การผลิตน้ำมันชีวภาพจากไพโรไลซีสในเฟสของเหลวของเนื้อไม้กระถินยักษ์

นาย ชลวิทย์ บวรวงศ์พิทักษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2553

BIO-OIL PRODUCTION FROM LIQUID PHASE PYROLYSIS OF GIANT LEUCAENA WOOD

Mr. Chonlawit Borwornwongpitak

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science
Chulalongkorn University
Academic Year 2010

Thesis Title BIO-OIL PRODUCTION FROM LIQUID PHASE PYROLYSIS OF GIANT LEUCAENA WOOD
By Mr. Chonlawit Borwornwongpitak
Field of Study Petrochemistry and Polymer Science
Thesis Advisor Assistant Professor Prasert Reubroycharoen, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

S. Hannongbua
.... Dean of the Faculty of Science
(Professor Supot Hannongbua, Dr.rer.nat.)

THESIS COMMITTEE

.... Chairman
(Professor Pattarapan Prasassarakich, Ph.D.)

.... Thesis Advisor
(Assistant Professor Prasert Reubroycharoen, Ph.D.)

W. Trakarnpruk
.... Examiner
(Associate Professor Wimonrat Trakarnpruk, Ph.D.)

Chanatip Samart
.... External Examiner
(Assistant Professor Chanatip Samart, Ph.D.)

ชลวิทย์ บวรวงศ์พิทักษ์ : การผลิตน้ำมันชีวภาพจากไพโรไลซีสในเฟสของเหลวของเนื้อไม้กระถินยักษ์ (BIO-OIL PRODUCTION FROM LIQUID PHASE PYROLYSIS OF GIANT LEUCAENA WOOD) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ผศ.ดร. ประเสริฐ เรียบร้อยเจริญ, 85หน้า.

งานวิจัยนี้ทำการศึกษาการผลิตน้ำมันชีวภาพจากไพโรไลซีสในเฟสของเหลวของเนื้อไม้กระถินยักษ์โดยใช้เดกเคนเป็นตัวทำละลาย ทำการทดลองในเตาปฏิกรณ์ที่อุณหภูมิ 350 องศาเซลเซียส, ความดันไฮโดรเจนเริ่มต้น 10 บาร์, เวลาในการทำปฏิกิริยา 2 ชั่วโมง, ชีวมวล 10 กรัมและตัวทำละลายเดกเคน 40 กรัมพร้อมกับตัวเร่งปฏิกิริยา ZSM-5, NiMo/Al_2O_3 และ Pt/Al_2O_3 ร้อยละ 10 โดยน้ำหนักเพื่อหาตัวเร่งปฏิกิริยาที่เหมาะสม ผลิตภัณฑ์ของเหลวนำไปทดสอบด้วยเครื่อง GC-MS, CHN และ Karl Fischer titration ผลการวิเคราะห์จากเครื่อง CHN พบว่า NiMo/Al_2O_3 เป็นตัวเร่งปฏิกิริยาที่เหมาะสมในการผลิตน้ำมันชีวภาพที่มีปริมาณออกซิเจนต่ำถึงร้อยละ 10.02 และให้ผลิตภัณฑ์น้ำมันชีวภาพร้อยละ 4.30 ดังนั้นจึงใช้ NiMo/Al_2O_3 เพื่อศึกษาอิทธิพลของปัจจัยอื่นๆและพบภาวะที่เหมาะสมในการผลิตน้ำมันชีวภาพ อิทธิพลของอุณหภูมิ (250, 300, 350, 400 องศาเซลเซียส), เวลาในการทำปฏิกิริยา (30 นาที, 1, 2, 4 ชั่วโมง), ความดันไฮโดรเจนเริ่มต้น (5, 10, 20, 30 บาร์), ปริมาณตัวเร่งปฏิกิริยา (ร้อยละ 1, 5, 10, 20 โดยน้ำหนัก) และก๊าซที่ใช้ทำปฏิกิริยา (ไฮโดรเจน, ไนโตรเจน) พบว่าอุณหภูมิในการทำปฏิกิริยาเป็นปัจจัยที่มีอิทธิพลมากที่สุดซึ่งให้ปริมาณน้ำมันและออกซิเจนเท่ากับร้อยละ 8.60 และ 8.50 โดยน้ำหนักตามลำดับที่อุณหภูมิ 400 องศาเซลเซียส เมื่อเพิ่มเวลาในการทำปฏิกิริยาปริมาณน้ำมันและออกซิเจนจะเพิ่มจนถึงจุดอิ่มตัวเช่นเดียวกันกับปริมาณตัวเร่งปฏิกิริยา เวลาในการทำปฏิกิริยาและปริมาณตัวเร่งที่เหมาะสมที่สุดคือ 2 ชั่วโมงและร้อยละ 10 โดยน้ำหนักโดยพิจารณาจากปริมาณน้ำมันและออกซิเจน ความดันไฮโดรเจนเริ่มต้นมีอิทธิพลน้อยและก๊าซไนโตรเจนให้น้ำมันชีวภาพสูงกว่าก๊าซไฮโดรเจน

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อ..
ปีการศึกษา 2553 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก........

5272271123 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS : PYROLYSIS / LIQUEFACTION / DEOXYGENATION /BIOMASS

CHONLAWIT BORWORNWONGPITAK: BIO-OIL PRODUCTION FROM LIQUID PHASE PYROLYSIS OF GIANT LEUCAENA WOOD. ADVISOR: ASST. PROF. PRASERT REUBROYCHAREON, Ph.D., 85pp.

In this study, bio-oil was produced from the liquid phase pyrolysis of Giant Leucaena wood in the presence of decane solvent. Firstly experiment was conducted in an autoclave reactor at following condition; reaction temperature of 350°C, initial pressure 10 bar of hydrogen, residence time of 2 hr, biomass of 10 g and decane as a solvent of 40 g with the different catalyst types, 10% by mass of ZSM-5, NiMo/Al_2O_3 and Pt/Al_2O_3 to find the optimum catalyst type. The liquid products were characterized by GC-MS, CHN analysis and Karl Fischer titration. The result from CHN analysis showed that NiMo/Al_2O_3 was the optimum catalyst to produce bio-oil with lowest oxygen content, 10.02 % and the oil yield was 4.30 %wt therefore NiMo/Al_2O_3 was chosen for studying the influence of other parameters and find the optimum condition for bio-oil production. The influence of temperatures (250, 300, 350, 400°C), residence times (30 minutes, 1, 2, 4 hours), initial pressures of hydrogen (5, 10, 20, 30 bar), catalyst dosages (1, 5, 10, 20%wt) and reaction gases (H_2, N_2) were studied. It was found that the reaction temperature is the most influencing parameter for oil yield and oxygen content which were 8.60 %wt and 8.50 %, respectively at 400°C. Increase in residence time and catalyst dosage also increased oil yield and decreased oxygen content to the saturation point. The residence time of 2 hr and 10%wt of catalyst gave the lowest oxygen content and the highest oil yield. Initial pressure of nitrogen showed higher oil yield and lower oxygen content than hydrogen as reaction gas.

Field of Study : Petrochemistry and Polymer Science Student's Signature ....
Academic Year : 2010 Advisor's Signature ....

ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to his advisor, Assist. Prof. Dr. Prasert Reubroycharoen for his excellent supervision, inspiring guidance and encouragement throughout his research. The author also would like to acknowledge Prof. Dr. Pattarapan Prasassarakich, Assoc. Prof. Dr. Wimonrat Trakarnpruk and Assist. Prof. Dr. Chanatip Samart for serving as chairman and members of thesis committee, respectively.

Many thanks for the technicians of the Department of Chemical Technology, Chulalongkorn University.

The author also gratefully acknowledged the funding support from Center for Petroleum, Petrochemical and Advanced Materials (NCE-PPAM), Energy Research Institute of Chulalongkorn University and the PTT Public Company Limited.

Finally, the author wishes to express his deep gratitude to his family for their love, support, understanding and encouragement throughout graduate study.

CONTENTS

page

page

LIST OF TABLES

page

LIST OF FIGURES

page

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Due to the depletion of non-renewable resources, such as fossil fuels and increasing of energy consumption, population, economic developments and environmental concerns of greenhouse emission. Biomass is viewed as one of alternative renewable resources which are environmentally friendly and sustainable in nature. It has negligible content of sulphur, nitrogen and ash, which give lower emission of SO_2, NO_x and soot than conventional fossil fuel [1]. Biomass is consisted of structural constituents (hemicellulose, cellulose and lignin) and minor amounts of extractives which can be converted to energy via thermochemical and biochemical processes. Biochemical processes are generally slow processes and yield single or specific products but thermochemical processes are rapid and yield multiple and complex products, additionally catalysts are often employed to improve the product quality, which can be divided into gasification, pyrolysis and liquefaction. For liquefaction, biomass can be decomposed to small molecules in presence of solvent with or without catalyst and small molecules are unstable and reactive, and can repolymerize into oily compounds [2]. However, it should be noticed that in comparison with fossil fuels, biomass much less carbon and more oxygen and has a low heating value. Generally in producing fuels from biomass, one overall objective is to remove oxygen. Biomass feedstocks often contain 40-60 wt.% oxygen and conventional fuel and oils typically have only under 1 % .

In this work, liquid phase pyrolysis or thermochemical liquefaction is mainly aimed at obtaining bio-oil by conversion of giant leucaena wood, fast growing leguminous tree in decane as solvent at moderate temperature and hydrogen pressure in the presence of ZSM-5, Ni/Mo and Pt/Al_2O_3 as catalyst to reduce the amount of oxygen by deoxygenation reaction and moisture which cause low heating value of bio-oil and to increase depolymerization to gain more oil yield.

1.2 Objective

1. To study bio-oil production from liquid phase pyrolysis of giant Leucaena wood.
2. To study the factors that affect to the quality of bio-oil production from liquid phase pyrolysis of giant Leucaena wood.
3. To find optimum condition for bio-oil production from liquid phase pyrolysis of giant Leucaena wood.

1.3 Scope of the research

The research procedures were carried out as follows:

1. Literature review.
2. Study of parameters that affect to the process of bio-oil production from liquid phase pyrolysis of giant leucaena wood to find the optimum condition for bio-oil production.
    - Temperature
    - Catalyst types
    - Catalyst dosage
    - Holding time
    - Initial pressure
3. Characterization of bio-oil.
    - CHN analysis
    - Gas chromatography-mass spectrometry (GC-MS)
    - Gas chromatography (GC)
    - Karl Fischer Titration

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Chemical structure and basic components of biomass

Biomass is a organic matter that can be defined as hydrocarbon material which mainly consists of carbon, hydrogen, oxygen and nitrogen in a mixture of structural constituents of hemicelluloses$(C_5H_8O_4)_m$, cellulose$(C_6H_{10}O_5)_x$ and lignin$[C_9H_{10}O_3(OCH_3)_{0.9\text{-}1.7}]_n$ [3]. The proportion of these wood constituents depend on species, Hardwoods have a higher proportion of cellulose, hemicelluloses and extractives than softwoods, but softwoods have a higher proportion of lignin [4]. Understanding of the chemical structure and major organic components in biomass are very important in the development of processes for producing derived fuels and chemicals [4].

Cellulose is a linear crystalline polysaccharide, with general formula $(C_6H_{10}O_5)_n$. Cellulose is a remarkable pure organic polymer, consisting of units of anhydroglucose held together in a giant straight-chain molecule. These anhydroglucose units are bound together by β-(1,4)-glycosidic linkages. Due to this linkage, cellobiose is established as the repeat unit for cellulose chains [5].

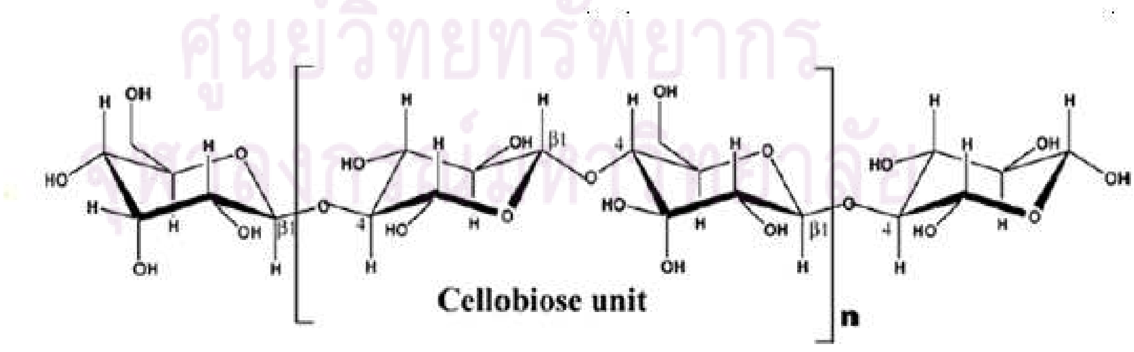


Figure 2.1 Chemical structure of cellulose [4].

The second major chemical species in wood are the hemicelluloses. They are amorphous polysaccharides, such as xylans, galactoglucomannans, arabinogalactans, glucans and galactans. The hemicelluloses, unlike cellulose, not only contain glucose units, but they are also composed of a number of different pentose and hexose monosaccharides. Hemicelluloses tend to be much shorter in length than cellulose, and the molecular structure is slightly branched. Unlike cellulose, hemicelluloses consist of different monosaccharide units. In addition, the polymer chains of hemicelluloses have short branches and are amorphous.

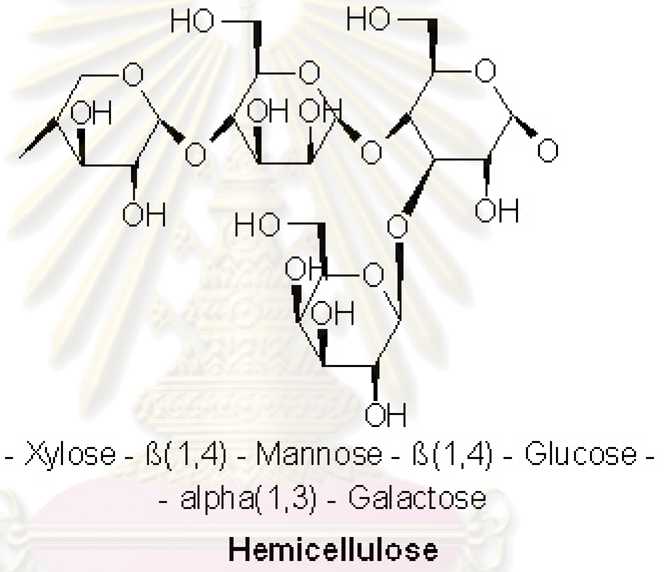


Figure 2.2 Chemical structure of hemicelluloses [6].

Lignin are highly branched aromatic polymers. The chemical formula of lignin is $C_{20}H_{19}O_{14}N_2$. Lignin is a complex, high molecular weight polymer built of hydroxyl phenyl propane units. Lignin is a completely different polymeric material, being highly crosslinked and having phenolic structures as the monomeric base. Lignin is a large, crosslinked macromolecule. It is relatively hydrophobic and aromatic in nature. The molecule consists of various types of substructures, which appear to repeat in a random manner. Lignin is a macromolecule, which consists of alkyl phenols and has a complex three dimensional structure. Lignin is covalently linked with xylans in the case of hardwoods and with galactoglucomannans in softwoods. Pyrolysis of lignin during combustion, yields a range of products, of which the most characteristic ones are methoxy phenols. The most important components in lignin are guaiacol and syringol and their derivatives.

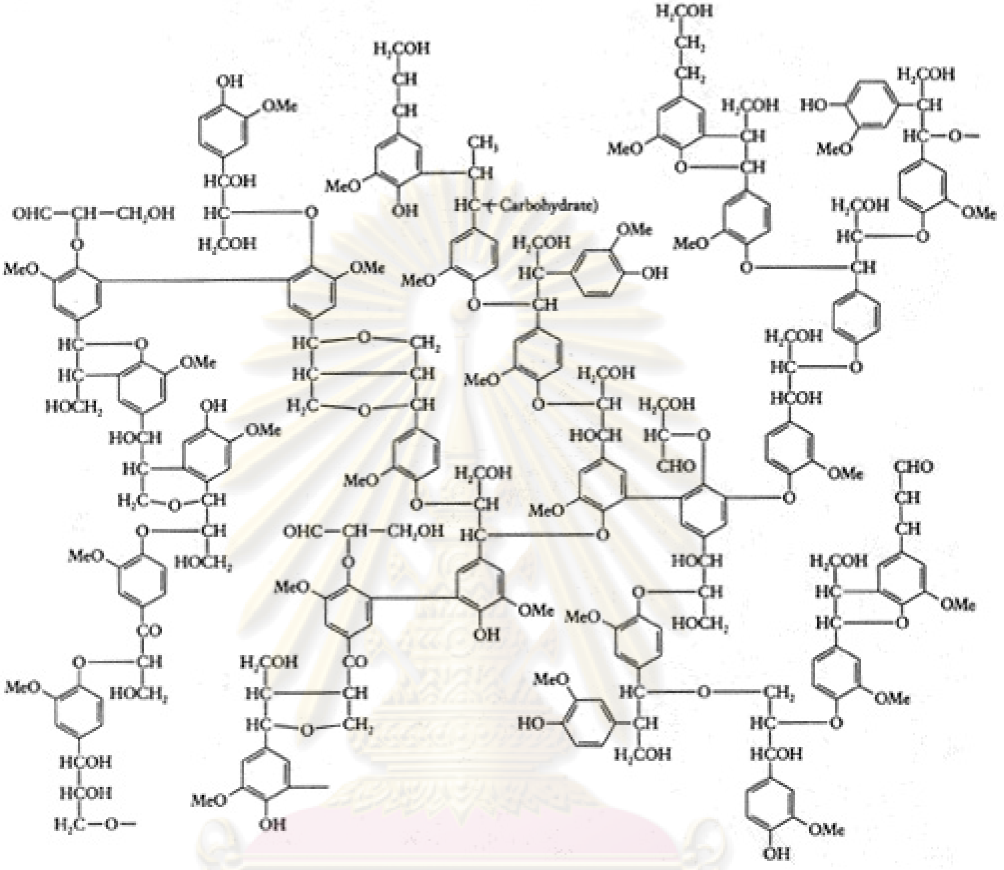


Figure 2.3 Chemical structure of lignin [6].

2.2 Attractiveness of Leucaena leucocephala

The fluctuation in the price of fossil fuels in the world market and the problems in the global warming. The Ministry of Natural Resources and Environment had the policy of providing alternative energy sources and interest in planting fast-growing tree as renewable energy

Leucaena leucocephala (Lam.) de Wit. is one of the most productive and versatile multi-purpose tree legumes suitable for tropical conditions and fast-growing tree, it take 5-6 years to be able to cut down this tree to use. The genus has its origin in Central America and Mexico where it has been used as a source of edible pods, forage for domestic animals, poles for construction, firewood and shade in permanent plantations. Leucaena has always primarily been used as high quality forage for ruminants, but it has also been valued for fuelwood, charcoal, timber and pulpwood. Leucaena is one of the few trees from which wood is used for both the industrial and non industrial purposes. Wood of leucaena is generally described as being strong, light in weight, easy to work and able to give attractive finish. These qualities make leucaena wood suitable to a wide range of uses, ranging from the traditional small scale use by farmers and small holders to the more recent utilization by large scale industries for pulp and energy generation. L. leucocephala has porous wood structure, longer fiber than that of other hardwoods, high holocellulose, cellulose and low lignin content with xylan type hemicellulose making it a suitable raw material in pulp and paper industry [1].

2.3 Biomass to energy conversion processes

Biomass is a mixture of hemicelluloses, cellulose, lignin and minor amount of extractives which can be converted to bioenergy by thermochemical or biochemical processes. The primary difference between biochemical and thermochemical conversion is that biochemical processes are generally slow processes which yield single or specific products such as ethanol or methane. On the other hand, thermochemical processes are rapid and yield multiple and often complex products. Additionally, catalysts are often employed to improve the product quality. Figure 2.4 shows of possible pathways of producing energy and products from biomass resources.

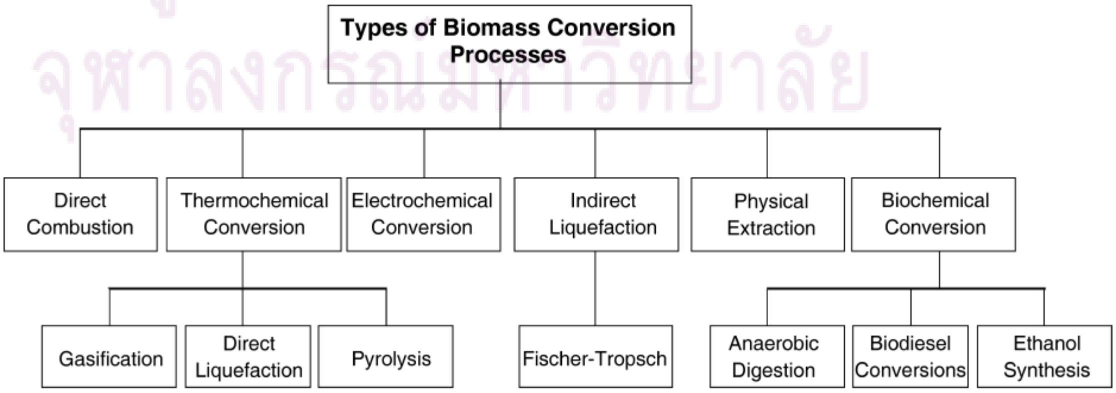


Figure 2.4 Types of biomass conversion processes [7].

2.3.1 Thermochemical processes for production of bio-oil

The thermochemical conversion processes have two basic approaches. The first is the gasification of biomass and its conversion to hydrocarbons. The second approach is to liquefy biomass directly by high-temperature pyrolysis and high-pressure liquefaction.

2.3.1.1 Pyrolysis process

Pyrolysis is the thermochemical process that converts organic materials into usable fuels. Pyrolysis produces energy fuels with high fuel-to-feed ratios, making it the most efficient process for biomass conversion and the method most capable of competing with and eventually replacing non-renewable fossil fuel resources. Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon-rich gas mixture, an oil-like liquid and a carbon-rich solid residue. Rapid heating and rapid quenching produce the intermediate pyrolysis liquid products, which condense before further reactions break down higher molecular weight species into gaseous products. High reaction rates minimize char formation. Under some conditions, no char is formed. At higher fast pyrolysis temperatures, the major product is gas.

2.3.1.1.1 Conventional pyrolysis

Conventional pyrolysis is defined as the pyrolysis which occurs under a slow heating rate. This condition permits the production of solid, liquid, and gaseous pyrolysis products in significant portions. Slow pyrolysis of biomass is associated with high charcoal continent at low temperature (675–775 K) and gas at high temperature. At present, the preferred technology is fast or flash pyrolysis at high temperatures with very short residence times [4].

2.3.1.1.2 Fast pyrolysis

Fast pyrolysis is a process in which a material, such as biomass, is rapidly heated to high temperatures in the absence of air. If the aim is the production of mainly liquid or gaseous products a fast pyrolysis is recommended. In recent years fast pyrolysis process for biomass has attracted a great deal of attention for maximizing liquid yields. Fast pyrolysis processes produce 60–75 wt.% of liquid bio-oil, 15–25 wt.% of solid char, and 10–20 wt.% of noncondensable gases, depending on the feedstock used. If the purpose were to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. If the purpose were to maximize the yield of fuel gas resulting from biomass pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred. There are four essential features of a fast pyrolysis process (1) very high heating and heat transfer rates are used, which usually requires a finely ground biomass feed, (2) a carefully controlled pyrolysis reaction temperature is used, often in the 700–775 K range, (3) short vapor residence times are used (typically < 2 s), and (4) pyrolysis vapors and aerosols are rapidly cooled to give bio-oil [4].

2.3.1.2 Liquefaction process

In the liquefaction process, biomass is converted to liquefied products through a complex sequence of physical structure and chemical changes. The feedstock of liquefaction is usually a wet matter. In the liquefaction process, biomass is decomposed into small molecules. These small molecules are unstable and reactive, and can repolymerize into oily compounds with a wide range of molecular weight distribution. Liquefaction can be accomplished directly or indirectly. Direct liquefaction involves rapid pyrolysis to produce liquid tars and oils and condensable organic vapors. Indirect liquefaction involves the use of catalysts to convert non-condensable, gaseous products of pyrolysis or gasification into liquid products. Alkali salts, such as sodium carbonate and potassium carbonate, can act as catalysts for the hydrolysis of cellulose and hemicellulose, into smaller fragments. The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation. In the liquefaction process, the amount of solid residue increases in proportion to the lignin content. Lignin is a macromolecule consisting of alkyl phenols, and has a complex three-dimensional structure. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin above 500 K and that the radicals have a random tendency to form a solid residue through condensation or repolymerization. The changes during liquefaction process involve all kinds of processes such as solvolysis, depolymerization, decarboxylation, hydrogenolysis, and hydrogenation. Solvolysis results in micellar-like substructures of the biomass. The depolymerization of biomass leads to smaller molecules. It also leads to new molecular rearrangements through dehydration and decarboxylation. When hydrogen is present, hydrogenolysis and hydrogenation of functional groups, such as hydroxyl groups, carboxyl groups, and keto groups also occur [5].

