxygen	2.71
Sulfur	0.12
HHV(MJ/kg)	45

3.3.2 Thermogravimetric analysis (TGA) of raw material

In this study, TGA was performed to get an overview of the thermal behavior of the feedstock. From Figure 3.2 it can be seen that the thermal decomposition of NR started approximately at 300°C and more than 95 % of NR was decomposed when temperature reached about 480°C. Same study has been reported by Mohapatra and Nando (2014) (Mohapatra & Nando, 2014). In NR, the degradation of Poly-isoprene was occurred which was pure hydrocarbon. The high percentage of weight loss observed from TGA analysis indicated that 350-400°C was found to be a suitable temperature for maximizing NR conversion into liquid product.

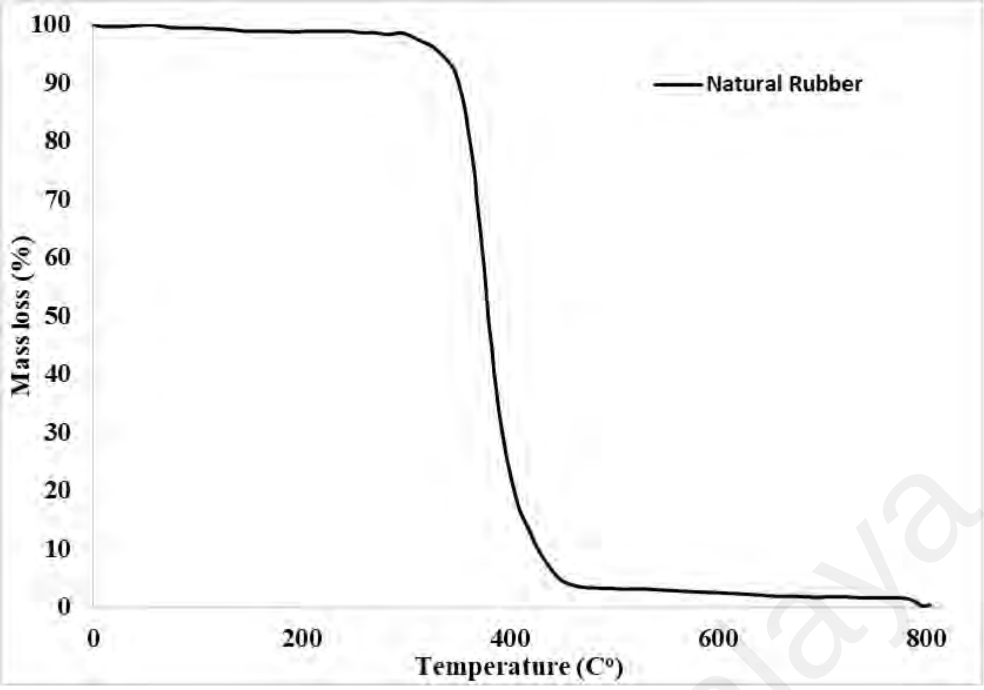


Figure 3-2: TGA curve for natural rubber

3.3.3 Effect of operating parameters on products

3.3.3.1 Effect of temperature and corresponding pressure

For this study, the time and H_2O/NR mass ratio were kept constant at 30 mins and 3:1 respectively whereas, the temperature was varied at 300, 325, 350, 375, and 400°C with the corresponding pressures of 54, 62, 70, 92, and 95 bar respectively to observe their effect on product yield. All the experiments were performed below supercritical conditions. The Figure 3.3 showed that the yield of liquid product was increased from 69 to 76 wt% as the temperature rose from 300 to 375°C. However, further increase in temperature didn’t show any significant effect on liquid yield increment. In contrast to liquid, the tar yield was decreased with the increase of temperature. The lowest tar yield of 8.26 wt% was achieved at 400°C. The tar yield was lesser than the liquid yield due to the presence of low ash and fixed carbon in the NR. The gaseous products were always the lowest fraction and were only detected at temperatures above 300°C in depolymerization process. The gas yield obtained was 4-8 wt% within the temperature range of 300-400°C. Moreover, the yield of gas products increased slightly with increasing temperatures due to cracking of the liquid product, where same phenomena has been described by many researchers (S. Park & Gloyna, 1997; L. Zhang et al., 2016). Water soluble fraction showed similar trend as liquid oil. That is, the yield of water soluble fraction increased with the increment of temperature up to 375°C, after which a slight decrease in yield was observed. In figure 3.3, σ represents standard deviation.

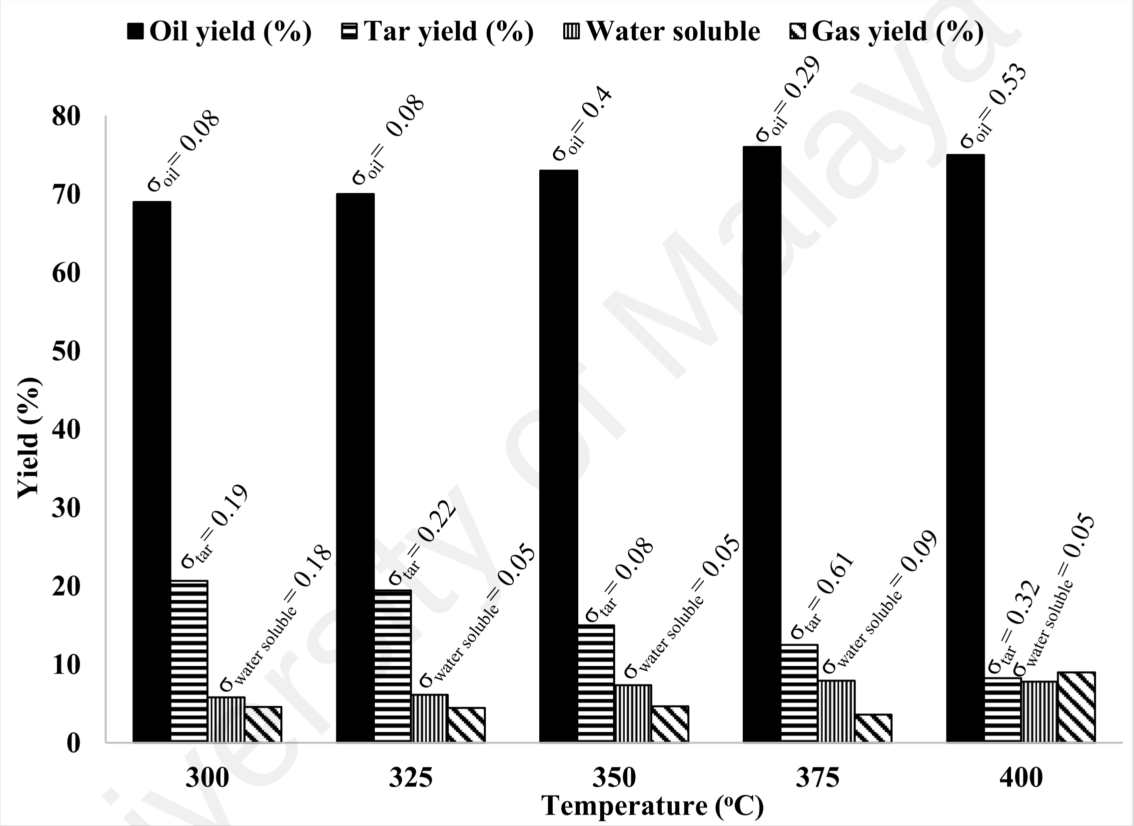


Figure 3-3: The effect of temperature on oil yield

3.3.3.2 Effect of water to natural rubber mass ratio

Normally, in hydrous pyrolysis the addition of water made the conversion milder than that of the direct pyrolysis of biomass. In this study, the effect of the different H_2O/NR mass ratios was varied at 1:1, 2:1, 3:1, 4:1 and 5:1 with corresponding pressures of 52, 61, 70, 52.4, and 51 bar. The temperature and time were fixed at 375°C and 30 mins respectively. It was found that the increase in liquid yield was observed linearly as the ratio of water increased from 1:1 to 4:1, while the maximum liquid product of 76 wt.% was obtained at 375^{o}C with H_2O/NR mass ratio and reaction time of 3:1 and 30 mins respectively. This phenomenon can be described by the presence of water in the process. As water can behave an a nucleophile, the increase of H_2O ratio in NR has led to the increase in the concentration of nucleophiles (D. T. Chen et al., 1995), which also enhances the attack possibility of the polymer backbone, engendering fragmentation of the polymer molecules and leading to higher liquid products yield. In addition, at same operating conditions, the tar and gas yield were estimated to be 12.5 and 4 wt% respectively. From figure 3.4, it can be seen that the amount of evolved gas increased as H_2O/NR mass ratio slightly increased from 1:1 to 3:1. However, the further increase of H_2O/NR mass ratio didn't show any significant effect on gas yield. Furthermore, it was found that the difference in H_2O/NR mass ratio had no significant effect on the water soluble fraction. The highest water soluble fraction of yield 7.9 wt% was obtained at H_2O/NR mass ratio of 4:1. The trend is shown in figure 3.4.

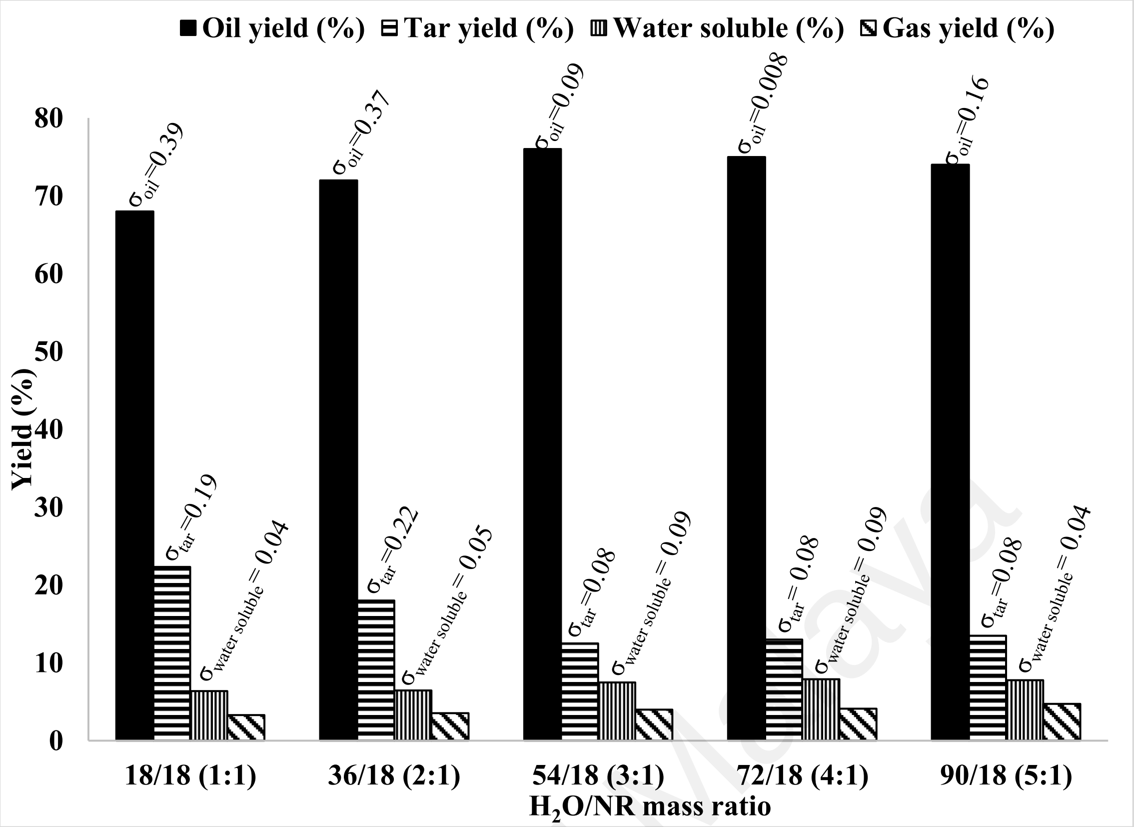


Figure 3-4: The effect of H_2O/NR mass ratio on liquid product yield

3.3.3.3 Effect of reaction time

The influence of reaction time on products was conducted at the temperature of 375°C, and with a H_2O/NR mass ratio of 3:1 with varying times from 15 to 75 min. From Figure 3.5, it can be observed that the conversion of liquid product increased steadily with reaction times from 15 min to 30 min. The residence time of 30 min at 375°C was observed to be sufficient to depolymerize the NR for the production of 76 wt% of liquid product. However, the further prolonging the holding time didn't show any significant effect on the liquid product yield. The longer the reaction time, the higher cost of process needed. Moreover, different reaction times didn't show any significant change on tar and gas yield. Same phenomena has been explained by Zhang et al (L. Zhang et al., 2016).

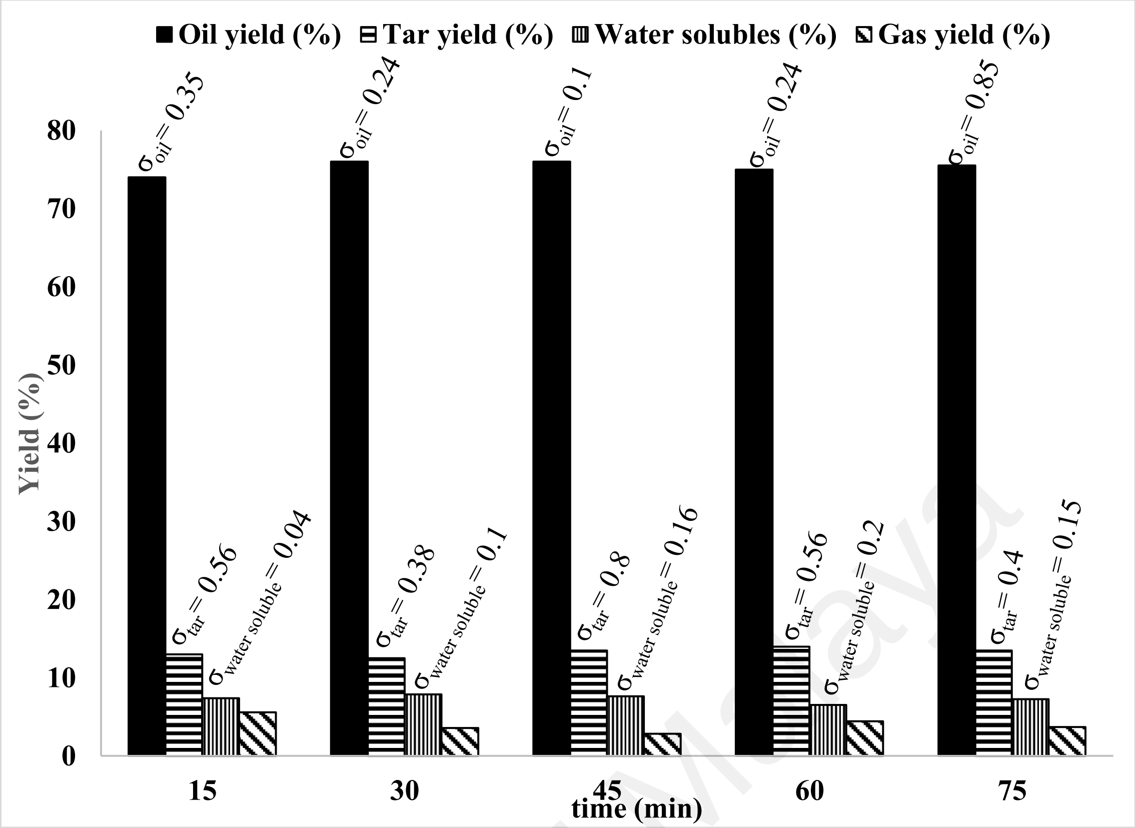


Figure 3-5: The effect of residence time on oil yield

3.3.4 Characterization of liquid products

3.3.4.1 Elemental analysis and HHV

Table 3.2 shows the elemental analysis and calorific values of liquid products obtained through the hydrous pyrolysis of NR at different operating parameters. Natural rubber is mainly consists of high amounts of hydrocarbons contents (carbon and hydrogen), which makes it a potential raw material for the synthesis of high grade liquid product. The elemental analysis showed that the carbon and hydrogen contents in the liquid product increased with the increase of temperature, whereas, the H_2O/NR mass ratio showed the opposite trend for carbon contents. For all liquid products, the nitrogen contents were always lower than the nitrogen present in NR. The oxygen contents in the liquid product were found to be larger than that of NR. It is due to the fact that usually water gets incorporate into liquid products during hydrous pyrolysis (L. Zhang et al., 2016). The increase in temperature favored the depolymerization of NR which also results in the decrease of nitrogen contents in liquid products. The same phenomena has been reported by Zhang et al (L. Zhang et al., 2016). The HHV was approximately between 42 to 45 MJ/kg for all liquid products. The calorific value of liquid product obtained from the hydrous pyrolysis of NR is close to the petroleum fractions derived from the crude oil (44 MJ/kg) (Ahmad et al., 2016).

Table 3-2: Effect of operating parameter on liquid product characteristics

Characteristics	Temperature (°C)[a]					H_2O/ NR ratio[b]					Time (min)[c]				
	300	**325**	**350**	**375**	**400**	**1: 1**	**2:1**	**3:1**	**4:1**	**5:1**	**15**	**30**	**45**	**60**	**75**
Physical properties															
Viscosity (cP)	713	41.1	23.2	**14.6**	14	45.2	39.6	**14.6**	7.3	7.2	46.2	**14.6**	13	7.3	7.23
pH	7.68	7.25	7.26	**7.33**	7.74	6.76	7.35	**7.26**	6.88	7.1	7.35	**7.26**	7.33	7.26	7.68
Density (g/ml)	0.85	0.85	0.87	**0.86**	0.82	0.84	0.82	**0.86**	0.82	0.8	0.82	**0.86**	0.87	0.86	0.85
Elemental Analysis															
HHV (MJ/kg)	42.3	43.46	44.29	**45.43**	45.66	43.41	43.34	**45.43**	44.99	45.08	43.33	**45.43**	45.78	44.64	45.63
Carbon	80.17	81.87	82.72	**84.62**	84.89	85.93	85.87	**84.62**	82.93	82.97	85.87	**84.62**	85.62	82.72	83.65
Hydrogen	11.58	11.76	12	**12.11**	12.15	10.36	10.4	**12.11**	12.34	12.41	10.4	**12.11**	12	12.23	12.54
Nitrogen	0.45	0.5	0.41	**0.41**	0.52	0.91	0.38	**0.41**	0.76	0.47	0.38	**0.41**	0.41	0.41	0.45
Oxygen	7.58	5.68	4.63	**2.67**	2.22	2.53	3.11	**2.67**	3.78	3.94	3.14	**2.67**	1.74	4.47	3.17
Sulfur	0.22	0.19	0.24	**0.19**	0.22	0.27	0.24	**0.19**	0.19	0.21	0.21	**0.19**	0.23	0.17	0.19
Energy recovery (%)	71.19	71.18	75.77	**78.98**	75.93	65.41	66.28	**75.07**	74.81	73.95	71.07	**77.03**	77.12	76.02	76.07
ECR	0.326	0.341	0.334	**0.334**	0.361	0.168	0.278	**0.344**	0.445	0.551	0.363	**0.334**	0.334	0.339	0.339

[a] H_2O/NR mass ratio = 3:1, time = 30min

[b] Temperature = 375°C, time = 30min

[c] Temperature = 375°C, H_2O/NR mass ratio = 3:1

3.3.4.2 Viscosity, density, and pH value

Table 3.2 shows the viscosity, density, and pH values of liquid products obtained at different operating conditions. From table 3.2, it can be seen that the viscosity decreased when the temperature of the process increased. At 300°C, a high value of viscosity was obtained to be 713 cP, however, at 325°C a very significant change in viscosity was measured to be 41.13 cp. It is due to the fact that less degree of depolymerisation occurred at lower temperature of 300°C (D. T. Chen et al., 1995). The final viscosity value was obtained 14 cP when temperature reached to 400°C. Furthermore, the H_2O/NR mass ratio and reaction time also showed the same trend like the effect of temperature. The increase in H_2O mass ratio results in the decrease of viscosity of liquid product. The increase in contact time decreased the viscosity of the oil due to the high extend of deploymerisation of NR, same finding has been reported by Chen et.al.(1995) (D. T. Chen et al., 1995). The optimum condition of process was resulted in the oil with viscosity of 14.61 cP. In contrast to viscosity, it can see that the variation of temperature, H_2O/NR mass ratio, and residence time did not show any significant effect on the density of oil products. At optimum conditions (374°C, H_2O/NR mass ratio= 3:1 and 30 min), the density of oil product was reported to be 0.859 g/ml, which was close to the density of diesel which was 0.82 g/ml. For pH analysis, the results showed that no significant improvement on pH value of liquid product when the operating parameters were changed. The average value of pH obtained was 7.26.

From all the quantitative and analytical data, it can be seen that the operating conditions of 375°C, H_2O/NR ratio 3:1, and 30mins were found to be the best and optimum.

3.3.4.3 Fourier transform infrared (FTIR) spectroscopy analysis

The results of FTIR analysis showed that all of the obtained oils had similar characteristics in term of chemical bonds (functional groups), where four major peaks were clearly observed during the analysis. Based on this finding, the discussion of FTIR analysis in this section was only emphasized on the liquid product obtained at optimum conditions of 375°C, H_2O/NR mass ratio of 3:1 and 30 min. As shown in Figure 3.6, the FTIR analysis identified that C-H, CH_2, and CH_3 were the most abundant chemical bonds detected in liquid product produced from the hydrous pyrolysis of NR. The function group of C-H bending was generally found at peaks between 864-919 cm^{-1}, which indicated the presence of vinyl and aromatic compounds.

A strong peak which found around 1450 cm^{-1} indicated the presence of methylene group (CH_2), while an additional strong peak about 1375 cm^{-1} was detected as a methyl group (CH_3). The functional groups related to methyl and methylene were also detected at high wavelength frequencies above 2500 cm^{-1}, where methyl and methylene groups were detected at peak of 2857 cm^{-1} and 2924 cm^{-1} respectively. From FTIR results it can be seen that the methyl and methylene groups were found as the dominant compounds. The same functional groups have also been reported by many authors from the deploymerisation of polyisoprene, which the methyl and methylene groups were recognized as major components in NR (Cataldo, 1998; F. Chen & Qian, 2002).

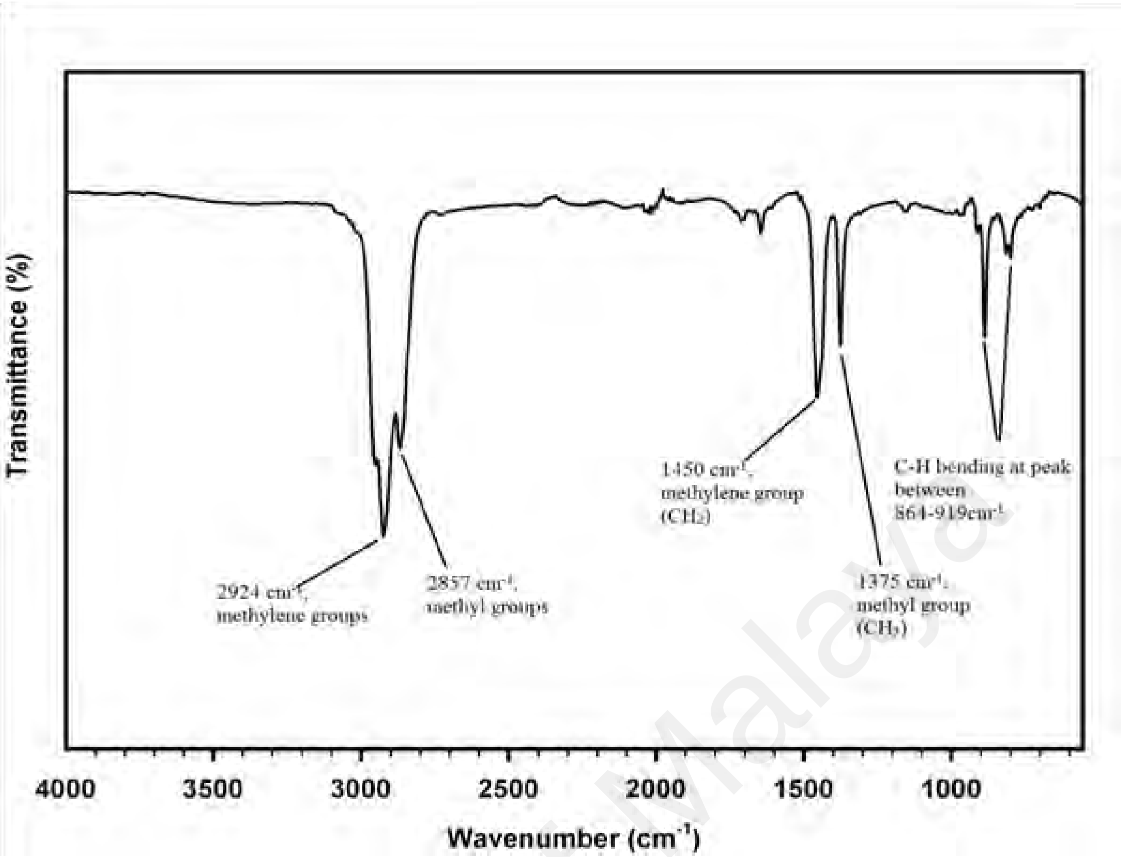


Figure 3-6: FTIR spectra for liquid product samples obtained at 375°C

3.3.4.4 GC/MS analysis

In this study, GC/MS analysis was performed to determine the nature and type of compounds present in the oil obtained under different conditions of temperature and H_2O/NR mass ratio, as these parameters had significant influence on oil quantity and quality. The detected compounds were identified by searching an MS library database, and the results were listed in Table 3.3. There are a great number of compounds but their peak areas are very low, thus are not examined in this study. During the analysis, numerous compounds that could be grouped as aromatics, alkyl, alcohols, alkenes, aldehydes and ketones were detected.

From Table 3.3, it can be seen that many compounds in the oil were identified as alkenes. The most dominating compounds in alkene were D-Limonene and isoprene.

Besides, aromatics were found to be the second most dominant species in all of the obtained oils. The greatest proportion of aromatics in the oils was mostly derived from toluene, xylene and benzene. The third dominating species was identified as Alkyls. Thus, it can be noted that alkenes was confirmed as the compounds with the highest concentrations in the oils, then following by alkyls, aromatics, aldehydes, alcohols, and ketones.

From Table 3.3, it also can be seen that the increase in temperature affected the oil compounds. The percentage areas of alkenes and aromatics showed the increasing trend with the increase of temperature. In Alkenes, at the temperature of 300^{o}C, the formation of D-limonene is less as compared to the temperature of 400^{o}C, due to the less depolymerization of poly-isoprene at 300^{o}C. Therefore, with the increase in temperature, the yield of D-limonene was found higher due to the conversion of isoprene radicals into D-limonene (Danon, van der Gryp, Schwarz, & Görgens, 2015; Pakdel, Pantea, & Roy, 2001). For aromatics, at high temperature the yields of aromatic hydrocarbons also increased. It is suggested that the main pathway to the aromatic compounds maybe accomplished at the expense of D-limonene (F. Chen & Qian, 2002; Cunliffe & Williams, 1998). On the other hand, alcohols showed the opposite trend when the amount of alcoholic compounds decreased with the rise of temperature. The decrease in alcohol compounds resulted in the reduction of oxygen contents in the oil subsequently improving its quality.