2.3.2 Thermal decomposition of cellulose, hemicelluloses and lignin

Previous study [8] showed the behavior of thermal degradation of main components in biomass. From the figure 2.5 hemicellulose started its decomposition easily with the weight loss mainly happened at 220–315^{o}C. It got the maximum mass loss rate at 268^{o}C and there was still 20% solid residue left even at 900^{o}C. Cellulose pyrolysis was focused at a higher temperature range 315–400^{o}C with the maximum weight loss rate 2.84 wt.%/^{o}C attained at 355^{o}C. When temperature was higher than 400^{o}C, almost all cellulose was pyrolyzed with a very low solid residue 6.5 wt.%/^{o}C left. Among the three components, lignin was the most difficult one to decompose. Its decomposition happened slowly under the whole temperature range from ambient to 900^{o}C. Cellulose and hemicelluloses form mainly volatile products on heating due to the thermal cleavage of the sugar units. The lignin forms mainly char since it is not readily cleaved to lower molecular weight fragments. The progressive increase in the pyrolysis temperature of the wood led to the release of the volatiles thus forming a solid residue that is different chemically from the original starting material. Cellulose and hemicelluloses initially break into compounds of lower molecular weight [5].

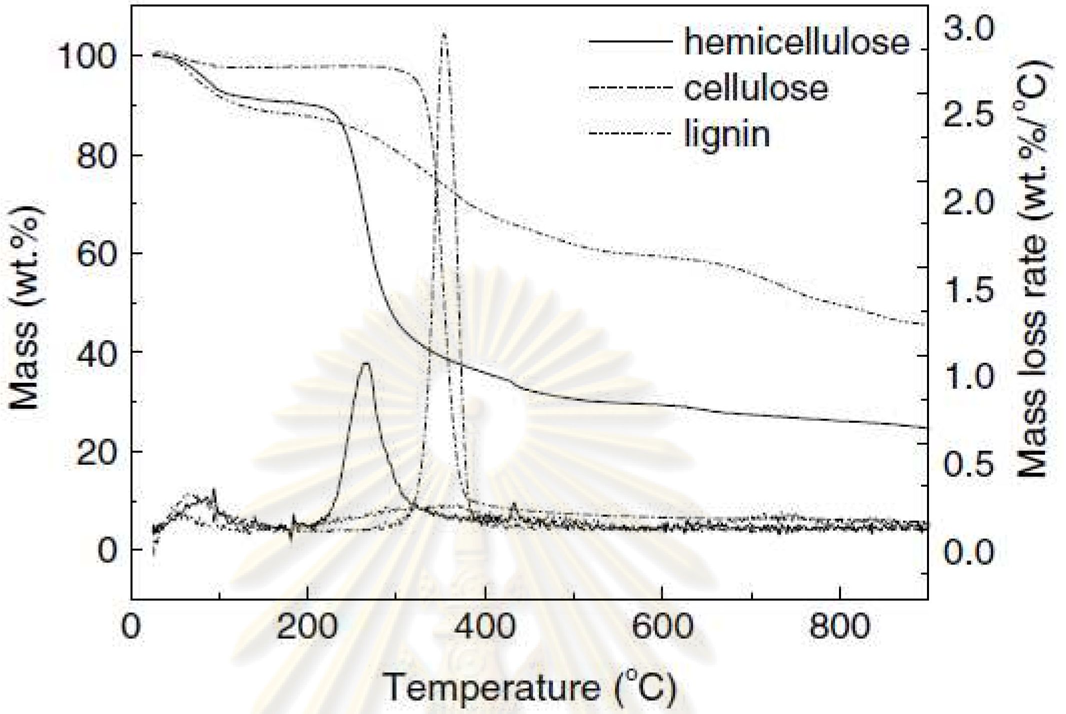


Figure 2.5 Pyrolysis curves of hemicellulose, cellulose and lignin in TGA [8].

2.3.3 Characteristics of bio-oil

Bio-oil is liquid product from biomass pyrolysis. It also has other names, pyrolysis oil and bio-crude. Bio-oil are the mixture of oxygenated compounds containing carbonyl, carboxyl and phenolic groups derived from depolymerization and fragmentation of cellulose, hemicelluloses and lignin. The main drawbacks of bio-oil is composition of bio-oil consist of large amount of oxygen atoms and water contents that lead to low heating vaule. Bio-oil [9] has a content of water as high as 15–30 wt% derived from the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage. The presence of water lowers the heating value and flame temperature, but on the other hand, water reduces the viscosity and enhances the fluidity, which is good for the atomization and combustion of bio-oil in the engine. The oxygen content of bio-oil is usually 35-40 % depend on the type of biomass and the severity of pyrolytic processes. The high oxygen content leads to the lower energy density than the conventional fuel by 50% and immiscibility with hydrocarbon fuels also. Bio-oil also has higher viscosity than petroleum derived hydrocarbon oil. The viscosity of bio-oil depends on nature of the feedstock, temperature of pyrolysis process, thermal degradation degree and catalytic cracking, water content of the bio-oil and pyrolysis process used [4].

Table 2.1 The properties of bio-oil from biomass pyrolysis compared to petroleum heavy fuel oil [9].

Physical property	Bio-oil	Heavy fuel oil
Moisture content (wt%)	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Element composition (wt%)		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3
Ash	0-0.2	0.1
HHV (MJ/kg)	16-19	40
Viscosity (at 50 ^{o}C) (cP)	40-100	180
Solid (wt%)	0.2-1	1
Distillation residue (wt%)	up to 50	1

2.3.3.1 Composition of bio-oil.

The 99.7% of bio-oil, a complex mixture containing carbon, hydrogen and oxygen, is composed of acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin derived phenols and extractible terpene with multi-functional groups [9].

Table 2.2 Chemical composition of pyrolysis liquid [4].

Major components	Mass %
Water	20-30
Lignin fragment: insoluble pyrolytic lignin	15-30
Aldehydes: formaldehyde, acetaldehyde, hydroxacetaldehyde, glyoxal, methylglyoxal	10-20
Carboxylic acids: formic acid, propanoic, butyric, pentanoic, hexanoic,glycolic (hydroxyacetic)	10-15
Carbohydrates: cellobiosan, α-Dlevoglucosan, oligosaccharides, 1.6-anhydroglucofuranose	5-10
Phenols: phenol, cresols, guaiacols, syringols	2-5
Furfurals	1-4
Alcohols: methanol, ethanol	2-5
Ketones: acetol (1-hydroxy-2-propanone), cyclopentanone	1-5

2.3.4 Catalytic upgrading of bio-oil.

The deleterious properties of low heating value, high viscosity, thermal instability and corrosiveness are the obstacles to replace of fossil fuel. Table 2.3 compares some of bio-oil with those of conventional transport fuels. Bio-oil contains some heavy aromatic compounds and this contrast with gasoline and diesel which comprise of mixture of hydrocarbon with relatively low carbon chain lengths of 5-10 and 12-20, respectively. The H/C ratio in bio-oil is in the range 1.2-1.4 and this is closer to aromatic than to alkanes. The O/C ratio in bio-oil is high, 0.5, the consequence of high level of oxygen is bio-oil is not sufficiently stable and is also corrosive and immiscible with petrofuels [56]. Bio-oils can be upgraded into a liquid transportation fuel by different routes. Hydrodeoxygenation with typical hydrotreating catalysts, typically sulfided CoMo or NiMo supported on alumina. Zeolite upgrading or forming emulsions with the diesel fuel. Alternatively, bio-oils and chars can be converted into H_2 or syngas by steam-reforming. The purposes of using catalysts are to enhance the cracking reactions of the heavy molecules in pyrolysis products resulting in the production of lighter and less viscous bio-oil, reduce the formation of carboxylic acids making bio-oil less corrosive, and enhance the formation of more valuable products like hydrocarbon that can increase the heating value of the bio-oil [4].

Table 2.3 Some features of bio-oil, gasoline and diesel [10].

	Bio-Oil	Gasoline	Diesel
Carbon chain length	Up to 100	5-10 branched alkanes, aromatics	12-20 linear alkanes
H/C ratio	1.2-1.4	1-2	2
O/C ratio	0.5	0	0

2.3.4.1 Hydrotreating reaction.

Hydrotreating (hydrodeoxygenation, HDO) eliminates oxygen in the form of water however CO_2 can be also formed. For this elimination, catalysts and hydrogen are necessary. Hydrodeoxygenation consists of a family of reactions such as hydrogenation, cracking and decarboxylation. Cracking and hydrogenation are the rate determininh step.

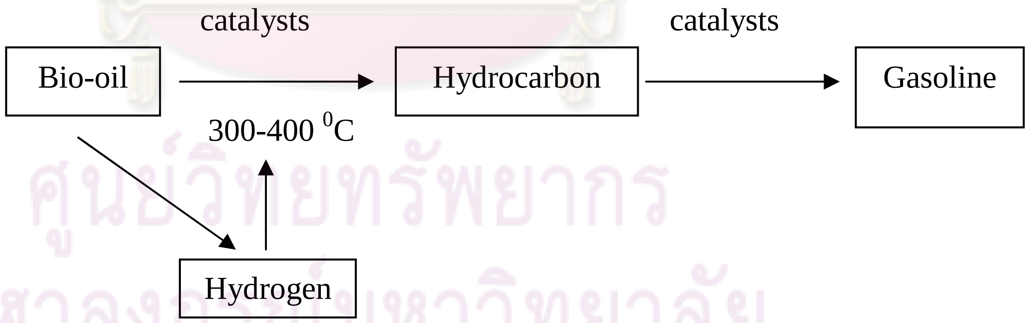


Figure 2.6 Scheme of bio-oil upgrading via hydrodeoxygenation [10].

Most hydrodeoxygenation of bio-oils has focused on sulfided $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts, which are used for hydrotreating industrial feedstocks. These catalysts have shown to be active in the upgrading of bio-oils. Hydrodeoxygenation of bio-oils involves treating bio-oils at moderate temperatures (575–875 K) with high-pressure H_2 in the presence of heterogeneous catalysts to remove the oxygen in form of CO_2 and H_2O and form saturated C–C bonds. The energy content of the fuel is significantly increased, and the stability of the fuel increases during hydrodeoxygenation. Gutierrez et al. [11] studied hydrodeoxygenation of guaiacol in a batch system using commercial alumina supported CoMo and NiMo catalysts under a total pressure of 8.0 MPa in the temperature range from 475 to 625 K. The results of the study showed that the conversion of guaiacol and the amount of hydrodeoxygenation products were higher on the NiMo than on the CoMo catalyst at the lowest temperatures tested (475–575 K). Thus, the NiMo catalyst was more active than the CoMo in this temperature range.

2.3.4.2 Cracking of bio-oil.

Another approach to deoxygenation of bio-oil catalytic cracking. Catalytic cracking is normally performed over solid acid catalysts such as aluminosilicate and zeolite. This approach does not required added hydrogen and oxygen is eliminated in the form of water and CO_2. As compare to hydrotreating, cracking gives a higher value transport fuel product because of higher aromatic content. However, the yields are lower and the amount of coke formed is relatively high. The yields obtained in the process reach 50–60% of the theoretical maximum. The liquid product obtained by cracking as the product obtained by hydrotreating demands further refining to produce gasoline or diesel hydrocarbons [10]. Zeolites are often used as catalyst to improve the product from biomass pyrolysis. The zeolites contain a suitable porous structure and possess the acidic properties necessary for the cracking of large polymeric molecules as well as oxygenates formed from the biomass.

The pyrolysis of wood based biomass has been performed in the presence of H-ZSM-5 catalyst obtaining an increase of the aromatic fraction in the bio-oil. The acid sites of the catalyst promote a series of dehydration, decarbonylation, decarboxylation, isomerization and dehydrogenation reactions, converting the oxygenated products generated in the pyrolysis process into more stable aromatic compounds, mainly naphthalene, ethylbenzene and xylenes. The shape selectivity and the acid properties of the catalysts are crucial parameters in the choice of the fast pyrolysis catalysts. For example silicalite and ZSM-5 had the same pore structure but different acid sites and the aromatic yield changed from about 26 wt% to below 10 wt.% passing from ZSM-5 to silicalite catalyzed reaction. Indeed the use of zeolite Beta, Y and silica–alumina lead to the production of large amounts of coke as the main product. High heating rates and catalyst to feed ratios are needed to ensure that pyrolized biomass compounds enter the pores of the ZSM-5 catalyst and that thermal decomposition is avoided. As a consequence, product selectivity was a function of the active site and pore structure of the catalyst [12].

2.3.5 Effect of processing parameters

2.3.5.1 Effect of temperature

The effect of temperature on the compounds existing in liquid products obtained from biomass samples via thermochemical conversion processes generally effect on the yield of liquids due to extended biomass fragmentations with increase in temperature. When the temperature is sufficiently larger than the activation energies for the bond cessation, the extensive biomass depolymerization occurs. This increases both concentration of free radicals and probability of repolymerization of fragmented species. The competition among hydrolysis, fragmentation and repolymerization reactions defines the role of temperature. Depolymerization of biomass is a dominant reaction during initial stages of pyrolysis. Repolymerization becomes active at later stages that leads to the formation of char. Increasing temperature usually yields higher amounts of bio oil. The suitable temperature for production of oil yield also depends on biomass types. Influence of temperature on the yield of bio-oil initially increase when increase in temperature to the maximum point and then increase in temperature actually inhabits biomass conversion. Very high temperature is not usually suitable for production of liquid oils both in terms of operational cost and liquid oil yield. The reason for this behavior is high temperature lead to formation of gas and recombination of free radical reaction that lead to char formation [13]. Liu et al. [14] summarized the results of oil yield with water, ethanol and acetone as liquefaction solvent at various temperature shown in figure 2.7. It was observed that oil yield increased with increasing temperature up to a certain value and decreased thereafter due to the formation of solid by cyclization, condensation and re-polymerization of liquid products and formation of gases from degradation of the liquid products.

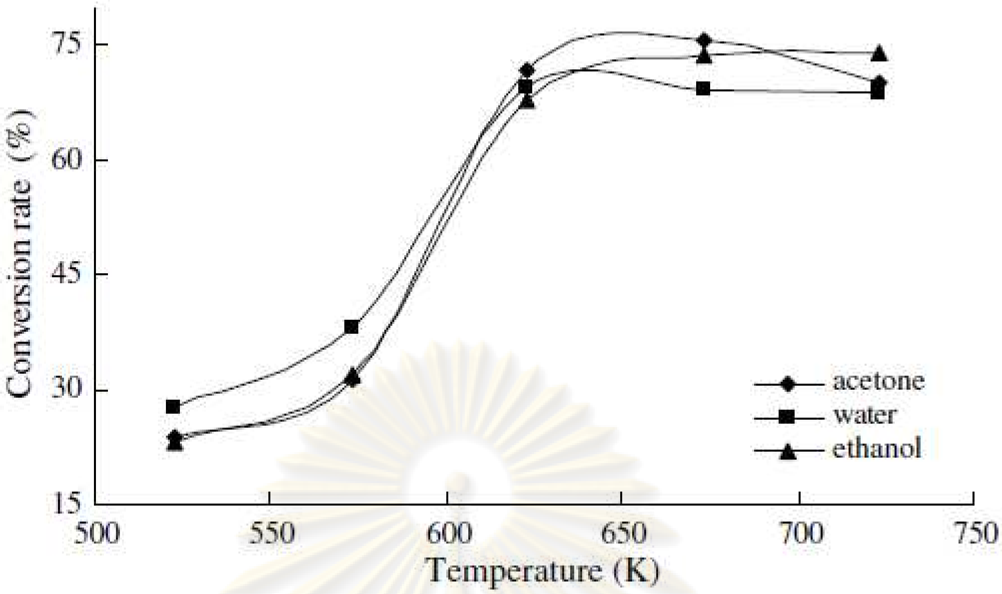


Figure 2.7 Effect of solvent type on pinewood conversion rate as a function of temperatures [14].

In the pyrolysis of biomass, the most interesting temperature that produce maximum oil yield range from 625 and 775 K. Table 2.4 shows pyrolysis reactions at different temperatures. At higher temperatures, the rather large molecules present in the liquid and residual solid are broken down to produce smaller molecules which enrich the gaseous fraction. Low temperatures and high residence times favor the production of char, while the higher temperatures and short residence times lead to high liquid production [4].

Table 2.4 Pyrolysis reactions at different temperatures [4].

Condition	Process	Products
Below 575 K	Free radical formation, elimination of water and depolymerization	Formation of carbonyl and carboxyl, evolution of CO and CO_2 and mainly a charred residue
Between 575 and 725 K	Breaking of glycosidic linkages of polysaccharide by substitution	Mixture of levoglucosan, anhydrides and oligosaccharides in the form of a tar fraction
Above 725 K	Dehydration, rearrangement and fission of sugar units	Formation of carbonyl compounds such as acetaldehyde, glyoxal and acrolein
Above 775 K	A mixture of all above processes	A mixture of all above products
Condensation	Unsaturated products condense and cleave to the char	A highly reactive char residue containing trapped free radicals

2.3.5.2 Effect of pressure.

Pressure maintains single-phase media for liquefactions process. This single phase liquefaction is necessary to avoid large enthalpy inputs required for phase change of solvents. By maintaining pressure above the critical pressure of medium, the rate of hydrolysis and biomass dissolution can be controlled that may enhance favorable reaction pathways thermodynamically for production of liquid fuels or for gas yield. Pressure also increases solvent density. High-density medium penetrates efficiently into molecules of biomass components, which results in enhanced decomposition and extraction. Catalytic runs actually decreased the amount of oil with increase in pressure, which can be attributed to blocking of catalyst active sites by high-density solvent. Pyrolysis of biomass depends on breakage of C–C linkages. When pressure is increased will increase in local solvent density that causes cage effect for these bonds. This cage effect inhibits C–C bonds breakage, which ends up in low fragmentations. Thus, variation of pressure in supercritical liquefaction may not play an important role for overall liquid oil yields.

2.3.5.3 Effect of hydrogen gas.

Hydrogen gas has the same role to hydrogen donor solvent that stabilizes the fragmented products of liquefaction by inhibition the condensation, cyclization, or repolymerization of free radicals, and reduce char formation. Equations (1) and (2) show the concept for stabilization of aromatic radicals(Ar•) of lignin by hydrogen gas to useful liquid oil products.

$$Ar\bullet + H_2 \rightarrow ArH + H\bullet \qquad (1)$$

$$Ar\bullet + H\bullet \rightarrow ArH \qquad (2)$$

The figure 2.8 showed that higher reactivity of CO and H_2 stabilized more of fragmented radicals during liquefaction. Probably biomass radicals show more affinity of towards H_2 or CO and get stabilize easily. Less amount liquid oils in N_2 environment is mainly due to its low reactivity comparatively. This discussion shows that reactive gases are better options than inert gases. H_2 gas or mixture of CO/H_2 gases is recommendable as reducing gases. Usage CO as reducing gas may be ignored due to its hazardous nature [13].

However pure hydrogen gas is not profitable to use in thermal conversion because of it high cost. Syngas is a hydrogen rich gas that can be other options to replace pure hydrogen in thermal conversion processes such as liquefaction or pyrolysis of biomass [18]. Comparing H_2 gas to hydrogen donor solvents. Hydrogen donor solvents are the more favorable option to hydrogenate the biomass fragments. These solvents not only donate hydrogen but also act as hydrogen transport vehicle to support hydrogenation reaction in the system

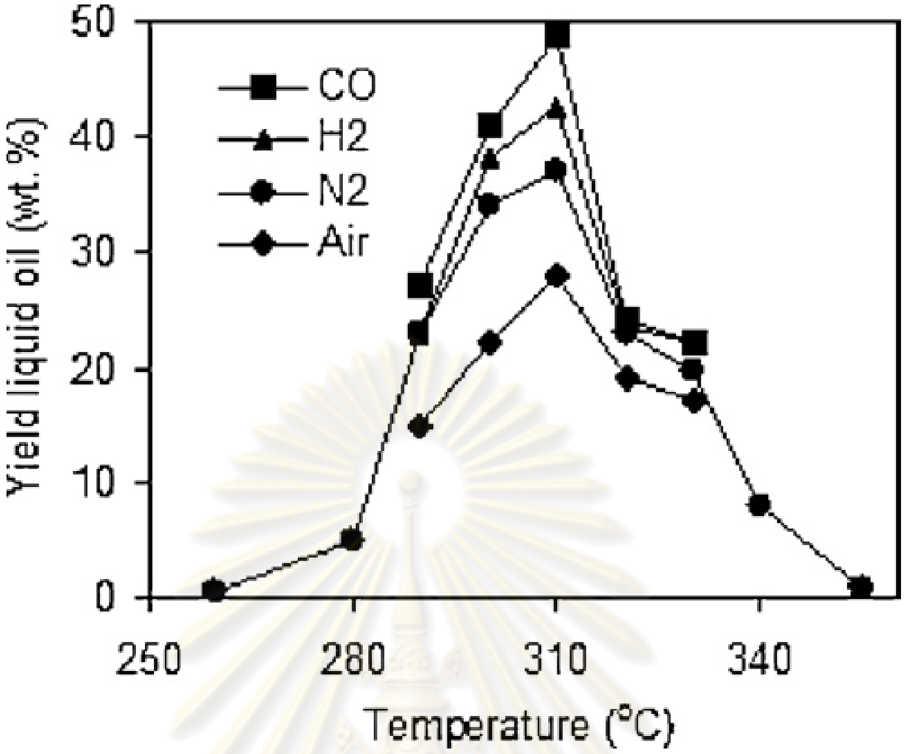


Figure 2.8 The effect of reducing gases on liquid oil yield [15].

2.3.5.4 Effect of residence time.

The effect of residence time has been studied in many research. For longer residence time will decrease in heavy oil yield to obtain more light oil yield and also produce more gas yield. To obtain high liquid oil yield, it is necessary to inhibit the decomposition of lighter products by addition of reducing agents like tetraline, hydrogen, and syngas can stabilize the radicals and products. In general, oil yield reaches a maximum before decreasing for very long residence times due to undesirable recondensation while gas yield and biomass conversion increase continuously until the saturation point.

2.3.5.5 Effect of heating rate.

Slow heating rates usually lead to the formation of char residue due to secondary reactions. Secondary reactions become also dominant at very high heating rates which results in high gas yields as in case of supercritical liquefaction. Moreover, liquid oil yield is not very sensitive to large variations in high heating rates. Suitable heating rates can lead extensive fragmentation and minimal secondary reactions. On such bases, moderate heating rates may be enough to overcome heat transfer limitations and to produce high liquid oil amounts.

2.4 Literature review

In 2009 , Yip et al. [16] investigated the liquefaction of bamboo in various solvents including phenol, ethylene glycol and ethylene carbonate with different liquid ratios (2:1, 3:1, 5:1, 10:1), and reaction times that used for this process were 2, 6, 10, 14 and 18 hours to see the effect of those parameters. The process was catalyzed by hydrochloride acid at 180^{o}C. The liquefaction yield increased when the reaction time was increased to 14 hours and a further increase in the reaction time to 18 hours might result in recondensation and reduce the liquefaction yield. Phenol was the optimal solvent with a yield up to 99% at the liquid ratio of 10:1, while the highest yield of using ethylene glycol and ethylene carbonate as a solvent were only 69% and 80%, respectively. When using phenol as a solvent the liquefaction yield increased slightly with increasing in the liquid ratio. When ethylene carbonate was used as a solvent the liquefaction yield showed no obvious differences among the liquid ratio of 2:1-5:1 but it increased significantly at a ratio of 10:1. And the optimal liquid ratio for EG is 5:1. From the results of the FT-IR spectra of the solid residues and the raw bamboo showed that cellulose, hemicelluloses and lignin were almost decomposed when using phenol as solvent. The gel permeation chromatography (GPC) results of the liquid products showed that the high molecular weight of bamboo decreased significantly to around 1800 g mol/1 after liquefaction. The gas chromatography and mass spectrometry (GC–MS) analysis showed that low boiling point products of liquefied bamboo were similar regardless of the type of solvent used. All of the components found by GC–MS could be divided into aromatic and non-aromatic compounds. Despite the different solvents used, several components with the same compositions were obtained, including benzoic acid methyl ester (RT = 7.366), 1,4Benzenedicarboxylic acid, dimethyl ester (RT = 13.27) and 1,3-Benzenedicarboxylic acid, dimethyl ester (RT = 13.426). These results indicated that resemblances in the liquefaction mechanism exist among the liquefaction processes although different kinds of chemicals were used as solvents.

In 2003 , Zhong et al. [17] studied on the liquefaction of four commonly used woody materials, Cunninghamia lanceolata, Fraxinus mandshurica, Pinus massoniana Lamb. and Populus tomentosa Carr in the reaction temperature range of 553.15-633.15 K. Both non-catalytic and catalytic liquefaction were performed. The non-catalytic liquefaction results showed that the yield of heavy oil decreased with increasing lignin content, while the yield of residue showed the opposite tendency. For the four woody materials studied, the highest heavy oil yield of about 31% was obtained for F. mandshurica at the reaction temperature of 573.15 K. The catalytic liquefaction results showed that K_2CO_3 could greatly reduce the residue yield, while its effect on the heavy oil yield was lignin content dependent, and generally, the effect became weaker with decreasing lignin content. The present work again showed that a catalyst was necessary to obtain a high oil yield and a low residue yield, and with K_2CO_3 as a catalyst, the heavy oil yield could be as high as 30% and the residue yield could be lower than 10%.

In 2008 , Liu et al. [14] studied the solvent effect on the pinewood liquefaction process. The solvents that used in this experiment were water, acetone and ethanol in the conditions of temperature range 523-723 K, initial pressure 1 MPa, reaction time 20 min, biomass 10 g and solvent 60 g. Among the three tested solvents, acetone had the best effect on the conversion in all the tested temperature and the highest conversion were 74.2%, 69.4% and 75.9% with ethanol, water and acetone as solvent, respectively. The different conversion in liquefaction process may due to the polarity constant values of the solvent. Higher conversion was obtained in solvent with higher polarity. The highest yield reached 18.6%, 26.5% and 20.0% at 573 K, 673 K and 673 K for water, ethanol and acetone as the solvents, respectively. The oil yield increased with increasing temperature up to a certain value and decreased for all the tested solvents due to the formation of solid by cyclization, condensation and repolymerization of the liquid products and formation of gases from degradation of the liquid products. From GC-MS analysis, the most constituted compounds in all three different solvents were phenol derivatives hydrocarbon and solvent type markedly affected the product distribution. The liquefaction process that used water as solvent had the shortest product distribution rang with only 44 compounds identified in the oil product. For acetone and ethanol as solvents in liquefaction process showed long product distributions that were the methyl- or ethyl-ester compounds due to esterification reaction for ethanol solvent.

In 2006 , Wang et al. [18] investigated direct liquefaction of sawdust under syngas with and without catalyst. The experiment of sawdust liquefaction was tested at 300^{o}C, 1 wt% Mo catalyst, initial gas pressure of 2.0 MPa and reaction time of 30 min. The effect of different catalyst preparation methods including mechanical mixing, impregnation and ultrasonic treatment with or without solvents on liquefaction were compared. The sample loaded catalyst with ultrasonic treatment showed the highest yield of oil and lowest yield of preasphaltene and asphaltene in all with or without solvents due to the well disperation of the catalyst. Hydrogen-donor solvent played an important role in sawdust liquefaction. From this research tetralin and toluene were used as solvent and the result showed that tetralin as a kind of hydrogen donor solvent showed a more remarkable effect on conversion and product distribution than toluene as a kind of non-hydrogen donor solvent by its hydrogen donor and hydrogen transportation ability to improve the hydrogenation and hydrocracking reactions with inhibition of polycondensation while hydrogen gas displayed less action in promoting hydrogenation reaction and enhancing catalyst ability. Gaseous hydrogen and catalyst showed significant functions in the presence of solvent. Higher temperature was favorable of thermal decomposition, hydrogenation and hydrocracking reactions.

In 2002 , Rezzoug et al. [19] investigated the liquefaction of wood in two steps, solvolysis in ethylene glycol or recycled ethylene glycol solvent and catalytic hydrotreatment at high pressure of the solvolysis product. For the solvolysis step, the liquefaction yield was limited by the acidity of reactant media and the formation of a coke-like residue. When using recycled solvolytic oil instead of fresh ethylene–glycol, the conversion into liquid was also reduced and the viscosity of the solution strongly increased. For the upgrading step NiMo provided a higher hydrogenating activity and higher deoxygenation than CoMo which gave more light fraction and less heavy fraction than CoMo catalyst. The initial pressure of hydrogen affected to the increasing of oil yield and removal of oxygen. When the initial hydrogen pressure increased from 3 to 9 MPa the light fraction increased from 11.3 to 26.2% and also the gas fraction rose due to the cracking and depolymerisation of long chain molecules in the heavy fraction led to the formation of gases and light products. Increasing the ratio tetralin/solvolysis oil from 0.5 to 3 resulted in a regular increase in the light fraction and a regular decrease in both the heavy and gas fractions because tetralin, good hydrogen donor solvent, transfered radical hydrogen to degrade wood and obtained desired product and also stabilized the free radicals to prevent condensation into heavy molecules. From the results showed that the process condition of initial pressure of 6 MPa, using NiMo as a catalyst and reaction temperature of 350 ^{0}C could upgrade oil into less than 2% of oxygen content.

In 2002 , Yang et al. [20] investigated the pyrolysis characteristics of three main components (hemicellulose, cellulose and lignin) of biomass by using thermogravimetric analyzer (TGA) with differential scanning calorimetry (DSC) detector and a pack bed. The releasing of main gaseous products from biomass pyrolysis in TGA were on-line measured using Fourier transform infrared (FTIR) spectroscopy. In thermal analysis, the pyrolysis of hemicellulose and cellulose occurred quickly, with the weight loss of hemicellulose mainly happened at 220 – 315^{o}C and that of cellulose at 315 – 400^{o}C. However, lignin was more difficult to decompose, as its weight loss happened in a wide temperature range from 160 to 900^{o}C and the generated solid residue was very high (40 wt.%). The main gaseous products from pyrolyzing the three components were similar, including CO_2, CO, CH_4 and some organics. CO_2 gas releasing was mainly caused by the primary pyrolysis, while secondary pyrolysis was the main source for releasing of CO and CH_4. Hemicellulose showed higher CO and CO_2 yield, while lignin displayed higher CH_4 releasing. Organic compounds (C=O, C–O–C, etc.) were mainly released out at low temperatures about 200–400^{o}C and 300–450^{o}C from hemicellulose and cellulose, respectively. Nevertheless, almost no organic compound was detected from lignin pyrolysis. The difference might be due to the inherent variance among the chemical structure of the three components, such as hemicellulose appeared more C=O contained organic compounds, while higher contents of OH and C–O were found with cellulose and more methoxyl groups with lignin.

In 2009 , Fisk et al. [21] studied the liquid phase upgrading of bio-oil over a series of supported Pt catalysts. Pt/Al_2O_3 showed the highest activity for deoxygenation, the oxygen content of the bio-oil decreasing from an initial value of 41.4 wt% to 2.8 wt% after upgrading. The gas composition was constant for different catalysts, CO_2 being the most abundant product and CO was lower due to high water-gas shift activity of Pt catalyst. GC–MS analysis of the oil showed it to be highly aromatic, the major components corresponding to alkyl-substituted benzenes and cyclohexanes. CO_2 was formed as the major gaseous product with lower yields of H_2 and C_1–C_6 hydrocarbons. Possible pathways for Pt catalyzed bio-oil deoxygenation were proposed in this research which light oxygenates were converted through two main pathways, reforming to reject the oxygen as CO_2 and produce H_2. The second pathway involving C–O bond scission and hydrogenation to produce alkanes with H_2O as the coproduct in a minor pathway. In a parallel process, aromatics undergo C–O cleavage or hydrogenation, affording benzenes and cyclohexanes.

In 2010 , Miskolczi et al. [22] studied of pyrolysis Malaysian refuse derived fuels (RDF) in continuously stirred batch reactor at 450 °C in the presence and absence of catalyst. It was concluded that pyrolysis of RDF produced higher gas and pyrolytic oil yields in the presence of catalysts. The highest amount of gases was found by the use of ZSM-5 catalyst (27.8%), while highest oil yields in the presence of Y-zeolite (17.8%). Gases consisted of CO_X, hydrogen and hydrocarbons. NiMo catalyst and Co–Mo catalyst had increased both the yields of CO and CO_2 and promoted the isomerization reactions. In pyrolytic oil the concentrations of aromatics, branched and non-branched compounds were also affected with the presence of catalysts. E.g. the highest increase in isomerization of main carbon frame and aromatization reactions was found in the case of Y-zeolite and ZSM-5. Phenol, benzene 1,3-diol and methyl-phenol content of pyrolytic oil obtained by non-catalytic pyrolysis could be decreased with 39.4%, 36.9% and 26.9% over CoMo catalyst, respectively. Sulphur, nitrogen and chlorine were found as contaminants in pyrolytic oils. The contaminant concentrations could be reduced by using catalysts, especially with NiMo catalyst and CoMo catalyst. Catalysts influenced the concentration of impurities both in the case of char and heavy oil, and especially the level of sulphur, nitrogen and chlorine could be reduced in heavy oils while catalysts were used. The

Results have shown that catalysts only slightly affected the composition and yields of products, but it was a very important result that the catalysts mainly the CoMo and NiMo catalysts have showed activity in Cl, N and S, as contaminants level decreased. Furthermore those catalysts could shift the oxygen containing hydrocarbons to oxygen free hydrocarbons.

In 2010 , Chen et al. [23] investigated the co-deoxy-liquefaction of biomass and vegetable oil under the condition of different temperatures (350-500^{o}C) and residence time as well as catalyst using HZSM-5. Result showed that the product yields from 350 to 500^{o}C under the residence time of 20 min the oil yield varied from 12.41% to 18.89% and the oil yield reached a maximum of 18.89% at the reaction temperature of 400 ^{0}C. At 500^{o}C the yield of the oil dropped remarkably to 12.41% for the higher temperature leading to the deep cracking of the mixture into gas products. The yield trend was consistent with the yield without catalyst but the difference was that the oil yield with catalyst was higher than that of no catalyst. It was found that at higher reaction temperature increased the gaseous product especially CO_2 and gas hydrocarbon (C_1-C_6) due to the breaking of long chain compounds to small molecule compounds. The formation of large quantities of CO_2 was advantageous for removing oxygen atoms. From GC-MS results showed that low temperature was favorable for the formation of diesel-like products, while high temperature caused more gasoline-like products.

CHAPTER III

EXPERIMENTAL

3.1 Materials

All Chemicals used in this experiment were listed in table 3.1.

Table 3.1 List of chemicals and sources

Chemicals	Source
Decane ($CH_3(CH_2)_8CH_3$) 99.99%	Sigma-Alorich
Hydrogen gas (99.99% purity)	Praxair
Nitrogen gas (99.99% purity)	Praxair
Standard synthesis gas of 1% CO, 1% CH_4 1% H_2 and 1% CO_2 balanced with N_2	BOC Scientific
Zeolite (commercial grade of ZSM-5)	PTT Research and Technology Institute
NiMo/ Al_2O_3 (commercial grade)	PTT Research and Technology Institute
Pt/Al_2O_3 (1 wt% of Pt)	Sigma-Alorich
Carbon disulfide (CS_2)	MERCK
Giant leucaena wood	PTT Research and Technology Institute

3.2 Instruments and equipments

- Autoclave reactor
- External electrical furnace
- Temperature controller
- Thermocouple
- Pressure gate
- pressure controller
- Rotary evaporator
- Ultrasonic bath
- Hot plate
- Oven
- Magnetic stirrer

- Pipette 5 and 10 mL
- Thermometer
- Beaker 50, 100 and 250 mL
- Dropper
- Spoon
- Dessicator
- Aluminium foil
- Sampling bag
- Weight papers
- Filter papers (number 42)
- Filter flask

3.3 Liquid-phase pyrolysis of Giant leucaena wood procedure.

1. Giant leucaena wood was employed as raw material. It was sieved to less than 75 µm and then dried under vacuum for 12 h at 110 ^{0}C before use.
2. The proximate and ultimate analyses of the giant leucaena wood were tested, given in Table 3.2.
3. The reaction was carried out in a 85 ml stainless steel autoclave with stirrer and the autoclave can be operated at a maximum pressure of 10 MPa.
4. The autoclave was heated with an external electrical furnace to the desired temperature the experimental apparatus was shown in Fig. 3.1.

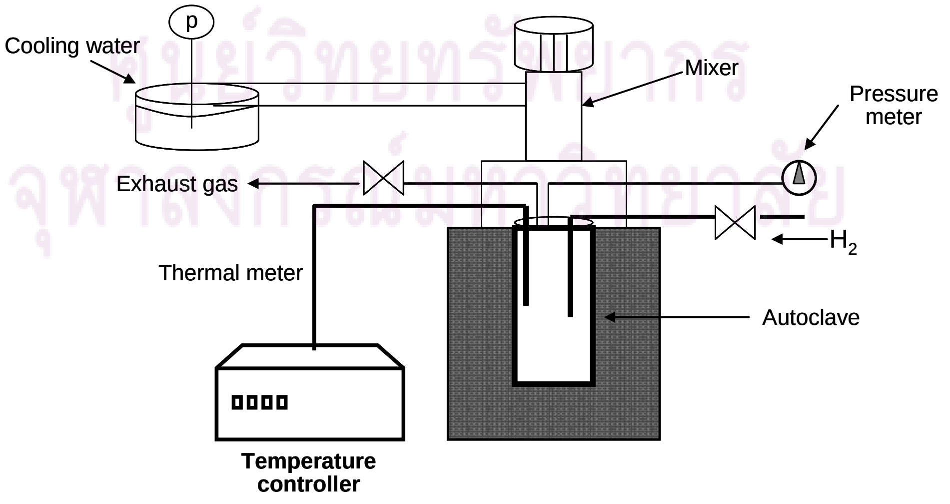


Figure 3.1. The outline of experimental apparatus.

5. In each test, the reactor was filled up with 10 g of dried giant leucaena wood, 40g of decane as solvent(the ratio of biomass to solvent is 1 : 4) in the presence of Zeolite (ZSM-5), NiMo/Al_2O_3 and Pt/Al_2O_3.
6. The air inside the autoclave was purged by hydrogen gas for three times, then pressure in the autoclave was held with hydrogen gas to avoid solvent vaporization.
7. After the autoclave was heated to the reaction temperature, the reaction was held then the autoclave was cooled to room temperature quickly by cool water.
8. All the products including gas, liquid and residue were collected for analysis and conversion calculation.

Table 3.2 The proximate and ultimate analyses of the giant leucaena wood.

Proximate analysis (wt%)	
Moisture	9.69
Volatile	79.48
Ash	2.06
Fixed carbon	8.78
Ultimate analysis (wt%)	
C	49.99
H	6.188
O	43.019
N	0.803

9. The separation process was begun after the reaction was cooled down to room temperature, shown in Fig 3.2.
10. The gaseous products were removed from the autoclave and then the autoclave was opened.
11. The solid and liquid products were separated by vacuum filtration then the solid product or residue was dried at 110 ^{0}C for 12 hours to calculate the conversion.
12. The liquid products including oil and decane were separated by rotary evaporator under vacuum at 80 ^{0}C.

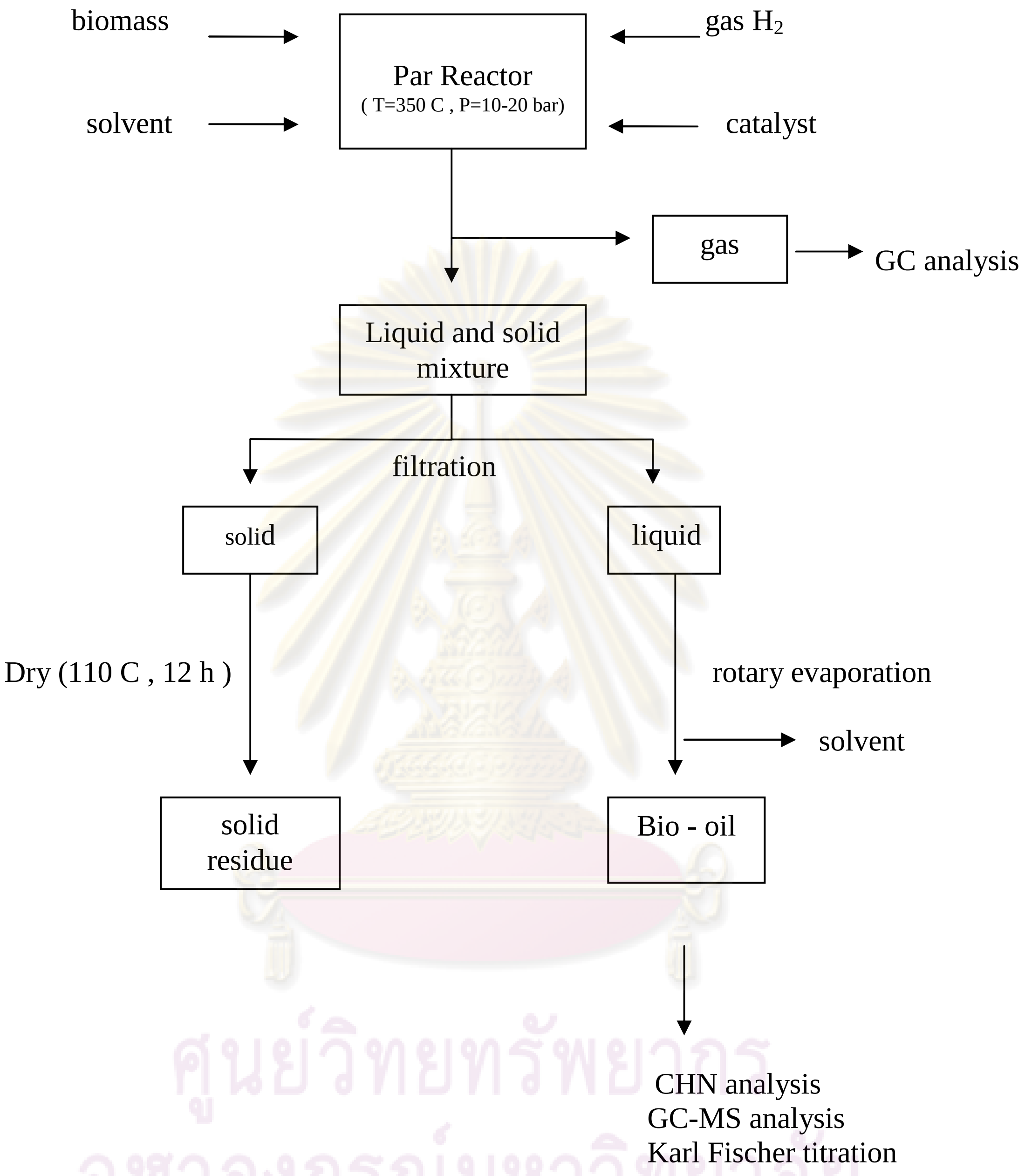


Figure 3.2. The diagram for separation of liquid phase pyrolysis products.

3.3.1 The influence of the parameters on the liquid-phase pyrolysis process.

The effect of the parameters on the oil yield and oxygen content was investigated listed as follows:

1. The effect of reaction temperature (250^{o}C, 300^{o}C, 350^{o}C and 400^{o}C).
2. The effect of catalysts (ZSM-5, Pt/Al_2O_3 and NiMo/Al_2O_3).
3. The effect of catalysts dosage (1 wt%, 5 wt%, 10wt% and 20 wt%).
4. The effect of reaction time (30 minutes, 1 hour, 2 hours and 4 hours).
5. The effect of hydrogen pressure (5 bar, 10 bar, 20 bar and 30 bar).

3.4 Product analysis.

3.4.1 Gas chromatography-mass spectrometry (GC-MS)

Bio-oill was analyzed on the GC-MS QP2010 series instrument. The GC column was 30 m x 0.25 mm x 0.25 µm with helium as the carrier gas. The column oven was programmed with starting temperature at 40 ^{0}C for 2 minutes with heat rate 15 ^{0}C/min to 230 ^{0}C and hold for 5 minutes. After a solvent cut time of 2 minutes, full scan mass spectra were acquired from 40 – 700 m/z. The identification of the peaks was based on computer matching of the mass spectra with the National Institute of Standards and Technology (NIST) library.

3.4.2 CHN analysis

The elemental composition, carbon (C), hydrogen (H) and nitrogen (N) of wood sample along with bio-oil products were analyzed with LECO CHN-2000 Analyzer, and the error of the equipment is within ±0.7%. The composition of O estimated by the assumption that only the elements C,H,O and N are contained in wood.

3.4.3 Gas chromatography

Gaseous products were analyzed by GC-2014 from Shimadzu to analyze the amount and composition of gaseous products. The condition used for analyzing shown below in Table 3.3.

Table 3.3 The optimum condition of gas chromatography.

Carrier gas	He 99.999%
Column	Unibeads C packed
Injector temperature	120°C
Column temperature	Temperature program 50°C 3min 180°C (20°C/min) 180°C 8min
Detector temperature	200°C
Detector	Thermal conduct detector (TCD)

3.4.4 Karl Fischer titration

Mettler Toledo volumetric Karl Fischer compact titrator V20 was used in this experiment to measure the amount of water in the oil product. It can determine from 100 ppm to 100% water, quickly and precisely.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The effect of catalyst types on the yield and oxygen content.

The effect of various catalysts on oil yield and oxygen content was investigated at reaction temperature of 350^oC, initial hydrogen pressure of 10 bar, residence time of 2 hours and 10 wt% of catalyst to compare the effect of each type of catalyst and also two and three different types of catalysts were tested to work together to obtain the maximum oil yield and the lowest oxygen content. The best result of catalyst type will be used in the next step to vary other parameters (reaction temperature, residence time, catalyst dosage, initial pressure of hydrogen) to find the optimum condition for producing bio-oil with high oil yield and low oxygen content.

Table 4.1 Bio-oil and char yields obtained from liquid phase pyrolysis with different type of catalysts.

% **Yield**								
Catalyst types	***Non-catalyst***	***ZSM-5***	***NiMo/ Al_2O_3***	***Pt/Al_2O_3***	***ZSM-5 + NiMo/ Al_2O_3***	***ZSM-5 + Pt/Al_2O_3***	***NiMo/ Al_2O_3 + Pt/Al_2O_3***	***ZSM-5 + NiMo/ Al_2O_3 + Pt/Al_2O_3***
Char	50.50% ± 1.25	47.50% ± 0.94	42.30% ± 1.53	44.40% ± 0.73	45.20% ± 0.42	41.90% ± 0.51	38.30% ± 0.52	41.90% ± 1.12
Bio-oil	3.90% ± 0.24	4.00% ± 0.15	4.30% ± 0.21	5.30% ± 0.16	4.50% ± 0.14	4.70% ± 0.18	5.00% ± 0.22	4.40% ± 0.15

Condition : temperature 350^oC, hydrogen pressure 10 bar, 10 wt% of catalyst/biomass, residence time 2 hours.

From table 4.1, there were insignificant differences on oil yields with different type of catalyst used. The oil yield ranged from 3.90 wt% in the non-catalytic condition to 5.30 wt% in the presence of Pt/Al_2O_3 as catalyst. The lack of oil yield is thought to be partially due to loss in the oil separation from decane solvent during the evaporation. Biomass feedstock also affected to oil yield because major biomass components such as lignin, hemicelluloses and cellulose behaved differently to thermal degradation. In general, presence of high cellulose and hemicelluloses contents in biomass yielded more bio-oil. Table 4.2 showed oil and char yield obtained from different type of biomass, Giant Leucaena, sawdust, rice straw and algae. Algae showed the highest oil yield that might be due to higher cellulose and hemicelluloses contents than Giant Leucaena, rice straw and sawdust, respectively.

Table 4.2 Bio-oil and char yields obtained from liquid phase pyrolysis with different type of biomass.