All the liquid products obtained from the liquefaction of NR via hydrous pyrolysis process should good fuel properties. The yield of oil products was found high 76% which is very good. Moreover, the presence of high hydrocarbon (hydrogen and carbon) contents increased the HHV of liquid oil. The oxygen contents of oil samples were also low (less than 10%) which improved the quality of oil by making in non-corrosive in nature. Moreover, oxygen content is also representative of water contents and results of oxygen contents also showed that the water content of oil was also low. Low water contents improves the combustion properties of oil. The low viscosity of oil obtained at optimum conditions was good enough to use as a fuel. Viscosity describes the flow property and low viscosity oil is good for the atomization in engines.

Table 3-3: Major compounds (% of total peak area by GC-MS) exist in liquid products obtained from hydrous pyrolysis of natural rubber at different temperature.

GCMS analysis of oil samples for major compounds (% of total peak area by GC-MS)						
Compounds	**Identified compounds (%)**					
	Temperature[a]			**H_2O/NR ratio[b]**		
	300°C	**375°C**	**400°C**	**2:1**	**3:1**	**4:1**
	Aromatics					
Toluene	1.86	3.56	4.3	2.76	3.56	3.89
o-Xylene	1.99	2.01	3.32	1.97	2.01	3.01
Benzene, 1,2,4-trimethyl-	1.76	2.89	3.45	2.45	2.89	3.21
Benzene, 1-methyl-3-(1-methylethyl)-	1.96	2.21	3.23	2.12	2.21	2.56
o-Cymene	1.89	—	—	0.34	—	—
Total	9.46	10.67	14.3	9.64	10.67	12.67
	Alkyl					
Cyclopentane, 1,3-dimethyl-, cis-	2.45	3.56	4.3	3.27	3.56	3.74
Cyclopentane, ethyl-	6.35	8.54	2.04	7.74	8.54	6.94
Heptane, 2,4-dimethyl-	1.2	1.23	1.4	1.45	1.23	1.78
2-Hexene, 2-methyl-	—	0.54	1.11	1.11	0.54	0.82
Total	10	13.87	8.85	13.57	13.87	13.28
	Alcohols					
Cyclohexanol	3.32	—	—	—	—	—
2-Hydroxymethylcyclopentanol (trans)	3.65	3	2	3.25	3	2.76

Total	6.97	3	2	3.25	3	2.76
	Ketones					
Cyclohexanone	1.81	—	—	1.57	—	—
7-Oxabicyclo[4.1.0]heptane	1.41	1.4	1.54	1.52	1.4	1.49
Total	3.22	1.4	1.54	3.09	1.4	1.49
	Alkenes					
D-Limonene	26.89	50.33	25.85	30.67	34.77	34.67
Cyclohexene, 3,5-dimethyl-	—	1.04	2.78	0.88	1.04	2.32
1,3-Cyclopentadiene, 5,5-dimethyl-2-propyl-	1.64	1.88	2	1.68	1.88	1.73
Isoprene	33.13	15.56	28	21.45	25	26.43
Total	61.66	62.69	59	54.68	62.69	65.15
	Aldehydes					
5-Hexenal	1.94	3.59	2.9	2.54	3.59	3.14
Total	1.94	3.59	2.9	2.54	3.59	3.14
Total (%)	93.25	95.22	97.22	86.77	95.22	98.49

[a] H_2O/NR mass ratio = 3:1, time = 30min

[b] Temperature = 375°C, time = 30min

3.3.5 Mechanism of natural rubber liquefaction

Natural rubber (NR) is biosynthesized organic material, which primarily consists of polyisoprene as a main constituent. During hydrous pyrolysis, NR is decomposed and depolymerized to fragments of lighter molecules, and then these unstable fragments rearranged through condensation, cyclization, dehydrogenation, and polymerization to form new compounds in a bio crude products (Cheng et al., 2017).

Liquefaction of NR is initiated by radical reaction (Danon et al., 2015). The monomer radicals are formed by β-scission reaction with respect to double bond in the main polymer chain. These monomer radicals are also known as allylic radicals. These radicals are highly reactive due to which they undergo alkylation and intramolecular cyclization reaction and yield different compounds which belong to the family of alkenes and alkyls. At high temperature, the decomposition and dehydrogenation reaction of cyclic compounds from alkenes leads to the formation of aromatic hydrocarbons (X. Zhang, Wang, Ma, & Chang, 2008). The other group of families such as alcohols, ketones and aldehydes are formed due to hydrolysis reaction (Cheng et al., 2017). The proposed mechanism of NR liquefaction is shown in Figure 3.7.

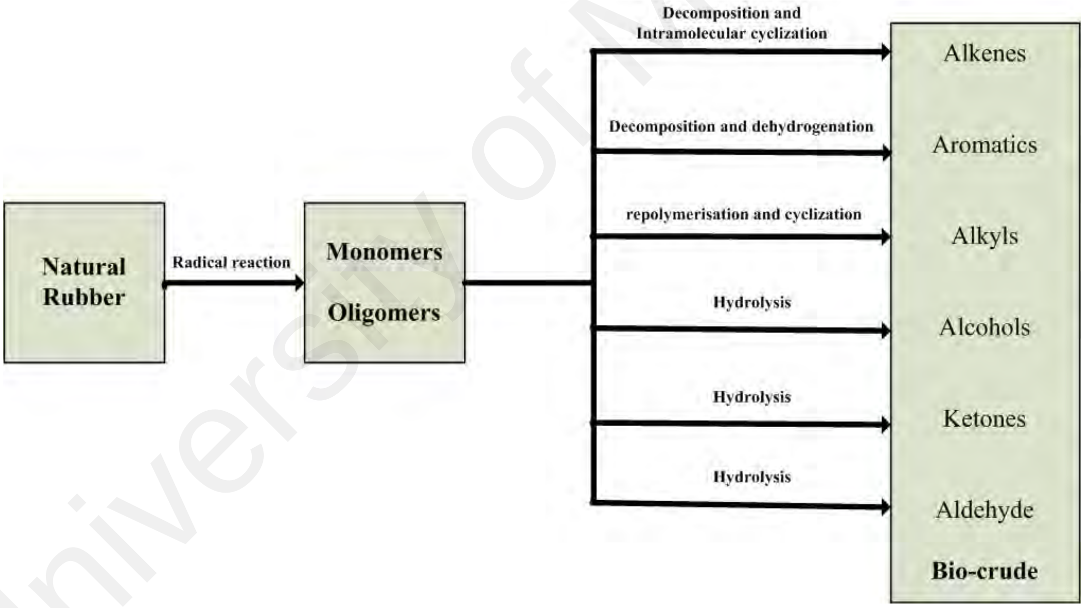


Figure 3-7: Mechanism of natural rubber liquefaction

3.3.6 Energy potential (EP) from pyrolysis oil

In Malaysia, the NR has been widely used for many industrial applications, such as medical equipments, rubber shoes, condoms, latex gloves, bio-materials, conveyer belts, electrical insulations, automotive mats and tires. However, not all of the produced NR is utilized; therefore, the un-utilized NR data from Malaysian NR statistic was used to estimate the energy potential. From year 2010 to 2014, the average amount of NR produced in Malaysia was estimated to be 884,656 tons, whereas, the average consumption was found to be 436,783 tons. The rest 50.62% (447,873 tons) of un-utilized NR can be converted in to liquid fuels. On the bases of data available, following calculations were made by using equation (3.3):

$$EP = (Feedstock \times oil\ yield\%) \times HHV_{oil} \qquad (3.3)$$

The oil from the hydrous pyrolysis of NR has a HHV of 45 MJ/kg with 76wt% yield. Hence, the total energy contained in the oil is shown in table 3.5.

Table 3-4: Projection of Energy potential from Natural rubber based oil

Feedstock (tons/year)	Liquid yield (kg/year)	HHV (MJ/year)	HHV (PJ/year)	million barrel of oil/year
447,873	340,383,480	15317256600	15	2.5

From the estimation, it can be seen that the energy potential that can be obtained from Malaysian NR derived oil is 15 PJ/year. In terms of barrel of oil equivalent, 15 PJ/year of energy is equivalent to 2.5 million barrels of oil per year. This energy potential has been calculated under optimum conditions. This energy potential is estimated by only using fresh NR before its use for other applications. In addition, more energy potential can also be achieved by utilizing the NR waste such as discarded rubber gloves, condoms, balloons, pharmaceutical rubber items, rubber shoes, and scrap tire.

3.4 Conclusions

In this study, the hydrous pyrolysis technique has been successfully used to convert natural rubber into liquid fuels. The experiment was performed in autoclave batch reactor under a nitrogen atmosphere. The operating condition of 375°C, H_2O/natural rubber mass ratio= 3:1, and 30 mins were found to be the most optimum and suitable to maximize the production of liquid oil. At optimum operating conditions the yield of liquid product (bio-oil), tar, water soluble fraction, and gas obtained were 76 wt%, 12.5 wt%, 7.9 wt% and 4 wt%, respectively. The elemental analysis showed that the amount of sulfur present in the oil from NR was very low. The viscosity, density, pH and HHV of obtained oil were 14.16 cP, 0.859 g/ml, 7.261, and 45 MJ/kg respectively. The FTIR analysis identified that C-H, CH_2, and CH_3 were the most abundant chemical bonds detected in the oil. The GC-MS analysis showed that the major constituents of oil were D-limonene, isoprene, chain hydrocarbons and aromatic compounds. Based on the characteristic results, in term of fuel properties, the oil from NR was found to be more suitable compared to the oil derived from scrap tire. The use of NR to produce the liquid fuel by hydrous pyrolysis could result in an increase of energy potential by 15 PJ per year, which was equivalent to 2.5 million barrels of oil per year.

CHAPTER 4: LIQUEFACTION OF NATURAL RUBBER TO PRODUCE FUELS AND CHEMICALS USING VARIOUS ALCOHOL SOLVENTS

4.1 Introduction

Natural rubber (NR) is an organic material obtained from *Hevea brasiliensis* tree which is widely used as a raw material to produce polymer products (Ahmad et al., 2016). There are numerous products that have been created using this material such as surgical equipment, biological-materials, clothing, insulations, rubber tires, rubber bands, sports items, etc (Ahmad et al., 2016; Ahmad, Abnisa, & Wan Daud, 2018). The variety of products produced showed that this material plays an important role in the industrial and manufacturing sectors. This fact is also supported by the availability of abundance source of NR. As one of the major producers, Malaysia produced 821,274 tonnes average quantity of NR annually from 2010 to 2016. However, the average consumption was found lower approximately 55% only (Malaysian Rubber Research and Development Board, 2017). This condition lead to the drastic decrease in NR price in the mentioned year period (Olaniyi et al., 2013). As impact the land for NR plantation has been degraded and occupied for the other commodities which mainly dominated by palm oil, and as consequences it also affected the rubber farmers and environmental issue (Hai, 2000; Saswattecha et al., 2016).

It is a challenge on how to ensure the high rubber consumption and products produced also have high demand in the market. In this regard, converting the NR into the intermediate product would be an interesting option. Basically, most of NR is directly utilized to produce the final product without involving the chemical conversion process (Kohjiya & Ikeda, 2014). Certainly, by converting NR into the intermediate product will open the new opportunity to break up the drawbacks of NR utilization. Chemical feedstock is one of examples of the intermediate product, it can be directly used and it can also be used to make other value-added products. The use of NR to produce chemical feedstock can be a step toward a more sustainable rubber industry.

NR can be converted into valuable chemical commodities by thermal conversion processes. Among them, pyrolysis and hydrothermal liquefaction are very well known processes. During the pyrolysis of NR, high temperature (400-600^{o}C) is required for the depolymerization of long chain polymeric compound to small hydrocarbons (Ahmad et al., 2016; Demirbaş, 2000). As a consequence, high temperature process requires high energy consumption thereby increasing the budget of the process. According to Farret and Simões, all processes that consume high energy for making a commodity become less economical and attractive (Farret & Simões, 2006). The depolymerization can be conducted at lower temperature by manipulating other process parameters such as increasing the pressure, introducing the hydrogen gas, use of catalyst and use of solvent. However, there are a few difficulties related to the utilization of a catalyst, it is a consumable and so it increases the process expenses; catalyst have a small lifespan owing to its deactivation; the catalyst may lead to high level of solid deposit, thereby increasing the operational cost in terms of its separation and disposal (Scheirs & Kaminsky, 2006). Similarly, the use of hydrogen gas is expensive, also the hydrogen handling process involves safety aspect and considerable amount of complicated equipment.

The use of solvent seems to be a positive approach as the solvent provides milder conditions for the degradation of organic matter to produce liquid products. This approach is actually used in the thermal liquefaction process under corresponding pressure condition. Many studies have shown that the role of solvent in this process can effectively help to liquefy the biomass with high liquid yield obtained (Jin et al., 2014; Sarwono, Pusfitasari, & Ghozali, 2016; Tian, Li, Liu, Zhang, & Lu, 2014). Moreover, it also showed that the low temperature in the range of 250-400^{o}C was found to be enough to complete the process. In brief, Gollakota et al. concluded that the low operating temperature, high energy efficiency and low solid residue yield are the key features of hydrothermal liquefaction process, which make it more superior than that of pyrolysis (Gollakota et al., 2018).

Water is a common solvent used in hydrothermal liquefaction since it is cheap, abundant, polar in nature and non-hazardous (Ahmad et al., 2016; Chan et al., 2017; Onwudili & Williams, 2008). However, water has some drawbacks as it results in low liquid yield and the oil products tend to have high oxygen contents, high corrosivity and high viscosity (Biswas et al., 2017; Sarwono et al., 2016). Durak has enlisted the features required for the selection of good solvent: non-acidic, high proticity, low boiling point, easily separable from the product, have low critical points and also improves the quality and quantity of oil (Durak, 2015). Organic solvents such as acetone, decane, hexane and toluene are usually considered to be the good solvents for the production of bio oil from different biomasses. Jin et al. conducted the liquefaction of microalga biomass using sub/supercritical acetone. The result from their experimental work showed that the maximum bio-oil yield of 60 wt.% was achieved at 290°C (Jin et al., 2014). Also, the addition of acetone improved the HHV and reduced the viscosity in contrast to the bio-oil obtained from thermal liquefaction using water as a solvent (Jin et al., 2014). Like acetone, decane was also investigated as an organic solvent in thermal liquefaction process. It was reported that the use of decane in hydrothermal liquefaction of *Nannochloropsis sp.* as a solvent gives high liquid yield of about 39% (Valdez, Dickinson, & Savage, 2011). Sarwono and Pusfitasari performed the thermal liquefaction of palm oil empty fruit bunch at 350^{o}C using hexane and they were reported that hexane gave the conversion of 17 – 25.25 % (Sarwono & Pusfitasari, 2017). Subsequently, Sarwono et al. also tried to use toluene to liquefy the palm oil empty fruit bunch at 350^{o}C and the result showed that higher conversion was found (35.76%) (Sarwono et al., 2016). Hence most of the previous studies showed that organic solvents improved the liquid yield at lower temperatures. In order to obtain versatile family of compounds, there are also other types of organic solvent that can be employed for the thermal liquefaction process such as alcohols under supercritical conditions. The benefit of using alcohols as a solvent is that alcohols are good hydrogen donors which provide milder degradation environment to convert organic material into bio-oil (Liu, Li, & Li, 2017). Furthermore, alcohols in supercritical condition are more superior than subcritical water in the liquefaction process (Brand & Kim, 2015). Also, due to the presence of hydrogen bonding (-OH group), the separation of alcohol from oil is easy as compared to non-alcohol organic solvents. Thus, more exploration is needed on the use of alcohols as a solvent in hydrothermal liquefaction process for better conversion and yields.

Currently, there is no literature available on the thermal liquefaction of NR using alcohol solvents. Therefore, the main objective of this current study is to perform the thermal liquefaction of NR using different alcohols (methanol, ethanol, and propanol) to produce of value-added chemicals. The influence of diverse operating conditions such as temperature, alcohol to NR mass ratio and reaction time on product quantity were studied comprehensively. The role of alcohol solvent and its recovery process were also discussed in this report. In addition, the liquid product was analyzed through numerous analyzers to assess its quality.

4.2 Experimental

4.2.1 Materials

The sample of NR used in this study was obtained from Malaysian Rubber Board. Particle size of NR was cutoff into small about 3-5 mm and it was then characterized by proximate and ultimate analyses, as well as thermogravimetric analysis (TGA). The results of NR characterization were presented in previous chapter 3. It was showed that NR is sulfur free material with high carbon and hydrogen contents, which making it good potential source for the synthesis of liquid fuels. Furthermore, various organic solvents such as methanol, ethanol, and propanol were used in this study obtained from Sigma-Aldrich Co. The N_2 gas with 99.99% purity was used to purge off the trapped air inside the autoclave to develop a non-reactive atmosphere.

4.2.2 Experimental Method

The whole experimental system was manufactured by Amar equipment's Pvt Ltd, Mumbai Maharashtra, India. An autoclave (SS 316) batch reactor with volume capacity of 1 liter was employed to conduct the hydrothermal liquefaction experiment. Autoclave comprised of electrically heated furnace for heating it to desire temperatures. Methanol, ethanol, and propanol were used as a reaction solvent in this investigation individually. The whole experimental setup and method of products separation was shown in Figure (4.1).

The experimentation was conducted by feeding NR and organic solvent in the reactor, then sealed and purged with N_2 gas to make the non-reactive atmosphere at 1.5 atm inside the reactor. The autoclave was heated electrically to reach the required temperature which was observed using K-type thermocouple. Since the experimentation was performed in a sealed reactor, the release of warm gaseous product raised the pressure inside the autoclave. Subsequently, hydrothermal liquefaction experimentation was exposed to autogenous pressure whose magnitude depend upon process temperature. Three different sets of experimental runs were conducted in current investigation for each solvent. First set of experimental runs were performed at various temperature settings within the range of 250 to 375°C with the increment of 25°C while keeping constant solvent/NR mass ratio (1:1) and time (30 mins). Second set of experimental runs were carried out by employing diverse solvent/NR mass ratio (solvent/NR=0.5:1, 1:1, 1:2, 1:3, and 1:4) at temperature and time of 325°C and 30 mins respectively. The last set of experimental runs were performed by changing the process time from 15 to 75 mins with the increase of 15 mins at 325°C, and solvent/NR mass ratio of 1:1. The cooling coil system was employed to cool down the reactor to ambient temperature after the process was completed.

After the completion of process, the autoclave was cooled to the room temperature by using chilling coils. The gaseous commodities were vented out and the liquid product was transferred to separating funnel where three layers were obtained comprising of solvent solution, oil, and heavy dense liquid in a very small amount. This heavy dense viscous liquid was considered as a tar. The solvent and oil were separated from the tar using a micropipette. The tar inside the funnel and reactor vessel was rinsed with solvent several times to ensure all of them were recovered. Alcohol was recovered from products by using rotary evaporator system (Büchi Rotavapor R-215) under reduced pressure at 45-50° C. Collected tar was dried at the boiling point of each solvent used, and then quantified. The diagram of the whole process flow and product separation method has been in supplementary material. The key emphasis of current investigation was on oil and therefore only oil product was analyzed.

Oil, tar, and gases were considered as the products from the liquefaction of NR, whereas the oil was considered as a key product. The gaseous products were not collected because of restrictions in experimental setup design. The oil and tar was collected and their weight were measured. The gaseous products were estimated by the calculating the difference. The yields of liquefaction products were calculated by using equation (4.1).

$$\text{Yield}(\%) = \frac{\text{Weight of product}}{\text{Weight of NR}} \times 100 \qquad (4.1)$$

The yield of gaseous products and other light end losses were projected by the difference: Gas+loss% = 100-(Oil yield + solid residue yield). All the experimental sets were replicated 3 times under the same settings to authenticate the experimental results.

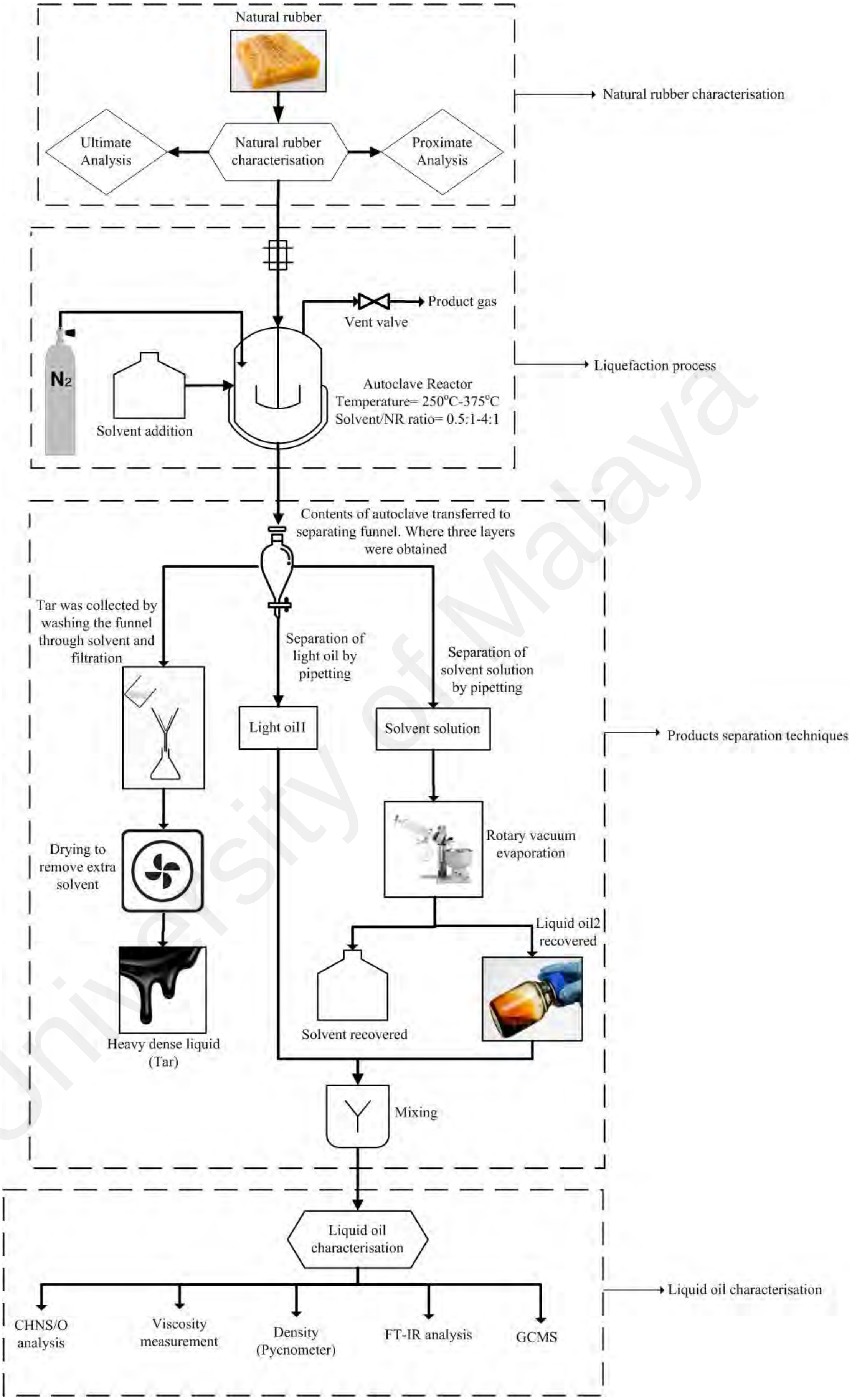


Figure 4-1: Graphical presentation of experimental system

4.2.3 Product characterization

Characterization is an important factor to assess the quality of produced oil. Normally, characterization is divided into two categories; Physical characterization and Chemical characterization. Physical characterization comprises the determination of different physical properties such as density (ρ) and viscosity (η). In current study, the density (ρ) and viscosity (η) of liquid products were estimated using a pycnometer and Brookfield viscometer respectively, and all measurements were conducted at ambient temperature of 26°C. PerkinElmer CHNO/S, portable pH meter, Fourier-transform infrared spectroscopy (FTIR), and gas chromatograph–mass spectrometer (GCMS) were used to determine the chemical properties of oil. The pH values of oil products were determine using Fischer Scientific pH meter (accuracy ±0.01) at ambient temperature. PerkinElmer Frontier FTIR spectrometer was used to perform the FTIR spectroscopy of oil samples within the wavelength frequencies of 450–4500 cm^{-1} with a resolution of 4 cm^{-1}. The ultimate analysis of oil products were conducted with CHNO/S analyzer model 2400 PerkinElmer. Elemental analysis data obtained from CHNO/S analyzer was used to compute the high heating value (HHV) using Dulong formula (equation 4.2) (L. Zhang et al., 2016).

$$\mathrm{HHV}\left(\frac{MJ}{kg}\right) = 0.338\mathrm{C} + 1.428\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) + 0.095\mathrm{S} \tag{4.2}$$

The identification of various compounds present in oil were carried out using Shimadzu GCMS-2010 plus. The specification of capillary column and method for the analysis used in this study was same as it was used in chapter 3.

The experimental runs were performed 3times to avoid the chances of error and to generate reproducible data. Furthermore, the standard deviation (SD) was calculated for the replicated experimental runs for oil and tar yield. The values of gas yield which were obtained by the difference were also used for the calculation of SD using SD correlation. This data describes the error analysis, originality and reproducibility of results. Moreover, to minimalize the edge of error and to produce more realistic and accurate results, each of the equipment that used for analysis has been calibrated and checked by using standards to obtain the accuracy of result measurement of every product from all experimentations.

4.3 Results and discussion

4.3.1 Influence of process conditions on products using different alcohols

4.3.1.1 Influence of process temperature

Three sets of experiments were performed using methanol, ethanol, and propanol in current investigation. For all solvents, solvent/NR mass proportion and time were kept constant at 1:1 and 30 mins respectively while, the process temperature was changed from 250 to 375°C with the different corresponding pressures. The Figure 4.2, 4.3 and 4.4 show the effect of temperature on product yield with all solvents. Where it can be seen that the yield of liquid product was increased as the temperature increased from 250 to 325°C. At 325°C, the highest liquid yield obtained were 84.12 wt%, 85.98 wt%, and 89.53 wt% with methanol, ethanol, and propanol respectively. Whereas, previous study in chapter 3 showed that the highest liquid yield of 76 wt% was obtained at optimum condition (375°C, NR/H_2O mass ratio=1:3, 30mins) using water as a solvent. From liquid yield values, it can be observed that there is slight difference between the liquid yields obtained using different alcohols. Further rise in process temperature does not showed any major positive influence on oil yield. The highest oil yield was obtained using propanol. It is because propanol donates more hydrogen as compared to methanol and ethanol which can be explained by solvolysis process and depolymerization of monomers into small molecules (Brand, Hardi, Kim, & Suh, 2014).