Yield (wt%)				
Biomass types	Giant leucaena	Algae	Rice straw	Sawdust
Bio-oil	8.6 ± 0.22	16.5 ± 0.41	5.9 ± 0.28	4.9 ± 0.22
Char	34.8 ± 1.18	31.3 ± 1.47	41.3 ± 1.28	43.8 ± 0.97

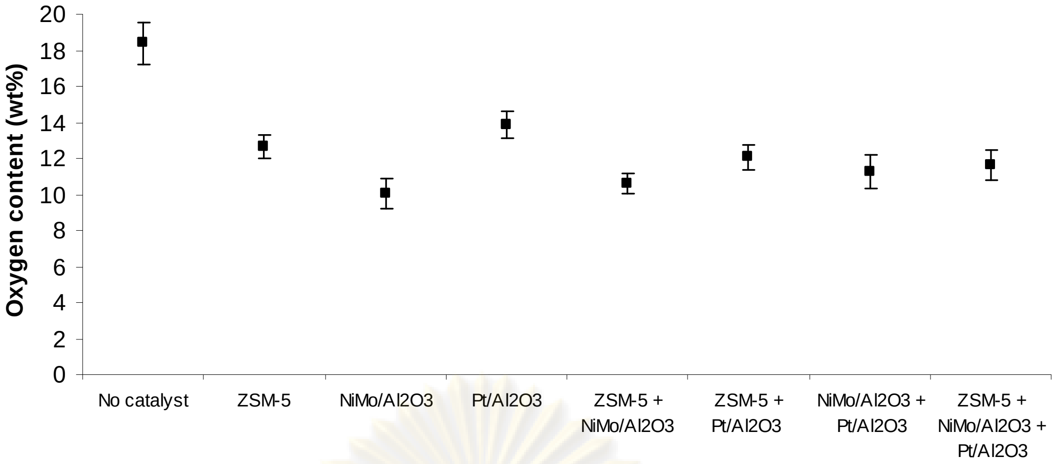
Condition ; temperature of 400°C, initial hydrogen pressure of 10 bar, residence time of 2 hours and 10 wt% of $NiMo/Al_2O_3$

Figure 4.1 showed that the presence of catalysts had significant effect on oxygen content. Non-catalytic condition gave the highest oxygen content of 18.40 wt%, whereas catalytic condition with $NiMo/Al_2O_3$ gave the lowest oxygen content of 10.02 wt%. Based on literature reviews [24], [22], [4], [19], it was summarized that $NiMo/Al_2O_3$ which is used as an industrial hydrotreating catalyst was more active in hydrodeoxygenation and hydrogenation than ZSM-5 and Pt/Al_2O_3.

Table 4.3 The water content in bio-oil and decane after evaporation.

Water content (wt%)								
Catalyst types	Non catalyst	ZSM-5	$NiMo/Al_2O_3$	Pt/Al_2O_3	ZSM-5 + $NiMo/Al_2O_3$	ZSM-5 + Pt/Al_2O_3	$NiMo/Al_2O_3$ + Pt/Al_2O_3	ZSM-5 + $NiMo/Al_2O_3$ + Pt/Al_2O_3
Bio-oil	0.0741 ± 0.008	0.0531 ± 0.013	0.0424 ± 0.007	0.0542 ± 0.014	0.0571 ± 0.021	0.0317 ± 0.014	0.0623 ± 0.009	0.0695 ± 0.012
Decane	0.4821 ± 0.016	0.4311 ± 0.085	0.6084 ± 0.086	0.5561 ± 0.081	0.5361 ± 0.l02	0.5724 ± 0.093	0.4182 ± 0.124	0.6731 ± 0.071

Condition : temperature 350°C, hydrogen pressure 10 bar, 10 w%t of catalyst/biomass, residence time 2 hours.



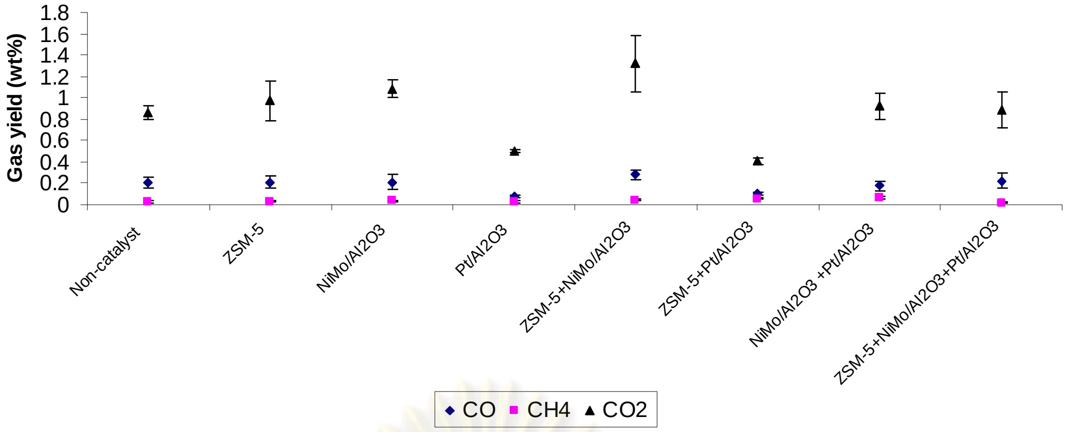
Condition : temperature 350^{o}C, hydrogen pressure 10 bar, 10 wt% of catalyst/biomass, residence time 2 hours.

Figure 4.1 The oxygen content of bio-oil from various catalysts.

In this research, the water content in the oil product was measured by Karl Fischer which showed a very small amount of water in oil and part of water was converted by water gas shift reaction which converted water and carbon monoxide to hydrogen and carbon dioxide. ZSM-5 + Pt/Al_2O_3 seem to be the best catalyst to get lowest water content in oil.

Figure 4.2 showed that the gas yields that produced from liquid-phase pyrolysis were CO, CO_2 and CH_4. The CO_2 was the most abundant product in the contrast the formation of CO was negligible due to water-gas shift activity of catalysts used in this research mean that CO was mostly shifted to CO_2 [21]. The amount of CO and CO_2 could be refered to decomposition of oxygenate molecules via decarboxylation and/or hydrodeoxygenation related to the result from CHN analysis of oxygen content of liquid-phase pyrolysis in the presence of $NiMo/Al_2O_3$ and ZSM-5. Both catalysts gave the oil with the lowest oxygen content, 10.02 wt% and 12.64 wt% respectively, and also gave high CO_2 and CO content [13]. Figure 4.2 also showed that when used both of $NiMo/Al_2O_3$ and ZSM-5 together, the gas yield reached to the highest amount compared to other conditions.

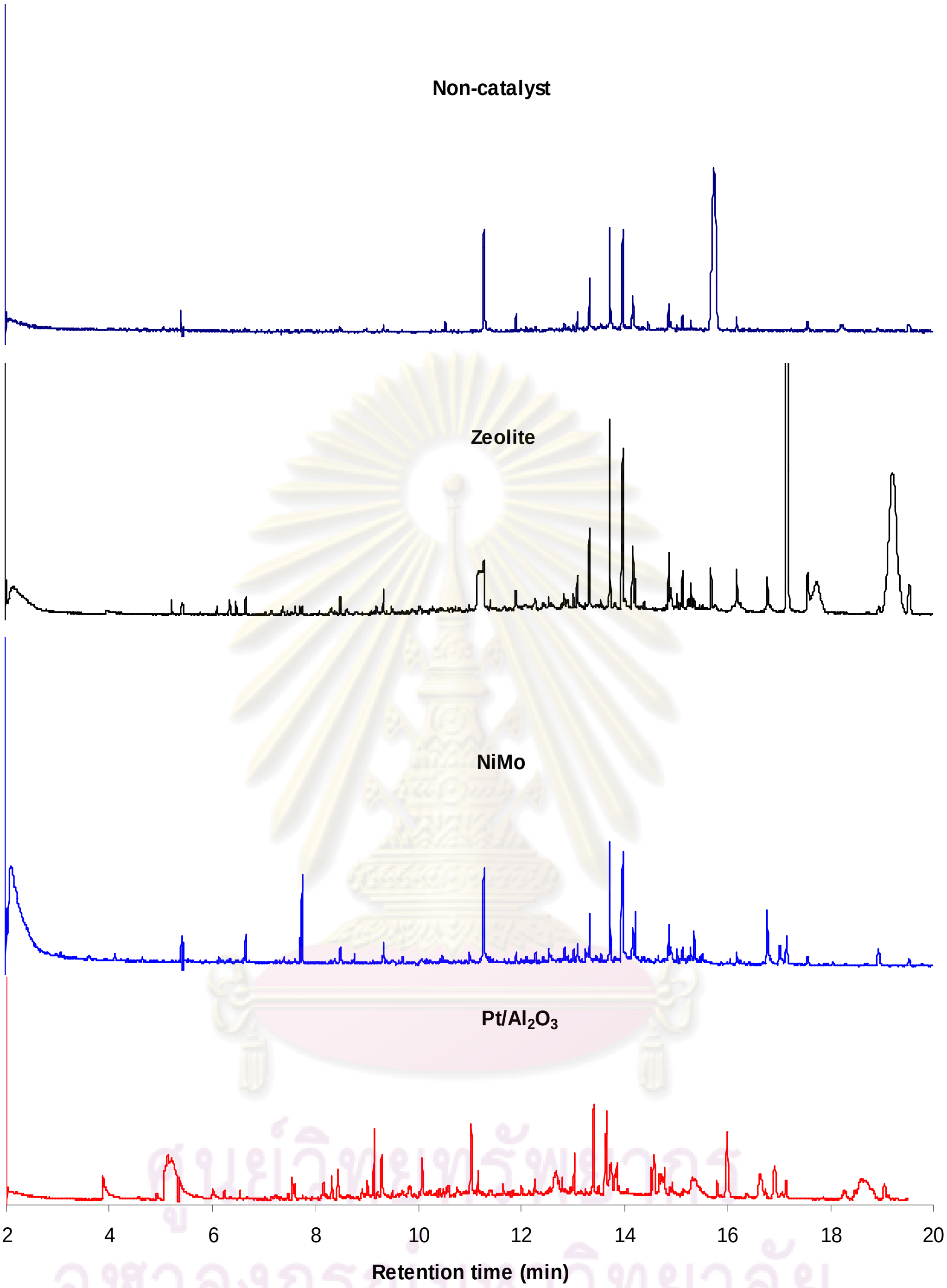
Water gas shift reaction $H_2O + CO \rightarrow H_2 + CO_2$ (4.1)



Condition : temperature 350^{o}C, hydrogen pressure 10 bar, 10 %wt of catalyst/biomass, residence time 2 hours.

Figure 4.2 The gas yields of liquid-phase pyrolysis with various catalysts.

All of the components found by GC-MS could be divided into aromatic and non-aromatic compounds as shown in Figure 4.3. Despite the different catalysts used, several components with the same compositions were obtained, including 2-methoxy-4-propyl-phenol (RT = 9.141), diethyl phthalate (RT = 11.030), 1,2-benzenedicarboxylic acid (RT = 13.020) and hexadecanoic acid (RT = 13.407). These results indicated that the resemblances in the liquid-phase pyrolysis mechanism.



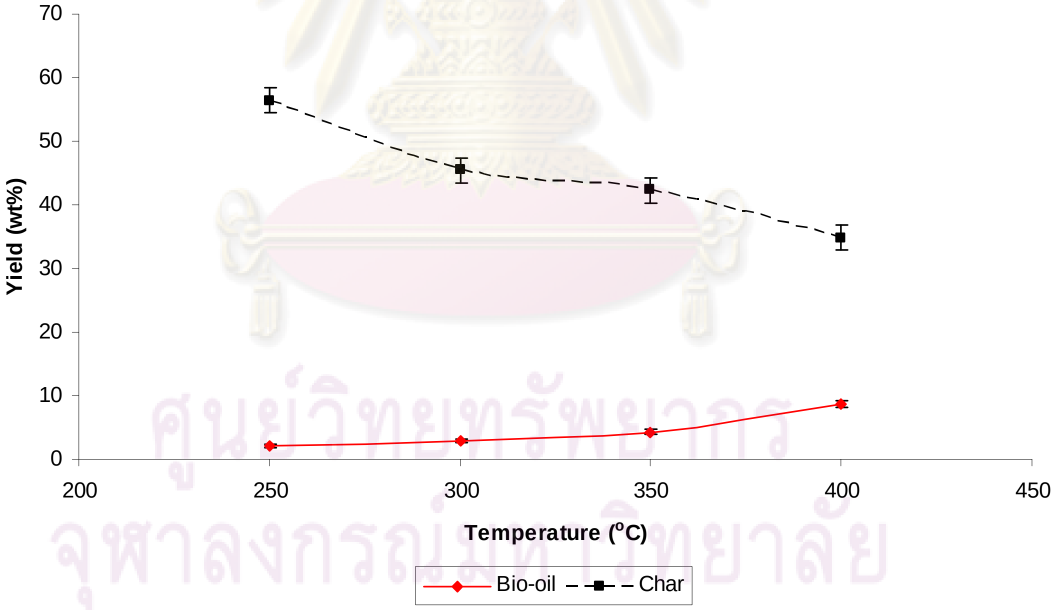
Condition : temperature 350°C, hydrogen pressure 10 bar, 10 %wt of catalyst/biomass, residence time 2 hours.

Figure 4.3 The GC-MS results of oil product from liquid-phase pyrolysis in the presence of various catalysts.

Figure 4.3 showed GC-MS results of the oil products from liquid-phase pyrolysis in the presence of NiMo/Al_2O_3, ZSM-5 and Pt/Al_2O_3. NiMo/Al_2O_3 showed less peaks of phenol and phenolic derivatives than ZSM-5 and Pt/Al_2O_3 with more straight chain products consisting of nonanal (RT = 6.542), tridecane (RT = 7.567), decanal (RT = 7.608), and heneicosane (RT = 13.892). Comparing non-catalytic process to catalytic process, GC-MS results indicated that liquid-phase pyrolysis without catalysts exhibited less product distribution and more oxygenated compounds than catalytic liquid-phase pyrolysis mainly consisting of diethyl phthalate (RT = 11.033), 1,2-benzenedicarboxylic acid (RT = 13.025) and 9-Octadecenoic acid (RT = 13.408) .

4.2 The effect of reaction temperature the yield and oxygen content.

The influence of temperature on the compounds existing in liquid product obtained from liquid-phase pyrolysis of Giant leucaena wood was examined in relation to the yield, oxygen content and composition of the oil products. The experiment was performed at reaction temperatures of 250, 300, 350 and 400°C in the presence of NiMo/Al_2O_3 (10 wt%) as a catalyst, residence time of 2 hours and initial hydrogen pressure of 10 bar.

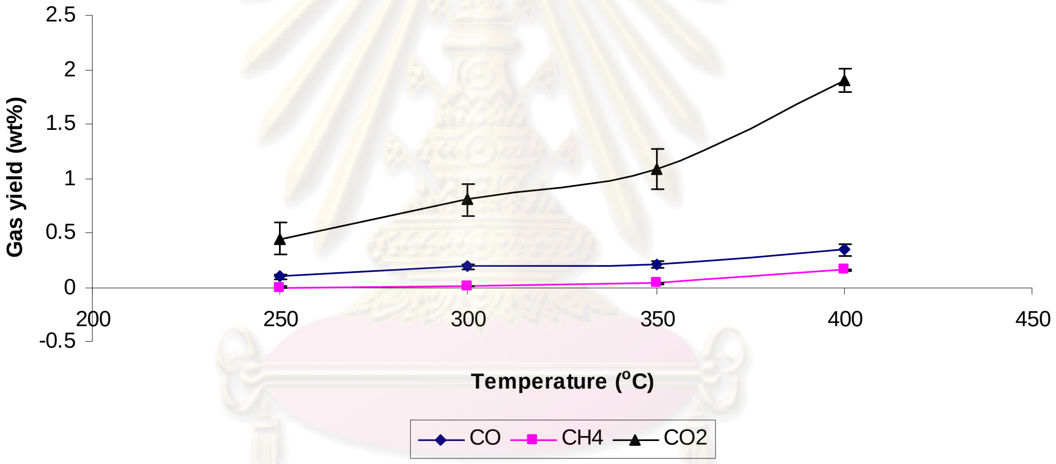


Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, residence time 2 hours.

Figure 4.4 The bio-oil and char yields obtained from liquid-phase pyrolysis with different reaction temperatures.

Influence of temperature in the yield is shown in the figure 4.4. The oil yield increased from 2.10 wt% to 8.60 wt% when the temperature increased from 250 to

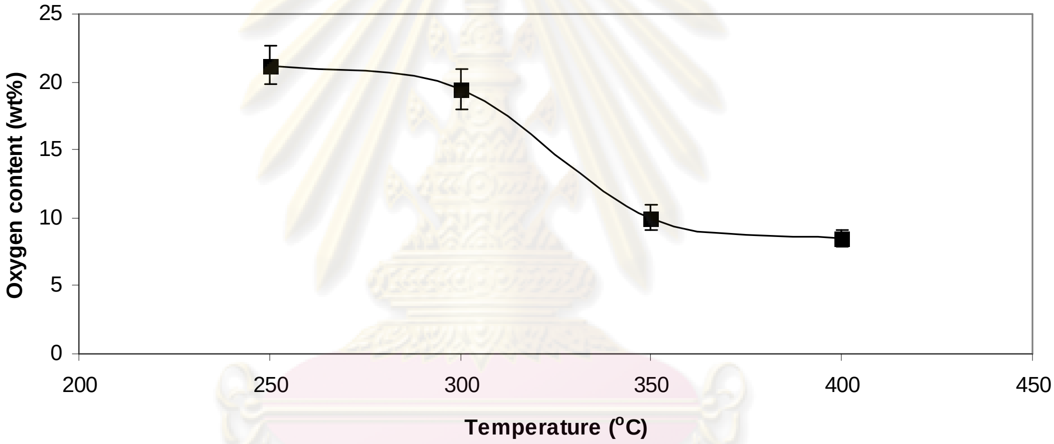
400^{o}C in the contrast, the char yield decreased from 56.40 wt% to 34.80 wt%. It could be explained by the higher reaction temperature, the easier in decomposition of biomass. When the temperature is larger than the activation energies for bond breaking, the extensive depolymerization occured. This increases both concentration of free radicals and probability of repolymerization of fragmented species. At low reaction temperature, 250^{o}C, depolymerization occured with very low rate so the result showed high char yield, because biomass was not decomposed result in less oil yield compared to higher reaction temperature. The reaction temperature also effect to gas yield, higher reaction temperature increased the gas yield which is consisted of CO_2, CO and CH_4. This higher gas yield may be due to the secondary decomposition from light oil to gaseous products that became active at high temperature which lead to the formation of gas [13].



Condition : hydrogen pressure 10 bar, 10 %wt of $NiMo/Al_2O_3$, residence time 2 hours.

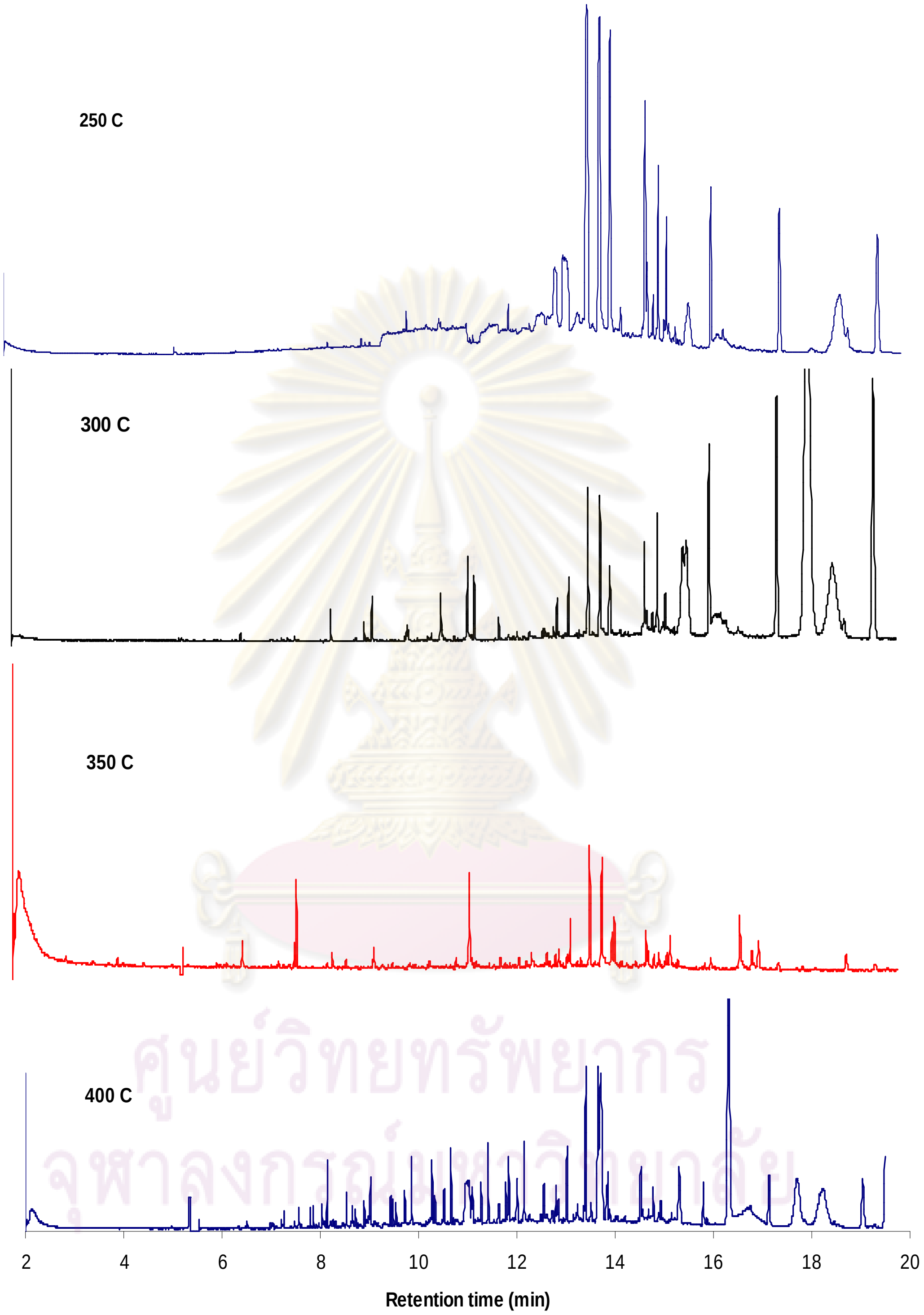
Figure 4.5 The gas yields of liquid-phase pyrolysis with different reaction temperature.

The influence of temperature to oxygen content was shown in figure 4.6. Oxygen content decreased from 21.24 wt% to 8.50 wt% as temperature increased from 250 to 400^{o}C due to high temperature also facilitated the removal of oxygen by both of deoxygenation and catalytic cracking reactions. These could be confirmed by GC-MS results in figure 4.7. Reaction temperature of 250^{o}C and 300^{o}C showed less products due to incomplete decomposition and the major products of 2-methoxy-4-(1-propenyl)-phenol (RT = 9.858), 2,6-dimethoxy-4-(2-propenyl)-phenol (RT = 11.475), heneicosane (RT = 12.492), 5-tert-butyl-1,2,3-benzenetriol (RT = 10.492) and 1-(2,6-dihydroxy-4-methoxyphenyl)-1-butanone (RT = 12.350), which are oxygenated compounds. All of these peaks that appeared at reaction temperature of 250^{o}C and 300^{o}C almost completely disappeared at reaction temperature of 350^{o}C to gaseous products and new compounds which were less oxygenated and complex compounds such as nonanal (RT = 6.542), tridecane (RT = 7.567), decanal (RT = 7.608), and heneicosane (RT = 13.892). GC-MS result of 400^{o}C showed the major peaks of long chain hydrocarbon such as dodecane (RT = 7.558), tridecane (RT = 7.558), 2-methyl-5-propyl-nonane (RT = 7.800), 3-methyl-undecane (RT = 7.858) and heptadecane (RT = 9.475) and also showed less phenol derivatives due to thermal cracking to yield smaller molecules and less oxygenated compounds.



Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, residence time 2 hours.

Figure 4.6 The oxygen content of bio-oil from different reaction temperature.

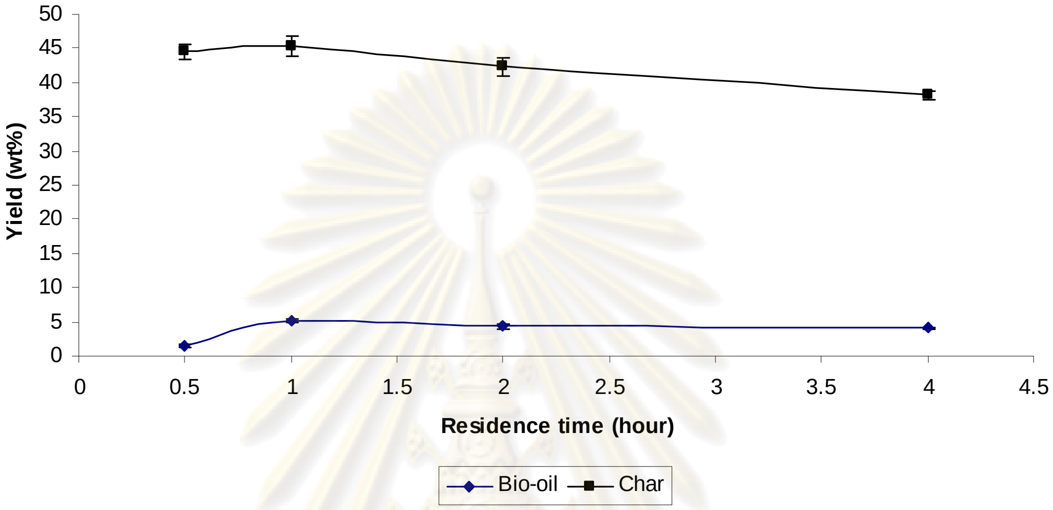


Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, residence time 2 hours.