In contrast to liquid product, from figure 4.3 and 4.4 it can be seen that the yields of tar and gas+loss were obtained in low proportion respectively. The yield of tar was observed reduced with the rise of temperature. With the highest liquid yield condition of 325°C, the tar yield of 6 wt% was obtained using propanol. Different with tar, the gas+losses generally increased with the increasing of temperature. This increment in gas+losses yield was because of the cracking of liquid products as high temperature, where the same phenomena has been reported by other researchers (S. Park & Gloyna, 1997; L. Zhang et al., 2016). At 325°C, the gas+losses yield of 4.47 wt% was obtained for propanol. σ represents the standard deviation.

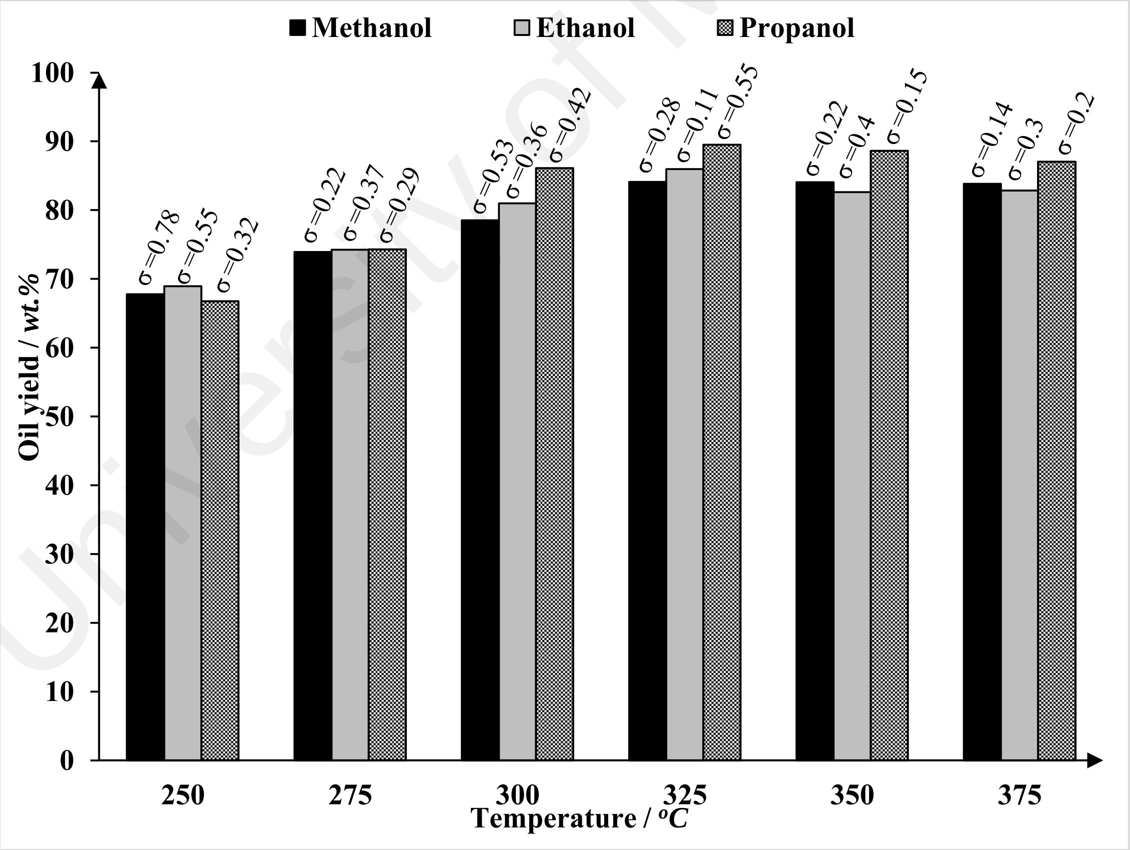


Figure 4-2 Influence of temperature on oil yield using different alcohols

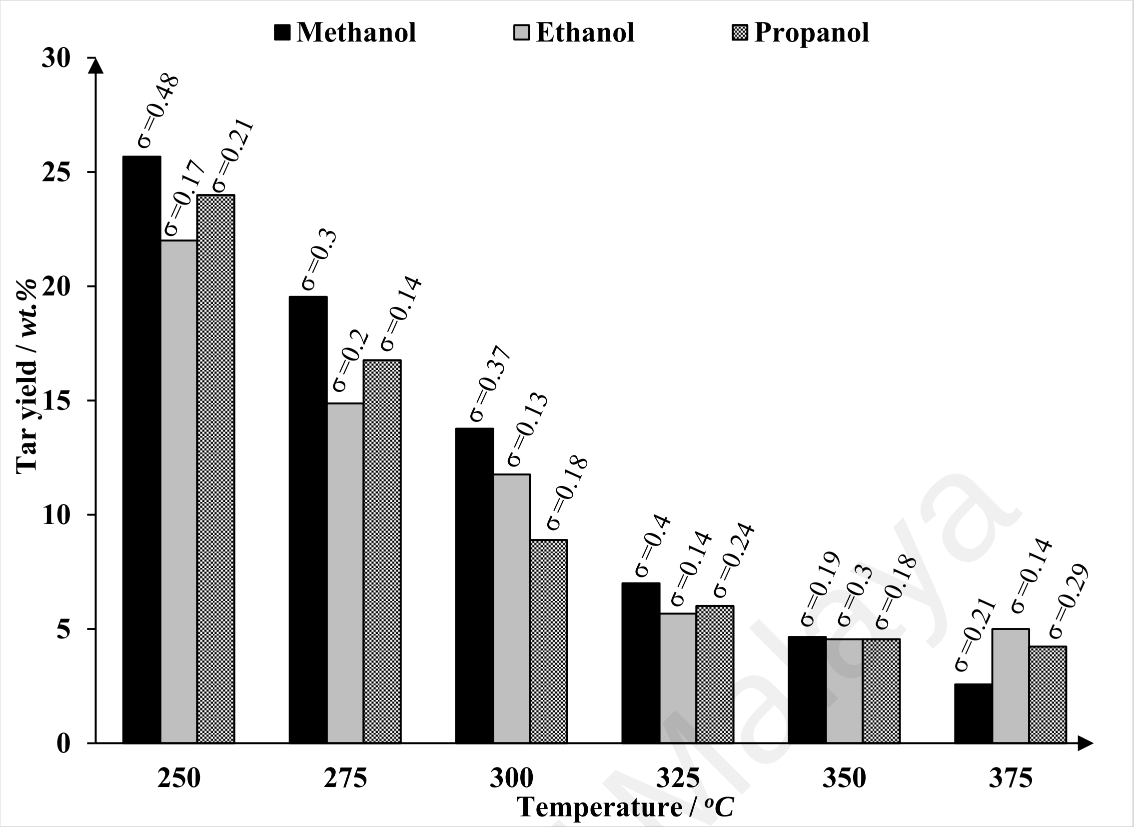


Figure 4-3: Influence of temperature on tar yield using different alcohols

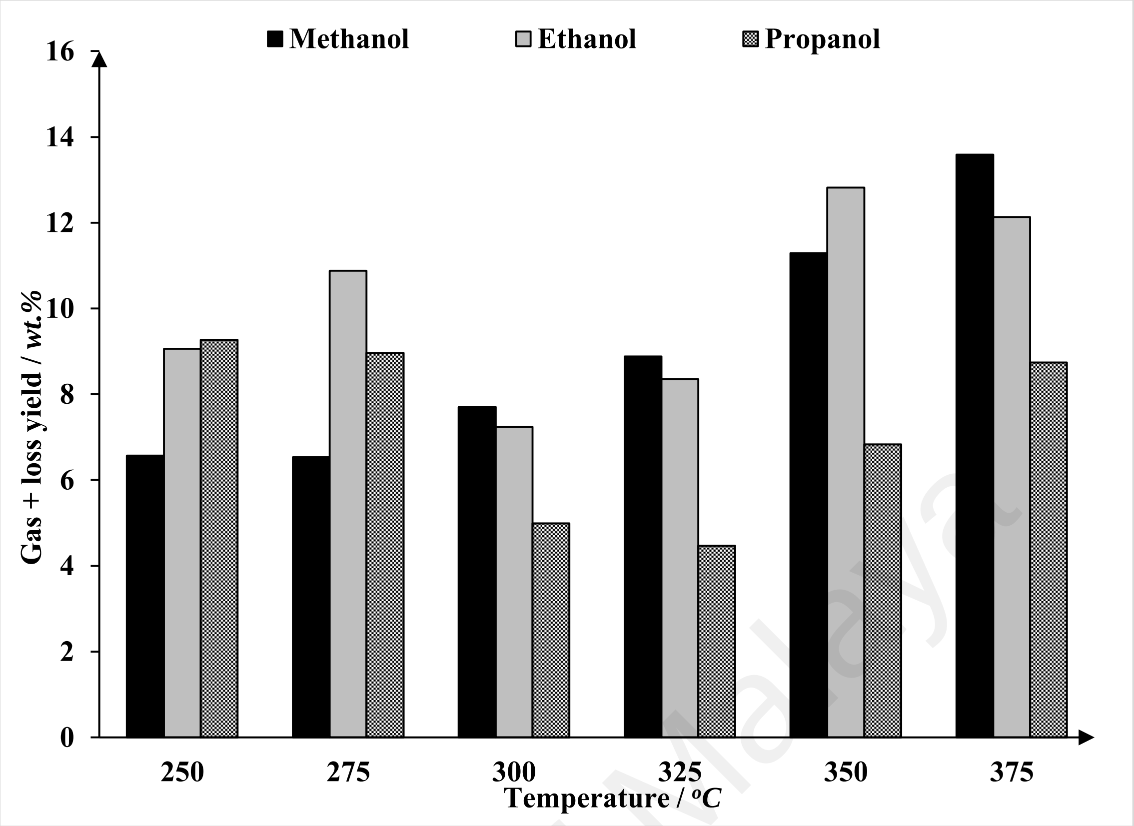


Figure 4-4: Influence of temperature on gas+loss yield using different alcohols.

4.3.1.2 Influence of solvent to natural rubber (NR) mass ratio

The influence of the different organic solvent/NR mass ratios was varied at 0.5:1, 1:1, 2:1, 3:1, and 4:1 and the result showed in figure 4.5, 4.6, and 4.7. However, the process time and temperature were kept constant at 30 mins and 325°C respectively. Figure 4.5 showed that the oil yield decrease linearly as the mass proportion of solvent raised from 1:1 to 4:1. When the mass ratio of solvent and NR is equal, the maximum liquid product (89.53 wt.%) was obtained by using propanol, while the liquid yields of 84.12 wt.% and 85.98 wt.% were obtained for methanol and ethanol, respectively. The increase of solvent ratio was tend to increase the yield of gas product, where, it can be seen clearly in Figure 4.7. This phenomenon can be described by possible alkylation reactions between alcohols and liquefied NR intermediates (Biswas et al., 2017). Moreover, polar protic solvents (alcohol) would assist the process by better dissolving and stabilizing reaction intermediates due to which they give high conversion rates, high oil, and high gas yields (Huang & Yuan, 2015; Yang et al., 2009). Thus, the presences of large amount of alcohol would provide the high degradation environment which also causes the cracking of liquid product into (small molecules) gaseous products.

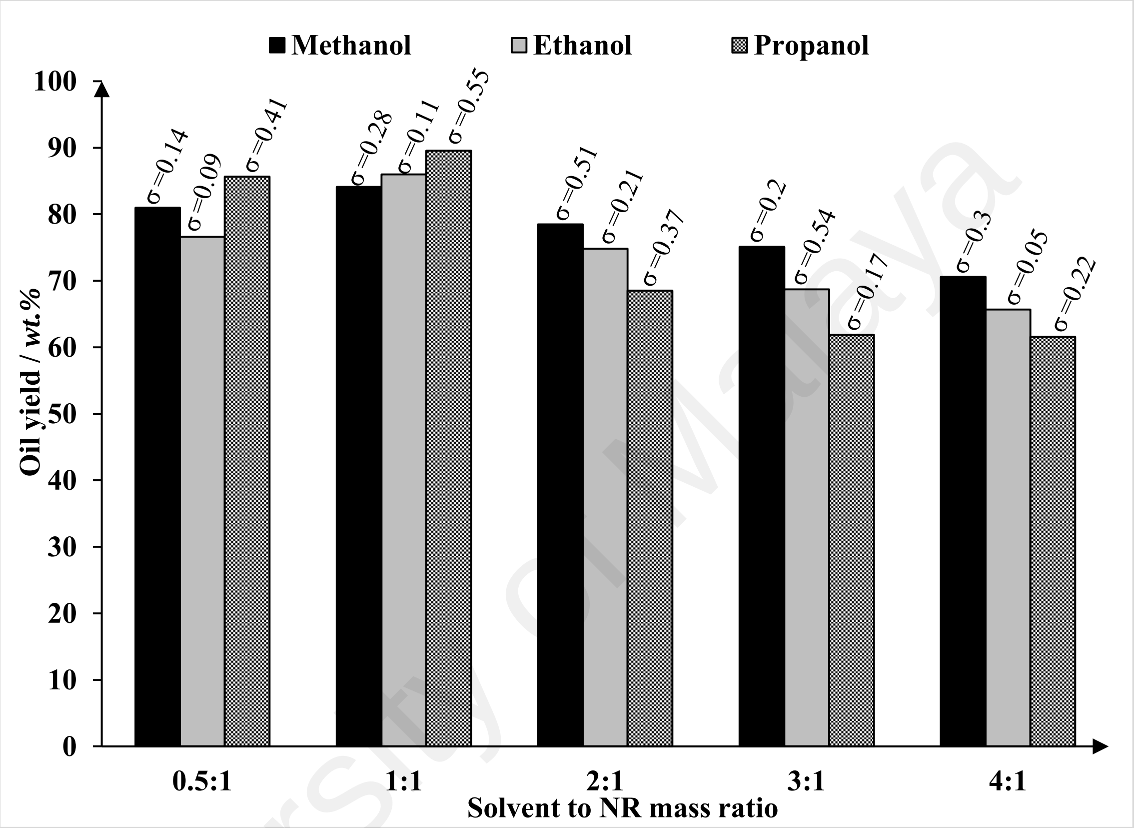


Figure 4-5: Influence of solvent to NR mass ratio on oil yield using different alcohols.

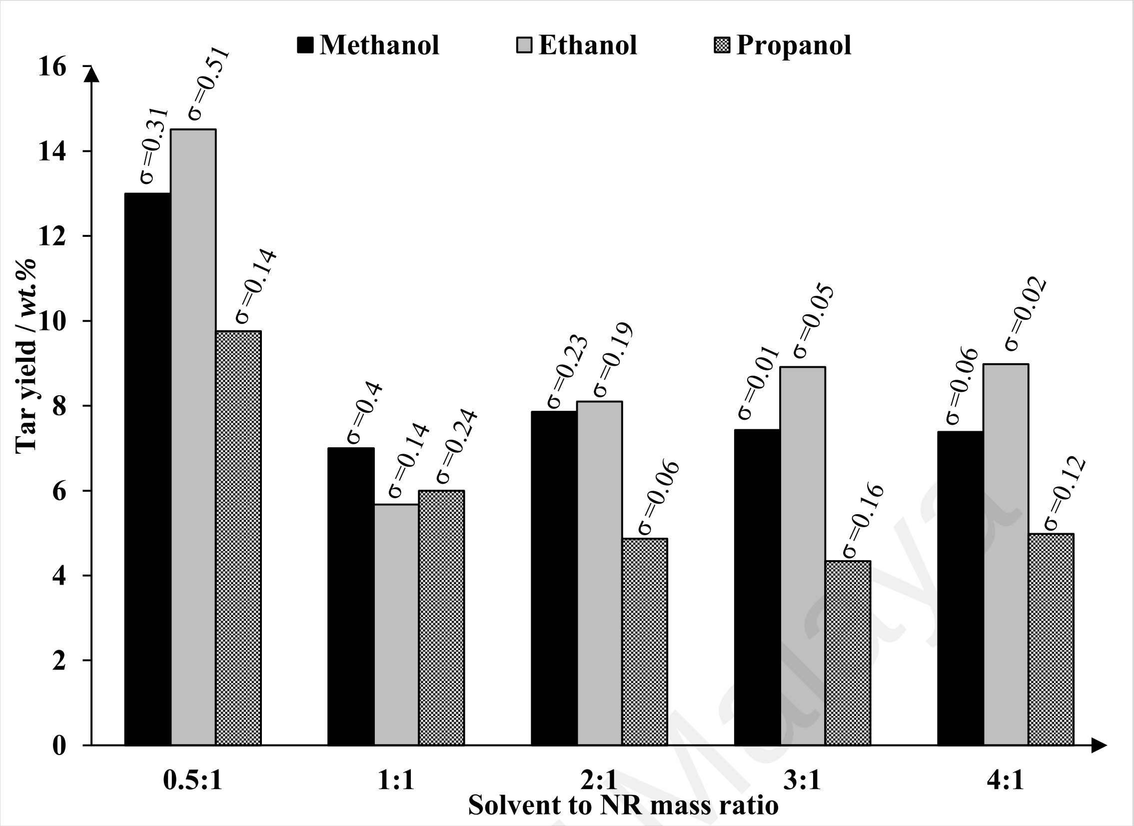


Figure 4-6: Influence of solvent to NR mass ratio on tar yield using different alcohols

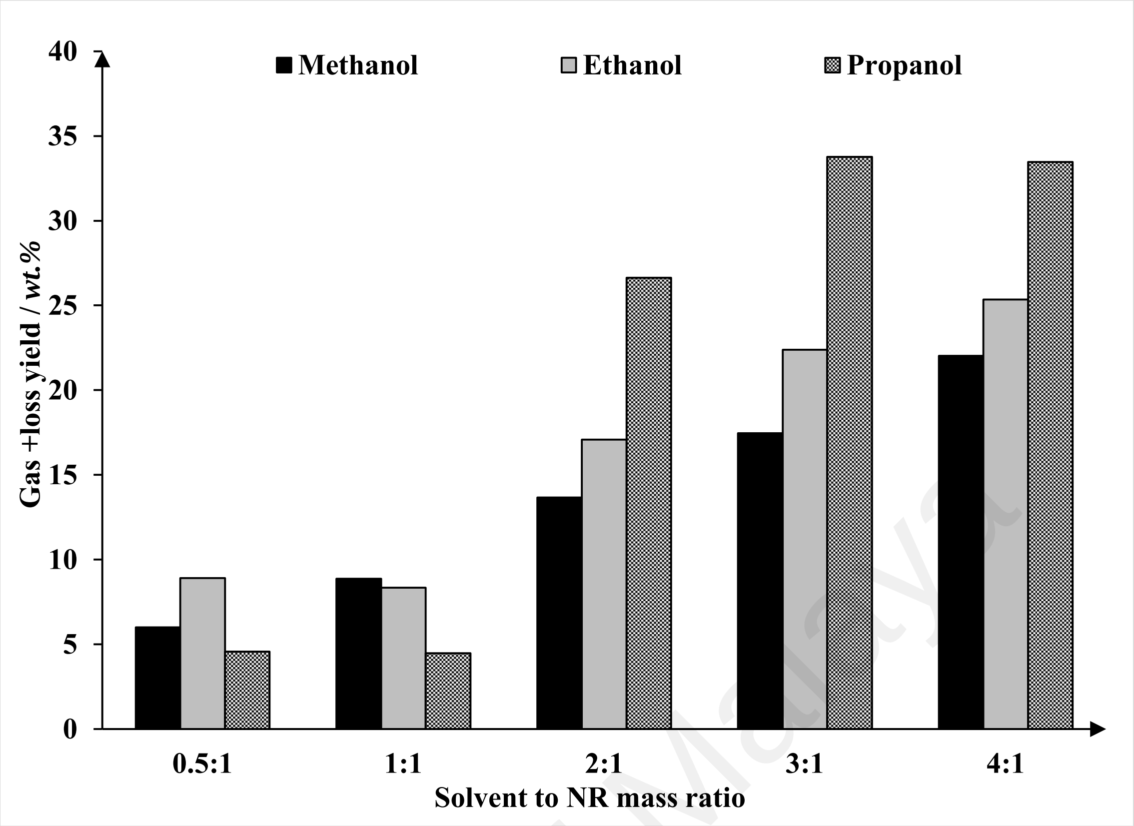


Figure 4-7: Influence of solvent to NR mass ratio on gas+loss using different alcohols

4.3.1.3 Influence of reaction time

The effect of residence time on product yield were carried out at 325°C, and with a solvent/NR mass proportion of 1:1 by changing time interval from 15 min to 75 min. Figure 4.8, showed that the yield of oil raised up gradually with rise in residence times from 15 min to 30 min. The reaction duration of 30 min was found adequate for the liquefaction of NR for the maximum production of oil yield (89.53 wt. %) using propanol. Whereas, liquid yield of 84.12 wt.% and 85.98 wt.%, was obtained using methanol and ethanol as a solvent respectively. However, the additional extending the reaction time do not showed any major influence on the oil yield. Also, varying the holding times also did not show any notable effect on gaseous product and tar yields. Similar findings were also described by Zhang et al (L. Zhang et al., 2016). Trend of different reaction times with product yields were shown in figure 4.8, 4.9, and 4.10.

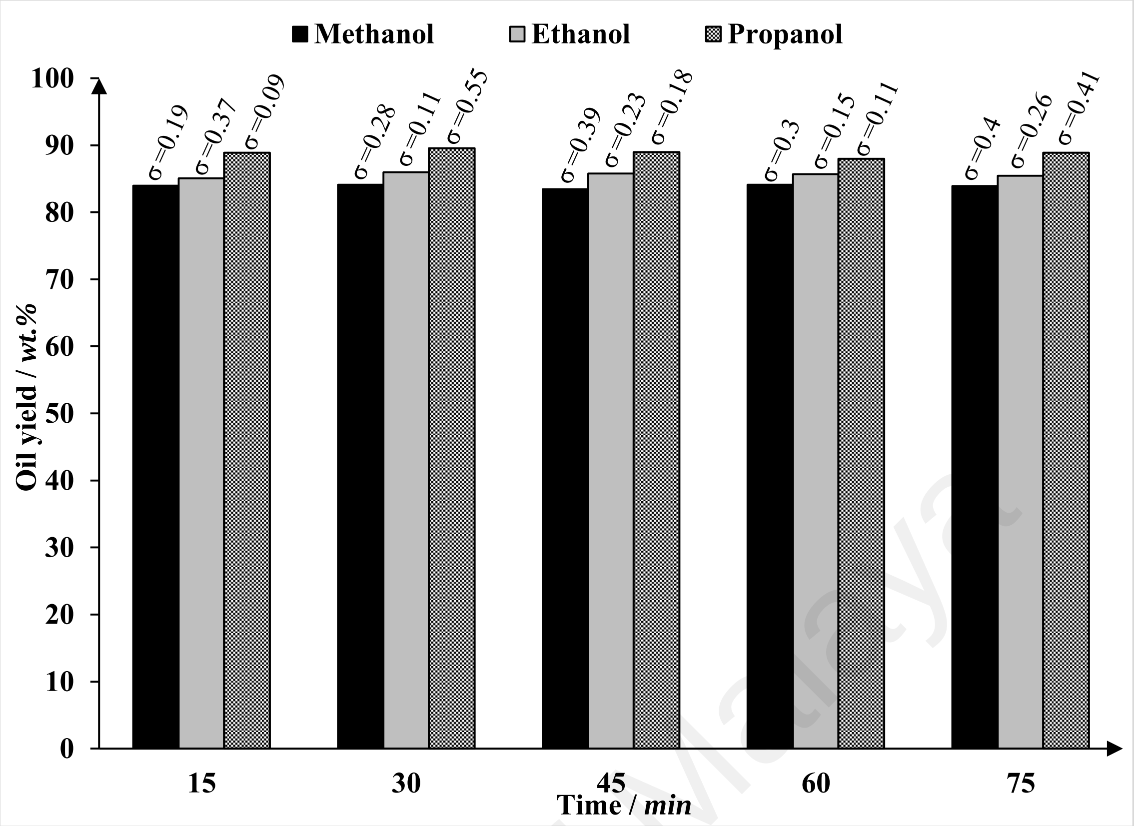


Figure 4-8: Influence of residence time on oil yield using different alcohols.