Figure 4.7 The GC-MS results of oil product from liquid-phase pyrolysis in the presence of various reaction temperatures.

4.3 The effect of residence time on the yield and oxygen content.

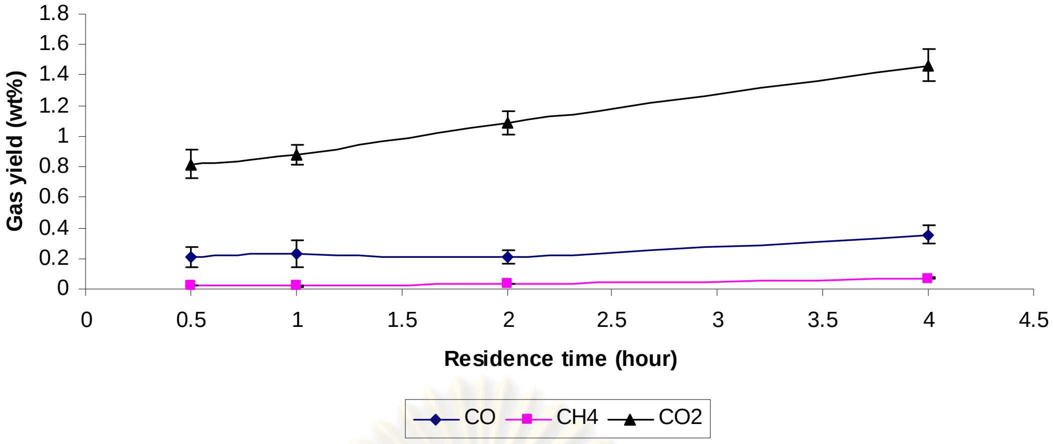
The influence of residence time on the compounds existing in liquid product obtained from liquid-phase pyrolysis of Giant leucaena wood was examined. The experiment was performed at residence time of 30 minutes, 1 hour, 2 hours and 4 hours in the presence of NiMo/Al_2O_3 (10 wt%) as a catalyst, reaction temperature of 350^{o}C and initial hydrogen pressure of 10 bar.



Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, temperature 350^{o}C.

Figure 4.8 The yields of liquid-phase pyrolysis with different resident time.

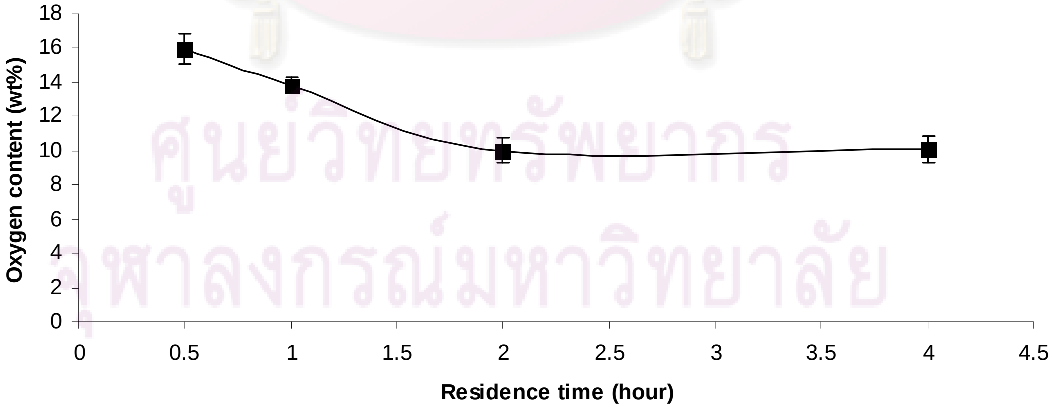
The results showed that increasing residence time will increase oil yield to the maximum point at 1 hour and then slightly decrease in oil yield with longer resident time. At the residence time of 30 minutes the oil yield was the lowest only 1.5 wt% compared to the residence time of 1 hour which reached the highest oil yield of 5.2 wt% . In contrast, char yield decreased from 45.40 wt% to 38.20 wt% when increasing the residence time from 30 minutes to 4 hours, respectively, resulting from the decomposition of oil to form gaseous products occurred. In figure 4.9, gas yield (CO, CO_2 and CH_4) increased when increasing the residence time. The longer residence time gave more chance for the secondary reaction that could convert heavy intermediates to liquids, gases, or residues products.



Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, temperature 350^oC.

Figure 4.9 The gas yields of liquid-phase pyrolysis with different residence time.

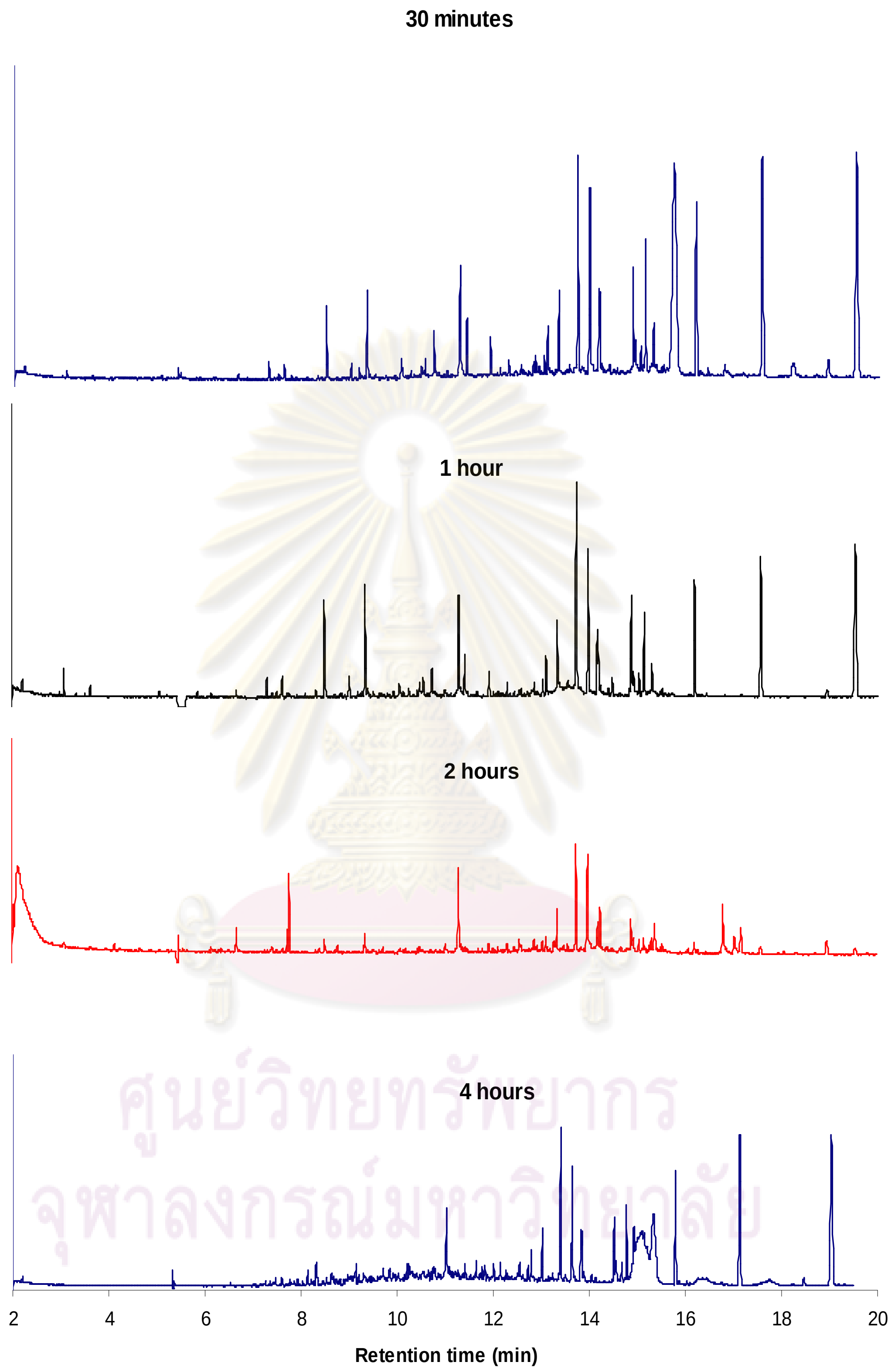
Figure 4.10 showed the oxygen content of different residence time. Oxygen content decreased when increasing the residence time to the minimum point of 2 hours and then showed insignificant in decreasing oxygen content. The oxygen content decreased from 15.91 wt% to 13.82 wt% to 10.02 wt% and 10.07 wt% with increasing in residence time from 30 minutes to 4 hours, respectively. It is clear that liquid-phase pyrolysis with 2 hours was an appropriate residence time to obtain low oxygen content products.



Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, temperature 350^oC.

Figure 4.10 The oxygen content of bio-oil from different residence time.

The compositions of oil products with different resident times were analyzed by GC-MS shown in figure 4.11. For GC-MS results of liquid-phase pyrolysis with different residence time showed some components with the same compositions including ethyloleate (RT = 14.933), octadecanoic acid, methyl ester (RT = 14.675), 9-octadcanoic acid, methyl ester (RT = 14.558), hexadecanoic acid, ethyl ester (RT = 13.850), dibutyl phthalate (RT = 13.650), 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester (RT = 13.025), isopropyl myristate (RT = 12.725), 3,8-dimethylundecane (RT = 12.550), and diethyl phthalate (RT = 11.025). It was obvious that GC-MS results of residence time at 30 minutes and 1 hour showed significantly peak of 2-methoxy-4-propyl-phenol (RT = 9.142) and 4-ethyl-2-methoxy-phenol (RT = 8.317) which were disappeared by cracking reaction at residence time at 2 and 4 hours. The residence time of 2 hours gave new compounds of tridecane (RT = 7.567) and decanal (RT = 7.608) that were decomposed and disappeared with the residence time at 4 hours, resulting in less product distribution due to longer residence time facilitated the formation of gaseous products.

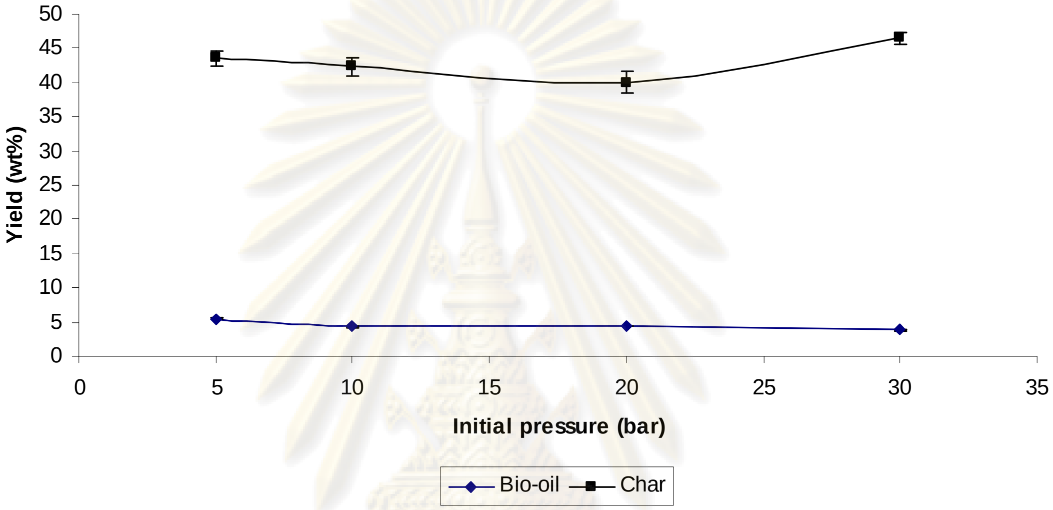


Condition : hydrogen pressure 10 bar, 10 %wt of NiMo/Al_2O_3, temperature 350^oC.

Figure 4.11 The GC-MS results of oil product from liquid-phase pyrolysis in the presence of various residence times.

4.4 The effect of initial pressure of hydrogen on the yield and oxygen content.

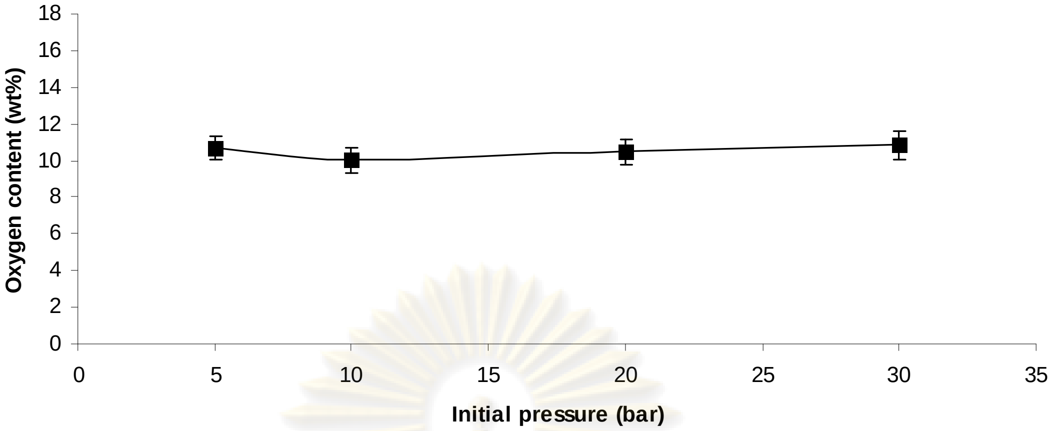
The influence of initial pressure of hydrogen on the compounds existing in liquid product obtained from liquid-phase pyrolysis of Giant leucaena wood was examined in relation to the yield, oxygen content and composition of the oil products with four different initial pressures of 5 , 10, 20 and 30 bar in the presence of $NiMo/Al_2O_3$ (10 wt%) as a catalyst, reaction temperature of 350°C and residence time of 2 hours.



Condition : residence time 2 hours, 10 %wt of $NiMo/Al_2O_3$, temperature 350 °C.

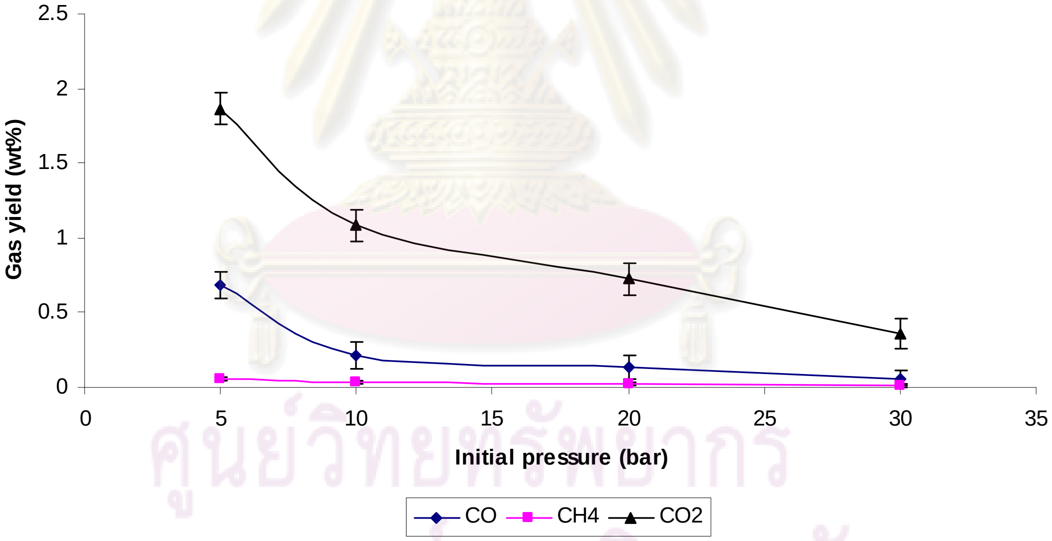
Figure 4.12 The yields of liquid-phase pyrolysis with different initial pressures of hydrogen.

Figure 4.12 showed that increase in initial pressure of hydrogen showed insignificant difference in oil and char yield. The initial pressures of hydrogen of 5, 10, 20, 30 bar gave 5.40 wt%, 4.30 wt%, 4.40 wt% and 3.90 wt% for oil yield and 43.60 wt%, 42.30 wt%, 40.00 wt% and 46.50 wt% for char yield, respectively. The oil yield at initial pressure of 30 bar was less than initial pressure of 5 bar although higher initial pressure was applied which could be attributed to blocking of catalyst active sites by increasing solvent density [13] and normally using hydrogen gas or other reducing gases were to stabilize the free radicals to inhibit repolymerization. In this case, high pressure of 30 bar inhibited the free radicals to form oil product by stabilizing free radicals while it was not decomposed completely and it was still complexes molecules that may cause more char yield. Figure 4.14 showed that initial pressure at 5 bar had the highest gaseous products. The oxygen content also showed that the initial pressures of 5, 10, 20 and 30 bar exhibited 10.67 wt%, 10.02 wt%, 10.50 wt% and 10.85 wt% of oxygen, respectively.



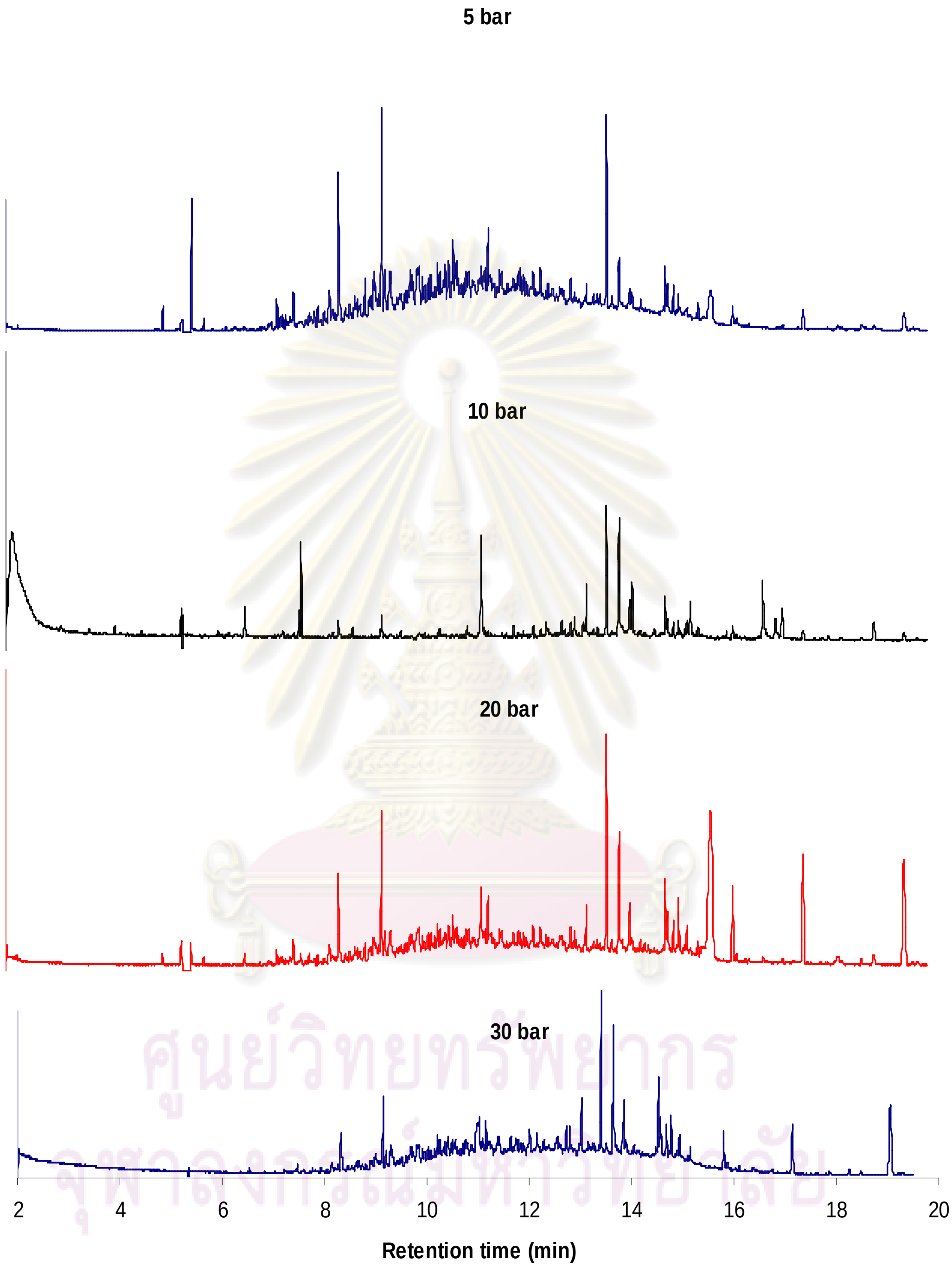
Condition : residence time 2 hours, 10 %wt of NiMo/Al_2O_3, temperature 350^{o}C.

Figure 4.13 The oxygen content of bio-oil from different initial pressures.



Condition : residence time 2 hours, 10 %wt of NiMo/Al_2O_3, temperature 350^{o}C.

Figure 4.14 The gas yields of liquid-phase pyrolysis with different initial pressures of hydrogen.



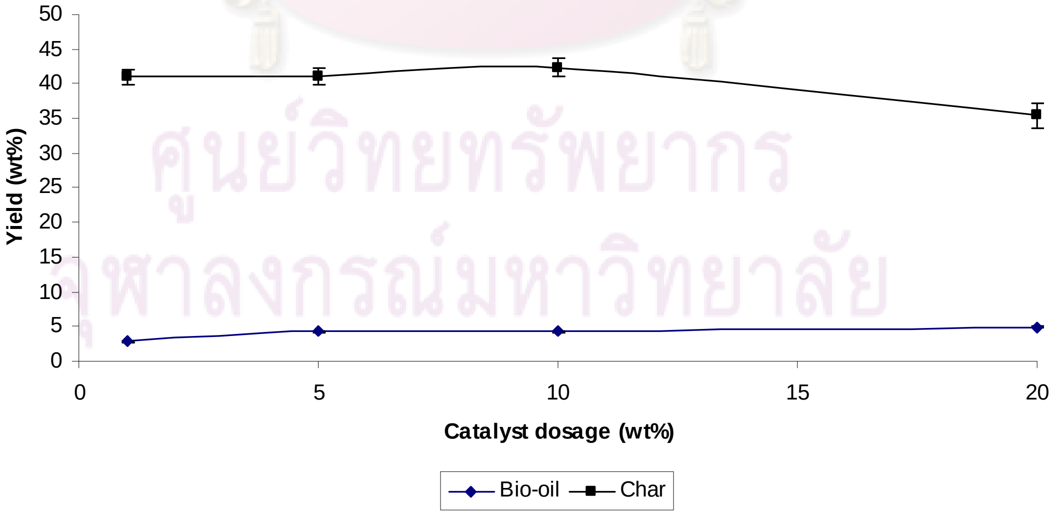
Condition : residence time 2 hours, 10 %wt of NiMo/Al_2O_3, temperature 350^oC.

Figure 4.15 The GC-MS results of oil product from liquid-phase pyrolysis in the presence of various initial pressures of hydrogen.

According to GC-MS analysis results in figure 4.15, the compounds which obtained from different initial pressures almost had the same compositions. The major compounds for all tests were 4-ethyl-2-methoxy-phenol (RT = 8.325), 2,6-dimethyl-1,4-benzenediol (RT = 9.008), 2-methoxy-4-propyl-phenol (RT = 9.142), 2,3,5-trimethyl-1,4-benzenediol (RT = 9.683), 2,5-dimethyl-1,4benzenedicarboxaldehyde (RT = 9.917), 2,3-dimethyl-1H-indole (RT = 10.200), 6-methyl-5-(1-methylethyl)-5-hepten-3-yn-2-ol (RT = 10.350), 5-methoxy-2,3,4-trimethyl-phenol (RT = 10.408), 1,2,3-trimethoxy-5-methyl-benzene (RT = 10.492), diethyl phthalate (RT = 11.033), 3-methyl-4-propyl-2,4-hexadienedioic acid (RT = 11.158), 2,5-dimethyl-3-phenylfuran (RT = 11.733), hexadecanoic acid, methyl ester (RT = 13.408), 1,2-benzenedicarboxylic acid, butyl octyl ester (RT = 13.650), hexadecanoic acid, ethyl ester (RT = 13.850), 9-octadecenoic acid (RT = 14.567).

4.5 The effect of catalyst dosage on the yield and oxygen content.

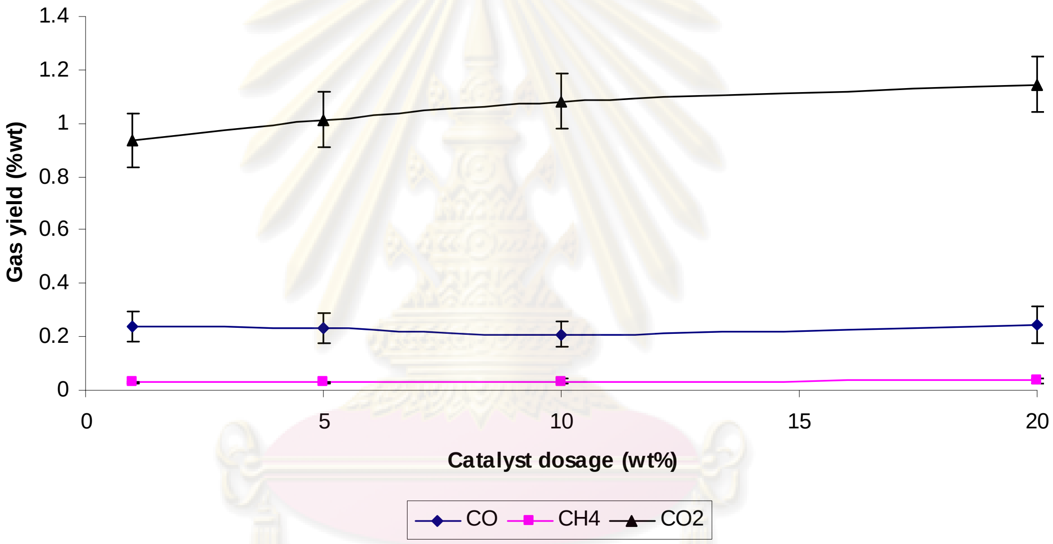
The influence of catalyst dosage on the compounds existing in liquid product obtained from liquid-phase pyrolysis of Giant leucaena wood was examined in relation to the yield, oxygen content and composition of the oil products with four different amount of catalysts of 1 , 5, 10 and 20 wt% with initial pressure of hydrogen of 10 bar, reaction temperature of 350^{o}C and residence time of 2 hours.



Condition : residence time 2 hours, initial pressure 10 bar, temperature 350^{o}C.

Figure 4.16 The yields of liquid-phase pyrolysis with different amount of catalysts.

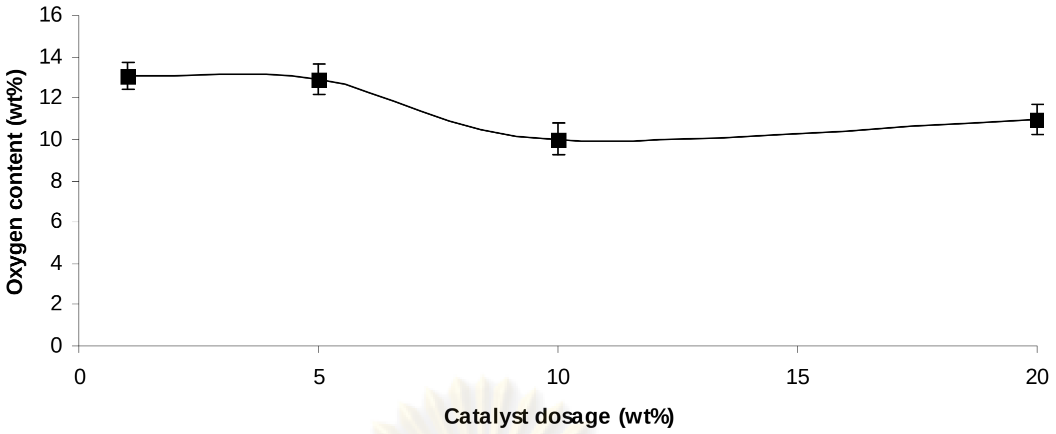
Increasing the catalyst dosage resulted in a increment of oil yield from 2.80 wt% with NiMo/Al_2O_3 1 wt% to 4.90 wt% with NiMo/Al_2O_3 20 wt%. It was also observed that increasing in catalyst dosage affected to decrease of char yield especially at NiMo/Al_2O_3 20 wt% char yield showed significant decreasing because large amount of catalyst dosage caused more depolymerization reaction to decompose complex molecules of biomass and form oily compounds. Figure 4.17 showed the gas yield obtained from liquid-phase pyrolysis with different catalyst dosages indicating that the increase in catalyst dosage resulted in higher gas yield. According to the information above, it can be concluded that more catalyst dosage promoted depolymerization process to yield more liquid and gaseous products.



Condition : residence time 2 hours, initial pressure 10 bar, temperature 350°C.

Figure 4.17 The gas yields of liquid-phase pyrolysis with different catalyst dosage.

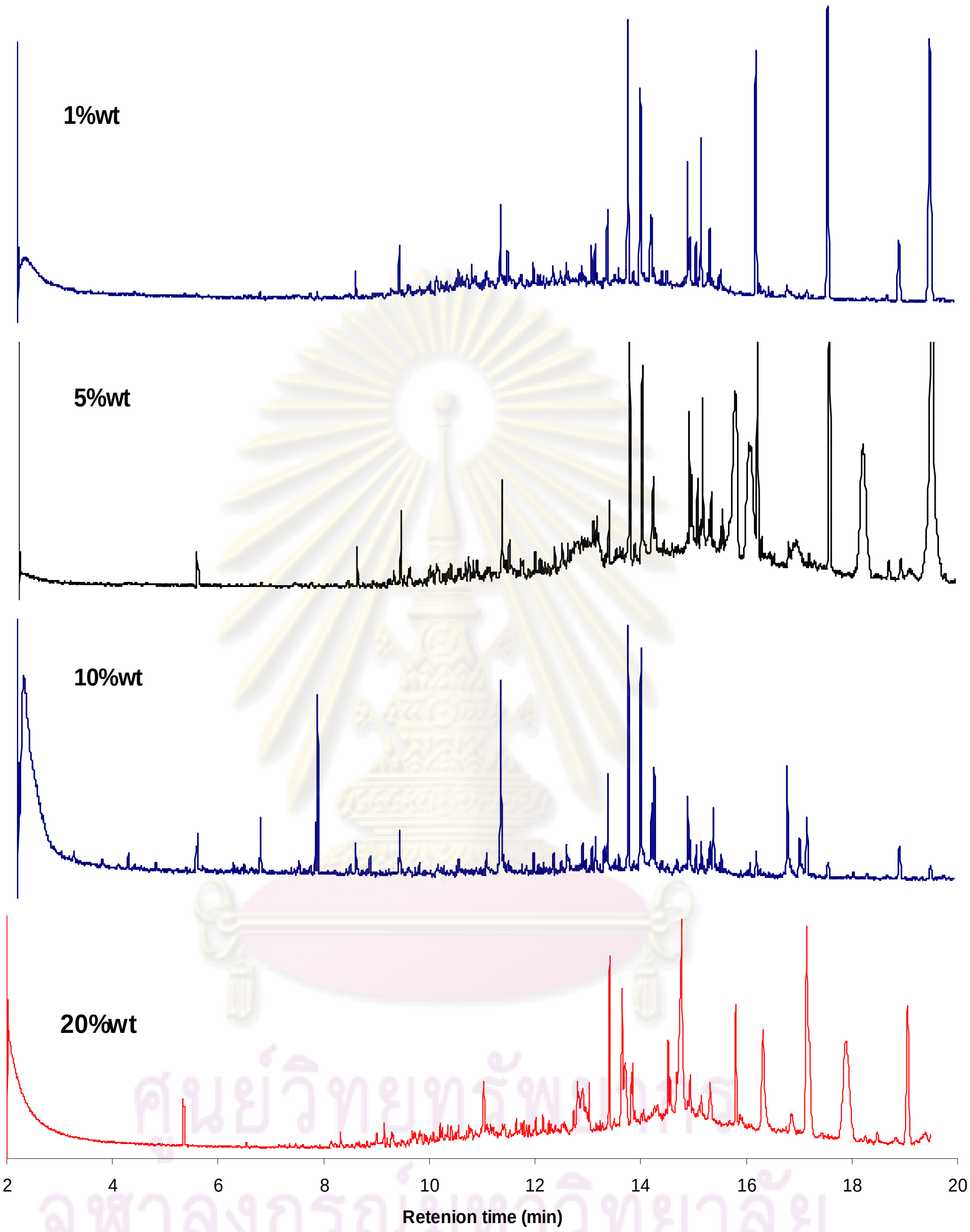
In figure 4.18, the oxygen content decreased to minimum value of 10.02 wt% with catalyst dosage 10 wt% and seem to be constant with more catalyst dosage. More catalyst dosage could promote both of cracking and hydrodeoxygenation by increasing gas yield of CO_2, CO and water



Condition : residence time 2 hours, initial pressure 10 bar, temperature 350^{o}C.

Figure 4.18 The oxygen content of bio-oil from different catalyst dosages.

The compositions of oil products were analyzed by GC-MS (figure 4.19) indicating that the increase in catalyst dosage had an effect on the composition of oil product. There were several compounds with the same composition in this case such as 2-methoxy-4-propyl-phenol (RT = 9.142), diethyl phthalate (RT = 11.033), hexadecanoic acid, methyl ester (RT = 13.408), heneicosane (RT = 13.892), 9-octadecanoic acid, methyl ester (RT = 14.525) and ethyl 9-hexadecenoate (RT = 14.933). In the case of 1wt% of catalyst showed more oxygenated compounds and complex molecules such as 2,5-dimethoxybenzyl alcohol (RT = 9.825), 3-(3-methylphenyl)-2-propenoic acid (RT = 9.958), 2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-5-(3-hydroxy-1-propenyl)-7-methoxy-3-benzofuranmethanol (RT = 10.017), 2-[[[2-(4-hydroxyphenyl)ethyl]amino]methyl]-1,4-benzenediol (RT = 10.075), 6-hydroxy-4,4,5,8-tetramethyl-2-chromanone (RT = 10.400) and 1,2,3-trimethoxy-5-methyl-benzene (RT = 10.483) which disappeared with more catalyst dosage due to the decomposition to smaller molecules and oxygen removal.



Condition : residence time 2 hours, initial pressure 10 bar, temperature 350°C.

Figure 4.19 The GC-MS results of oil product from liquid-phase pyrolysis in the presence of various catalyst dosages.

4.6 The effect of reaction gas on the yield and oxygen content.

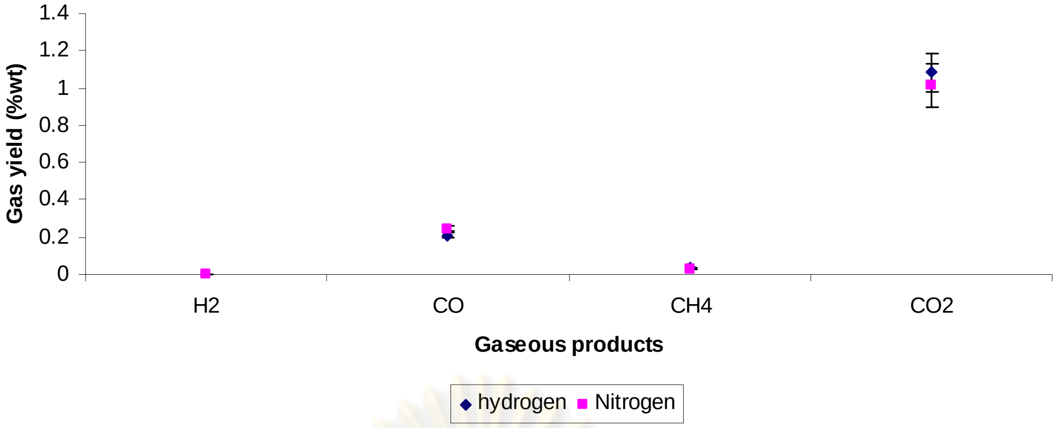
The influence of reaction gas (hydrogen and nitrogen) on the compounds existing in liquid product obtained from liquid-phase pyrolysis of Giant leucaena wood was examined in relation to the yield, oxygen content and composition of the oil products with the condition of $NiMo/Al_2O_3$ 10 wt% and initial pressure of gas at 10 bar, reaction temperature of 350°C and residence time of 2 hours.

Table 4.4 The yields of liquid-phase pyrolysis with different reaction gases.

Yield (wt%)		
Reaction gases / Product	Hydrogen	Nitrogen
Bio-oil	4.30 ± 0.14	8.00 ±0.78
Char	42.30 ±1.02	41.60 ± 1.12

Condition : residence time 2 hours, initial pressure 10 bar, temperature 350°C, 10 %wt of $NiMo/Al_2O_3$.

According to table 4.4 the oil yield with nitrogen was 8 wt% which was higher than that with hydrogen (only 4.30 wt%). The role of reaction gases was generally to stabilize the fragmented product of liquid-phase pyrolysis by inhibition the condensation, cycliczation and re-polymerization of free radicals to reduce the char formation [13]. In this case, hydrogen was very effective for stabilizing the fragmented products and the pyrolysis of biomass normally produced hydrogen via water gas shift reaction. Too much hydrogen as a stabilizer inhibited the formation of the oil products by terminating the free radical. In the other hand, nitrogen an inert gas could not terminate the free radical resulting in high oil yield. Comparing to literature review of study the effect of reactor gases to fast pyrolysis of corncob showed the same result that corncob pyrolysis under N_2 atmosphere gave a yield of oil fraction more than H_2 atmosphere because more vapors were converted into non-condensable gases especially CO_2 in the case of H_2 atmosphere [25].

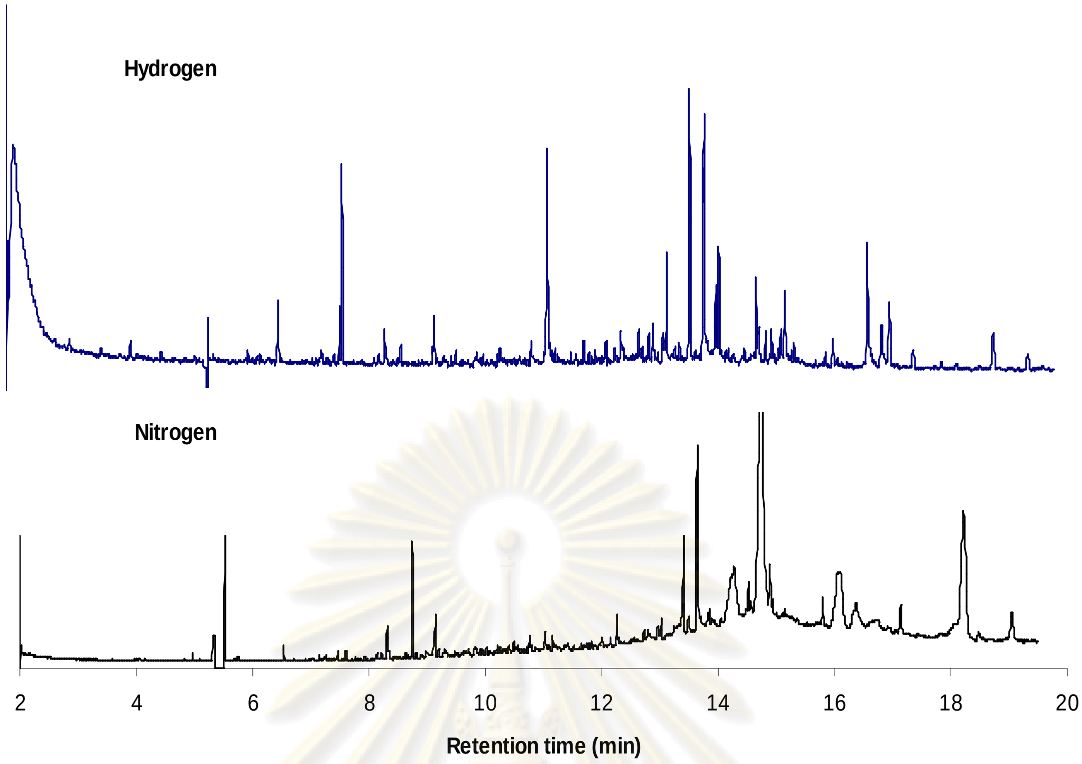


Condition : residence time 2 hours, initial pressure 10 bar, temperature 350°C, 10 %wt of NiMo/Al_2O_3.

Figure 4.20 The gas yields of liquid-phase pyrolysis with different reducing gases types.

In figure 4.20, the CO_2 was the most abundant product in gas yield for both nitrogen and hydrogen cases. It was found that hydrogen was produced in small amount, 0.0012 wt%, in liquid-phase pyrolysis using nitrogen as reaction gas. Figure 4.20 showed that using hydrogen and nitrogen almost had the same amount of gas yield. The influence of reaction gas types on oxygen content was also investigated and it was found that nitrogen exhibited only 8.00 wt% of oxygen content which was slightly lower than hydrogen with 10.02 wt% of oxygen content.

The compositions of oil products were analyzed by GC-MS indicating that some compounds of oil product from liquid-phase pyrolysis with nitrogen had the same composition to hydrogen such as nonanal (RT = 6.533), 4-ethyl-2-methoxy-phenol (RT = 8.317), 2-methoxy-4-propyl-phenol (RT = 9.142), diethyl phthalate (11.033), tetradecanoic acid (RT = 12.258), pentadecanoic acid (RT = 12.958), 1,2-benzenedicarboxylic acid (RT = 13.025), Hexadecanoic acid and methyl ester (RT = 13.4008).



Condition : residence time 2 hours, initial pressure 10 bar, temperature 350°C, 10 %wt of NiMo/Al_2O_3.

Figure 4.21 The GC-MS results of oil product from liquid-phase pyrolysis in the presence of different reaction gases .

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The results have shown that there were insignificant differences on oil yields with different types of catalysts and NiMo/Al_2O_3 used as a catalyst showed the lowest oxygen content and moderate oil yield which were 10.02 wt% and 4.30 %wt, respectively. The major parameters that affected on yield, oxygen content and compositions of bio-oil were reaction temperature, residence time, catalyst dosage, type of reaction gases and initial pressures. Temperature was the most influencing parameter for liquid oil yield and/or biomass conversion. Increase in temperature affected to increase in oil and gas yield and decrease in oxygen content because increase in temperature extended biomass fragmentations and high temperature also facilitated removal of oxygen by both of deoxygenation and catalyst cracking. Reaction temperature of 400^{o}C showed the highest oil yield of 8.60 %wt, as well as the lowest oxygen content of 8.50 wt%. The GC-MS analysis showed that all of peaks that appeared at reaction temperature at 250^{o}C and 300^{o}C almost completely disappeared at reaction temperature of 400^{o}C which showed the major peaks of long chain hydrocarbon. The residence time also affected to the oil yield and oxygen content. Considering the residence time, the residence time of 2 hour showed the lowest oxygen content (10.02 wt%). Increase in catalyst dosage resulted in a increase of oil yield from 2.80 %wt with NiMo/Al_2O_3 of 1 wt% to 4.90 wt% with NiMo/Al_2O_3 of 20 wt%. It can be concluded that high catalyst dosage and long residence time promoted depolymerization process to yield more liquid product. Increase in initial pressure of hydrogen showed insignificantly difference in oil and char yield. The initial hydrogen pressure of 10 bar showed the lowest oxygen content of 10.02 wt%. The effect of reaction gases showed that nitrogen was a better reaction gas than hydrogen because hydrogen is very effective in stabilizing the free radical and fragmented products to inhibit the formation of the oil products In conclusion, the optimum condition was reaction temperature of 400^{o}C, 10 wt% of NiMo/Al_2O_3, residence time of 2 hours and reaction gas of nitrogen.

5.2 Recommendation

The future research, study of the chemical structure, major organic components formation, the effect of the amount of Ni, Mo and Al_2O_3 on yield and oxygen content and catalytic mechanism for producing low oxygen content with higher oil yield are very important.

REFERENCES

[1] Charles, M. and Akwasi, B. Catalytic pyrolysis-GC/MS of lifnin from several sources. Fuel Processing Technology. 91 (2010): 1446-1458.

[2] Selhan, K., Thallada, B., Akinori, M. and Yusaku, S. Effect of Rb and Cs carbonates for production of phenol from liquefaction of wood biomass. Fuel. 83 (2004): 2293-2299.

[3] Serdar, Y. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management. 45 (2004): 651-671.

[4] Mustafa, B., Mehmet, B., Elif, K. and Havva, B. Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. Energy Conversion and Management. 50 (2009): 3147-3157.

[5] Demirbas, A. Biorefineries for biomass upgrading facilities. [Online]. Available from http://www.springer.com/978-1-84882-720-2. [2009, October 4].

[6] Rebel. Bioenergy [Online]. Available from: http://wiki.lamk.fi/display/rebwp7/Bioethanol+production+of+2nd+generation.[2010, June 8].

[7] Javaid, A. and Nor, A. A review on process condition for optimum bio-oil yield in hydrothermal liquefaction of biomass. Renewable and sustainable Energy Review. 15 (2011): 1615-1624.

[8] Haiping, Y., Rong, Y., Hanping, C., Dong Ho, L. and Chuguang, Z. Characteristics of hemicelluloses, cellulose and lignin pyrolysis. Fuel. 86 (2007): 1781-1788.

[9] Zhang, Q., Chang, J., Wang, T. and Xu, Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Conversion and Management. 48 (2007): 87-92.

[10] Dmitri, B. and Julian, R. Catalytic for conversion of biomass to fuels via pyrolysis and gasification: A review. Catalysis Today. (2011).

[11] Gutierrez, A., Domine, M. and Salantausta, Y. Co-processing of upgraded bioliquids in standard refinery units-fundamentals. Proceedings of the 15th European biomass conference and exhibition, Berlin, 2007.

[12] Carlo, P. and Aldo, B. Biomass to fuel: The role of zeolite and mesoporous materials. Microporous and Mesoporous Materials. (2011).

[13] Javaid, A. and Nor, A. A review on process condition for optimum bio-oil yield in hydrothermal liquefaction of biomass. Renewable and sustainable Energy Review. 15(2011): 1615-1624.

[14] Zhengang, L. and Fu-Shen, Z. Effect of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management. 49(2008): 3498-3504.

[15] Sudong, Y., et al. Subcritical hydrothermal liquefaction of cattle manure to bio-oil: Effect of conversion parameters on bio-oil yield and characterization of bio-oil. Bioresource Technology. 101(2010): 3657-3664.

[16] Joanne, Y., Meijuan, C., Y.S., S. and Siucheong, Y. Comparative study of liquefaction process and liquefied products from bamboo using different organic solvents. Bioresource Technology. 100(2009): 6674-6678.

[17] Chongli, Z. and Xiaomin, W. A comparative experimental study on the liquefaction of wood. Energy. 29(2004): 1731-1741.

[18] Gang, W., Wen, Li., Baoqing, L., Haokan, C. and Jan, B. Direct liquefaction of sawdust under syngas with and without catalyst. Chemical Engineering and Processing. 46(2007): 187-192.

[19] Sid-Ahmed, R. and Richard, C. Liquefaction of wood in two successive step: solvolysis in ethylene-glycol and catalytic hydrotreatment. Applied Energy. 72(2002): 631-644.

[20] Haiping, Y., Rong, Yan., Hanping, C., Dong Ho, L. and Chuguang, Z. Characteristics of hemicelluloses, cellulose and lignin pyrolysis. Fuel. 86(2007): 1781-1788.

[21] Courtney A, F., Tonya, M., Yaying, Ji., Mark, C., Czarena, C. and Sam A, L. Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. Applied Catalyst A: General. 358(2009): 150-156.

[22] Miskolczi, N., Borsodi, N., Buyong, F., Angyal, A. and Williams, P. Product of pyrolytic oils by catalytic pyrolysis of Malaysian refuse-derived fuels in continuously stirred batch reactor. Fuel Processing Technology. (2011).

[23] Yigang, C., Fan, Y., Libin, W., Chao, W. and Zhengyu, Y. Co-deoxy-

liquefaction of biomass and vegetable oil to hydrogen oil: influence of temperature, resisdence time, and catalyst. Bioresource Technology. 102(2011): 1933-1941.