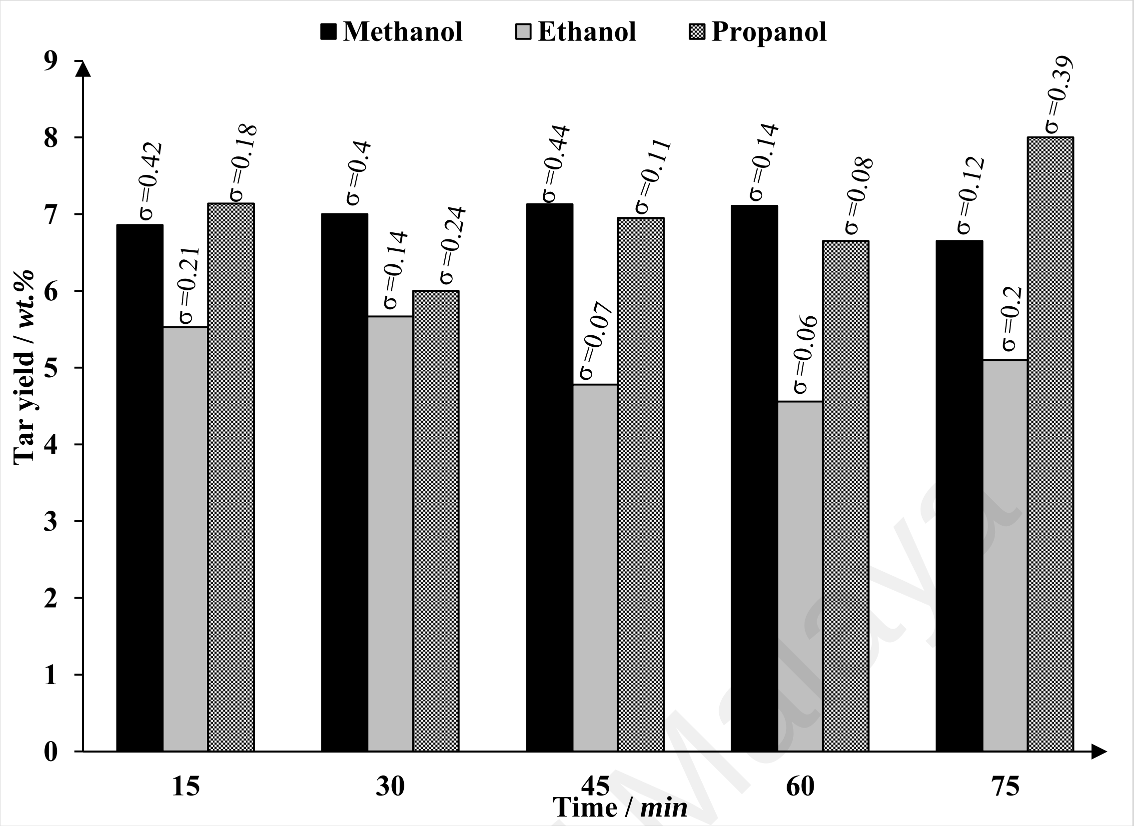


Figure 4-9: Influence of residence time on tar yield using different alcohols

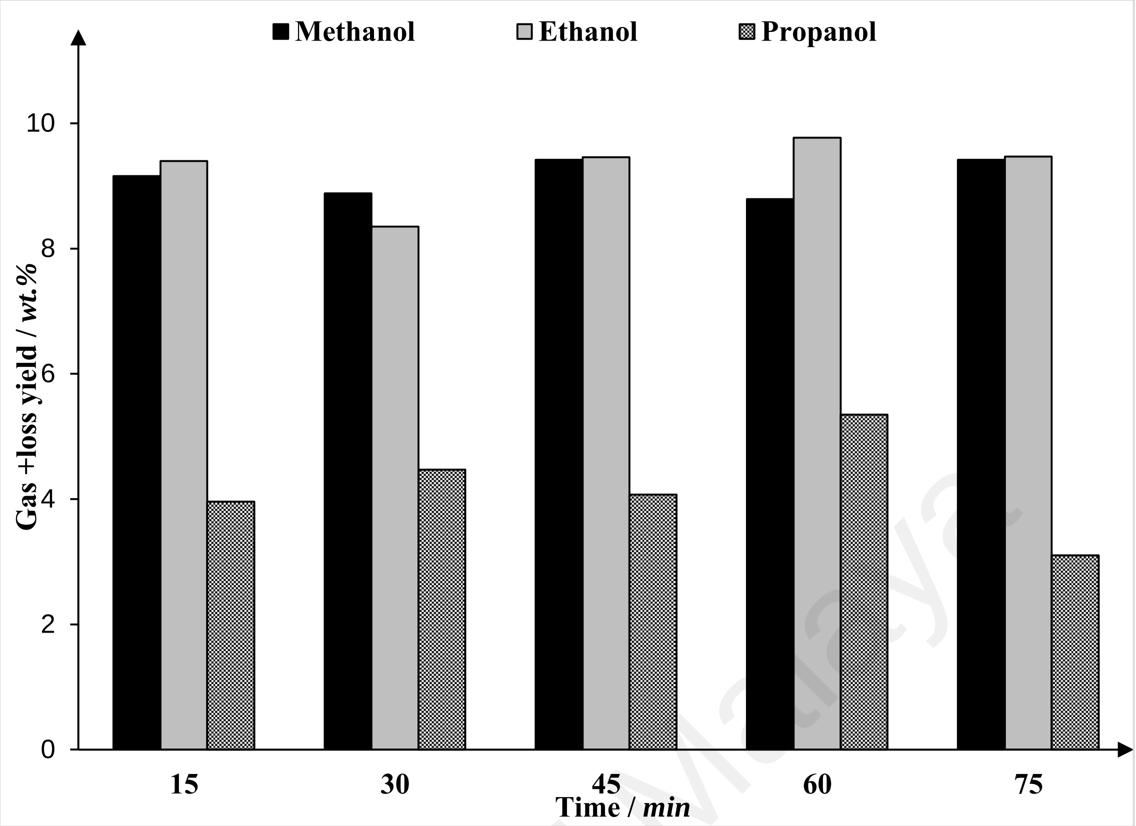


Figure 4-10: Influence of residence time on gas+loss yield with different alcohols

4.3.2 Optimum parameters and the role of solvent

Based upon results, it can be seen that the temperature of 325°C, alcohol to NR ratio of 1:1, and the reaction time of 30 mins were found as optimum conditions to maximize the production of liquid products. Under these conditions, the highest liquid yield of 84.12 wt%, 85.98 wt%, and 89.53 wt% were achieved using methanol, ethanol, and propanol as a solvent respectively. The results highlighted that the propanol gave the highest liquid yield which is due to fact that propanol has more hydrogen. Approximately, 97 % of alcohols were recovered in all the cases.

This study showed that the propanol has significant improvement on the liquid yield and energy density. Alcohol solvents have low critical points as compared to water and it is easy to achieve these milder conditions in thermal liquefaction process. Alcohol solvents have low dielectric constant which enhance the solubility of product fragments and therefore improves the liquefaction process (Biswas et al., 2017). Furthermore, alcohols not only act as a solvent to decompose the raw material but they also become a source of hydrogen donor for the production of high yield oil. The presence of hydrogen in alcohol solvent could stabilize the fragments and intermediates formed during the thermal liquefaction and prevent them from repolymerization to produce tar (Zhen Fang et al., 2008; Jena & Das, 2011; Singh, Bhaskar, & Balagurumurthy, 2015).

4.3.3 Characterization of liquid products

In this section, the characteristics of liquids products were reported on the basis of maximum liquid yield obtained at optimum conditions with three different alcohols. The conditions of 325°C, 1:1 solvent/NR ratio, and 30min were found to be optimal parameters for the highest production of liquid-oil. However, for comparison purposes, some results of liquid characteristics from different operating parameters also presented in this section.

4.3.3.1 Ultimate analysis and HHV

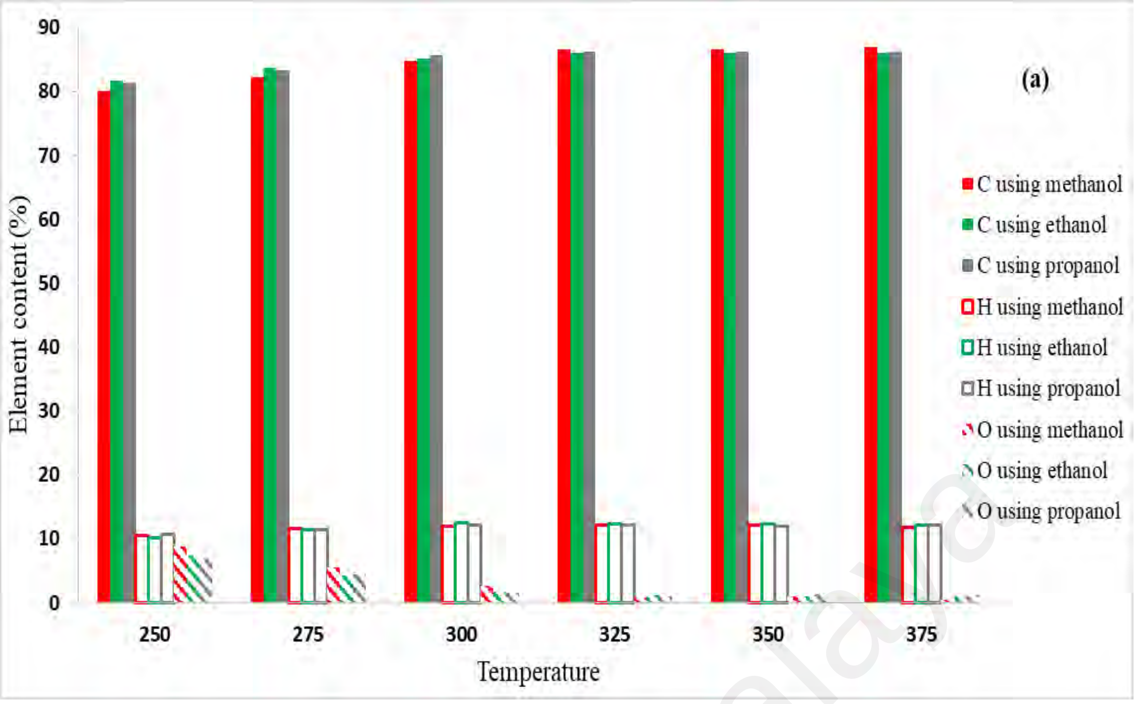
The results of elemental analysis and HHV of liquid products from different alcohols were shown in Table 4.1. From Table 4.1, it showed that the use of alcohol in hydrothermal liquefaction of NR has significantly improved the value of carbon and hydrogen contents, which is very important for increasing the energy density of liquid. The average carbon and hydrogen contents for all liquid product were obtained higher than 86% and 12%, respectively. In contrast, the oxygen contents were observed to be lower, where the value was obtained in the range of 0.77% to 1.1%. In addition, the average of value of HHV was estimated to be 46 MJ/kg. All the liquid products obtained using different alcohols showed that the nitrogen contents were lesser than the nitrogen contents existing in NR. This elemental analysis results have proven that the alcohols solvent can provide a better fuel quality compared to water as commonly used solvent in hydrothermal liquefaction (Ahmad et al., 2018; Toor et al., 2011).

An additional experiment were performed to assess the influence of different operating parameters on the oil properties and the result were given in Figure 4.5 (a) and 4.5 (b). The increasing of carbon and hydrogen contents were observed as the temperature increased, where the increasing of the solvent in feedstock only improved the carbon contents. The oxygen contents were remain lower than 10% in all the operating conditions. The rise in temperature reduced the oxygen contents significantly which led to improve the HHV of liquid product. In addition, the sulfur and nitrogen contents were not showed any significant change by applying different operating parameters. For all the oil samples, the HHV was approximately obtained between 40 to 46 MJ/kg at different operating conditions using different alcohols. In chapter 3, the HHV of oil achieved through the hydrothermal liquefaction of NR was marked nearly to diesel quality (44 MJ/kg).

Good fuel characteristic were obtained from NR based oil using different alcohol solvent. The highest oil yield 89% was obtained using propanol solvent. Due to which this solvent is highly recommended for the production of NR based oil on a large scale. Furthermore, the presence of high hydrogen and carbon contents and low sulfur contents made it good potential alternative eco-friendly fuel. High hydrogen and carbon contents contribute to improve the heating value of oil. The presence of sulfur contents in the may cause environmental issue by releases SOx. The oxygen contents of oil samples were also low (less than 10%) which improved the quality of oil by making in non-corrosive in nature. Moreover, oxygen content is also representative of water contents and results of oxygen contents also showed that the water content of oil was also low. Low water contents improves the combustion properties of oil. The low viscosity of oil obtained at optimum conditions was good enough to use as a fuel. Viscosity describes the flow property and low viscosity oil is good for the atomization in engines. Moreover, the pH value of oil samples were almost neutral in all the cases making them non-acidic.

Table 4-1: Characteristics of liquid products obtained at optimum conditions using different alcohols (solvent/NR mass ratio = 1:1, temperature = 325°C, time = 30mins).

Characteristics	Methanol	Ethanol	Propanol
Physical properties			
Viscosity (cP)	11.7	12.4	12.6
pH	8.5	8.03	8.16
Density (g/ml)	0.82	0.86	0.85
Elemental Analysis			
Carbon	86.54	86.02	86.16
Hydrogen	12.07	12.24	12.21
Nitrogen	0.41	0.41	0.42
Oxygen	0.77	1.1	1.02
Sulfur	0.21	0.23	0.19
HHV (MJ/kg)	46.36	46.37	46.39



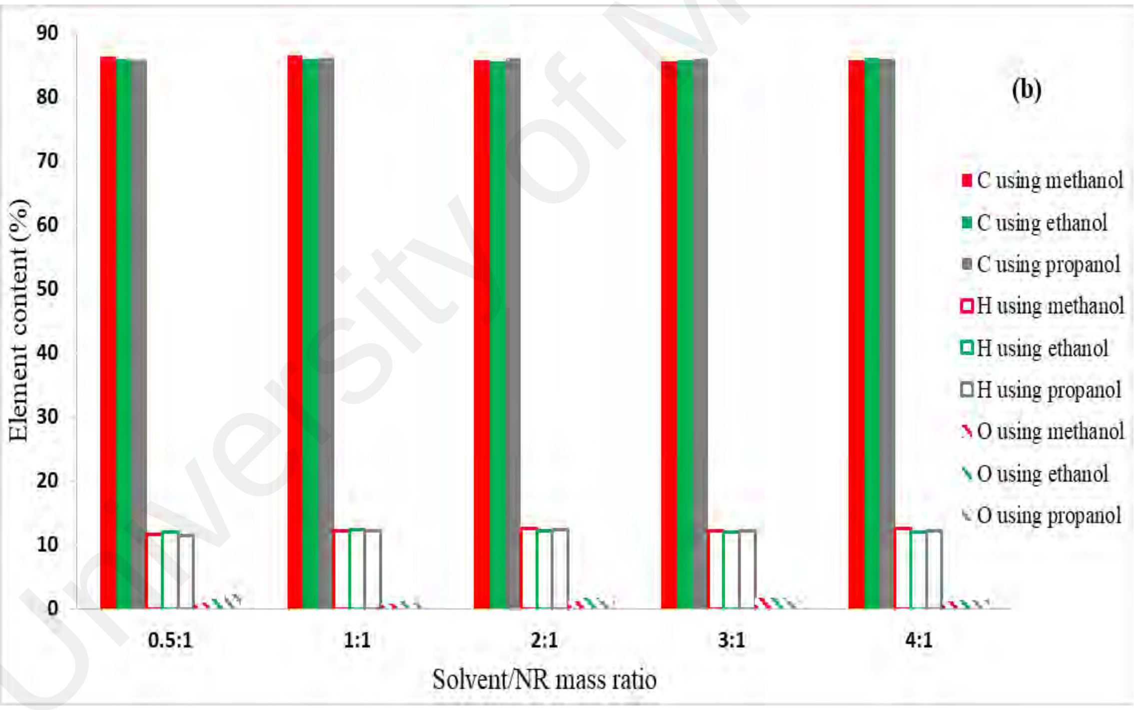


Figure 4-11: (a). Effect of temperature on carbon, hydrogen and oxygen contents using different alcohols. (b). Effect of solvent/NR mass ratio on carbon, hydrogen and oxygen contents using different alcohols.

4.3.3.2 Physical properties and pH value

The results from Table 4.1 showed that the value of viscosities were observed within the range of 11.7cP to 12.6cP. This range was significantly different with the viscosity of the oil obtained by the hydrothermal liquefaction of NR using water. At the same temperature condition, the viscosity of obtained oil using water was reported to be 41.1cP (Ahmad et al., 2018). Kanaveli et al. noted that high viscous oil lowers the quality of fuel in terms of poor flow, poor atomization, and low volatility, causing incomplete combustion, engine deposits, and piston ring sticking (Kanaveli, Atzemi, & Lois, 2017). In contrast to viscosity, the density of oil produced has showed no much considerable influence by the use of diverse solvents. At optimal operating parameters, the average density of oil samples were estimated to be 0.8 g ml^{-1}. As for pH analysis, the outcomes indicated that there was no major change on oil's pH value when different alcohols were applied. The mean pH value achieved was 8 indicating the obtained oil has basic nature.

4.3.3.3 Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra shown that all oil samples nearly had same features in the respect of functional groups (chemical bonds), where five main peaks were noticeably detected in the spectra. These peaks identified as methyl, methylene, aromatics, vinyl, and carbonyl group. Figure 4.6 showed that, CH_2, CH_3, and C─H were chief abundant functional groups identified in the oil synthesized through the hydrothermal liquefaction of NR using different alcohols. The chemical bond of C=C bending and C─H bending were mostly observed at peaks between 816- 953 cm^{-1}, which showed the existence of aromatic and vinyl based compounds. A peak was observed at 1104-1159 cm^{-1} in the FTIR spectra of ethanol and propanol indicating the functional group of C─O stretching. C─O functional groups normally shows the presence of primary, secondary alcohols, aldehydes and ketones. A strong peak which was observed at 1454 cm^{-1} showed the existence of methylene group (CH_2), whereas the methyl group (CH_3) was identified with a strong peak at 1376 cm^{-1}.At wavelength frequency above 2500 cm^{-1}, the chemical bonds associated to methyl and methylene were also identified. At peak 2866 cm^{-1} and 2924 cm^{-1}, methylene and methyl groups were spotted respectively. From FTIR analysis showed that the methylene and methyl groups were most dominant functional groups. In chapter 4, almost the similar chemical bonds were reported using water as a solvent for the depolymerisation of NR.

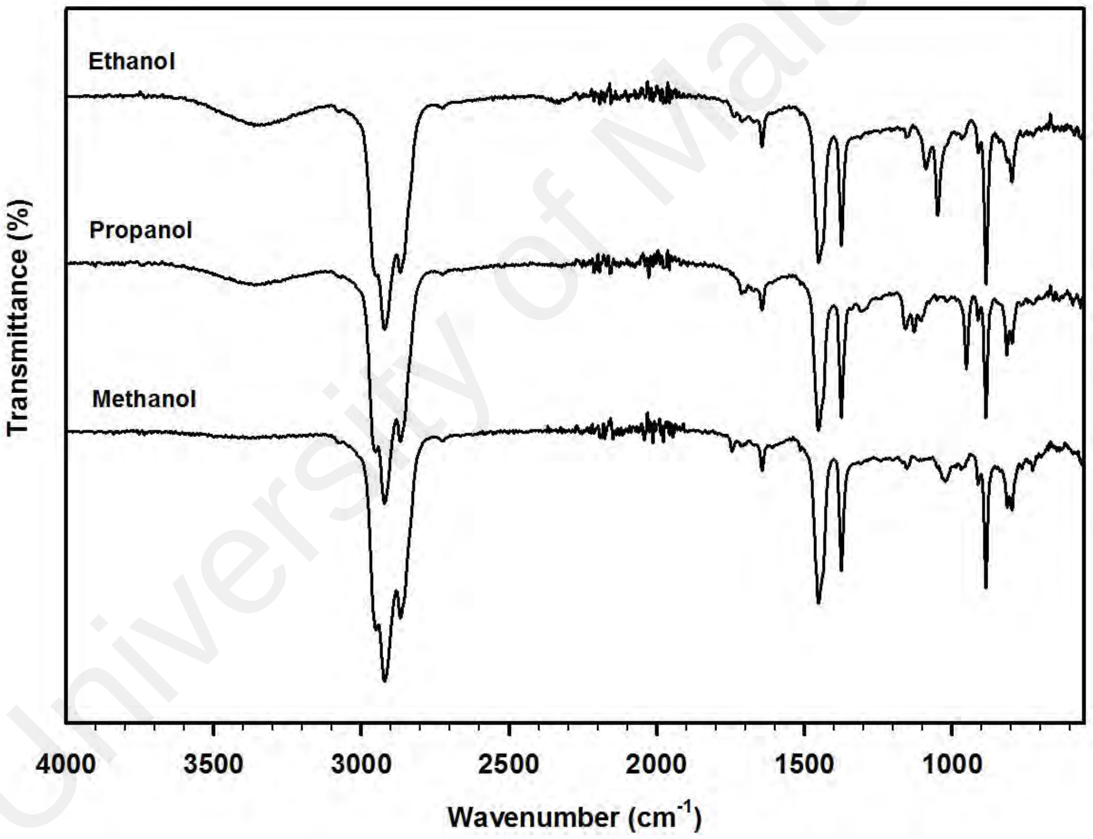


Figure 4-12: FTIR spectra for liquid products using different alcohols at optimum conditions

4.3.3.4 GC/MS analysis

The GCMS study was conducted to define the category and kind of compounds existing in the oil that has obtained using diverse alcohols at optimum parameter. The identified compounds were recognized by searching a mass spectrometry library databank, and the results of analysis were shown in Table 4.2. There were large number of compounds that were identified but their peak areas were small, hence they were not inspected in current investigation. In GCMS study, various compounds that can be categorized as alkenes, aromatics, alcohols, ketones, alkyl, and aldehydes were noticed.

Table 4.2 showed that most of the compounds present in oil were recognized as alkenes. D-Limonene and isoprene were the most governing species found in alkene. Moreover, the second most dominating kind was identified as aromatics compounds. The highest percentage of aromatics in the oil was mainly resulting from 1,2,4-Trimethylbenzene, o-xylene, and toluene. Alkyls were recognized as third prominent class in the obtained oil. Hence, from the analysis it can be concluded that the alkenes were present with maximum proportion in oil, then followed by aromatics, alkyls, ketones, alcohols, and aldehydes. Malevich et al, used propanol for the liquefaction of rubber (consisting of 25.4% of NR and 27.7% of synthetic NR rest were carbon black and other ingredients) (Malevich, Yusevich, & Shashok, 2014). It was reported that high liquid yield was obtained using propanol, which indicates the interaction of solvent molecules with material being processed. Moreover, it was also reported that the amount of cyclic and alkenes (olefin) based compounds were high when propanol was used in the process.

Table 4.2 also showed that in alkenes, the concentration of D-limonene is highest when using propanol as a solvent under optimal operating parameters. Whereas, the concentration of isoprene is less. This is due to the depolymerisation of polyisoprene high at 325°C using propanol to form isoprene radicals. These isoprene radical subsequently undergoes dimerization reaction to form D-limonene. Moreover, the aromatic hydrocarbons formed due to the degradation and dehydrogenation of alkene based cyclic compounds (F. Chen & Qian, 2002; Cunliffe & Williams, 1998; X. Zhang et al., 2008). Furthermore, the presences of alcoholic compound is mainly due to degradation of monomers with solvent (Cheng et al., 2017).

From GCMS results, it can be seen that D-limonene is the most dominating compound in the liquid oil. Therefore, it is important to discuss the mechanism for the formation of D-limonene from NR. During depolymerization of NR, the first step is the degradation of polyisoprene to isoprene monomers (intermediate radicals A and B as shown in figure 7(a).) via a β– scission mechanism. Isoprene radicals then undergoes dimerization (intramolecular cyclisation) to form dipentene (D-limonene) (Cheng et al., 2017; X. Zhang et al., 2008).

The concentration of D-limonene was found to be the highest around 51.23 % and then followed by isoprene 10.65 % when using propanol as a solvent under optimum operating parameters. These two compounds are categorized as alkenes and have potential use as value-added chemicals. Recovery of these chemicals by using extraction techniques will lead to increase in the utilization of NR in the global market. The most common techniques that are used for the separation of D-limonene from liquid product is distillation (Murillo et al., 2006; C. Roy, Chaala, & Darmstadt, 1999), or by the selective condensation of the reactor outlet (Williams & Brindle, 2003). Pakdel et al. studied the synthesis of D-limonene from tire based oil extensively and successfully extracted the 95% of D-limonene through distillation (Danon et al., 2015). Subsequently, Pakdel et al. extracted the D-limonene from tire derived oil using large capacity reactor and the obtained fractions of D-limonene was within the range of 50 and 92 wt% (Pakdel et al., 2001). Similarly, Stanciulescu and Ikura also performed the double distillation of a tire based oil and achieved 75% of pure D-limonene (Stanciulescu & Ikura, 2007)

D-limonene is an important substance in the pharmaceutical industry to produce skin creams, cancer medicine, solvent for cholesterol, pathogens neutralizer, wound healer and heartburn relief. In addition, D-limonene is also used as a flavoring agent, dishwashing liquid, floor cleaner, cosmetics, and odour control agent. Some studies reported that hydrogenated D-limonene can also be used as a fuel additives and it can also be used for the production of high energy density fuels (Jongedijk et al., 2015; Kang & Lee, 2016; Tracy, Chen, Crunkleton, & Price, 2009; Whitworth, 1990). The statistical data showed that over 45 kilo-tons of D-limonene was needed in 2015 and it is predicted to exceed 65 kilo-tons by the year 2023, with estimated gains at above 5%. The production of D-limonene through this process may be promoted as an alternative way to fulfill its future demand.

Besides D-limonene, the liquid product also comprised other hydrocarbon compounds which make this liquid suitable to be proposed as alternative fuel. The other important compounds for fuel detected in liquid are aromatics (12.54%), alkyls (10.8%), and alkene (13.37%). The results of analysis showed that liquid product exhibits good fuel properties in terms of high HHV (46 MJ/kg), and low oxygen contents (1.02%). These characteristics of liquid product are very close to that of conventional fuel oil that were reported in the literature (Kaye, 2018) and it can be upgraded for high quality fuel.

Aromatics are second most dominating compounds in liquid oil. Aromatics are produced at high temperature. It is reported that, at higher temperatures, limonene was not stable and was decomposed or transformed into aromatic compounds via a dehydrogenation or recombination reaction. The mechanism of secondary cracking of limonene was shown in figure 4.7(b) (Pakdel et al., 2001; X. Zhang et al., 2008).

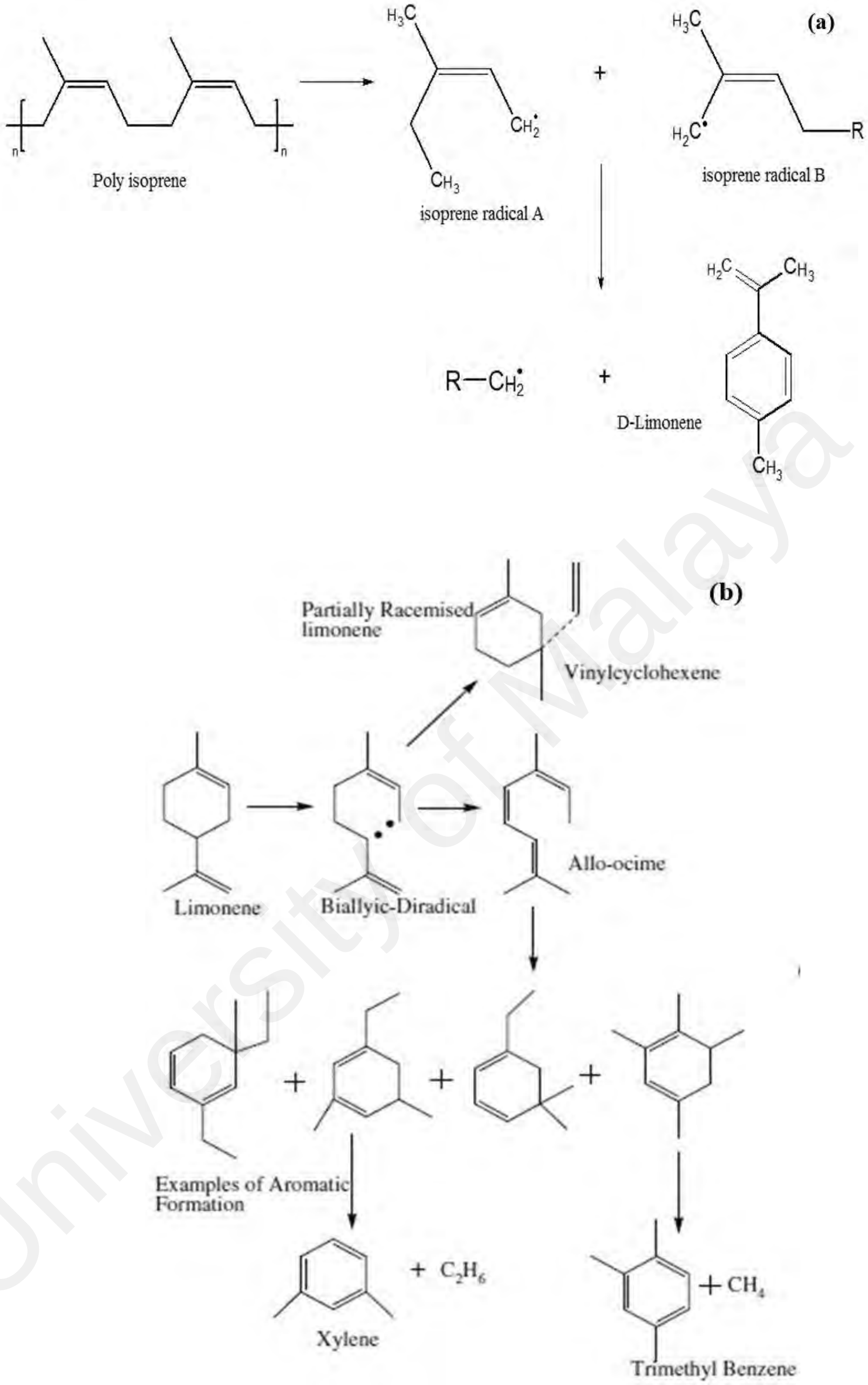


Figure 4-13 (a). Reaction mechanism of Poly isoprene to D-limonene, (b). Reaction mechanism for D-limonene to aromatics

Table 4-2: Main compounds present in oil obtained from hydrothermal liquefaction of natural rubber using diverse alcohols at optimum conditions (325ºC, solvent/natural rubber mass ratio= 1:1, and 30mins) as recognized in GC-MS examination.