[24] Ying, X., Tiejun, W., Longlong, M., Qi, Z. and Lu, W. Upgrading of liquid fuel from the vacuum pyrolysis of biomass over the Mo-Ni/Al_2O_3 catalysts. Biomass and Bioenergy. 33(2009): 1030-1036.

[25] Huiyan, Z., Rui, X., Denghui, W., Guangying, H., Shanshan, S., Jubing, Z.and Zhaoping, Z. Biomass fast pyrolysis in a fluidized bed reactor under N_2, CO_2, CO, CH_4 and H_2 atmospheres. Bioresource Technology. 102(2011): 4258-4264.

APPENDICES

Appendix A

Calculation of CO_2, CO, CH_4 yields from liquid phase pyrolysis of Giant leucaena wood.

From PV = nRT

P = pressure (atm), V = volume (L), n = mole (mol), R = constant and T =temperature (K)

The example for calculation of gas yields.

Weight of biomass	10 g
Reaction temperature	350°C
Residence time	2 hours
Catalyst	10 wt% $NiMo/Al_2O_3$
Initial pressure	10 bar
Final pressure after cooling	15.5 bar
The different pressure	5.5 bar
R (constant)	0.0820513 atm L /mol K
Free volume of reactor for gaseous product	45 ml

Area of standard gases

CH_4 1 vol%	CO 1 vol%	CO_2 1 vol%
7693	1998	3349

Area of gaseous product

CH_4	CO	CO_2
15675	14778	81426

From PV = nRT

P = pressure (atm), V = volume (L), n = mole (mol), R = constant and T = temperature (K)

n = PV/RT

Therefore,

Mole of CH_4 = [5.5 x (((15675 / 7693) x 45) / 100)] / [0.08206 x 298]
= 5.06 / 24.45
= 0.21 mmol = 0.00021 mol

Mole of CO_2 = [5.5 x (((81426 / 3349) x 45) / 100)] / [0.08206 x 298]
= 60.17 / 24.45
= 2.46 mmol = 0.00246 mol

Mole of CO = [5.5 x (((14778 / 1998) x 45) / 100)] / [0.08206 x 298]
= 18.32 / 24.45
= 0.75 mmol = 0.00075 mol

Therefore, calculation of % yield by comparing to the weight of biomass 10 g and

Mw of CH_4 = 16
Mw of CO_2 = 44
Mw of CO = 28

% yield of CH_4 = [((0.00021 x 16) x 100) / 10]
= 0.0336 %

% yield of CO_2 = [((0.00246 x 44) x 100) / 10]
= 1.0824 %

% yield of CO = [((0.00075 x 28) x 100) / 10]
= 0.21 %

Appendix B

Table B-1 Calculation of %yield from liquid phase pyrolysis with biomass 10 g and decane (solvent) = 40 g

Weight (g) / Condition	Solid and liquid mixture	Liquid products (bio-oil + decane)	Decane (after evaporation)	Bio-oil (after evaporation)	Solid product	%yield of bio-oil	%yield of char
Temperature 350^{o}C, hydrogen pressure 10 bar, 10 wt% of catalyst/biomass, residence time 2 hours.							
Non-catalyst	44.7	28.82	26.6	0.39	5.05	3.9	50.5
ZSM-5	43.6	23.58	21.9	0.4	4.75	4	47.5
NiMo/ Al_2O_3	44.36	27.79	25.8	0.43	4.23	4.3	42.3
Pt/Al_2O_3	44.16	28.35	26.88	0.53	4.44	5.3	44.4
ZSM-5 + NiMo/ Al_2O_3	46.29	28.49	26.05	0.45	4.52	4.5	45.2
ZSM-5 + Pt/Al_2O_3	44.46	26.68	25.28	0.47	4.19	4.7	41.9
NiMo/ Al_2O_3 + Pt/Al_2O_3	45.8	28.04	25.58	0.5	3.83	5	38.3
ZSM-5 + NiMo/ Al_2O_3 + Pt/Al_2O_3	45.42	27.54	25.13	0.44	4.19	4.4	41.9
Vary temperatures (^{o}C), hydrogen pressure 10 bar, 10 wt% of NiMo/ Al_2O_3, residence time 2 hours.							
250^{o}C	46.9	26.84	25.93	0.21	5.64	2.1	56.4
300^{o}C	45.38	26.24	24.76	0.29	4.54	2.9	45.4
350^{o}C	44.36	27.79	25.8	0.43	4.23	4.3	42.3
400^{o}C	44.32	31.15	28.22	0.86	3.48	8.6	34.8
Vary residence times (hr), temperature 350^{o}C, hydrogen pressure 10 bar, 10 wt% of NiMo/ Al_2O_3.							
0.5 h	43.75	26.04	23.6	0.15	4.45	1.5	44.5
1 h	45.56	27.27	25.1	0.52	4.54	5.2	45.4
2 h	44.36	27.79	25.8	0.43	4.23	4.3	42.3
4 h	46.05	28.73	27.13	0.41	3.82	4.1	38.2
Vary initial pressures of hydrogen (bar), temperature 350^{o}C, residence time 2 h, 10 wt% of NiMo/ Al_2O_3.							
5 bar	45.28	29.94	27.41	0.54	4.36	5.4	43.6
10 bar	44.36	27.79	25.8	0.43	4.23	4.3	42.3

Weight (g) / Condition	Solid and liquid mixture	Liquid products (bio-oil + decane)	Decane (after evaporation)	Bio-oil (after evaporation)	Solid product	%yield of bio-oil	%yield of char
20 bar	45.14	27.43	25.25	0.44	4.0	4.4	40
30 bar	45.82	26.97	25.08	0.39	4.65	3.9	46.5
Vary catalyst dosages (%wt), initial pressure of hydrogen 10 bar, temperature 350^{o}C, residence time 2 h.							
1 %wt	44.94	28.63	27.62	0.28	4.1	2.8	41
5 %wt	44.12	28.61	26.67	0.43	4.11	4.3	41.1
10 %wt	44.36	27.79	25.8	0.43	4.23	4.3	42.3
20 %wt	45.55	29.72	27.86	0.49	3.54	4.9	35.4
Vary reaction gases (%wt), initial pressure 10 bar, temperature 350^{o}C, residence time 2 h, 10 wt% of NiMo/ Al_2O_3.							
Nitrogen	45.17	30.23	28.04	0.8	4.16	8	41.6
Hydrogen	44.36	27.79	25.8	0.43	4.23	4.3	42.3

Table B-2 Major compounds in bio-oil using different catalysts.

Compound names	**Retention time**	**Catalyst**			
		Non-catalyst	**ZSM-5**	**NiMo/ Al_2O_3**	**Pt/ Al_2O_3**
2-amino-1-phenyl-1-propanol	2.108	0.69			
cyclobutanol	2.317	0.31			
hydroxyurea	3.675	0.19			
cyclobutanol	4.983	0.21			
phenol	5.142		0.29		4.58
hydroxyurea	5.983	0.29			
2-methyl-phenol	6.000		0.14		
3-methyl-phenol	6.233				0.31
4-methyl-phenol	6.242		0.29	0.13	
2-methoxy-phenol	6.358		0.18		
nonanal	6.542		0.25	0.96	
2-amino-N-ethylpropanamide	6.600	0.21			
2-methylaminomethyl-1,3-dioxolane	7.225	0.19			
hexanal	7.267			0.39	
2-methoxy-4-methyl-phenol	7.467		0.16		
2-amino-N-ethylpropanamide	7.542	0.31			
1,2-benzenediol	7.550				0.85
tridecane	7.567		0.14	0.66	
decanal	7.608			2.08	0.38
2-ethoxy-4-methylphenol	8.158		0.27		
3-methyl-1,2-benzenediol	8.158				0.72
4-ethyl-2-methoxy-phenol	8.325		0.33	0.56	0.84
4-methyl-1,2-benzenediol	8.433				1.07
2-ethoxy-propane	8.792	0.35			
4-ethyl-1,3-benzenediol	8.908				0.60
2,5-dimethyl-1,4-benzenediol	9.008		0.25		0.85
5-methyltetradecane	9.017				
2-methoxy-4-propyl-phenol	9.142		0.38	0.82	1.76
4-ethyl-1,2-benzenediol	9.283				1.84
4-ethyl-2-methoxy-phenol	9.675				0.35
5-isopropyl-3,3-dimethyl-2-methylene-2,3-dihydrofuran	9.817		0.36		
4-ethyl-2-methoxy-phenol	9.817				0.58
dimethylamine	9.958	0.12			
4-propyl-1,3benzenediol	10.067				1.51
4-ethyl-1,2-dimethoxy-benzene	10.408				0.37
Undecanoic acid	10.767			0.77	
2-cyano-acetamide	10.842	0.25			
Diethyl phthalate	11.033	4.76	0.82	4.31	3.29
3-hydroxy-.alpha.-	11.150	0.19			

Compound names	**Retention time**	**Catalyst**			
		Non-catalyst	**ZSM-5**	**NiMo/ Al_2O_3**	**Pt/ Al_2O_3**
[(methylamino)methyl]-benzenemethanol					
3,4-diethyl -2,4-hexadienedioic acid,dimethyl ester	11.150		0.17		0.68
1,4-bis(methoxymethyl)-2,3,5,6-tetramethyl-benzene	11.383				0.47
15-methyl-hexadecanoic acid, methyl ester	12.008		0.41		0.38
2-cyano-acetamide	12.142	0.10			
2,5-dimethyl-3-phenylfuran	12.158		0.28	0.25	
Tetradecanoic acid	12.258		0.21	0.48	0.43
1,4-butanediol	12.308	0.38			
1,2-dimethyl-cyclopentane	12.508			0.16	
hexadecane	12.550		0.28		
2,5-dimethyl-3-hexanone	12.550	0.33			
2,6,11-trimethyldodecane	12.558			0.37	
Hexyl octyl ether	12.592			0.30	
2-hydroxy-benzoic acid, 2-ethylhexyl ester	12.608		0.26		
2-propenamide	12.625	0.19			
9-octadecenamide	12.675				3.02
Methyl 3,6-anhydro-glucopyranoside	12.725	0.27			
Isopropyl myristate	12.733		0.25	0.28	
2-amino-N-methylpropanamide	12.908	0.38			
Pentadecanoic acid	12.958		0.11	0.45	
(1-methylethyl)-cyclopentane	12.992			0.36	
1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester	13.017		1.68		
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	13.025	2.36		1.55	1.02
12-methyl-Tetradecanoic acid	13.158			1.21	
pentadecane	13.242		0.18	0.37	
Hexadecanoic acid, methyl ester	13.408	3.76	2.62	3.49	2.65
Oleic acid	13.492				0.39
3-methyl-heneicosane	13.525	0.25			
1,2-benzenedicarboxylic acid, butyl octyl ester	13.650	3.85	3.12	6.43	3.55
decylamide	13.700		0.27		
Hexanedioic acid, bis(2-ethylhexyl)ester	13.742				2.63

Compound names	**Retention time**	**Catalyst**			
		Non-catalyst	**ZSM-5**	**NiMo/ Al_2O_3**	**Pt/ Al_2O_3**
1,3-dioxolane	13.758	0.26			
Hexadecanoic acid, ethyl ester	13.850	1.87		1.66	1.43
heneicosane	13.892		0.42	1.47	0.24
1-bromo-8-tetrahydropyranyloxyoctane	14.017			0.17	
Octadecanoic acid, methyl ester	14.058		0.18		
Heneicosyl-cyclopentane	14.325			0.26	
5-methyl-1-heptene	14.442			0.32	
9-octadecanoic acid, methyl ester	14.525	1.74	0.83	1.28	0.74
7-octadecenoic acid, methyl ester	14.558		0.42		
Octadecanoic acid, methyl ester	14.675				0.74
15-methyl-Hexadecanoic acid, methyl ester	14.683		0.29	0.44	
Ethyl 2-aminoethanimidoate	14.683	0.34			
1,54-dibromotetrapentacontane	14.733				1.34
Octadecanoic acid, 2-(2-hydroxyethoxy)ethyl ester	14.883				0.37
1-hydroxy-cyclopropanecarboxylic acid, (2,6-di-t-butyl-4-methylphenyl)ester	14.892		0.28		
Ethyl 9-hexadecenoate	14.933	0.42	0.46	0.57	0.38
hexadecanamide	15.000			1.12	
tetradecylamide	15.000		0.25		
N,N-dimethyl-urea	15.108	0.23			
2-oxo-hexadecanoic, methyl ester	15.150				0.71
1-methyl-7-(1-methylethyl)-phenanthrene	15.317		0.67		
2-amino-1-propanol	15.958	0.28			
1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester	15.992				3.86
9-octadecenamide	16.375		1.24	3.25	
tetradecanamide	16.608			1.25	
Glyoxylic acid	16.708	0.10			
Hexanedioic acid, bis(2-ethylhexyl) ester	16.742		33.21	1.43	0.39
2-methyl-2-propenoic acid, oxiranylmethyl ester	17.792	0.10			

Compound names	Retention time	Catalyst			
		Non-catalyst	ZSM-5	NiMo/ Al_2O_3	Pt/ Al_2O_3
1,2-benzenedicaboxylic acid, diisooctyl ester	18.475		0.27	0.96	

Table B-3 Major compounds in bio-oil using different reaction temperature.

Compound names	Retention time	Temperature			
		250 ^oC	300 ^oC	350 ^oC	400 ^oC
4-methyl-phenol	6.242			0.13	
nonanal	6.542			0.96	
hexanal	7.267			0.39	
tridecane	7.567			0.66	0.21
decanal	7.608			2.08	
5-propyldecane	7.800				0.23
3-methylundecane	7.858				0.22
5-methyltetradecane	8.033				0.33
4-methyldodecane	8.142				0.67
2,4,6-trimethyl-phenol	8.250				0.10
4-ethyl-2-methoxy-phenol	8.325		0.36	0.56	
tridecane	8.533				0.41
5-butylnonane	8.650				0.37
3,5-dimethyldodecane	8.892				0.25
2,6-dimethoxy-phenol	8.975		0.30		
5-methyltetradecane	9.017				0.76
2-methoxy-4-propyl-phenol	9.142		0.54	0.82	
1,2-benzenedicarboxylic acid, diethyl ester	9.408	0.84			
tetradecane	9.433				0.36
heptadecane	9.475				0.29
2,6,10,14-tetramethyl-hexadecane	9.717				0.64
2-methoxy-4-(1-propenyl)-phenol	9.858	0.67	0.40		
2,5-dimethyltridecane	9.858				0.81
1,2-benzenedicarboxylic acid, diethyl ester	10.200	0.30			
nonadecane	10.275				0.67
heptadecane	10.333				0.41
5-tert-butyl-1,2,3-benzenetriol	10.492	1.45	0.62		
8-hexylpentadecane	10.517				0.45
1-(4-hydroxy-3-methoxyphenyl)-2-propanone	10.525		0.16		

Compound names	Retention time	Temperature			
		250 ^{o}C	300 ^{o}C	350 ^{o}C	400 ^{o}C
7-methylpentadecane	10.658				0.80
Undecanoic acid	10.767			0.77	
Diethyl phthalate	11.033		1.43	4.31	0.76
heneicosane	11.100				0.73
3,4-diethyl -2,4-hexadienedioic acid,dimethyl ester	11.150		0.78		
8-heptyl-pentadecane	11.275				0.48
hexadecane	11.417				1.01
2,6-dimethoxy-4-(2-propenyl)phenol	11.475	1.85			
Methyl tetradecanoate	11.692	0.44			
heneicosane	11.775				0.47
2,6-dimethoxy-4-(2-propenyl)-phenol	11.842	0.76			
2-phenyl-4-hydroxy-5-methyl-pyrimidine	11.892	0.63			
Tridecanoic acid, methyl ester	12.000	0.50			
octacosane	12.000				0.79
3-ethyl-5-(2-ethylbutyl)-octadecane	12.125	1.68			
heptadecane	12.150				1.05
2,5-dimethyl-3-phenylfuran	12.158			0.25	
Tetradecanoic acid	12.258	0.68		0.48	
1-(2,6-dihydroxy-4-methoxyphenyl)-1-butanone	12.350	0.37			
heneicosane	12.492	1.84			
1-dodecanol	12.500		0.13		
1,2-dimethyl-cyclopentane	12.508			0.16	
hexadecane	12.550		0.15		0.56
2,6,11-trimethyldodecane	12.558			0.37	
Hexyl octyl ether	12.592			0.30	
2-hydroxy-benzoic acid, 2-ethylhexyl ester	12.617		0.09		
Isopropyl myristate	12.617	0.81			
Isopropyl myristate	12.733		0.15	0.28	0.33
10-methylnonadecane	12.842				0.39
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	12.942	5.15			
Pentadecanoic acid	12.958			0.45	
(1-methylethyl)-cyclopentane	12.992			0.36	
1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester	13.017		0.95		0.91
1,2-benzenedicarboxylic acid	13.025			1.55	
12-methyl-Tetradecanoic acid	13.158			1.21	
octacosane	13.192	2.37			

Compound names	Retention time	Temperature			
		250 ^{o}C	300 ^{o}C	350 ^{o}C	400 ^{o}C
pentadecane	13.242			0.37	
Methyl 11,14-octadecadiynoate	13.300	0.58			
2,2,5,5-tetramethyl-4-(p-fluorophenyl)-3-imidazoline-3-oxide	13.333		0.13		
tetratricontane	13.367				0.28
Hexadecanoic acid, methyl ester	13.408	8.19	1.81	3.49	1.61
2-butyl-1-octanol	13.492	0.90			
1-methoxy-13-methyl-hexadecane	13.508				0.34
Dibutyl phthalate	13.642	8.69	2.62		2.44
1,2-benzenedicarboxylic acid, butyl octyl ester	13.650			6.43	
Hexadecanoic acid, ethyl ester	13.850		1.51	1.66	0.98
heneicosane	13.892			1.47	
1-bromo-8-tetrahydropyranyloxyoctane	14.017			0.17	
Hexadecanoic acid, 1-methylethyl ester	14.033	1.01			
8-hexyl-8-pentylhexadecane	14.275	0.37			
Heneicosyl-cyclopentane	14.325			0.26	
1-cyclohexylethanol	14.358		0.11		
Methyl trans-4-(2-nonylcyclopentyl)butanoate	14.417	0.23			
5-methyl-1-heptene	14.442			0.32	
9-octadecanoic acid, methyl ester	14.525	2.82	1.42	1.28	0.65
7-octadecenoic acid, methyl ester	14.558	1.02	0.38		0.20
3,3-dimethyl-4-dimethylamino-2-phenyl-2-butanol	14.600		0.27		
Octadecanoic acid, methyl ester	14.675	0.84	0.37		0.20
15-methyl-Hexadecanoic acid, methyl ester	14.683			0.44	
olealdehyde	14.733		0.17		
Oleic acid	14.883	0.34	0.32		
Ethyl 9-hexadecenoate	14.933	1.31	0.61	0.57	0.31
Ethyl oleate	14.975	0.38			
1,7-dimethyl-1,7-octanediol	14.992		0.21		
hexadecanamide	15.000			1.12	
Octadecanoic acid, ethyl ester	15.100	0.20			
squalene	15.275		3.88		
1,2-benzenedicarboxylic acid, mono(2-ethylhexyl)ester	15.308				1.57
3-(4-methoxyphenyl)-2-propenoic acid, 2-ethylhexyl ester	16.033	0.34	0.93		
3,5,24-trimethyltetracontane	16.092	0.32			

Compound names	Retention time	Temperature			
		250 °C	300 °C	350 °C	400 °C
9-octadecenamide	16.375		0.18	3.25	
tetradecanamide	16.608			1.25	
Hexanedioic acid, bis(2-ethylhexyl) ester	16.742			1.43	
6-[7-nitrobenzofurazan-4-yl]amino-Morphinan-4,5-epoxy-3,6-di-ol	18.467	0.71			
1,2-benzenedicaboxylic acid, diisooctyl ester	18.475		0.55	0.96	

Table B-4 Major compounds in bio-oil using different residence time.

Compound names	Retention time	Residence time			
		30 min	1 hr	2 hr	4 hr
2,4-dimethylheptane	3.058		0.23		
4-methyloctane	3.592		0.10		
4-methyl-phenol	6.242			0.13	
nonanal	6.542			0.96	
hexanal	7.267			0.39	
2-methoxy-4-methyl-phenol	7.467	0.11	0.23		
3,4-dimethyl-3-cyclohexen-1-carboxaldehyde	7.475				0.16
tridecane	7.567			0.66	
decanal	7.608			2.08	0.18
1,5,5-trimethyl-6-methylene-cyclohexene	8.142				0.40
4-ethyl-2-methoxy-phenol	8.317	0.62	0.92	0.56	0.60
2-methoxy-.alpha.-2-propenyl-benzenemethanol	8.633				0.37
1-phenyl-2,5-dimethyl-1,3-hexanedione	8.892				0.11
2,6-dimethoxy-phenol	8.975	0.10			
3-(2,4-dihydroxybenzoylhydrazono)-N-mesitylbutyramide	8.983		0.10		
2-methoxy-4-propyl-phenol	9.142	0.57	1.20	0.82	0.32
2,4,6-trimethyl-1,3-benzenedimethanol	9.708				0.49
1,2,3-trimethoxybenzene	9.825	0.26			
Hexyl 4-hydroxy-3-methoxybenzoate	9.825		0.17		
Benzeneacetic acid, 3-tetradecylester	9.858				0.58

Compound names	Retention time	Residence time			
		30 min	1 hr	2 hr	4 hr
2,3,4,5-tetramethylbenzaldehyde	9.908				0.23
2,3-dimethyl-1H-indole	10.200		0.10		
1-bromo-dodecane	10.033				0.34
2-isopropylphenyl-thiourea	10.150				0.19
2,3-dimethyl-1H-indole	10.200				0.27
Pentamethylbenzoic acid	10.242				0.63
2,3,4,4a,5,6,7,8-octahydro-2-hydroxy-[.alpha./.beta.]-2,4a-dimethyl-naphthalene	10.400				0.29
5-tert-butyl-1,2,3-benzenetriol	10.492	0.37	0.31		
1-(4-hydroxy-3-methoxyphenyl)-2-propanone	10.525	0.10			
5-methoxy-6,7-dimethyl-benzofuran	10.558				0.59
2-methyl-dodecane	10.658				0.17
1-naphthyl octanoate	10.750		0.12		
1-(1H-indol-3-yl)-ethanone	10.750				0.29
Undecanoic acid	10.767	0.10		0.77	
1,2-dimethyl-4-methylene-3-phenyl-cyclopentene	10.792				0.32
Diethyl phthalate	11.033	1.61	1.31	4.31	2.26
4-(4-methoxyphenyl)-3-buten-2-one	11.100				0.45
3,4-diethyl -2,4-hexadienedioic acid,dimethyl ester	11.150	0.46	0.39		
5,8-dimethyl-1,2,3,4-tetrahydro-1-naphthol	11.217				0.28
1-(decyloxy)decane	11.275				0.22
2-ethyl-2-propyl-hexanoic acid, methyl ester	11.417				0.51
hexadecane	11.825	0.10			
15-methyl-hexadecanoic acid, methyl ester	12.008	0.13	0.13		0.32
1-(decyloxyl)decane	12.150				0.40
2,5-dimethyl-3-phenylfuran	12.158			0.25	
Tetradecanoic acid	12.258	0.10		0.48	
Octyl formate	12.500	0.13			
1,2-dimethyl-cyclopentane	12.508			0.16	
3,8-dimethylundecane	12.550	0.17	0.14		0.29
2,6,11-trimethyldodecane	12.558			0.37	
Hexyl octyl ether	12.592			0.30	
Isopropyl myristate	12.733	0.14	0.16	0.28	0.37
n-decanoic acid	12.950				0.10
Pentadecanoic acid	12.958			0.45	
(1-methylethyl)-cyclopentane	12.992			0.36	
1,2-benzenedicarboxylic acid, bis(2-	13.017	0.73	1.25		

Compound names	Retention time	Residence time			
		30 min	1 hr	2 hr	4 hr
methylpropyl)ester					
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	13.025			1.55	0.99
12-methyl-Tetradecanoic acid	13.158			1.21	
2,6,10-trimethyl-dodecane	13.233	0.16			
pentadecane	13.242			0.37	
Hexadecanoic acid, methyl ester	13.408	1.77	2.25	3.49	2.55
2,7-dimethyl-1-octanol	13.483	0.15			
Dibutyl phthalate	13.642	1.95	1.72		
1,2-benzenedicarboxylic acid, butyl octyl ester	13.650			6.43	2.56
Tetrahydro-2,2-dimethyl-5-(1-methylethyl)-furan	13.708	0.17			
Hexadecanoic acid, ethyl ester	13.850	1.19	1.04	1.66	1.58
heneicosane	13.892			1.47	
4,6-dimethyldodecane	13.892	0.10			
1-bromo-8-tetrahydropyranyloxyoctane	14.017			0.17	
Methyl heptacosanoate	14.050	0.10			
Heneicosyl-cyclopentane	14.325			0.26	
5-methyl-1-heptene	14.442			0.32	
9-octadecenoic acid, methyl ester	14.525	0.89	0.99	1.28	1.24
7-octadecenoic acid, methyl ester	14.558	0.34	0.39		0.49
Octadecanoic acid, methyl ester	14.675	0.32	0.20		0.36
15-methyl-Hexadecanoic acid, methyl ester	14.683			0.44	
(8Z)-14-methyl-8-hexadecen-1-ol	14.733	0.10			
Ethyl oleate	14.933	0.40	0.48	0.57	2.15
hexadecanamide	15.000			1.12	
2,3,5,8-tetramethyldecane	15.142	0.10			
9-hexadecenoic acid, octadecyl ester	15.142				3.94
3-(4-methoxyphenyl)-2-propenoic acid, 2-ethylhexyl ester	16.042	0.10			
9-octadecenamide	16.375			3.25	
tetradecanamide	16.608			1.25	
Hexanedioic acid, bis(2-ethylhexyl) ester	16.742			1.43	
squalene	17.750	0.52			
1,2-benzenedicarboxylic acid, diisooctyl ester	18.467	0.29			
1,2-benzenedicaboxylic acid, diisooctyl ester	18.475			0.96	

Table B-5 Major compounds in bio-oil using different pressure of hydrogen gas.