Compounds	Identified compounds (%)		
	Methanol	Ethanol	Propanol
	Aromatics		
Toluene	4.21	3.83	4.32
o-Xylene	1.82	2.25	1.93
1,2,4-Trimethylbenzene	3.11	3.35	2.89
m-Cymene	1.16	1.22	1.19
1-Isopropyl-2-methylbenzene	1.86	2.18	2.21
Total	12.16	12.83	12.54
	Alkyls		
Cyclohexane, methyl-	2.73	2.17	3.11
Cyclopentane, ethyl-	5.14	5.65	4.54
Heptane	3.15	1.96	2.76
2-Hexene, 2-methyl-	-	0.45	0.39
Total	11.02	10.23	10.8
	Alcohols		
Perilla Alcohol	0.86	-	-
Cyclohexanol	-	0.42	0.53
cis-1,2-Cyclo octanediol	0.64	0.85	1.21
2-methyl-1,3-butadiene	0.71	1.31	1.15
Total	2.21	2.58	2.89
	Ketones		
Methyl vinyl ketone	-	1.28	1.54
2-Propenal, 2-methyl-	1.43	-	1.53
Cyclohexanone	2.65	2.31	-

Total	4.08	3.59	3.07
	Alkenes		
D-Limonene	42.21	32.86	51.23
Isoprene	18.43	27.76	10.65
3,5-Dimethylcyclohexene	1.05	2.05	1.51
1,3-Cyclopentadiene,5,5-dimethyl-2-propyl-	2.11	1.85	1.21
Total	63.8	64.52	64.6
	Aldehydes		
5-Hexenal	2.67	3	2.79
Total	2.67	3	2.79
Total (%)	95.94	96.7	96.69

4.4 Conclusions

This study showed that NR can be converted into valuable intermediate products through thermal liquefaction process using different alcohol solvents. The conversion has successfully transformed the solid NR into the liquid product which are beneficial for the storage and transportation. With the equal ratio of propanol and NR, the highest liquid yield (89.53 wt.%) was obtained at the temperature and reaction time of 325°C and 30 mins respectively. The liquid product has two potential uses as a chemical feedstock and as a renewable fuel by upgradation. D-limonene was found to be the most dominating compound present in the liquid that can be extracted by distillation process and then used as a chemical feedstock in many industrial applications. Furthermore, the characteristics of product showed that this liquid can also be used for as a future renewable fuel production since it has a high energy density and low sulfur content which make the liquid more environmental friendly.

CHAPTER 5: LIQUEFACTION OF NATURAL RUBBER AND SCRAP TIRE TO LIQUID FUELS

5.1 Introduction

Shortening of fossil fuels and their effects of greenhouse gas emission has become a very famous and leading problem from the last few years, which subsequently convinced the scientists to develop alternative fuels to substitute these fossil fuels (AldoVieira et al., 2009; Dell et al., 2014). Therefore, researchers are utilizing different biomasses for the synthesis of biofuel. The oil obtained from biomasses exhibits low calorific value within the range of 30 to 36 MJ/kg due to the presence of high amount of oxygen contents (Crocker, 2010). Moreover, the biomass based oil found to be acidic in nature due to low pH value (Kruse, Funke, & Titirici, 2013).

Due to these issues, some other alternative should be invented. That alternative should be available in huge quantity and easily available. In this regard, Natural rubber (NR) and scrap tires (ST) should be considered. Natural rubber is also one of the available sources that have a potential to meet future energy requirements. Natural rubber is a vigorous, premeditated and exceptional feedstock used in huge quantities globally (Rogers & Cornish, 2005). Natural rubber is a polymeric compound of Isoprene, i.e. Poly-isoprene $(C_5H_8)n$ with smalle quantity of impurities such as other organic compounds and water (Morton, 1999). Similarly, ST usually consists 40-52.2% of NR and other components of ST are carbon black, metal, textile, sulfur and additives (A. K. Basu, 2009; Evans & Evans, 2006; Funazukuri et al., 1987). This ST can be used for the liquid fuel production.

Different thermal conversion processes are available, among them hydrothermal liquefaction technique is the best process that gives maximum liquid yield and lower temperatures. Normally, hydrothermal liquefaction process uses water as a solvent. This solvent acts as a catalytic medium of the organic reaction to take places subsequently breaking down the material into lighter molecule fractions. There lighter fractions are very reactive and undergoes different polymerisation reaction, condensation reaction and intramolecular cyclization reaction to produce high yield oil.

In this objective,a comparative study was performed by converting NR and ST into liquid fuel using hydrothermal liquefaction process. The yield of oil obtained from both materials was estimated and reported. Moreover, different analytical techniques were used to assess the properties of liquid oil samples obtained from NR and ST.

5.2 Experimental

5.2.1 Materials

The natural rubber (NR) with SMR L grade (Malaysian Standard Rubber) was obtained from Malaysian Rubber Board. The NR used was chopped to particle size of approximately 3-5 mm. The NR was characterized using Thermogravimetric analysis (TGA). The proximate and ultimate analyses of NR were also performed. Distilled water that used as a reaction medium in this study was produced from Auxilab S.L, QUARTZ. Moreover, the inert nitrogen gas with 99 % purity was used to create a non-oxidative environment inside the reactor. For comparative study, the scrap tires (ST) used in this experiment were categorized as truck tires. The steel and textile netting components of the tire were removed and the tires were grinded to obtain the desired particle size of 1-2 mm.

5.2.2 Experimental method

Autoclave batch reactor made up of SS316 was used in this study obtained from Amar Equipment Private Limited, Mumbai, India. The reactor was heated electrically using furnace. The reactor was also equipped with thermocouple, pressure gauge, safe value, vent value and a stirrer. The reactor system was attached to computer to give required temperature set point to the controller. This control system was feedback control system.

The two sets of experiments were performed. In the 1st set, NR was used for its conversion in to liquid fuel. For both cases, the solvent used was water and the water to NR and water to scrap tire mass ratio was set to 3:1(54g: 18g). The temperature of 375°C was employed and it was set by giving command on a computer. The reaction time of 30minutes was provided for the reaction to carryout.

After the process was done, the heater was switched off and the reactor was cool down to room temperature by cooling coils system. Three products were obtained liquid, tar, and gas products, where the liquid was considered to be the main product. The gas product was not collected due to limitations in reactor design. The liquid products and tar were collected and weighted. The gas product was calculated by the material balance. The yields of products were calculated by dividing its mass by the mass of NR loaded into the autoclave batch reactor, equation (5.1) was used for that purpose.

$$\text{Product Yield}(\%) = \frac{\text{wt. of product}}{\text{wt. of NR}} \times 100 \qquad (3.1)$$

The yield of product gas was estimated by the subtraction: 100-(Oil yield + tar yield + water soluble).

5.2.3 Raw material and product characterization

The elemental analysis of raw material was performed using CHNS/O analyzer model 2400, whereas, the proximate analysis of raw material was conducted using ASTM standard (ASTMD 3173 and ASTMD3175) methods. The TGA analysis was performed using model NETZSCH STA 449F3. The TGA study of NR and scrap tire were conducted with 10 C^o/min heating rate to investigate their thermal characteristics. The analysis was carried out within the temperature range of 28^{o}C to 800^{o}C in the presence of nitrogen atmosphere. The flowrate of nitrogen purge gas was 20 mL/min. 11.58 mg and 10.76 mg of NR and scrap tire samples respectively were used to carry the analysis.

After the completion of reaction time, the whole mixture inside the reactor was transferred in a 50 mL conical centrifuge tubes and subjected to centrifugation process at 3200 RPMs for 20 mins. As a result, three separate layers were obtained, consisted of oil layer at the top, water in the middle and solid at the bottom. The oil sample was collected by using micropipette, while the remaining portion in funnel was filtered out using whatman filter papers. The residue obtained on filter paper was dried in an over at 110^{o}C and weighted. The filtrate left was considered as water (aqueous phase). Using solvent extraction technique, water soluble fractions were extracted. The quantitative analysis of water soluble fraction was provided in this study. However, the main focus of this study was on liquid oil. Hence, the product characterizations were done only for liquid oil.

The physical analysis of liquid includes the viscosity (η) and density (ρ). The viscosity (η) of the liquid was estimated by using methods described in previous chapters. Several chemical analysis were performed using pH meter and CHNS/O analyzer. Results and discussion

5.3 Results and discussions

5.3.1 Elemental and proximate analysis of raw materials

Ultimate and proximate analyses of any materials are very important since they provide information about the chemical and elemental composition of materials. From Table 5.1, it can be seen that the volatile matter in NR is 89.98 % whereas for ST it was estimated to be 66.76%. The fixed carbon and ash contents in NR were 4.71 % and 3.60 % respectively. While for ST, the fixed carbon and ash contents were calculated to be 28.53% and 3.56%. It is reported that high volatile contents in organic material provides high volatility and reactivity, which subsequently favors the production high quantity of liquid and gas products, whereas the presence of fixed carbon leads to the formation of char (Jahirul et al., 2012). Moreover, it can also be seen that NR consists of high hydrocarbons as compared to ST. The carbon and hydrogen contents in NR were estimated to be 83.63 % and 11.97 % respectively. On the other hand, the carbon and hydrogen contents in ST were estimated to be 82.59% and 8.17% respectively. Furthermore, the Table 5.1 is also showing that the NR is sulfur free material with low oxygen contents, whereas ST exhibits high sulfur contents of 2.18%. The high amount of carbon and hydrogen contents have positive effect on the HHV, whereas, high oxygen contents reduces the HHV (Abnisa & Wan Daud, 2015). Therefore, the presence of high hydrocarbons, high HHV, volatile matter and less sulfur clearly showed that the properties of NR is better than ST and makes NR a reliable and suitable alternative material to produce liquid fuels.

Table 5-1: Characteristics of natural rubber and scrap tire

Characteristics	Natural rubber	Scrap tire
Proximate Analysis (wt.%)		
Volatile matter	89.98	66.76
Fixed carbon	4.71	28.53
Ash	3.60	3.56
Moisture	1.71	1.15
Ultimate Analysis (wt.%)		
Carbon	83.63	82.59

Hydrogen	11.97	8.17
Nitrogen	1.58	0.92
Oxygen	2.71	6.14
Sulfur	0.12	2.18
HHV(MJ/kg)	45	40

5.3.2 TGA analysis of raw materials

In this study, TGA was performed to get an overview of the thermal behavior of the feedstock. From Figure 5.1 it can be seen that the thermal decomposition of NR started approximately at 300°C and more than 95 % of NR was decomposed when temperature reached about 480°C. Same study has been reported by Mohapatra and Nando (2014) (Mohapatra & Nando, 2014). This decomposition was found to be higher than ST, where ST decomposition was only observed around 52 % at temperature of 480°C. The low decomposition of ST was due to the presence of stearic acid, extender oil, plasticizers, and other additives (Abnisa & Wan Daud, 2015). However, in NR, the degradation of Poly-isoprene was occurred which was pure hydrocarbon. The high percentage of weight loss observed from TGA analysis indicated that 350-400°C was found to be a suitable temperature for maximizing NR conversion into liquid product.

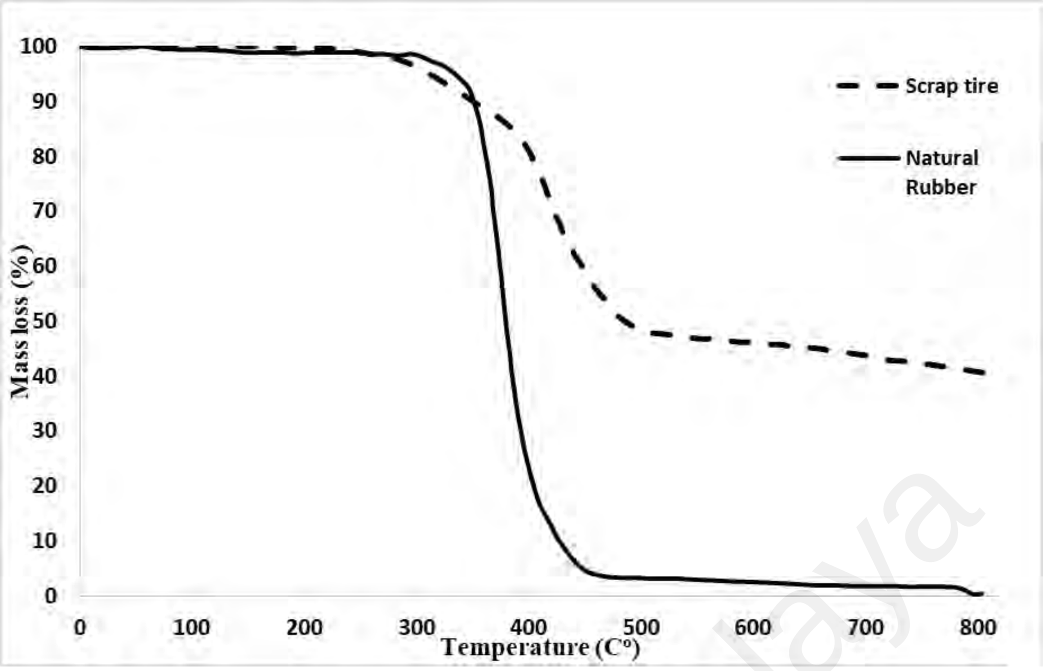


Figure 5.1: TGA curve for natural rubber and scrap tire

5.3.3 Product yields and characterization results

The process conditions of 375°C, H_2O/material ratio 3:1 and 30 minutes were employed to carry out the hydrothermal liquefaction of NR and scrap tire as comparative study. The data comparison between the liquid products from NR and scrap tire is shown in Table 5.2. The results showed that the liquid yield from scrap tire obtained was 25 wt.%. This yield was observed to be very low as compared to the oil yield produced from NR which was 76%. The less oil yield from scrap tire was due to the incomplete degradation at lower temperature and pressure. It is reported that to carry out the effective degradation of scrap tire, water in super critical condition (374°C and 22.1 MPa) is recommended during hydrous pyrolysis (Funazukuri et al., 1987; L. Zhang et al., 2016). Under super critical water, the liquid product yield of 44 to 58% can be achieved from scrap tire (Ahmad et al., 2016).

Based on the quality aspects, it can be seen from Table 5.1 that the density of the scrap tire based oil at 26°C was 0.900 g/ml. It was denser than the oil obtained from NR, which was typically about 0.859 g/ml. The density is much related to the liquid mass flow rate, which significantly affects the performance of fluid atomizers. Another property that has also been given the effect to atomization quality is viscosity. The oil from scrap tire has very high viscosity as compared to NR which was 531 cP at 26ºC. This high viscosity could become problematic in the long run that could include the difficulty to light the burners. It may also affect the fuel flow through pipes when poor atomization may result in the formation of carbon deposits on the burner tips or on the walls. The viscosity of oil obtained from NR was estimated to be 14.61cP.

The pH value of oil from scrap tire at room temperature was 4.65. This low pH was due to the presence of acidic compounds such as fatty acids (carboxylic acids and *n*-alkanoic acid) in the oil (Martínez et al., 2013; Rushdi et al., 2013; L. Zhang et al., 2016). In contrast, the oil from NR had pH value of 7.26, which makes it non-corrosive. It is reported that the oil with low pH value are very corrosive to aluminum, mild steel and nickel based materials (Abnisa et al., 2013).

The hydrogen contents of scrap tire oil was less than NR based oil showing that NR based oil was more enriched in hydrocarbon contents, which made it good to be used as fuel. However, the oxygen content of rubber tire oil was slightly lower than NR oil. During hydrothermal liquefaction of scrap tire, some sulfur contents were retained in the liquid product, which could result in toxic emissions such as SOx. The sulfur in scrap tire came from the vulcanization process. Whereas, the liquid product obtained from the hydrous pyrolysis of NR contained very low sulfur contents, which made it more reliable and environmental friendly.

Table 5-2: Comparison between the oil products obtained from natural rubber and scrap tire

Properties of Oil Products obtained at 375°C, H_2O/material mass ratio= 3:1, and 30 mins		
Characteristics	**Natural rubber**	**Scrap tire**
Physical properties		
Oil yield (%)	76	25
Viscosity (cP)	14.61	531
Density (g/ml)	0.859	0.900
pH	7.26	4.56
Ultimate Analysis		
HHV(MJ/kg)	43-45	44
Carbon (%)	84.62	84.3
Hydrogen (%)	12.11	11.65
Nitrogen (%)	0.41	0.49
Oxygen (%)	2.67	1.93
Sulfur (%)	0.19	1.63

5.4 Conclusion

Hydrothermal liquefaction of natural rubber and scrap tire was performed using autoclave batch reactor as a comparative study. At operating conditions of 375°C, H_2O/material mass ratio= 3:1, and 30 mins, NR gave the highest amount of oil yield with 76% where the oil yield obtained from ST was estimated to be 25%. This low yield was due to the presence of non-hydrocarbon additives in the ST. The result of characterization showed that NR and ST based oil contain high hydrocarbon contents due to which they have good HHV. However, elemental analysis showed that ST exhibits high sulfur contents making it non-ecofriendly. Moreover, ST based oil was appeared to be acidic in nature to be low pH.

CHAPTER 6: TECHNO-ECONOMIC STUDY OF LIQUEFACTION OF NATURAL RUBBER

6.1 Introduction

Natural rubber (NR) is usually obtained from the rubber tree, guayule plant, russian dandelion and rubber rabbitbrush (Roberts, 1988; Rogers & Cornish, 2005; J. van Beilen, 2006). It has been recognized as a vital, strategic and unique feedstock used in enormous quantities worldwide in different sectors, such as medical, transportation, clothing, and defense industries (Rogers & Cornish, 2005). This plant is also considered as the important crop for Malaysia, Indonesia, Thailand and several central African countries since it can provide the major share of export revenue (Barlow, 1970). The warm and humid tropical conditions of those countries make the NR grows optimally and yields best (Rogers & Cornish, 2005).

According to 2016 statistics, the NR production in Malaysia was reported to be 740 billion tonnes, whereas the NR consumption was estimated to be 488 billion tonnes (Malaysian Rubber Research and Development Board, 2017). This huge amount NR rubber has been mainly used for many industrial applications, such as medical equipment, rubber shoes, condoms, latex gloves, bio-materials, conveyer belts, electrical insulations, automotive mats and tires (Abdullah, 1994; Kohjiya & Ikeda, 2014). However, this high quantity of NR has also appealed the scientists to exploit it as a valuable feedstock for the synthesis of liquid fuels by depolymerization process (Niaounakis, 2013). In 1999, Kawser and Farid converted the natural rubber (NR) to liquid fuels using pyrolysis technique at 500^{o}C (Kawser & Farid, 2000). Then, in 2017, Ahmad et, al. improved the process by successfully converting the NR into liquid fuels at lower temperature by increasing the corresponding pressure (Ahmad et al., 2018). This technology was known as hydrothermal liquefaction technique, where 76 wt% of bio-oil yield was obtained at the optimum conditions of 375ºC, 92 bar, NR/water ratio 1:3, and 30 min reaction time. It was also reported that the bio-oil obtained from NR showed very good fuel properties in terms of low oxygen contents, high energy density, and zero sulfur contents. According to Ahmad et, al, these characteristics made NR based oil to be higher in rank as compared to the wood-biomass based oil. Based upon finding it can be assumed that it would be very advantageous to commercialize this method for the production of liquid fuels from NR on large scale. Ahmad et al., further improved the liquefaction process by utilization of organic solvents in the process and obtained the liquid yield of 89% using propanol as a solvent (Ahmad, Abnisa, & Wan Daud, 2019).

Ravignani et al., reported that whenever a first-hand process is considered for developing new process, substituting an existing process or a sequence of processes, the economic evaluation should be evaluated (Ravignani et al., 1982). The liquefaction of NR by using hydrothermal process was considered as brand-new way to produced liquid fuels recently. If this process is considered to be used in future, the economic assessment of the process in terms of capital investment cost, operating & maintenance cost, profitability index and ROI is need to be calculated to establish its feasibility and commerciality.

There are several methods that can be employed for the economic assessment of the process such as net future worth, pay-back time, net present worth, return on investment, and discounted cash-flow rate of return (Sinnott, 2005). Among these methods, the return on investment (ROI) is mostly chosen to evaluate the economic feasibility. The advantage of ROI is that it could be used as a rough guide for judging projects and when decisions have to be made on whether to install additional equipment to reduce operating costs (Sinnott, 2005). There are some information available in literature for the economic assessment of hydrothermal liquefaction processes using different feedstocks by ROI approach. A techno-economic study conducted by Shelley and El-Halwagi showed the promising economic feasibility of co-liquefaction plant of rubber tire and plastics operating at capacity of 300tons/day (Shelley & El-Halwagi, 1999). The capital and operating cost of the plant was estimated to be 55$MM and 8.509$MM respectively. The results showed that investment was profitable with the ROI of approximately 15% with oil priced at 20$/bbl. They studied the effect of capital cost and fuel selling price on ROI and observed that increasing the capital cost decreased the ROI whereas increasing the fuel selling price showed improvement of project's ROI. Ou et al., converted the defatted microalgae into fuel using hydrothermal liquefaction and hydroprocessing (Ou, Thilakaratne, Brown, & Wright, 2015). Process simulation and costs were estimated using CHEMCAD software, where the plant capacity was assumed to be 2000 tonnes/day. The calculations showed that total project investment was 504 M$ and the annual operating cost was 158 M$. The profitability of the investments were assessed by estimating the ROI to be 10%. In their study, it was noticed that raw material price and product yield had remarkable influence on ROI. They described that increasing the feedstock price reduced the ROI, whereas, high yield of fuel improved the profitability of the project. Similarly, Snowden-Swan et al. used the muncipale waste sludge to produce fuels using hydrotherrmal liquefaction and process upgradation (Lesley Snowden-Swan et al., 2016). Aspen plus economic analyzer was used for estimation of different costs and values. The capacity of hydrothermal liquefaction plant was set to be 100 ton/day. The results showed that the total capital investment of plant was 79.4M$, which was found to be profitable with ROI of 10%. They noted that the plant capacity played important role in improving the profitability of the project, increasing the plant capacity improved the ROI. Similar investigations have been reported by many authors. (Eggoni, 2016; Helmer, Høy, Miralles, Villamar, & A., 2018; Jarvis, Billing, Hallen, Schmidt, & Schaub, 2017; Jones et al., 2014; LJ Snowden-Swan et al., 2016).

In this study, Aspen Plus® economic analyzer was used to study the economics of hydrothermal liquefaction of NR to liquid fuels. Two cases models were developed; one for water and second for propanol. All the experimental data such as temperature, pressure, material and energy balance were used to create the simulation model. All the process equipment were sized and mapped on the basis of experimental based input data. The ROI, profitability index (PI), and payout period was calculated for the both cases in order to assess the economic feasibility.

6.2 Feedstock and methods

6.2.1 Feedstock

In this investigation the feedstock comprises of NR and a solvent with a processing capacity of 2000 tons feedstock per day. According to Malaysian rubber board statistic (2016), the 252 billion tonnes of NR remain un-utilized and this huge amount of NR can cover up the feedstock capacity of plant for the production of fuels. In Aspen Plus®, the type of components are divided into two categories: conventional components and non-conventional components. Since NR is a non-conventional component that listed in the software, the ultimate, proximate, and sulfur analysis data of NR were used to be added into the ULTANAL, SULFANAL, and PROXANAL data, respectively. The NR analysis used in this study was obtained from experimental results presented in chapter 3 is shown in Table 6.1.

Distilled water and isopropyl alcohol were two solvents selected in this study individually, they were available in software database and considered as conventional components. The molecular mass and boiling point of isopropyl alcohol is 60.1g/mole and 82.6^{o}C respectively. Two case study models were developed, where in first case, distilled water was employed with NR mass ratio of 3:1, whereas the equal ratio of isopropyl alcohol and NR mass was applied for the second case.

Table 6-1: Characteristics of natural rubber

Characteristics	**Natural rubber**
Proximate Analysis (wt.%)	
Volatile matter	89.98
Fixed carbon	4.71
Ash	3.60
Moisture	1.71
Ultimate Analysis (wt.%)	
Carbon	83.63
Hydrogen	11.97
Nitrogen	1.58
Oxygen	2.71
Sulfur	0.12
HHV(MJ/kg)	45

6.2.2 Process simulation

Aspen Plus® software was used to conduct the economics assessment of the process in current investigation. This software has been used widely in process design, analysis, process optimization and to carry out the economic evaluation of any chemical process (Sinnott, 2005). Rong et al. noted that different chemical processes such as gasification, distillation, pyrolysis, and many more can be modelled in this software by using various thermodynamic properties packages (Rong et al., 2017).

This study used Aspen Plus® version 9 which is equipped with the new feature of economic evaluation, which known as activated economics. This new feature is capable to perform capital and operating cost evaluations during early design stage of the process on large scale, where it helping the design engineers to assess the proposed design and allowing them to do screening on the basis of economic factors (T. A. Adams, 2017; Al-Malah, 2016; Intratec, 2013).

Normally, in Aspen Plus® designing a process starts by drawing a process flow sheet, then the components are added and the numerous operation conditions defined. The several types of equipment used in this study such as pump, separator, and reactor are represented by blocks. Streams connecting these blocks selected as material streams, where in each stream the temperature, pressure, flowrate and components were defined.

6.2.3 Process description and method

The figure 6.1 was shown the whole process flow diagram of liquefaction process. The designed plant was started by sketching the process flow diagram containing of the main components, a pump, a reactor with heating utility, cooler, and a phase separator. All the input feeds, recycle stream, output products, and streams between the components were drawn. There were two feed streams comprising of solvent and NR entering the system. NR was transferred to reactor directly while solvent stream to the reactor was pumped by using centrifugal pump. The solvent was also recycled after separation. In the case of water as a solvent, the mass flowrate of NR was set to 500 tons/day with the temperature and corresponding pressure were 375ºC and 92bar respectively. With this condition, the yield of bio-oil obtained was 76 wt. % and this yield was used in simulation. For isopropyl alcohol, around 1000 tons/day of NR was used with the temperature of 325ºC and corresponding pressure of 35bar, where under these conditions the bio-oil yield was obtained 89 wt. %. Table 6.2 was showed the input process parameters and product yield distribution used for the development of simulations in Aspen Plus®.

Table 6-2: Input operating conditions and product yield distribution

Process inputs and product yields		
Data input	**Water as a solvent**	**Propanol as a solvent**
Feedstock		
Natural rubber (tons/day)	500	1000
Solvent (tons/day)	1500	1000
Total feed (tons/day)	2000	2000
Hydrothermal liquefaction parameters		
Temperature (ºC)	375	325
Corresponding pressure (bar)	92	35
Natural rubber conversion (%)	99.9	99.9
Product yields		
Bio-oil (wt. %)	76	89
Gas (wt. %)	4	5
Tar (wt. %)	12.5	6
Water soluble (wt. %)	7.5	—

All the reaction conversions and yield data were simulated using available built-in RYield reactor block. The yield and composition used for the modelling were based upon experimental data. The composition was determined using GCMS analysis, and compounds that were identified in GCMS analysis were shown in Table 6.3.

Table 6-3: GCMS analysis of bio-oil obtained from NR liquefaction using water and propanol as a solvent

GC/MS analysis of oil samples for major compounds (% of total peak area by GC-MS)		
Compounds	**Water as a solvent [a]**	**Propanol as a solvent [b]**
	Aromatics	
Toluene	3.56	4.32
o-Xylene	2.01	1.93
1,2,4-Trimethylbenzene	2.89	2.89
Benzene,1-methyl-3-(1-methylethyl)-	2.21	-
m-Cymene	-	1.19
1-Isopropyl-2-methylbenzene	-	2.21
Total	10.67	12.54
	Alkyl	
Cyclohexane, methyl-	-	3.11
Cyclopentane, 1,3-dimethyl-, cis-	3.56	-
Heptane, 2,4-dimethyl-	1.23	-
Cyclopentane, ethyl-	8.54	4.54
Heptane	-	2.76
2-Hexene, 2-methyl-	0.54	0.39
Total	13.87	10.8
	Alcohols	
Cyclohexanol	-	0.53

2-Hydroxymethylcyclopentanol (trans)	3	-
cis-1,2-Cyclooctanediol	-	1.21
2-methyl-1,3-butadiene	-	1.15
Total	3	2.89
	Ketones	
7-Oxabicyclo[4.1.0]heptane	1.4	-
Methyl vinyl ketone	-	1.54
2-Propenal, 2-methyl-	-	1.53
Total	1.4	3.07
	Alkenes	
D-Limonene	34.77	51.23
Cyclohexene, 3,5-dimethyl-	1.04	1.51
1,3-Cyclopentadiene,5,5-dimethyl-2-propyl-	1.88	1.21
Isoprene	25	10.65
Total	62.69	64.6
	Aldehydes	
5-Hexenal	3.59	2.79
Total	3.59	2.79
Total (%)	95.22	96.69

[a] H_2O/NR mass ratio = 3:1, temperature = 375°C

[b] C_3H_7OH/NR mass ratio = 1:1, temperature = 325°C

After the completion of process, the product stream was assumed to be transferred into the separator unit. The component separator was selected to split fractions of gas, oil, tar, and recovered solvent. Similar separation method was also adopted by Haugstad in the study of hydrothermal liquefaction of Algae (Haugstad, 2017).

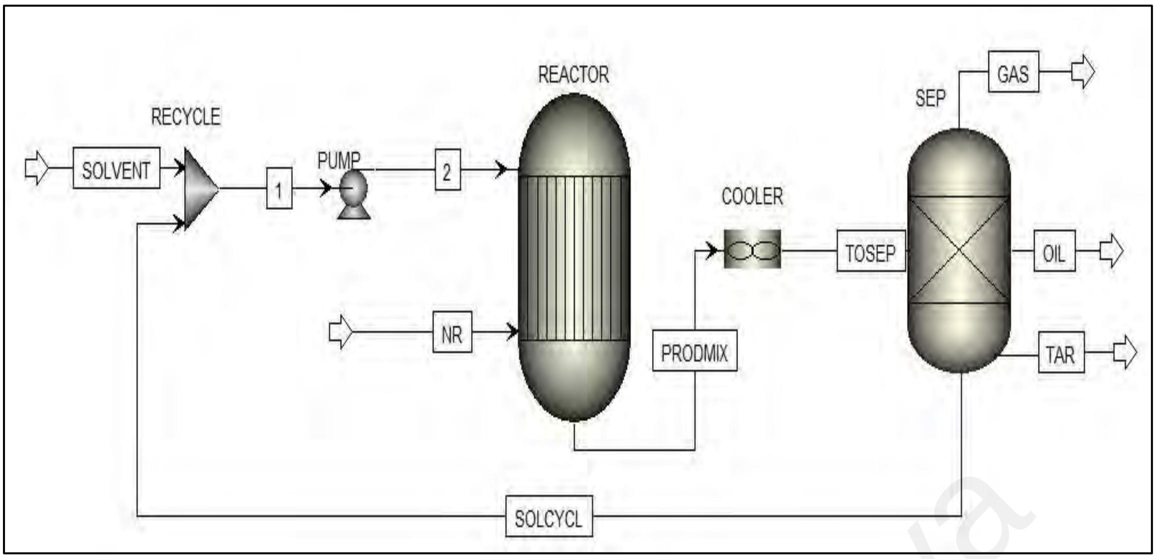


Figure 6-1: Simulation process flow diagram

For thermodynamic properties, the Soave-Redlich-Kwong (SRK) cubic equation of state was used to develop the simulation in Aspen Plus®. This method was found to be capable of both predicting immiscibility of crude oil with solvent, and reproduce results of miscibility and phase separation that were consistent with literature data (Tzanetis, Posada, & Ramirez, 2017).

Components present in the oil and gaseous products were added as a conventional compounds which were taken from available database in the Aspen Plus®. The gaseous components were considered as H_2, CO_2, CO, CH_4, C_2H_4, and C_2H_6 since they were found to be a major compounds in gas products during the conversion of natural rubber to liquid fuel by using thermal conversion process (Kan, Strezov, & Evans, 2017). The enthalpy and density of the non-conventional component was estimated using special HCOALGEN and DCHARIGT models available in Aspen Plus® software. These special models required the input data from ULTANAL, SULFANAL, and PROXANAL analyses.

6.2.4 Economic assessment

Economic study involves the evaluation of different expenditures, these different expenditure consisted of estimation of capital cost, operating cost and product selling price. Capital cost includes the procurement costs of various equipment such as, pumps, reactor with heating system, and separator. All the process equipment were sized and mapped on the basis of mass and energy balance and their costs were projected using Aspen Plus® economic analyzer. Annual operating cost normally depends upon the prices of feedstock, process utility, labor cost, and maintenance cost. As the cost of feedstock is unpredictable, in current study the feedstock price was set as the current selling price (1.33USD/kg) of NR in Malaysia. Furthermore, product selling price has a great influence on the profitability therefore the average price of crude oil (0.54 USD/liter) in last ten years was selected as the product selling price.

To assess profitability of whole project, rate of return (ROI) and profitability index (PI) were calculated. ROI measures the profit or loss made on an investment relative to the amount of money invested. ROI is usually expressed as a percentage and is typically used for financial decisions, to compare a company's profitability or to compare the efficiency of different investments. ROI can be calculated by using equation (6.1). PI helps to identify the relationship between the costs and benefits of a proposed project through the use of a ratio that can be calculated using equation (6.2). If the value of PI is less than 1, the project is considered no profitable. If PI is greater than 1 in that case the project is expected to be profitable.

$$\mathrm{ROI} = \left({}^{\text{Net profit}}\!/_{\text{Cost of investment}}\right) \times 100 \tag{6.1}$$

$$\mathrm{PI} = {}^{\text{Projects present value of future cash flow}}\!/_{\text{initial investment}} \tag{6.2}$$

6.3 Results and discussion

The total project investment for both cases that using water (case 1) and propanol (case 2) was shown in table 5.4. The total capital cost of the case 1 was estimated 4.96 million USD, while it was calculated 6.27 million USD for case 2. The result showed that the capital cost of case 2 was found higher. The reason behind this difference was due to the usage of high proportion of NR in case 2 subsequently increases cost of NR processing and handling in terms of equipment cost, equipment setting, piping, instrumentation, insulation, paint and electrical cost. The detailed project capital cost for both cases were shown in table 5.4.

Table 6-4: Total Project investments for both cases

Total Project investments		
Investments	**Case 1 (using water)**	**Case 2 (using propanol)**
Project capital cost (Million USD)		
Total Project Capital Cost	4.969	6.325
Purchased Equipment	1.59	1.89
Equipment Setting	0.01	0.1
Piping	0.274	0.353
Civil	0.023	0.029
Steel	0.02	0.021
Instrumentation	0.464	0.718
Electrical	0.504	0.52
Insulation	0.052	0.086
Paint	0.006	0.01
Other	1.233	1.601
G and A Overheads	0.066	0.083

Contract Fee	0.166	0.207
Contingencies	0.561	0.707
Operating cost (Million USD/year)		
Total operating cost	218.284	509.468
Total Operating Labor Cost	0.351	0.351
Total Maintenance Cost	0.027	0.022
Total Supervision Cost	0.307	0.307
Operating Charges	0.164	0.164
Plant Overhead	0.342	0.34
Total Raw Materials Cost	200.85	470.427
G and A Cost	16.169	37.738
Total Utilities Cost	0.075	0.119

Similarly, there was significant difference observed in the operating costs for both cases. The operating cost for case 2 was approximately 509 million USD/year which is higher as compared to the operating cost for case 1. Besides, the division the NR to solvent mass ratio, the general & administrative (G & A) cost also showed high influence on operating cost. G & A cost are expenses for running the business (rent, salaries, repairs, insurances, tax etc.) that is not directly associated with production of goods or services. However, it depends upon the plant capital cost while imposing annual tax and insurance rate, and also depends on subtotal operating cost. Normally, for calculation purpose G & A cost is calculated as 5-10 percent of sub-total operating cost. Therefore, case 2 has high subtotal operating cost thereby increasing its G & A costs compared to the case 1. The detailed summary of operating costs for both cases was presented in table 6.4.

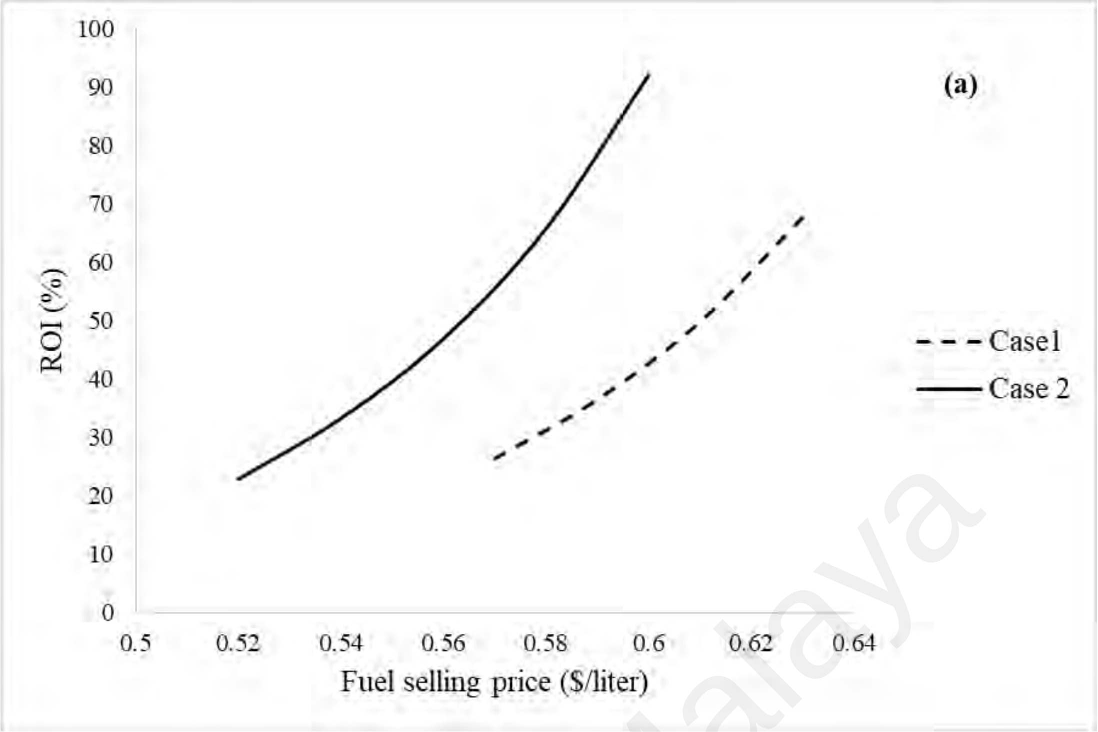
Table 6.5 is showing the product sales higher for case 2 as compared to case 1. It is due to fact that high yield of liquid fuel about 89wt% was obtained in case 2 thereby increasing the sales of products. The ROI and PI depends upon the prices of feedstock and on the product selling price. If feedstock price is low and the product selling price is high, it improves the ROI and PI of the project. In this study, both feedstock NR price (1.33 USD/kg) and product oil selling price (0.54 USD/liter) was fixed.

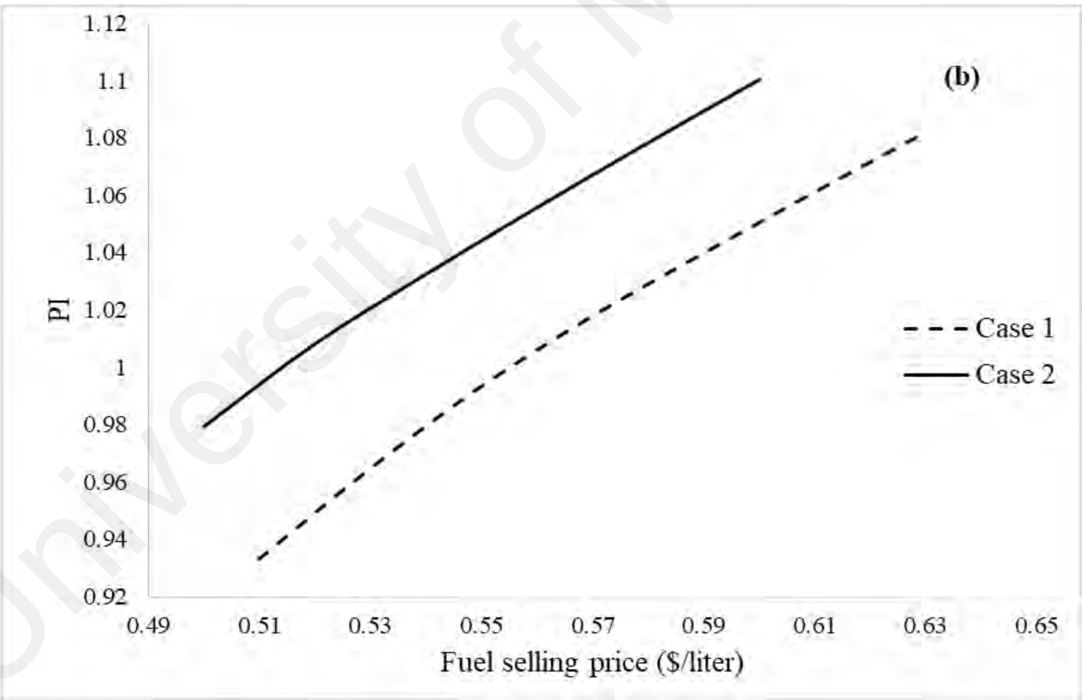
Even case 2 required the high capital and operating cost but ROI proved that it is more profitable as compared to the case 1 and showed ROI of 34.97%. While for case 1, ROI was calculated to be 24.51%. Same trend was also observed for the PI. The difference of 11% in ROI between both cases was due high product sales obtained in case 2. Due to this reason, the results also showed that the payout period of the case 2 less than case 1. The profitability of both cases in terms of ROI, PI, and payout period were shown in table 6.5.

Table 6-5. Project profitability for both cases

Project profitability		
Profit assessment	**Case 1 (using water)**	**Case 2 (using propanol)**
Total Product Sales	214 Million USD/Year	531 Million USD/year
ROI (Rate of Return)	24.51%	34.97%
PI (Profitability Index)	1.01772	1.05802
Payout period	11 Years	4 years

Moreover, for study purpose, the influence of fuel selling price on ROI, PI and Payout period was also observed and shown in figure 6.2(a), 6.2(b) and 6.2(c) respectively.


(a)
ROI (%)
100
90
80
70
60
50
40
30
20
10
0
0.5
0.52
0.54
0.56
0.58
0.6
0.62
0.64
Fuel selling price ($/liter)
Case1
Case 2


(b)
PI
1.12
1.1
1.08
1.06
1.04
1.02
1
0.98
0.96
0.94
0.92
0.49
0.51
0.53
0.55
0.57
0.59
0.61
0.63
0.65
Fuel selling price ($/liter)
Case 1
Case 2

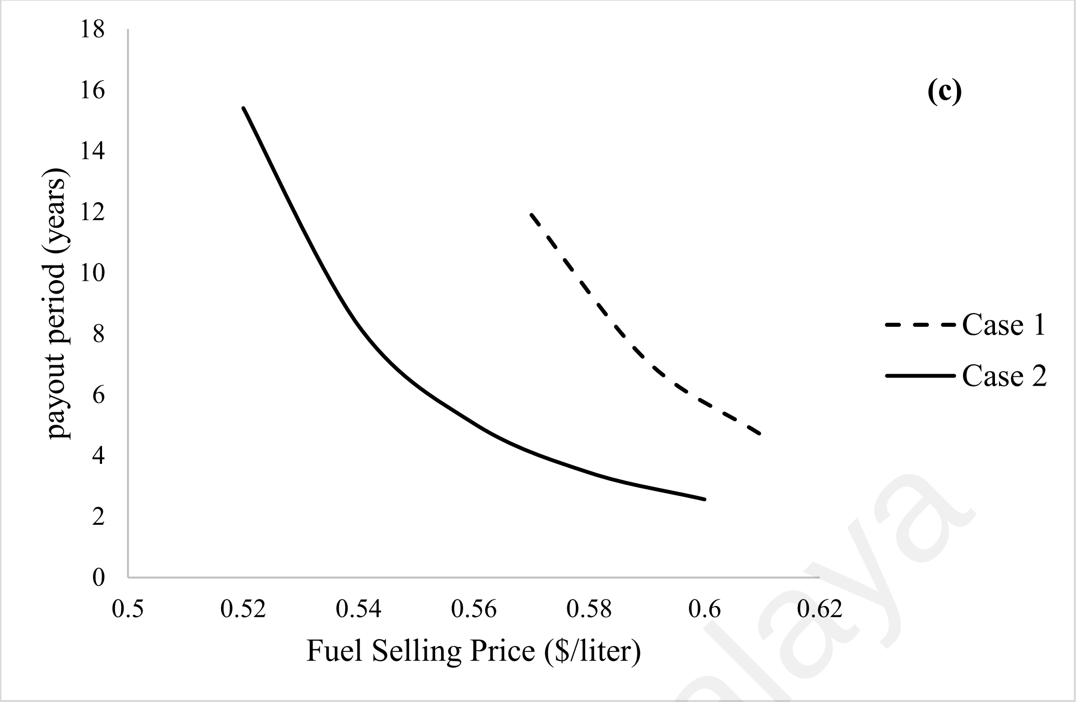


Figure 6-2: Effect of fuel selling price on (a) ROI. (b) PI, and (c) Payout period

From Figure 6.2(a) and 6.2 (b), showed that the increment in fuel selling price improved the value of ROI and PI. From Figure 6.2(b), it can be seen that at the fuel selling price of 0.56USD/liter the case 1 start becoming profitable. While for case 2 profitability started at the fuel selling price of 0.52 USD/liter. Figure 6.2(c) it showed the opposite trend to ROI and PI, rising of fuel selling price reducing the payout period. At fixed fuel selling price of 0.57 USD/liter, the payout period for case 1 and case 2 was calculated to be 11 year and 4 years respectively.

6.4 Conclusions

This study showed the economic assessment of hydrothermal liquefaction process of natural rubber using water (case 1) and propanol (case 2) as a solvent. Economic evaluation and simulation models were developed using Aspen plus ® software was based on experimental findings. The result showed that case 2 was found to be more profitable as compared to the case 1. ROI and PI for case 2 was estimated to be 34.97 % and 1.05 respectively, whereas, for the case 1, ROI and PI was calculated to be 24.51% and 1.01 respectively. The results showed that both process have a potential and can undergo for further upgradation of the product through hydrocracking and hydro-processing.

CHAPTER 7: CONCLUSION AND FUTURE RECOMMENDATION

7.1 Conclusion

In this chapter, we presented several conclusions based on the obtained results of this study. In first objective, the natural rubber (NR) was liquefied successfully to produce liquid fuels using hydrous pyrolysis technique. The study was performed in the autoclave batch reactor at different temperatures (300 to 400°C), with different water to natural rubber mass ratios (1:1 to 5:1) and different reaction times (15 to 75 mins). The effect of different parameters then was evaluated on the liquid product in term of quantity and quality. The results showed that the highest liquid yield of 76 wt% was obtained at temperature, H_2O/material mass ratio and time of 375°C, 3:1 and 30 min respectively. Among the parameters, temperature was found to be the most important parameter, showing a notable positive effect on the liquid oil quality and quantity. The characterization results showed that the oil had high energy density, low oxygen and sulfur contents, and non-acidic. The GC-MS analysis showed that the obtained oil was dominated by alkenes, aromatics and alkyls. From all characteristic results it showed that the oil from NR was more suitable to be used as fuel compare to the oil derived from scrap tire, where the study on hydrous pyrolysis of scrap tire was also provided in this manuscript as comparative study. In addition, the production of oil from the hydrothermal liquefaction of NR in Malaysia could contribute to achieve the energy potential about 1.5 EJ/year or equivalent to 250 million barrels of oil per year.

In the second objective, the liquefaction of natural rubber was effectively performed using different alcohol solvents to improve the quantity and quality of liquid product. The experiments were conducted in autoclave reactor at different temperatures (250 to 375°C), different solvent to natural rubber mass ratio (0.5:1 to 4:1), and at different reaction times (15 to 75mins). The results showed the maximum liquid yield was obtained 89.53 wt.% using propanol at optimum conditions, whereas, this result is considered higher about 13.53% compared to liquid-oil obtained using water as a solvent. Around 51.23% and 10.65% of liquid comprised of D-limonene and Isoprene respectively, which are being used as potential feedstock in different industrial sectors. Besides these compounds, the liquid product also consisted of other hydrocarbon such as aromatics, alkyls, and alkene with high HHV (46 MJ/kg), and low oxygen contents (1.02%). These properties make this liquid suitable to be used for substitution the conventional fossil fuels. In addition, alcohol solvents play an important role to facilitate the liquefaction process by providing milder process conditions and hydrogen donor. Among the solvents, propanol has significant improvement on the liquid yield, solvent recovery and energy density.

In last objective, the economic assessment of hydrothermal liquefaction of natural rubber was performed using water and propanol as a solvent. Two case models were developed based on experimental data, case 1 using water and case 2 using propanol as a solvent. The ratio proportion of natural rubber and solvent in case 1 was set to 3:1, whereas for case 2 it was set to be 1:1. Aspen Plus ® software was used to conduct the economic evaluation for both cases. The results showed that the case 2 was more profitable as compared to the case 1. The ROI for case 2 was estimated to be 34.97 %, this result is considered to be higher 11 % than the case 1. Besides, the payout period of the case 2 was found to be 4 year which is less as compare to case 1. In addition, the value of ROI and PI is showing that the both cases are economically feasible and they have a potential for the further upgradation by hydrocracking and hydro-processing for the extra refinement of products.

7.2 Future work and recommendation

The natural rubber can be as a feed with other feedstocks such as wood based biomasses to improve the quality of biomass based oil. For that purpose co-liquefaction of natural rubber along with other biomasses using suitable solvents can be conducted and evaluated. Moreover, the good characteristics of liquid oil obtained from NR could stimulate researchers to consider it for further upgradation by hydro-processing and hydrocracking. Furthermore, the rheology of NR based oil can be explored to assess it properties more deeply at different parameters. The most dominating compounds that were identified in the NR based oil can be separated using destructive or selective distillation for further exploration.

REFERENCES

Abas, N., Kalair, A., & Khan, N. (2015). Review of fossil fuels and future energy technologies. *Futures, 69*, 31-49. doi: http://dx.doi.org/10.1016/j.futures.2015.03.003

Abbas, Z. (2010). *Depolymerization of Pet and Other Plastic Wastes*: VDM Publishing.

Abdullah, I. (1994). Liquid Natural Rubber: Preparation and Application. In K. Ghiggino (Ed.), *Progress in Pacific Polymer Science 3* (pp. 351-365): Springer Berlin Heidelberg.

Abnisa, F., & Wan Daud, W. M. A. (2014). A review on co-pyrolysis of biomass: An optional technique to obtain a high-grade pyrolysis oil. *Energy Conversion and Management, 87*, 71-85. doi: http://dx.doi.org/10.1016/j.enconman.2014.07.007

Abnisa, F., & Wan Daud, W. M. A. (2015). Optimization of fuel recovery through the stepwise co-pyrolysis of palm shell and scrap tire. *Energy Conversion and Management, 99*, 334-345. doi: http://doi.org/10.1016/j.enconman.2015.04.030

Abnisa, F., Wan Daud, W. M. A., Ramalingam, S., Azemi, M. N. B. M., & Sahu, J. N. (2013). Co-pyrolysis of palm shell and polystyrene waste mixtures to synthesis liquid fuel. *Fuel, 108*, 311-318. doi: http://dx.doi.org/10.1016/j.fuel.2013.02.013

Aboyade, A. O., Carrier, M., Meyer, E. L., Knoetze, H., & Görgens, J. F. (2013). Slow and pressurized co-pyrolysis of coal and agricultural residues. *Energy Conversion and Management, 65*, 198-207. doi: http://dx.doi.org/10.1016/j.enconman.2012.08.006

Adams, T. A. (2017). *Learn Aspen Plus in 24 Hours*: McGraw-Hill Education.

Adams, T. N., Appel, B. S., Samson, P., & Roberts, M. J. (2004). Converting turkey offal into bio-derived hydrocarbon oil with the CWT thermal process West Hempstead, NY.

Agarwal, A. K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progress in Energy and Combustion Science, 33*(3), 233-271. doi: http://dx.doi.org/10.1016/j.pecs.2006.08.003

Aguado, J., & Serrano, D. P. (2006). *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels* (J. Scheirs Ed.): John Wiley & Sons.

Ahmad, N., Abnisa, F., & Daud, W. M. A. W. (2016). Potential use of natural rubber to produce liquid fuels using hydrous pyrolysis - A review. *RSC Advances, 6*, 68906-68921. doi: http://dx.doi.org/10.1039/C6RA09085K

Ahmad, N., Abnisa, F., & Wan Daud, W. M. A. (2018). Liquefaction of natural rubber to liquid fuels via hydrous pyrolysis. *Fuel, 218*, 227-235. doi: https://doi.org/10.1016/j.fuel.2017.12.117

Ahmad, N., Abnisa, F., & Wan Daud, W. M. A. (2019). Synthesis of valuable intermediate products from natural rubber under supercritical alcohol conditions. *Journal of Analytical and Applied Pyrolysis, 139*, 196-204. doi: https://doi.org/10.1016/j.jaap.2019.02.004

Ahmed, I., & Gupta, A. K. (2011). Characteristic of hydrogen and syngas evolution from gasification and pyrolysis of rubber. *International Journal of Hydrogen Energy, 36*(7), 4340-4347. doi: http://dx.doi.org/10.1016/j.ijhydene.2010.12.131

Al-Malah, K. I. M. (2016). *Aspen Plus: Chemical Engineering Applications*: Wiley.

Albert, H. E. (1939). *The Catalytic Hydrogenation of Rubber*: University of Akron.