Compound names	**Retention time**	**Hydrogen pressure**			
		5 bar	**10 bar**	**20 bar**	**30 bar**
4-methyl-phenol	6.242		0.13		
nonanal	6.542		0.96		
hexanal	7.267		0.39		
2-methoxy-4-methyl-phenol	7.467	0.47		0.37	
tridecane	7.567		0.66		
decanal	7.608		2.08		
3-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butanone	7.867	0.21			
2-ethoxybenzenemethanamine	8.058	0.24			
Trimethyl(2-methyl-1-propenylidene)-cyclopropane	8.150	0.60			
4-ethyl-2-methoxy-phenol	8.317	1.64	0.56	1.32	0.91
2,3a-dimethylhexahydrobenzofuran-7a-ol	8.458	0.52			
4-methoxybenzyl(4-hydroxybut-2-enyl)ether	8.533	0.46			
2-methoxy-.alpha.-2-propenyl-benzenemethanol	8.633	0.93			
4-ethyl-1,2-dimethoxybenzene	8.733	0.55			
2,3-dihydro-1H-inden-5-ol	8.892			0.44	0.29
4-hydroxy-4-phenylcyclohexanone	8.900	0.43			
2,5-dimethyl-1H-indole	8.933	0.40			
2-methoxybenzyl alcohol	9.008	1.83		0.55	0.58
2-methoxy-4-propyl-phenol	9.142	1.68	0.82	1.39	1.05
4-(3-hydroxy-1-propenyl)-2-methoxy-phenol	9.308			1.03	1.15
1-(2-methylphenyl)-2-propen-1-ol	9.308	1.49			
2,3,5-trimethyl-1,4-benzenediol	9.675	0.51			0.53
3-ethyl-1,2,4,5-tetramethylbenzene	9.708			0.96	0.91
4-ethyl-2-methoxy-phenol	9.808				0.73
2-methoxy-4-(2-propenyl)-phenol	9.858	2.02		1.24	
2,5-dimethyl-1,4-benzenedicarboxaldehyde	9.917	0.71		0.32	0.49
5-hydroxy-3-methyl-1-indanone	9.958				0.51
2-tert-butyl-4-methoxyphenol	10.017			0.49	0.75
2-methoxy-4-propyl-phenol	10.025	0.89			
4-propyl-1,3-benzenediol	10.075	0.83		0.39	
2,3-dimethyl-1H-indole	10.150			0.53	0.88
2,3-dimethyl-1H-indole	10.200	0.72		0.40	0.57
2-amino-1-(3-methoxyphenyl)ethanol	10.250			0.50	0.99
5-hydroxy-8,8-dimethyl-	10.250	1.67			

Compound names	Retention time	Hydrogen pressure			
		5 bar	10 bar	20 bar	30 bar
3,3a,4,5,6,7,8,8b-octahydroindeno[1,2-b]furan-2-one					
6,7-dimethoxy-1-styryl-1,2,3,4-tetrahydro-isoquinoline	10.350	0.83			1.38
2,6,6-trimethyl-1-cyclohexene-1-acetaldehyde	10.358			0.81	
4-ethyl-1,2-dimethoxybenzene	10.408	1.20			1.08
2,4,6-trimethyl-1,3-benzenedimethanol	10.417			0.67	
5-tert-butyl-1,2,3-benzenetriol	10.492	1.13		0.60	0.85
3-hydroxycarbofuran	10.525			0.34	
2-methoxy-4-propyl-phenol	10.558	1.31		0.62	
5-sec-butyl-1,2,3-benzenetriol	10.592			0.62	
3-methyl-butanoic acid	10.667			0.19	
(4-tert-butylphenyl)acetaldehyde	10.700			0.23	
6-ethyl-2-methylindolizine	10.750	0.69		0.91	
Undecanoic acid	10.767		0.77		
1,2-dimethyl-4-methylene-3-phenyl-cyclopentene	10.792	1.00			
Diethyl phthalate	11.033	0.93	4.31	1.59	1.17
1-(4-methylphenyl)-1,3-butanedione	11.100	1.41			0.80
3,4-diethyl -2,4-hexadienedioic acid,dimethyl ester	11.158	0.84		0.66	0.87
5,8-dimethyl-1,2,3,4-tetrahydro-1-naphthol	11.192	1.12			
2-(2-methoxy-1-propenyl)-1,3,5-trimethylbenzene	11.275				0.71
5,8-dimethyl-1,2,3,4-tetrahydro-1-naphthol	11.383				0.76
1-(3-methoxymethyl-2,5,6-trimethylphenyl)ethanol	11.383	0.72		0.50	
2,4-dimethyl-1-heptanol	11.417			0.52	1.32
2-ethyl-2-propyl-hexanoic	11.425	0.95			
2,5-dimethyl-3-phenylfuran	11.733	0.84		0.51	0.82
2,6-dimethoxy-4-(2-propenyl)-phenol	11.842	0.98		0.35	
15-methyl-hexadecanoic acid, methyl ester	12.008			0.54	1.70
8-methyl-8-heptadecanol	12.150	0.98			1.78
2,5-dimethyl-3-phenylfuran	12.158		0.25		
Tetradecanoic acid	12.258		0.48		0.49
1-(4-hydroxy-3-methoxyphenyl)-cyclopentane-1-carbonitrile	12.383	1.10			
1,2-dimethyl-cyclopentane	12.508		0.16		

Compound names	**Retention time**	**Hydrogen pressure**			
		5 bar	**10 bar**	**20 bar**	**30 bar**
hexadecane	12.550				1.39
2,6,11-trimethyldodecane	12.558		0.37		
Hexyl octyl ether	12.592		0.30		
2-hydroxy-benzoic acid, 2-ethylhexyl ester	12.617				1.07
Isopropyl myristate	12.725		0.28	0.24	1.34
Pentadecanoic acid	12.958		0.45		
(1-methylethyl)-cyclopentane	12.992		0.36		
1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester	13.017				1.59
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	13.025		1.55	0.65	
12-methyl-Tetradecanoic acid	13.158		1.21		
pentadecane	13.242		0.37		
Hexadecanoic acid, methyl ester	13.408	2.00	3.49	1.93	4.13
1,2-benzenedicarboxylic acid, butyl octyl ester	13.650	1.06	6.43	1.81	3.37
Hexadecanoic acid, ethyl ester	13.850	0.67	1.66	0.75	1.72
heneicosane	13.892		1.47		0.72
1-bromo-8-tetrahydropyranyloxyoctane	14.017		0.17		
Methyl heptacosanoate	14.050				0.56
Heneicosyl-cyclopentane	14.325		0.26		
5-methyl-1-heptene	14.442		0.32		
9-octadecenoic acid, methyl ester	14.525	0.52	1.28	0.86	1.46
7-octadecenoic acid, methyl ester	14.558	0.58		0.70	1.28
Octadecanoic acid, methyl ester	14.675				1.05
15-methyl-Hexadecanoic acid, methyl ester	14.683	0.43	0.44	0.33	
Ethyl oleate	14.933		0.57	0.29	0.89
hexadecanamide	15.000		1.12		
heneicosane	15.150				0.37
9-octadecenamide	16.375		3.25		
tetradecanamide	16.608		1.25		
Hexanedioic acid, bis(2-ethylhexyl) ester	16.742		1.43		
1,2-benzenedicaboxylic acid, diisooctyl ester	18.475		0.96		

Table B-6 Major compounds in bio-oil using different catalyst dosages.

Compound names	**Retention time**	**Catalyst dosage**			
		1%wt	**5%wt**	**10%wt**	**20%wt**
4-methyl-phenol	6.242			0.13	
nonanal	6.542			0.96	
hexanal	7.267			0.39	
tridecane	7.567			0.66	
decanal	7.608			2.08	
4-ethyl-2-methoxy-phenol	8.325	0.55		0.56	
2-methoxy-4-propyl-phenol	9.142	0.95	0.55	0.82	0.34
2,3,5-trimethyl-1,4-benzenediol	9.308				0.44
2,3,4,5-tetramethyl-benzaldehyde	9.708				0.68
4-ethyl-2-methoxy-phenol	9.808		0.31		
2,5-dimethoxybenzyl alcohol	9.825	1.04			
3-(3-methylphenyl)-2-propenoic acid	9.958	0.27			
2,3-dihydro-2-(4-hydroxy-3-methoxyphenyl)-5-(3-hydroxy-1-propenyl)-7-methoxy-3-benzofuranmethanol	10.017	0.50			
2-methoxy-4-propyl-phenol	10.017				0.21
4-propyl-1,3-benzenediol	10.067		0.28		
2-[[[2-(4-hydroxyphenyl)ethyl]amino]methyl]-1,4-benzenediol	10.075	0.31			
3-ethyl-1,2,4,5-tetramethyl-benzene	10.250				0.35
5-methoxy-2,3,4-trimethyl-phenol	10.350				0.25
6-hydroxy-4,4,5,8-tetramethyl-2-chromanone	10.400	0.75			
1,4dimethoxy-2,3-dimethylbenzene	10.408				0.40
1,2,3-trimethoxy-5-methyl-benzene	10.483	0.65			
3-methyl-5-(2,6,6-trimethyl-1-cyclohexenyl)-2-pentenoic acid	10.558				0.40
2-(2-penten-4-yl)-4-methyl-phenol	10.700				0.18
2-hexyloctanoic acid	10.750		0.39		
Undecanoic acid	10.767	0.61		0.77	
1,2,3,4-tetrahydro-5-nitro-naphthalene	10.867				0.43
Diethyl phthalate	11.033	2.44	1.06	4.31	1.49
4-(4-methoxyphenyl)-3-buten-2-one	11.100				0.56
3,4-diethyl -2,4-hexadienedioic acid,dimethyl ester	11.150	1.02	0.34		
6-methoxy-1-methyl-8-nitro-1,2-dihydroquinoline	11.208	0.39			0.38
3,4-dichloro-.alpha.-methyl-benzenemethanol	11.308	0.18			

Compound names	**Retention time**	**Catalyst dosage**			
		1%wt	**5%wt**	**10%wt**	**20%wt**
5,8-dimethyl-1,2,3,4-tetrahydro-1-naphthol	11.383		0.28		0.33
1-tert-butyl-3-(3-methoxyphenyl)-bicyclopentan	11.525				0.24
1-cyclopropyl-1-dodecanone	11.725	0.43			
2,5-dimethyl-3-phenylfuran	11.733				0.46
10-methyl-Heptadecanoic acid, methyl ester	12.008	1.08			0.40
5-nitrothiophene-2-carboxylic acid, n-tetradecanyl ester	12.150		0.53		
2,5-dimethyl-3-phenylfuran	12.158	0.54		0.25	0.58
Tetradecanoic acid	12.258	0.57	0.28	0.48	
2,3-dimethyl-2-(3-oxobutyl)-cyclohexanone	12.500	0.48			
1,2-dimethyl-cyclopentane	12.508		1.05	0.16	
hexadecane	12.550	0.39			
2,6,11-trimethyldodecane	12.558			0.37	
Hexyl octyl ether	12.592			0.30	
3,5,24-trimethyltetracontane	12.625		0.43		
Isopropyl myristate	12.733	0.87	1.76	0.28	
26-t-butyl-2,3,14,15-dibenzo-1,4,7,10,13,16,19,22-octaoxacyclotetracosa-2,14-diene	12.833		0.95		
Pentadecanoic acid	12.958	0.36		0.45	
(1-methylethyl)-cyclopentane	12.992			0.36	
1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester	13.017	1.54	0.72		
1,2-benzenedicarboxylic acid	13.025			1.55	0.72
12-methyl-Tetradecanoic acid	13.158		0.53	1.21	
pentadecane	13.242		0.49	0.37	
Hexadecanoic acid, methyl ester	13.408	4.47	2.78	3.49	2.34
1-methoxy-13-methyl-hexadecane	13.508		0.57		
Dibutyl phthalate	13.642	4.80			
1,2-benzenedicarboxylic acid, butyl octyl ester	13.650		3.73	6.43	2.80
Hexadecanoic acid, ethyl ester	13.850	2.37	1.53	1.66	
heneicosane	13.892	0.51	0.78	1.47	0.64
1-bromo-8-tetrahydropyranyloxyoctane	14.017			0.17	0.52
Octadecanoic acid, methyl ester	14.050	0.29	0.32		0.39
Heneicosyl-cyclopentane	14.325			0.26	0.60
5-methyl-1-heptene	14.442			0.32	
1,4-eicosadiene	14.483				0.58
9-octadecanoic acid, methyl ester	14.525	1.97	1.55	1.28	1.31

Compound names	**Retention time**	**Catalyst dosage**			
		1%wt	**5%wt**	**10%wt**	**20%wt**
Octadecanoic acid, methyl ester	14.675	0.92			
15-methyl-Hexadecanoic acid, methyl ester	14.683			0.44	
Octadecanoic acid, methyl ester	14.675	0.69			
Oxacyclohexadecan-2-one	14.733		0.45		
Octadecanoic acid	14.892		0.94		
Ethyl 9-hexadecenoate	14.933	1.04	0.65	0.57	1.07
hexadecanamide	15.000		0.63	1.12	
Ethyl tridecanoate	15.100	0.27			
Hexadecanoic acid, ethyl ester	15.108		0.36		0.80
2,6,10,14-tetramethyl-hexadecane	15.142	0.32			
heneicosane	15.150		0.56		
Tetracosanoic acid, methyl ester	15.225		0.44		
4,8-dimethyl-3,7-nonadienoic acid, methyl ester	15.275		0.67		
1,2-benzenedicarboxylic acid, mono(2-ethylhexyl)ester	15.308				1.67
n-methyltomatidine	15.867	0.39			
3-(4-methoxyphenyl)-2-propenoic acid, 2-ethylhexyl ester	16.033	0.21			
9-octadecenamide	16.375			3.25	
tetratriacontane	16.525		1.13		
tetradecanamide	16.608			1.25	
Hexanedioic acid, bis(2-ethylhexyl) ester	16.742			1.43	
1,2-benzenedicarboxylic acid, mono(2-ethylhexyl)ester	18.467	2.23			
1,2-benzenedicaboxylic acid, diisooctyl ester	18.475			0.96	0.39

Table B-7 Major compounds in bio-oil using different reducing gases.

Compound names	**Retention time**	**Reducing gases**	
		Nitrogen gas	**Hydrogen gas**
4-methyl-phenol	6.242		0.13
nonanal	6.542	0.12	0.96
hexanal	7.267		0.39
4-methyloctanoic acid	7.267	0.10	
tridecane	7.567		0.66
decanal	7.608		2.08
2,3-dimethoxytoluene	7.925	0.04	
Trimethyl(2-methyl-1-propenylidene)-cyclopropane	8.150	0.12	
Nonanoic acid	8.217	0.14	
4-ethyl-2-methoxy-phenol	8.317	0.32	0.56
Decanoic acid, methyl ester	8.742	0.80	
2,4-dimethoxyphenyl 3-phenylpropanoate	8.983	0.19	
2-methoxy-4-propyl-phenol	9.142	0.53	0.82
1,2,3,4-tetrahydro-1-methoxy-naphthalene	9.308	0.14	
N-(4-dimethylaminobenzylidenamino)-2-hydroxybenzenamide	9.475	0.23	
3-ethyl-1,2,4,5-tetramethylbenzene	9.708	0.11	
3-hydroxy-4-methoxybenzoic acid	9.825	0.29	
2,4,6-trimethyl-1,3-benzenedimethanol	10.408	0.19	
4-(4-methoxyphenyl)-3-buten-2-one	10.558	0.53	
(4-tert-butylphenyl)acetaldehyde	10.700	0.18	
Dodecanoic acid	10.750	0.39	
Undecanoic acid	10.767		0.77
Diethyl phthalate	11.033	0.57	4.31
3,4-diethyl -2,4-hexadienedioic acid,dimethyl ester	11.158	0.27	
3,3,4,6-tetramethyl-1-benzofuran-2(3H)-one	11.275	0.15	
2-ethyl-2-propyl-hexanoic acid, methyl ester	11.417	0.22	
2,5-dimethyl-3-phenylfuran	12.158		0.25
Tetradecanoic acid	12.258	0.66	0.48
1,2-dimethyl-cyclopentane	12.508		0.16
2,6,11-trimethyldodecane	12.558		0.37
Hexyl octyl ether	12.592		0.30
Isopropyl myristate	12.725	0.53	0.28
Pentadecanoic acid	12.958	0.45	0.45

Compound names	**Retention time**	**Reducing gases**	
		Nitrogen gas	**Hydrogen gas**
(1-methylethyl)-cyclopentane	12.992		0.36
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	13.025	0.49	1.55
12-methyl-Tetradecanoic acid	13.158		1.21
pentadecane	13.242	0.82	0.37
Hexadecanoic acid, methyl ester	13.408	1.64	3.49
9-octadecenoic acid	13.492	0.80	
n-hexadecanoic acid	13.633	3.63	
1,2-benzenedicarboxylic acid, butyl octyl ester	13.650		6.43
Hexadecanoic acid, ethyl ester	13.850	0.89	1.66
heneicosane	13.892		1.47
1-bromo-8-tetrahydropyranyloxyoctane	14.017		0.17
Methyl 7-methylhexadecanoate	14.050	1.01	
Hexacosanoic acid, methyl ester	14.225	6.01	
Heneicosyl-cyclopentane	14.325		0.26
5-methyl-1-heptene	14.442		0.32
9-octadecenoic acid, methyl ester	14.525	0.78	1.28
7-octadecenoic acid, methyl ester	14.558	0.89	
15-methyl-Hexadecanoic acid, methyl ester	14.683		0.44
Octadecanoic acid	14.883	1.11	
Ethyl oleate	14.933	0.75	0.57
hexadecanamide	15.000		1.12
Hexacosanoic acid, methyl ester	16.050	5.10	
9-octadecenamide	16.375		3.25
tetradecanamide	16.608		1.25
Hexanedioic acid, bis(2-ethylhexyl) ester	16.742		1.43
1,2-benzenedicaboxylic acid, diisooctyl ester	18.475	0.36	0.96

Table B-8 Major compounds in fragmentation of decane in presence of different catalysts.

Compound names	Retention time	Catalyst		
		ZSM-5	NiMo/ Al_2O_3	Pt/ Al_2O_3
1-methyl-2-methylene-cyclopentane	2.308	1.60		
2-methyl-heptane	2.417	3.87		
3-methylheptane	2.492	2.46		
1-ethyl-2-methyl-cyclopentane	2.642	1.44		
octane	2.783	4.75		0.15
3-ethyl-1,4-hexadiene	2.883	1.25		
1,3-dimethyl-benzene	3.625	5.10		
3-methyl-octane	3.683	1.13		
nonane	4.058	2.32		0.38
3-ethyl-2-methyl-1,3-hexadiene	4.508	0.89		
5,6-dimethylundecane	4.583			0.19
2-decene	4.792	0.60		
3,4,5-trimethyl-heptane	4.825		0.76	
1-ethyl-3-methyl-benzene	4.842	4.55		
decane	4.858			1.48
6-ethyl-2-methyl-decane	4.883		0.16	
2-methyl-nonane	4.900	1.25		1.07
3-methylnonane	4.967	2.33	3.54	2.46
1,2-dimethylcyclooctane	5.125			3.52
5-methyl-4-undecene	5.167	0.77		
1,2,3-trimethyl-benzene	5.225	0.83		
5-decene	5.258		0.13	
1-methyl-2-propyl-cyclohexane	5.275			0.12
dodecane	5.342			70.35
1,1-dimethyl-cyclohexane	5.567			0.16
butyl-cyclohexane	5.700			0.15
pentyl-cyclopentane	5.758			0.96
1-methyl-3-propyl-benzene	5.925	0.80		
1-methyl-4-propyl-benzene	5.967	1.57		
butyl-benzene	5.983			0.14
5-methyl-decane	6.033	0.45		
1,2-diethyl-benzene	6.042			0.24
1-methyl-2-propyl-benzene	6.100			0.55
2-methyl-decane	6.108	0.57		
3-methyl-decane	6.175	0.45		
undecane	6.508	0.85		

Compound names	Retention time	Catalyst		
		ZSM-5	NiMo/ Al_2O_3	Pt/ Al_2O_3
2-phenyl-3-propyl-hexane	7.108	0.60		
1-methyl-4-(1-methylpropyl)-benzene	6.992	0.43		
Diethyl phthalate	11.033	1.46	1.06	1.07
1,2-benzenedicarboxylic acid, bis(2-methylpropyl)ester	13.025	0.53	0.44	0.53
Hexadecanoic acid, methyl ester	13.408	0.86	0.83	0.98
Dibutyl phathalate	13.650	0.99	0.93	1.15
Hexadecanoic acid, ethyl ester	13.850	0.52	0.43	0.68
9-octadecanoic acid, methyl ester	14.517		0.31	0.46
E-11-hexadecenoic acid, ethyl ester	14.933		0.18	0.33

Table B-9 The water content in the bio-oil and decane after evaporation with different reaction temperature.

	Water content (wt%)			
Temperature	250 ^{0}C	300 ^{0}C	350 ^{0}C	400 ^{0}C
Bio-oil	0.0298	0.0306	0.0424	0.0532
Decane	0.3215	0.2358	0.6084	0.6729

Table B-10 The water content in the bio-oil and decane after evaporation with different residence time.

	Water content (wt%)			
Residence time	30 min	1 hour	2 hours	4 hours
Bio-oil	0.0354	0.0352	0.0424	0.0372
Decane	0.5341	0.4512	0.6084	0.5618

Table B-11 The water content in the bio-oil and decane after evaporation with different hydrogen pressure.

Water content (wt%)				
Hydrogen pressure	5 bar	10 bar	20 bar	30 bar
Bio-oil	0.0351	0.0424	0.0483	0.0731
Decane	0.0914	0.6084	0.6060	0.4286

Table B-12 The water content in the bio-oil and decane after evaporation with different catalyst dosage.

Water content (wt%)				
Catalyst dosage	1 wt%	5 wt%	10 wt%	20 wt%
Bio-oil	0.0441	0.0481	0.0424	0.0392
Decane	0.2972	0.2844	0.6084	0.4981

Table B-13 The water content in the bio-oil and decane after evaporation with different reducing gases.

Water content (wt%)		
Reducing gas	Hydrogen gas	Nitrogen gas
Bio-oil	0.0424	0.0261
Decane	0.6084	0.4811

VITA

Mr. Chonlawit Borwornwongpitak was born on March 10, 1987 in Ubonratchatanee province, Thailand. He received a Bachelor’s degree of Engineering and industrial technology, majoring in Petrochemicals and Polymeric Materials from Silpakorn University in 2009. He has pursued Master’s degree in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand since 2009 and finished his study in 2011.

<u>Presentation</u>

- 5-7 Jan 2011 Poster presentation “Bio-oil production from liquid phase pyrolysis of giant Leucaena wood” Pure and Applied Chemistry International Conference 2011 (PACCON2011) at Miracle Grand Hotel, Bangkok, Thailand.