AldoVieira, R. D., Breeze, P., Doble, M., Gupta, H., Kalogirou, S., Maegaard, P., . . . Kruthiventi, A. K. (2009). *Renewable energy focus handbook*: Elsevier.

Alkhatib, R., Loubar, K., Awad, S., Mounif, E., & Tazerout, M. (2015). Effect of heating power on the scrap tires pyrolysis derived oil. *Journal of Analytical and Applied Pyrolysis*. doi: http://dx.doi.org/10.1016/j.jaap.2015.10.014

Allen, N. S., & Edge, M. (1992). *Fundamentals of Polymer Degradation and Stabilization*: Springer Netherlands.

Anachkov, M. P., Rakovski, S. K., & Stefanova, R. V. (2000). Ozonolysis of 1,4-cis-polyisoprene and 1,4-trans-polyisoprene in solution. *Polymer Degradation and Stability, 67*(2), 355-363. doi: http://dx.doi.org/10.1016/S0141-3910(99)00137-8

Andresen, J., & Lim, X. Y. (2011). 6 - Pyrolysis processes and technology for the conversion of hydrocarbons and biomass. In M. R. Khan (Ed.), *Advances in Clean Hydrocarbon Fuel Processing* (pp. 186-198): Woodhead Publishing.

Anne Loppinet-Serani, C. A. (2014). Chapter 7 - Hydrolysis in Near- and Supercritical Water for Biomass Conversion and Material Recycling. In M. F. Vladimir Anikeev (Ed.), *Supercritical Fluid Technology for Energy and Environmental Applications* (pp. 139-156). Boston: Elsevier.

Arapogianni, A., Moccia, J., Pineda, I., & Wilkes, J. (2014). Avoiding fossil fuel costs with wind energy In S. Azau (Ed.): European Wind Energy Association.

Ateş, F. (2011). Co-pyrolytic Behaviors of Agricultural Wastes. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 34*(2), 111-121. doi: 10.1080/15567036.2010.509211

Aysu, T., & Küçük, M. M. (2013). Liquefaction of giant fennel (Ferula orientalis L.) in supercritical organic solvents: Effects of liquefaction parameters on product yields and character. *The Journal of Supercritical Fluids, 83*, 104-123. doi: http://dx.doi.org/10.1016/j.supflu.2013.09.001

Ballester, C., & Furió, D. (2015). Effects of renewables on the stylized facts of electricity prices. *Renewable and Sustainable Energy Reviews, 52*, 1596-1609. doi: http://dx.doi.org/10.1016/j.rser.2015.07.168

Barbose, G., Bird, L., Heeter, J., Flores-Espino, F., & Wiser, R. (2015). Costs and benefits of renewables portfolio standards in the United States. *Renewable and Sustainable Energy Reviews, 52*, 523-533. doi: http://dx.doi.org/10.1016/j.rser.2015.07.175

Barlow, C. (1970). Prospects for Natural Rubber. *Economic Record, 46*(4), 482-496. doi: 10.1111/j.1475-4932.1970.tb02507.x

Basu, A. K. (2009). *Tyres in Mining and Allied Sectors: Status and Outlook*: Allied Publishers.

Basu, P. (2010). *Biomass gasification and pyrolysis : practical design and theory*: Elsevier.

Beltrame, P. L., Bergamasco, L., Carniti, P., Castelli, A., Bertini, F., & Audisio, G. (1997). Hydrous pyrolysis of polystyrene. *Journal of Analytical and Applied Pyrolysis, 40–41*, 451-461. doi: http://dx.doi.org/10.1016/S0165-2370(96)00977-1

Berl, E. (1944). PRODUCTION OF OIL FROM PLANT MATERIAL. *Science, 99*(2573), 309-312. doi: 10.1126/science.99.2573.309

Bhattacharjee, S., Bhowmick, A. K., & Avasthi, B. N. (1993). Hydrogenation of epoxidized natural rubber in the presence of palladium acetate catalyst. *Polymer, 34*(24), 5168-5173. doi: http://dx.doi.org/10.1016/0032-3861(93)90265-C

Bhowmick, A. K., Rampalli, S., Gallagher, K., Seeger, R., & McIntyre, D. (1987). The degradation of guayule rubber and the effect of resin components on degradation at high temperature: Wiley-Blackwell.

Biller, P., & Ross, A. B. (2011). Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresource Technology, 102*(1), 215-225. doi: https://doi.org/10.1016/j.biortech.2010.06.028

Biswas, B., Arun Kumar, A., Bisht, Y., Singh, R., Kumar, J., & Bhaskar, T. (2017). Effects of temperature and solvent on hydrothermal liquefaction of Sargassum tenerrimum algae. *Bioresource Technology, 242*, 344-350. doi: https://doi.org/10.1016/j.biortech.2017.03.045

Blackley, D. C. (2012). *Polymer Latices: Science and technology Volume 2: Types of latices*: Springer Netherlands.

Blanc, G., Baptiste, C., Oliver, G., Martin, F., & Montoro, P. (2006). Efficient Agrobacterium tumefaciens-mediated transformation of embryogenic calli and regeneration of Hevea brasiliensis Müll Arg. plants. *Plant Cell Reports, 24*(12), 724-733. doi: 10.1007/s00299-005-0023-3

BOARD, I. W. M. (2006). *Technology Evaluation and Economic Analysis of Waste Tire Pyrolysis, Gasification, and Liquefaction*. (620-2006-0004). California Integrated Waste Management Board Retrieved from http://www.calrecycle.ca.gov/Publications/Detail.aspx?PublicationID=1174.

Boateng, A. A., Elkasabi, Y., & Mullen, C. A. (2016). Guayule (Parthenium argentatum) pyrolysis biorefining: Fuels and chemicals contributed from guayule leaves via tail gas reactive pyrolysis. *Fuel, 163*, 240-247. doi: http://dx.doi.org/10.1016/j.fuel.2015.09.062

Boden, T. A., Marland, G., & Andres, R. J. (2015). *Global Greenhouse Gas Emissions Data*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Retrieved from http://www3.epa.gov/climatechange/ghgemissions/global.html.

Brand, S., Hardi, F., Kim, J., & Suh, D. J. (2014). Effect of heating rate on biomass liquefaction: Differences between subcritical water and supercritical ethanol. *Energy, 68*, 420-427. doi: https://doi.org/10.1016/j.energy.2014.02.086

Brand, S., & Kim, J. (2015). Liquefaction of major lignocellulosic biomass constituents in supercritical ethanol. *Energy, 80*(Supplement C), 64-74. doi: https://doi.org/10.1016/j.energy.2014.11.043

Brunner, G. (2014). *Hydrothermal and Supercritical Water Processes* (Vol. 5): Elsevier Science.

Bushman, B. S., Scholte, A. A., Cornish, K., Scott, D. J., Brichta, J. L., Vederas, J. C., . . . Knapp, S. J. (2006). Identification and comparison of natural rubber from two Lactuca species. *Phytochemistry, 67*(23), 2590-2596. doi: http://dx.doi.org/10.1016/j.phytochem.2006.09.012

Carraher, C. E., & Seymour, R. B. (2007). *Seymour/Carraher's polymer chemistry*: CRC Press.

Cataldo, F. (1998). Thermal depolymerization and pyrolysis of cis-1,4-polyisoprene: preparation of liquid polyisoprene and terpene resin. *Journal of Analytical and Applied Pyrolysis, 44*(2), 121-130. doi: http://dx.doi.org/10.1016/S0165-2370(97)00081-8

Chaikumpollert, O., Sae-Heng, K., Wakisaka, O., Mase, A., Yamamoto, Y., & Kawahara, S. (2011). Low temperature degradation and characterization of natural rubber. *Polymer Degradation and Stability, 96*(11), 1989-1995. doi: http://dx.doi.org/10.1016/j.polymdegradstab.2011.08.010

Chan, Y. H., Quitain, A. T., Yusup, S., Uemura, Y., Sasaki, M., & Kida, T. (2017). Liquefaction of palm kernel shell in sub- and supercritical water for bio-oil production. *Journal of the Energy Institute*. doi: https://doi.org/10.1016/j.joei.2017.05.009

Chandra, V. (2006). *Fundamentals of Natural Gas: An International Perspective*: PennWell Corporation.

Chen, D. T., Perman, C. A., Riechert, M. E., & Hoven, J. (1995). Depolymerization of tire and natural rubber using supercritical fluids. *Journal of Hazardous Materials, 44*(1), 53-60. doi: http://dx.doi.org/10.1016/0304-3894(95)00047-X

Chen, F., & Qian, J. (2002). Studies on the thermal degradation of cis-1,4-polyisoprene. *Fuel, 81*(16), 2071-2077. doi: http://dx.doi.org/10.1016/S0016-2361(02)00147-3

Chen, J., Li, Z., Jin, L., Ni, P., Liu, G., He, H., . . . Ruan, R. (2010). Catalytic hydrothermal depolymerization of nylon 6. *Journal of Material Cycles and Waste Management, 12*(4), 321-325. doi: 10.1007/s10163-010-0304-y

Cheng, S., Wei, L., Julson, J., Kharel, P. R., Cao, Y., & Gu, Z. (2017). Catalytic liquefaction of pine sawdust for biofuel development on bifunctional Zn/HZSM-5 catalyst in supercritical ethanol. *Journal of Analytical and Applied Pyrolysis, 126*(Supplement C), 257-266. doi: https://doi.org/10.1016/j.jaap.2017.06.001

Chien, J. C. W., & Kiang, J. K. Y. (1979). Polymer reactions—X thermal pyrolysis of poly(isoprene). *European Polymer Journal, 15*(11), 1059-1065. doi: http://dx.doi.org/10.1016/0014-3057(79)90146-0

Coates, W., Ayerza, R., & Ravetta, D. (2001). Guayule rubber and latex content — seasonal variations over time in Argentina. *Industrial Crops and Products, 14*(2), 85-91. doi: http://dx.doi.org/10.1016/S0926-6690(00)00091-1

Crocker, M. (2010). *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*: RSC Publishing.

Cunliffe, A. M., & Williams, P. T. (1998). Properties of Chars and Activated Carbons Derived from the Pyrolysis of Used Tyres. *Environmental Technology, 19*(12), 1177-1190. doi: https://doi.org/10.1080/09593331908616778

Daily Prices of Natural Rubber (US dollar per 100 kg). (2015). from Association of Natural Rubber Producing Countries (ANRPC) http://www.anrpc.org/html/daily_prices.aspx

Danon, B., van der Gryp, P., Schwarz, C. E., & Görgens, J. F. (2015). A review of dipentene (dl-limonene) production from waste tire pyrolysis. *Journal of Analytical and Applied Pyrolysis, 112*, 1-13. doi: http://dx.doi.org/10.1016/j.jaap.2014.12.025

Dell, R. M., Moseley, P. T., & Rand, D. A. J. (2014). Chapter 3 - Unconventional Fuels. In R. M. D. T. M. A. J. Rand (Ed.), *Towards Sustainable Road Transport* (pp. 86-108). Boston: Academic Press.

Demirbas, A. (2007). *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*: Springer London.

Demirbaş, A. (2000). Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management, 41*(6), 633-646. doi: https://doi.org/10.1016/S0196-8904(99)00130-2

Dias De Oliveira, M. E., Vaughan, B. E., & Rykiel, E. J. (2005). Ethanol as Fuel: Energy, Carbon Dioxide Balances, and Ecological Footprint. *BioScience, 55*(7), 593-602. doi: 10.1641/0006-3568(2005)055[0593:eafecd]2.0.co;2

Dincer, I., & Rosen, M. A. (2013). Chapter 4 - Exergy, Environment And Sustainable Development. In I. D. A. Rosen (Ed.), *Exergy (Second Edition)* (pp. 51-73): Elsevier.

Dincer, I., & Zamfirescu, C. (2014). Chapter 3 - Fossil Fuels and Alternatives. In I. D. Zamfirescu (Ed.), *Advanced Power Generation Systems* (pp. 95-141). Boston: Elsevier.

Doble, M., Rollins, K., & Kumar, A. (2010). *Green Chemistry and Engineering*: Elsevier Science.

Durak, H. (2015). Thermochemical conversion of Phellinus pomaceus via supercritical fluid extraction and pyrolysis processes. *Energy Conversion and Management, 99*, 282-298. doi: http://dx.doi.org/10.1016/j.enconman.2015.04.050

Durak, H., & Aysu, T. (2014). Effects of catalysts and solvents on liquefaction of Onopordum heteracanthum for production of bio-oils. *Bioresource Technology, 166*, 309-317. doi: http://dx.doi.org/10.1016/j.biortech.2014.05.051

Eggoni, K. (2016). *Early-stage techno-economic analysis of renewable diesel production via hydrothermal liquefaction of filamentous fungi.* Iowa State University.

Energy, U. S. D. o. National Energy Information Centre, EIA, Washington, DC. from http://www.eia.gov/environment/

Engineers, N. B. C. (2010). *The Complete Book on Rubber Processing and Compounding Technology*: NIIR Project Consultancy Services.

Engineers, N. B. C. (2015). *The Complete Book on Biomass Based Products (Biochemicals, Biofuels, Activated Carbon)*: ASIA PACIFIC BUSINESS PRESS Inc.

Evans, A., & Evans, R. (2006). The Composition of a Tyre: Typical Components. Banbury Oxford, UK.

Everard, C. D., McDonnell, K. P., & Fagan, C. C. (2012). Prediction of biomass gross calorific values using visible and near infrared spectroscopy. *Biomass and Bioenergy, 45*, 203-211. doi: http://dx.doi.org/10.1016/j.biombioe.2012.06.007

Fang, Z. (Ed.). (2013). *Biofuels - Economy, Environment and Sustainability*: InTech.

Fang, Z., Sato, T., Smith, R. L., Inomata, H., Arai, K., & Kozinski, J. A. (2008). Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water. *Bioresource Technology, 99*(9), 3424-3430. doi: https://doi.org/10.1016/j.biortech.2007.08.008

Fang, Z., & Xu, C. C. (2014). *Near-critical and Supercritical Water and Their Applications for Biorefineries*: Springer Netherlands.

FAO. 2013: Food and Agriculture Organization of the United Nations.

FAO. (1992). *Commodity Review and Outlook: 1991/92*: Food and Agriculture Organization of the United Nations.

Farret, F. A., & Simões, M. G. (2006). *Integration of Alternative Sources of Energy*: Wiley.

Fukahori, Y. (2014). 14 - Use of natural rubber (NR) for vibration isolation and earthquake protection of structures. In S. Kohjiya & Y. Ikeda (Eds.), *Chemistry, Manufacture and Applications of Natural Rubber* (pp. 371-381): Woodhead Publishing.

Funazukuri, T., Takanashi, T., & Wakao, N. (1987). Supercritical extraction of used automotive tire with water. *Journal of Chemical Engineering of Japan, 20*(1), 23-27. doi: 10.1252/jcej.20.23

Gao, J., Jin, Z., & Pan, Z. (2012). Depolymerization of poly(trimethylene terephthalate) in hot compressed water at 240–320 °C. *Polymer Degradation and Stability, 97*(9), 1838-1843. doi: http://dx.doi.org/10.1016/j.polymdegradstab.2012.05.015

Garcìa-Pèrez, M., Chaala, A., & Roy, C. (2002). Co-pyrolysis of sugarcane bagasse with petroleum residue. Part II. Product yields and properties. *Fuel, 81*(7), 893-907. doi: http://dx.doi.org/10.1016/S0016-2361(01)00215-0

García, J., Pérez, O., Fdez-Polanco, F., & Cocero, M. (2003). Supercritical water as reaction media. Physical properties at supercritical conditions an overview.

Gollakota, A. R. K., Kishore, N., & Gu, S. (2018). A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews, 81*, 1378-1392. doi: https://doi.org/10.1016/j.rser.2017.05.178

Groover, M. P. (2010). *Fundamentals of Modern Manufacturing: Materials, Processes, and Systems*: John Wiley & Sons.

Groves, S. A., Lehrle, R. S., Blazsó, M., & Székely, T. (1991). Natural rubber pyrolysis: Study of temperature-and thickness-dependence indicates dimer formation mechanism. *Journal of Analytical and Applied Pyrolysis, 19*, 301-309. doi: http://dx.doi.org/10.1016/0165-2370(91)80051-9

Gupta, O. P. *Elements of Fuels, Furnaces and Refractories* (6th ed.): Khanna Publishers.

Hai, T. C. (2000). Land use and the oil palm industry in Malaysia. *WWF Global*.

Hall, W. J., Zakaria, N., & Williams, P. T. (2009). Pyrolysis of latex gloves in the presence of Y-zeolite. *Waste Management, 29*(2), 797-803. doi: http://dx.doi.org/10.1016/j.wasman.2008.06.031

Hallahan, D. L., & Keiper-Hrynko, N. M. (2004). Cis-prenyltransferases from the rubber-producing plants russian dandelion (taraxacum kok-saghyz) and sunflower (helianthus annus): Google Patents.

Han, K.-H., Shin, D. H., Yang, J., Kim, I. J., Oh, S. K., & Chow, K. S. (2000). Genes expressed in the latex of Hevea brasiliensis. *Tree Physiology, 20*(8), 503-510. doi: 10.1093/treephys/20.8.503

Hanif, M. U., Capareda, S. C., Iqbal, H., Arazo, R. O., & Baig, M. A. (2016). Effects of Pyrolysis Temperature on Product Yields and Energy Recovery from Co-Feeding of Cotton Gin Trash, Cow Manure, and Microalgae: A Simulation Study. *PLOS ONE, 11*(4), e0152230. doi: 10.1371/journal.pone.0152230

Haugstad, B. H. (2017). *Fuel Characterization and Process Analysis of Hydrothermal Liquefaction of Algae.* Universitetet i Agder; University of Agder.

Haykiri-Acma, H., & Yaman, S. (2010). Interaction between biomass and different rank coals during co-pyrolysis. *Renewable Energy, 35*(1), 288-292. doi: http://dx.doi.org/10.1016/j.renene.2009.08.001

He, B., Zhang, Y., Funk, T., Riskowski, G., & Yin, Y. (2000). Thermochemical conversion of swine manure: an alternative process for waste treatment and renewable energy production. *Transactions of the ASAE, 43*(6), 1827.

Heidenreich, S., & Foscolo, P. U. (2015). New concepts in biomass gasification. *Progress in Energy and Combustion Science, 46*, 72-95. doi: http://dx.doi.org/10.1016/j.pecs.2014.06.002

Helmer, P. T., Høy, H. N., Miralles, P. O., Villamar, C. D. E., & A., R. L. (2018). Renewable hydrocarbon fuels from hydrothermal liquefaction: A techno-economic analysis. *Biofuels, Bioproducts and Biorefining, 12*(2), 213-223. doi: doi:10.1002/bbb.1831

Higman, C., & van der Burgt, M. (2011). *Gasification*: Elsevier Science.

Hoel, M., & Kverndokk, S. (1996). Depletion of fossil fuels and the impacts of global warming. *Resource and Energy Economics, 18*(2), 115-136. doi: http://dx.doi.org/10.1016/0928-7655(96)00005-X

Höök, M., & Tang, X. (2013). Depletion of fossil fuels and anthropogenic climate change—A review. *Energy Policy, 52*, 797-809. doi: http://dx.doi.org/10.1016/j.enpol.2012.10.046

Hua, Y., Oliphant, M., & Hu, E. J. (2016). Development of renewable energy in Australia and China: A comparison of policies and status. *Renewable Energy, 85*, 1044-1051. doi: http://dx.doi.org/10.1016/j.renene.2015.07.060

Huang, H.-j., & Yuan, X.-z. (2015). Recent progress in the direct liquefaction of typical biomass. *Progress in Energy and Combustion Science, 49*, 59-80. doi: https://doi.org/10.1016/j.pecs.2015.01.003

Huang, H.-j., Yuan, X.-z., Zeng, G.-m., Liu, Y., Li, H., Yin, J., & Wang, X.-l. (2013). Thermochemical liquefaction of rice husk for bio-oil production with sub- and supercritical ethanol as solvent. *Journal of Analytical and Applied Pyrolysis, 102*(Supplement C), 60-67. doi: https://doi.org/10.1016/j.jaap.2013.04.002

Huffman, G. P., & Shah, N. (1997). *Feasibility study for a demonstration plant for liquefaction and coprocessing of waste plastics and tires.* Paper presented at the PREPRINTS OF SYMPOSIA-DIVISION OF FUEL CHEMISTRY AMERICAN CHEMICAL SOCIETY.

Hunseung Kang, Min Young Kang, & Kyung-Hwan Han. (2000). Identification of Natural Rubber and Characterization of Rubber Biosynthetic Activity in Fig Tree. *Plant Physiology, 123*. doi: http://dx.doi.org/10.1104/pp.123.3.1133

Ichsani, S., & Suhardi, A. R. (2015). The Effect of Return on Equity (ROE) and Return on Investment (ROI) on Trading Volume. *Procedia - Social and Behavioral Sciences, 211*, 896-902. doi: http://dx.doi.org/10.1016/j.sbspro.2015.11.118

Inc., S. (2015). Global natural rubber production from 2000 to 2015 (in 1,000 metric tons): Statista Inc.

International, A., & Lampman, S. (2003). *Characterization and Failure Analysis of Plastics*: A S M International.

Intratec. (2013). *Research Economics: Green Ethylene from Ethanol*: CreateSpace Independent Publishing Platform.

Jahirul, M., Rasul, M., Chowdhury, A., & Ashwath, N. (2012). Biofuels Production through Biomass Pyrolysis —A Technological Review. *Energies, 5*(12), 4952.

Jarvis, J. M., Billing, J. M., Hallen, R. T., Schmidt, A. J., & Schaub, T. M. (2017). Hydrothermal liquefaction biocrude compositions compared to petroleum crude and shale oil. *Energy & Fuels, 31*(3), 2896-2906.

Jena, U., & Das, K. C. (2011). Comparative Evaluation of Thermochemical Liquefaction and Pyrolysis for Bio-Oil Production from Microalgae. *Energy & Fuels, 25*(11), 5472-5482. doi: http://dx.doi.org/10.1021/ef201373m

Jin, B., Duan, P., Zhang, C., Xu, Y., Zhang, L., & Wang, F. (2014). Non-catalytic liquefaction of microalgae in sub-and supercritical acetone. *Chemical Engineering Journal, 254*, 384-392. doi: https://doi.org/10.1016/j.cej.2014.05.137

Jones, S. B., Zhu, Y., Anderson, D. B., Hallen, R. T., Elliott, D. C., Schmidt, A. J., . . . Drennan, C. (2014). Process design and economics for the conversion of algal biomass to hydrocarbons: whole algae hydrothermal liquefaction and upgrading: Pacific Northwest National Laboratory (PNNL), Richland, WA (US).

Jongedijk, E., Cankar, K., Ranzijn, J., Krol, S., Bouwmeester, H., & Beekwilder, J. (2015). Capturing of the monoterpene olefin limonene produced in Saccharomyces cerevisiae. *Yeast, 32*(1), 159-171. doi: https://doi.org/10.1002/yea.3038

Kalogirou, S. A. (2004). Solar thermal collectors and applications. *Progress in Energy and Combustion Science, 30*(3), 231-295. doi: http://dx.doi.org/10.1016/j.pecs.2004.02.001

Kan, T., Strezov, V., & Evans, T. (2017). Fuel production from pyrolysis of natural and synthetic rubbers. *Fuel, 191*, 403-410. doi: https://doi.org/10.1016/j.fuel.2016.11.100

Kanaveli, I.-P., Atzemi, M., & Lois, E. (2017). Predicting the viscosity of diesel/biodiesel blends. *Fuel, 199*, 248-263. doi: https://doi.org/10.1016/j.fuel.2017.02.077

Kang, A., & Lee, T. S. (2016). Chapter 2 - Secondary Metabolism for Isoprenoid-based Biofuels. In C. A. Eckert & C. T. Trinh (Eds.), *Biotechnology for Biofuel Production and Optimization* (pp. 35-71). Amsterdam: Elsevier.

Kawser, M. J., & Farid, N. A. (2000). Thermochemical processing of rubber waste to liquid fuel. *Plastics, Rubber and Composites, 29*(2), 100-104. doi: https://doi.org/10.1179/146580100101540851

Kaye, G. W. C. (2018). *Tables of Physical and Chemical Constants and Some Mathematical Functions (Classic Reprint)*: Fb&c Limited.

Kidena, K., Adachi, R., Murata, S., & Nomura, M. (2008). Hydrous pyrolysis of two kinds of low-rank coal for relatively long duration. *Fuel, 87*(3), 388-394. doi: http://dx.doi.org/10.1016/j.fuel.2007.05.009

Kim, I. J., Ryu, S. B., Kwak, Y. S., & Kang, H. (2004). A novel cDNA from Parthenium argentatum Gray enhances the rubber biosynthetic activity in vitro*. *Journal of Experimental Botany, 55*(396), 377-385. doi: 10.1093/jxb/erh039

Kohjiya, S., & Ikeda, Y. (2014). *Chemistry, Manufacture and Applications of Natural Rubber*: Elsevier Science.

Kroschwitz, J. I., & Mark, H. F. (2004). *Encyclopedia of Polymer Science and Technology*: John Wiley & Sons.

Kruse, A., Funke, A., & Titirici, M.-M. (2013). Hydrothermal conversion of biomass to fuels and energetic materials. *Current Opinion in Chemical Biology, 17*(3), 515-521. doi: https://doi.org/10.1016/j.cbpa.2013.05.004

Kumar, H. (2001). *Environmental Health Hazards*: IVY Publishing House.

Larsen, J. W. (1976). Conversion of waste rubber to fuel and other useful products: Google Patents.

Larsen, J. W., & Hu, J. (2006). Kerogen Chemistry. 8. Hydrous Pyrolysis of Rundle Kerogen: Source of the Oxygen in CO2 and Mineral Catalysis. *Energy & Fuels, 20*(1), 278-280. doi: 10.1021/ef050237m

Leggett, J. A. (2011). China's Greenhouse Gas Emissions and Mitigation Policies (U. S.-C. R. a. A. Society, Trans.): Congressional Research Service.

Leung, D. Y. C., & Wang, C. L. (1998). Kinetic study of scrap tyre pyrolysis and combustion. *Journal of Analytical and Applied Pyrolysis, 45*(2), 153-169. doi: http://dx.doi.org/10.1016/S0165-2370(98)00065-5

Lewan, M. D., Winters, J. C., & Mcdonald, J. H. (1979). Generation of Oil-Like Pyrolyzates from Organic-Rich Shales. *Science, 203*(4383), 897-899. doi: 10.1126/science.203.4383.897

Li, R., Jin, K., & Lehrmann, D. J. (2008). Hydrocarbon potential of Pennsylvanian coal in Bohai Gulf Basin, Eastern China, as revealed by hydrous pyrolysis. *International Journal of Coal Geology, 73*(1), 88-97. doi: http://dx.doi.org/10.1016/j.coal.2007.07.006

Liang, M., Wang, Z., Zheng, J., Li, X., Wang, X., Gao, Z., . . . Qian, Y. (2015). Hydrous pyrolysis of different kerogen types of source rock at high temperature-bulk results and biomarkers. *Journal of Petroleum Science and Engineering, 125*, 209-217. doi: http://dx.doi.org/10.1016/j.petrol.2014.11.021

Liu, H.-M., Li, H.-Y., & Li, M.-F. (2017). Cornstalk liquefaction in sub- and super-critical ethanol: Characterization of solid residue and the liquefaction mechanism. *Journal of the Energy Institute, 90*(5), 734-742. doi: https://doi.org/10.1016/j.joei.2016.07.004

Luque, R., & Speight, J. (2014). *Gasification for Synthetic Fuel Production: Fundamentals, Processes and Applications*: Elsevier Science.

Mahittikul, A., Prasassarakich, P., & Rempel, G. L. (2009). Hydrogenation of natural rubber latex in the presence of [Ir(cod)(PCy3)(py)]PF6. *Journal of Molecular Catalysis A: Chemical, 297*(2), 135-141. doi: http://dx.doi.org/10.1016/j.molcata.2008.09.006

Malaysian Rubber Research and Development Board. (2017). Natural Rubber Statistics. from Malaysian Rubber Board http://www.lgm.gov.my/

Malevich, N. N., Yusevich, A. I., & Shashok, Z. S. (2014). Features of the Thermal Liquefaction of Rubber in Water and Organic Solvents. *International Polymer Science and Technology, 41*(8), 15-20. doi: https://doi.org/10.1177/0307174X1404100804

Manuel, H. J., Dierkes, W., & Limited, R. T. (1997). *Recycling of Rubber*: Rapra Technology Limited.

Mark, H. F. (2013). *Encyclopedia of Polymer Science and Technology, Concise*: Wiley.

Martínez, J. D., Puy, N., Murillo, R., García, T., Navarro, M. V., & Mastral, A. M. (2013). Waste tyre pyrolysis – A review. *Renewable and Sustainable Energy Reviews, 23*, 179-213. doi: http://dx.doi.org/10.1016/j.rser.2013.02.038

Mazaheri, H., Lee, K. T., Bhatia, S., & Mohamed, A. R. (2010). Sub/supercritical liquefaction of oil palm fruit press fiber for the production of bio-oil: Effect of solvents. *Bioresource Technology, 101*(19), 7641-7647. doi: http://dx.doi.org/10.1016/j.biortech.2010.04.072

Menezes, M. B. C., Kim, S., & Huang, R. (2015). Return-on-investment (ROI) criteria for network design. *European Journal of Operational Research, 245*(1), 100-108. doi: http://dx.doi.org/10.1016/j.ejor.2015.03.009

Michels, R., Landis, P., Philp, R. P., & Torkelson, B. E. (1995). Influence of Pressure and the Presence of Water on the Evolution of the Residual Kerogen during Confined, Hydrous, and High-Pressure Hydrous Pyrolysis of Woodford Shale. *Energy & Fuels, 9*(2), 204-215. doi: 10.1021/ef00050a002

Miknis, F. P., Netzel, D. A., & Surdam, R. C. (1996). NMR Determination of Carbon Aromatization during Hydrous Pyrolysis of Coals from the Mesaverde Group, Greater Green River Basin. *Energy & Fuels, 10*(1), 3-9. doi: 10.1021/ef950143k

Minowa, T., Kondo, T., & Sudirjo, S. T. (1998). Thermochemical liquefaction of indonesian biomass residues. *Biomass and Bioenergy, 14*(5–6), 517-524. doi: http://dx.doi.org/10.1016/S0961-9534(98)00006-3

Minowa, T., Murakami, M., Dote, Y., Ogi, T., & Yokoyama, S.-y. (1995). Oil production from garbage by thermochemical liquefaction. *Biomass and Bioenergy, 8*(2), 117-120. doi: http://dx.doi.org/10.1016/0961-9534(95)00017-2

Mohamad, N., Mohamad Yusof, N. N., & Yong, T. L.-K. (2017). Furfural Production Under Subcritical Alcohol Conditions: Effect of Reaction Temperature, Time, and Types of Alcohol. *Journal of the Japan Institute of Energy, 96*(8), 279-284. doi: https://doi.org/10.3775/jie.96.279

Mohapatra, S., & Nando, G. B. (2014). Cardanol: a green substitute for aromatic oil as a plasticizer in natural rubber. *RSC Advances, 4*(30), 15406-15418. doi: 10.1039/C3RA46061D

Mohtasham, J. (2015). Review Article-Renewable Energies. *Energy Procedia, 74*, 1289-1297. doi: http://dx.doi.org/10.1016/j.egypro.2015.07.774

Mooibroek, H., & Cornish, K. (2000). Alternative sources of natural rubber. *Applied Microbiology and Biotechnology, 53*(4), 355-365. doi: 10.1007/s002530051627

Morton, M. (Ed.). (1999). *Rubber Technology* (3 ed.). Netherlands: Springer.

Munger, J. H. (1992). Recycling process, apparatus and product produced by such process for producing a rubber extender/plasticizing agent from used automobile rubber tires: Google Patents.

Muraza, O. (2015). Hydrous pyrolysis of heavy oil using solid acid minerals for viscosity reduction. *Journal of Analytical and Applied Pyrolysis, 114*, 1-10. doi: http://dx.doi.org/10.1016/j.jaap.2015.04.005

Murillo, R., Aylón, E., Navarro, M. V., Callén, M. S., Aranda, A., & Mastral, A. M. (2006). The application of thermal processes to valorise waste tyre. *Fuel Processing Technology, 87*(2), 143-147. doi: https://doi.org/10.1016/j.fuproc.2005.07.005

. Natural Rubber Statistics. (2015): Malaysian Rubber Board.

Nguyen, T. D. H., Maschietti, M., Belkheiri, T., Åmand, L.-E., Theliander, H., Vamling, L., . . . Andersson, S.-I. (2014). Catalytic depolymerisation and conversion of Kraft lignin into liquid products using near-critical water. *The Journal of*

Supercritical Fluids, 86, 67-75. doi: http://dx.doi.org/10.1016/j.supflu.2013.11.022

Niaounakis, M. (2013). *Biopolymers: Reuse, Recycling, and Disposal*: Elsevier Science.

Nor, H. M., & Ebdon, J. R. (1998). Telechelic liquid natural rubber: A review. *Progress in Polymer Science, 23*(2), 143-177. doi: http://dx.doi.org/10.1016/S0079-6700(97)00028-2

Nor, H. M., & Ebdon, J. R. (2000). Ozonolysis of natural rubber in chloroform solutionPart 1. A study by GPC and FTIR spectroscopy. *Polymer, 41*(7), 2359-2365. doi: http://dx.doi.org/10.1016/S0032-3861(99)00417-6

Obeid, W., Salmon, E., Lewan, M. D., & Hatcher, P. G. (2015). Hydrous pyrolysis of Scenedesmus algae and algaenan-like residue. *Organic Geochemistry, 85*, 89-101. doi: http://dx.doi.org/10.1016/j.orggeochem.2015.04.001

Olaniyi, A., Abdullah, A., Ramli, M., & Sood, A. (2013). *Agricultural land use in Malaysia: An historical overview and implications for food security* (Vol. 19).

Onwudili, J. A., & Williams, P. T. (2008). Hydrothermal gasification and oxidation as effective flameless conversion technologies for organic wastes. *Journal of the Energy Institute, 81*(2), 102-109. doi: https://doi.org/10.1179/174602208X301934

Ou, L., Thilakaratne, R., Brown, R. C., & Wright, M. M. (2015). Techno-economic analysis of transportation fuels from defatted microalgae via hydrothermal liquefaction and hydroprocessing. *Biomass and Bioenergy, 72*, 45-54. doi: https://doi.org/10.1016/j.biombioe.2014.11.018

P.M. Priyadarshan, P. S. G. a., K.O. Omokhafe. (2009). Breeding Hevea Rubber. In P. M. P. Shri Mohan Jain (Ed.), *Breeding Plantation Tree Crops: Tropical Species* (1 ed.): Springer-Verlag New York.

Pakdel, H., Pantea, D. M., & Roy, C. (2001). Production of dl-limonene by vacuum pyrolysis of used tires. *Journal of Analytical and Applied Pyrolysis, 57*(1), 91-107. doi: http://dx.doi.org/10.1016/S0165-2370(00)00136-4

Paradela, F., Pinto, F., Ramos, A. M., Gulyurtlu, I., & Cabrita, I. (2009). Study of the slow batch pyrolysis of mixtures of plastics, tyres and forestry biomass wastes. *Journal of Analytical and Applied Pyrolysis, 85*(1–2), 392-398. doi: http://dx.doi.org/10.1016/j.jaap.2008.09.003

Park, S., & Gloyna, E. F. (1997). Statistical study of the liquefaction of used rubber tyre in supercritical water. *Fuel, 76*(11), 999-1003. doi: http://dx.doi.org/10.1016/S0016-2361(97)00088-4

Park, Y., Hool, J. N., Curtis, C. W., & Roberts, C. B. (2001). Depolymerization of Styrene−Butadiene Copolymer in Near-Critical and Supercritical Water. *Industrial & Engineering Chemistry Research, 40*(3), 756-767. doi: 10.1021/ie000502l

Peacock, A. J., & Calhoun, A. R. (2006). *Polymer Chemistry: Properties and Applications*: Hanser Gardner Publications.

Pilusa, J., Shukla, M., & Muzenda, E. (2014). Economic assessment of waste tyres pyrolysis technology: a case study for Gauteng Province, South Africa.

Pilusa, T., Shukla, M., & Muzenda, E. (2013). *Tyre Derived Fuel as an Alternative fuel for CI engines*.

Pinto, F., Paradela, F., Gulyurtlu, I., & Ramos, A. M. (2013). Prediction of liquid yields from the pyrolysis of waste mixtures using response surface methodology. *Fuel Processing Technology, 116*, 271-283. doi: http://dx.doi.org/10.1016/j.fuproc.2013.07.012

Polhamus, L. G. (1962). *Rubber: botany, production, and utilization*: L. Hill.

Priya, P., Venkatachalam, P., & Thulaseedharan, A. (2006). Molecular cloning and characterization of the rubber elongation factor gene and its promoter sequence from rubber tree (Hevea brasiliensis): A gene involved in rubber biosynthesis. *Plant Science, 171*(4), 470-480. doi: http://dx.doi.org/10.1016/j.plantsci.2006.05.009

Priyadarshan, P. M. (2011). *Biology of Hevea Rubber*: CABI.

Public Health Statement for Toluene. (2015). from http://www.atsdr.cdc.gov/ToxProfiles/tp56-c1-b.pdf

R. V. Gadag, A. N. S. (2007). *Engineering Chemistry*: I.K. International Publishing House Pvt. Limited.

Rasutis, D., Soratana, K., McMahan, C., & Landis, A. E. (2015). A sustainability review of domestic rubber from the guayule plant. *Industrial Crops and Products, 70*, 383-394. doi: http://dx.doi.org/10.1016/j.indcrop.2015.03.042

Ravignani, G. L., Tipnis, V. A., & Mantel, S. J. (1982). Economic Feasibility of a New Process. *CIRP Annals, 31*(1), 339-340. doi: https://doi.org/10.1016/S0007-8506(07)63324-1

Ray, D. T., Foster, M. A., Coffelt, T. A., McMahan, C. (2010). Guayule: culture, breeding and rubber production. In B. P. Singh (Ed.), *Industrial crops and uses*. Wallingford, UK: CABI Publishers.

Roberts, A. D. (1988). *Natural rubber science and technology*: Oxford University Press.

Rodgers, M. B., & Abdullahi, A. A. (2016). Rubber Tires *Reference Module in Materials Science and Materials Engineering*: Elsevier.

Rogers, T. H., & Cornish, K. (2005). Rubber, Natural *Van Nostrand's Scientific Encyclopedia*: John Wiley & Sons, Inc.

Rong, B. G., Aguilera, A. F., Alopaeus, V., Christensen, L. P., Contreras-Zarazúa, G., Errico, M., . . . Herrera, V. S. (2017). *Process Synthesis and Process Intensification: Methodological Approaches*: De Gruyter.

Roy, C., Chaala, A., & Darmstadt, H. (1999). The vacuum pyrolysis of used tires: End-uses for oil and carbon black products. *Journal of Analytical and Applied Pyrolysis, 51*(1), 201-221. doi: https://doi.org/10.1016/S0165-2370(99)00017-0

Roy, C., Darmstadt, H., Benallal, B., & Amen-Chen, C. (1997). Characterization of naphtha and carbon black obtained by vacuum pyrolysis of polyisoprene rubber. *Fuel Processing Technology, 50*(1), 87-103. doi: http://dx.doi.org/10.1016/S0378-3820(96)01044-2

Rushdi, A. I., BaZeyad, A. Y., Al-Awadi, A. S., Al-Mutlaq, K. F., & Simoneit, B. R. T. (2013). Chemical characteristics of oil-like products from hydrous pyrolysis of scrap tires at temperatures from 150 to 400 °C. *Fuel, 107*, 578-584. doi: http://dx.doi.org/10.1016/j.fuel.2012.12.089

Sadaka, F., Campistron, I., Laguerre, A., & Pilard, J.-F. (2012). Controlled chemical degradation of natural rubber using periodic acid: Application for recycling waste tyre rubber. *Polymer Degradation and Stability, 97*(5), 816-828. doi: http://dx.doi.org/10.1016/j.polymdegradstab.2012.01.019

Sahgal, A. C. S. M. *Living Sci. 8 Silver Jubilee*: Ratna Sagar (P) Limited.

Samanya, J., Hornung, A., Apfelbacher, A., & Vale, P. (2012). Characteristics of the upper phase of bio-oil obtained from co-pyrolysis of sewage sludge with wood, rapeseed and straw. *Journal of Analytical and Applied Pyrolysis, 94*, 120-125. doi: http://dx.doi.org/10.1016/j.jaap.2011.11.017

Sánchez, M. E., Martínez, O., Gómez, X., & Morán, A. (2007). Pyrolysis of mixtures of sewage sludge and manure: A comparison of the results obtained in the laboratory (semi-pilot) and in a pilot plant. *Waste Management, 27*(10), 1328-1334. doi: http://dx.doi.org/10.1016/j.wasman.2006.07.015

Sarwono, R., & Pusfitasari, E. D. (2017). Degradation of palm oil empty fruit bunch (EFB) into bio-oil in sub-and supercritical solvents. *AIP Conference Proceedings, 1803*(1), 020010. doi: https://doi.org/10.1063/1.4973137

Sarwono, R., Pusfitasari, E. D., & Ghozali, M. (2016). Hydrothermal liquefaction of palm oil empty fruit bunch (EFB) into bio-oil in different organic solvents. *AIP Conference Proceedings, 1737*(1), 060015. doi: https://doi.org/10.1063/1.4949322

Saswattecha, K., Kroeze, C., Jawjit, W., & Hein, L. (2016). Options to reduce environmental impacts of palm oil production in Thailand. *Journal of Cleaner Production, 137*, 370-393. doi: https://doi.org/10.1016/j.jclepro.2016.07.002

Savage, P. E. (1999). Organic Chemical Reactions in Supercritical Water. *Chemical Reviews, 99*(2), 603-622. doi: 10.1021/cr9700989

Scheinost, P. L., J. Scianna, D.G. Ogle. (2010). Plant fact sheet for rubber rabbitbrush (Ericameria nauseosa). Pullman, WA. : USDA-Natural Resources Conservation Service, Pullman Plant Materials Center.

Scheirs, J., & Kaminsky, W. (Eds.). (2006). *Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels*: John Wiley & Sons.

Schmidt, P. F. (1985). *Fuel Oil Manual*: Industrial Press.

Shafiee, S., & Topal, E. (2009). When will fossil fuel reserves be diminished? *Energy Policy, 37*(1), 181-189. doi: http://dx.doi.org/10.1016/j.enpol.2008.08.016

Sharypov, V. I., Marin, N., Beregovtsova, N. G., Baryshnikov, S. V., Kuznetsov, B. N., Cebolla, V. L., & Weber, J. V. (2002). Co-pyrolysis of wood biomass and synthetic polymer mixtures. Part I: influence of experimental conditions on the evolution of solids, liquids and gases. *Journal of Analytical and Applied Pyrolysis, 64*(1), 15-28. doi: http://dx.doi.org/10.1016/S0165-2370(01)00167-X

Shelley, M. D., & El-Halwagi, M. M. (1999). Techno-economic feasibility and flowsheet synthesis of scrap tire/plastic waste liquefaction. *Journal of Elastomers and Plastics, 31*(3), 232-254.

Simmonds, N. W. (1994). Natural Rubber: Biology, Cultivation and Technology. Edited by M. R. Sethuraj and N. M. Matthew. Amsterdam and New York: Elsevier (1992), pp. xii + 610, US$231.00, Dfl 370.00. ISBN 0-444-88329-0. *Experimental Agriculture, 30*(02), 265-265. doi: doi:10.1017/S0014479700024315

Singh, R., Bhaskar, T., & Balagurumurthy, B. (2015). Effect of solvent on the hydrothermal liquefaction of macro algae Ulva fasciata. *Process Safety and Environmental Protection, 93*, 154-160. doi: https://doi.org/10.1016/j.psep.2014.03.002

Sinha, S., Agarwal, A. K., & Garg, S. (2008). Biodiesel development from rice bran oil: Transesterification process optimization and fuel characterization. *Energy Conversion and Management, 49*(5), 1248-1257. doi: http://dx.doi.org/10.1016/j.enconman.2007.08.010

Sinnott, R. K. (2005). *Chemical Engineering Design: Chemical Engineering*: Elsevier Science.

Snowden-Swan, L., Zhu, Y., Jones, S., Elliott, D., Schmidt, A., Hallen, R., . . . Maupin, G. (2016). Hydrothermal Liquefaction and Upgrading of Municipal Wastewater Treatment Plant Sludge: A Preliminary Techno-Economic Analysis: U.S. Department of Energy.

Snowden-Swan, L., Zhu, Y., Jones, S., Elliott, D., Schmidt, A., Hallen, R., . . . Maupin, G. (2016). *Hydrothermal Liquefaction and Upgrading of Municipal Wastewater Treatment Plant Sludge: A Preliminary Techno-Economic Analysis*.

Stanciulescu, M., & Ikura, M. (2007). Limonene ethers from tire pyrolysis oil: Part 2: Continuous flow experiments. *Journal of Analytical and Applied Pyrolysis, 78*(1), 76-84. doi: https://doi.org/10.1016/j.jaap.2006.04.006

Statista, I. (2015). Global consumption of natural and synthetic rubber from 1990 to 2015 (in 1,000 metric tons). http://www.statista.com/statistics/275399/world-consumption-of-natural-and-synthetic-caoutchouc/

Straka, P., & Bučko, Z. (2009). Co-gasification of a lignite/waste-tyre mixture in a moving bed. *Fuel Processing Technology, 90*(10), 1202-1206. doi: http://dx.doi.org/10.1016/j.fuproc.2009.05.021

Straka, P., KŘÍŽ, V., & BUČKO, Z. (2008). CO-GASIFICATION OF RUBBER WITH BROWN COAL. *Acta Geodyn. Geomater, 5*(151), 329-334.

Strande, L., & Brdjanovic, D. (2014). *Faecal Sludge Management: Systems Approach for Implementation and Operation*: IWA Publ.

Swanson, C. L., Buchanan, R. A., & Otey, F. H. (1979). Molecular weights of natural rubbers from selected temperate zone plants. *Journal of Applied Polymer Science, 23*(3), 743-748. doi: 10.1002/app.1979.070230309

Telmo, C., Lousada, J., & Moreira, N. (2010). Proximate analysis, backwards stepwise regression between gross calorific value, ultimate and chemical analysis of wood. *Bioresource Technology, 101*(11), 3808-3815. doi: https://doi.org/10.1016/j.biortech.2010.01.021

Tian, C., Li, B., Liu, Z., Zhang, Y., & Lu, H. (2014). Hydrothermal liquefaction for algal biorefinery: A critical review. *Renewable and Sustainable Energy Reviews, 38*, 933-950. doi: https://doi.org/10.1016/j.rser.2014.07.030

Toor, S. S., Rosendahl, L., & Rudolf, A. (2011). Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy, 36*(5), 2328-2342. doi: http://dx.doi.org/10.1016/j.energy.2011.03.013

. Top consumers of natural rubber worldwide in 2013 and 2014 (in 1,000 metric tons). (2015): Statista Inc.

Totten, G. E. (2003). *Fuels and Lubricants Handbook* (S. R. Westbrook & R. J. Shah Eds.). U.S.A: ASTM International.

Tracy, N. I., Chen, D., Crunkleton, D. W., & Price, G. L. (2009). Hydrogenated monoterpenes as diesel fuel additives. *Fuel, 88*(11), 2238-2240. doi: https://doi.org/10.1016/j.fuel.2009.02.002

Tzanetis, K. F., Posada, J. A., & Ramirez, A. (2017). Analysis of biomass hydrothermal liquefaction and biocrude-oil upgrading for renewable jet fuel production: The impact of reaction conditions on production costs and GHG emissions performance. *Renewable Energy, 113*, 1388-1398. doi: https://doi.org/10.1016/j.renene.2017.06.104

Valdez, P. J., Dickinson, J. G., & Savage, P. E. (2011). Characterization of Product Fractions from Hydrothermal Liquefaction of Nannochloropsis sp. and the Influence of Solvents. *Energy & Fuels, 25*(7), 3235-3243. doi: http://dx.doi.org/10.1021/ef2004046

van Beilen, J. (2006). *Alternative Sources of Natural Rubber: Outputs from the EPOBIO Project November 2006*: CPL Press.

van Beilen, J. B., & Poirier, Y. (2007a). Establishment of new crops for the production of natural rubber. *Trends in Biotechnology, 25*(11), 522-529. doi: http://dx.doi.org/10.1016/j.tibtech.2007.08.009

van Beilen, J. B., & Poirier, Y. (2007b). Guayule and Russian Dandelion as Alternative Sources of Natural Rubber. *Critical Reviews in Biotechnology, 27*(4), 217-231. doi: 10.1080/07388550701775927

van Beilen, J. B., & Poirier, Y. (2012). 30 - Plants as factories for bioplastics and other novel biomaterials. In A. A. M. Hasegawa (Ed.), *Plant Biotechnology and Agriculture* (pp. 481-494). San Diego: Academic Press.

Vaysse, L., Bonfils, F., Sainte-Beuve, J., & Cartault, M. (2012). 10.17 - Natural Rubber. In K. M. Möller (Ed.), *Polymer Science: A Comprehensive Reference* (pp. 281-293). Amsterdam: Elsevier.

Venkatachalam, P., Geetha, N., Sangeetha, P., & Thulaseedharan, A. (2013). Natural rubber producing plants: An overview. *African Journal oF Biotechnology, 12*. doi: 10.5897/AJBX12.016

Verheye, W. H. (2010). *Soils, Plant Growth and Crop Production*: Eolss Publishers Company Limited.

Vladimir Anikeev, & Fan, M. (2013). *Supercritical Fluid Technology for Energy and Environmental Applications*: Elsevier.

Wei, L.-g., Zhang, L., & Xu, S.-p. (2011). Effects of feedstock on co-pyrolysis of biomass and coal in a free-fall reactor. *Journal of Fuel Chemistry and Technology, 39*(10), 728-734. doi: http://dx.doi.org/10.1016/S1872-5813(11)60044-3

Whalen, M., McMahan, C., & Shintani, D. (2013). Development of Crops to Produce Industrially Useful Natural Rubber. In T. J. Bach & M. Rohmer (Eds.), *Isoprenoid Synthesis in Plants and Microorganisms* (pp. 329-345): Springer New York.

Whaley, W. G., & Bowen, J. S. (1947). *Russian Dandelion (kok-saghyz): An Emergency Source of Natural Rubber*: U.S. Department of Agriculture.

Whitworth, R. D. (1990). 4915707. United States Patent.

Williams, P. T. (2013). Pyrolysis of waste tyres: A review. *Waste Management, 33*(8), 1714-1728. doi: http://dx.doi.org/10.1016/j.wasman.2013.05.003

Williams, P. T., & Brindle, A. J. (2003). Temperature selective condensation of tyre pyrolysis oils to maximise the recovery of single ring aromatic compounds. *Fuel, 82*(9), 1023-1031. doi: https://doi.org/10.1016/S0016-2361(03)00016-4

Wingfield, R. C., Braslaw, J., & Gealer, R. L. (1984). Use of zinc and copper (I) salts to reduce sulfur and nitrogen impurities during the pyrolysis of plastic and rubber waste to hydrocarbons: Google Patents.

Wingfield, R. C., Braslaw, J., & Gealer, R. L. (1985). Pyrolytic conversion of plastic and rubber waste to hydrocarbons with basic salt catalysts: Google Patents.

. The World Factbook 2013-14. (2013). Washington, DC: Central Intelligence Agency.

Yan, H.-L., Zong, Z.-M., Li, Z.-K., Kong, J., Zheng, Q.-X., Li, Y., & Wei, X.-Y. (2017). Sweet sorghum stalk liquefaction in supercritical methanol: Effects of operating conditions on product yields and molecular composition of soluble fraction. *Fuel Processing Technology, 155*(Supplement C), 42-50. doi: https://doi.org/10.1016/j.fuproc.2016.02.011

Yan, H.-L., Zong, Z.-M., Zhu, W.-W., Li, Z.-K., Wang, Y.-G., Wei, Z.-H., . . . Wei, X.-Y. (2015). Poplar Liquefaction in Water/Methanol Cosolvents. *Energy & Fuels, 29*(5), 3104-3110. doi: 10.1021/ef502518n

Yang, Y., Gilbert, A., & Xu, C. (2009). Production of Bio-Crude from Forestry Waste by Hydro-Liquefaction in Sub-/Super-Critical Methanol. *American Institute of Chemical Engineers, Journal, 55*, 807-819. doi: https://doi.org/10.1002/aic.11701

Ye, J. L., Cao, Q., & Zhao, Y. S. (2008). Co-pyrolysis of Polypropylene and Biomass. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(18), 1689-1697. doi: 10.1080/15567030701268419

Yi, B.-k., Ma, C.-y., Chen, G.-f., & Chen, S.-y. (2009, 16-18 Oct. 2009). *Study on Pyrolysis of Used Tyre in Subcritical and Supercritical Water.* Paper presented at the Energy and Environment Technology, 2009. ICEET '09. International Conference on.

Yildirir, E., Onwudili, J., & Williams, P. (2015). Chemical Recycling of Printed Circuit Board Waste by Depolymerization in Sub- and Supercritical Solvents. *Waste and Biomass Valorization*, 1-7. doi: 10.1007/s12649-015-9426-8

Yokoyama, S.-y., Suzuki, A., Murakami, M., Ogi, T., Koguchi, K., & Nakamura, E. (1987). Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate. *Fuel, 66*(8), 1150-1155. doi: https://doi.org/10.1016/0016-2361(87)90315-2

Zhang, L., Zhou, B., Duan, P., Wang, F., & Xu, Y. (2016). Hydrothermal conversion of scrap tire to liquid fuel. *Chemical Engineering Journal, 285*, 157-163. doi: http://dx.doi.org/10.1016/j.cej.2015.10.001

Zhang, X., Wang, T., Ma, L., & Chang, J. (2008). Vacuum pyrolysis of waste tires with basic additives. *Waste Management, 28*(11), 2301-2310. doi: https://doi.org/10.1016/j.wasman.2007.10.009