Technology Assessment of Upgrading Bio-oil

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(Dr. Suzana Yusup)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

(REZITA SYARINA BINTI MOHD REDZUAN)

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Praise to the Almighty God for his mercy and kindness that the author has successfully completed this project within the time provided. Throughout these 2 semesters, it has greatly benefited the author in various aspects especially in engineering knowledge applied. Experiences gained are believed to be very useful to the author in her future career and endeavors. Hopefully all the information gained from this project may benefit others especially UTP students and staff for references. The successful completion of this project has been made possible through the help and support of many individuals and organizations

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ABSTRACT

This report is about the current progress on the proposed topic which is "Technology Assessment of Upgrading Bio-oil". The objectives of this project are to study on the methods available of upgrading the bio-oil in terms of the advantages and disadvantages of each method. The methods that have been identified to upgrade bio-oil are hydrotreatment, catalytic cracking, emulfication and steam reforming. For each of the technology, estimated cost analysis and iCON simulation will be done. The methodology for this project is identifying technology available for upgrading bio-oil, extensive research will be done by analyzing relevant journals and obtaining information from applicable books, comparing results and findings from journals, obtaining estimated cost analysis for each technology and modeling by using iCON process simulation. In term of material costs, the most feasible technology would be emulsification. However, emulsification did not change the physical properties of the upgraded bio-oil. Thus, emulsification can still caused corrosiveness to the equipment that uses the fuel. For the time being, iCON simulation can only be done for steam reforming. From the simulation, the optimum operating condition for steam reforming is 5 bar for operating pressure, operating temperature of 800 °C and steam to carbon ratio (S/C) of 5.

LIST OF FIGURES

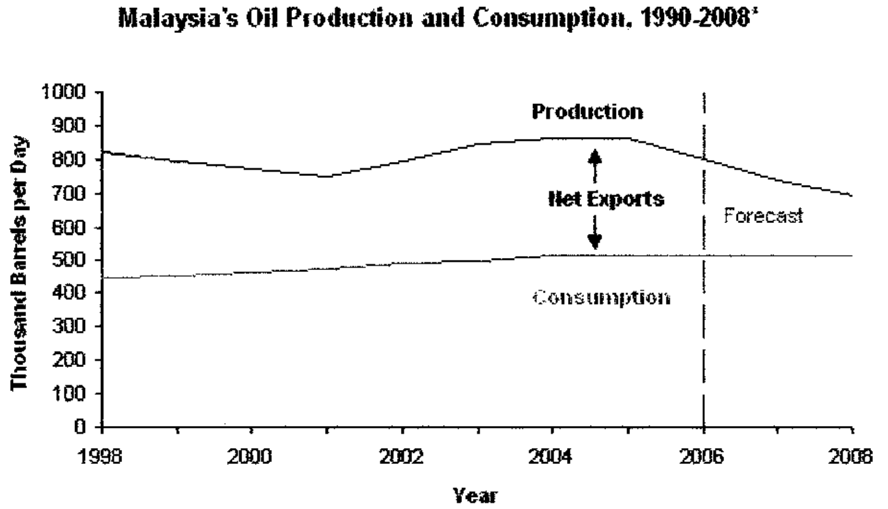
LIST OF TABLES

CHAPTER 1
PROJECT BACKGROUND

1.1 Background

As of January 2008, the proven oil reserves in Malaysia are 3.0 billion barrels as of January 2007, down from a peak of 4.6 billion barrels in 1996. The majority of Malaysia's oil reserves are located off the coast of peninsular Malaysia. Malaysia's national oil company, Petroliam Nasional Berhad (PETRONAS) and its various Production Sharing Contract (PSC) partners have been most active exploring offshore areas, especially in deepwater zone.

However, despite the exploration and production (E&P) that is still going on in Malaysia, the proven oil reserves in Malaysia declining. The Energy Information Administration (EIA) of the US government predicted that Malaysia's oil production will fall to 693 000 bbl/d in 2008, a 13 percent decrease from 2006 levels.



Source: EIA International Energy Annual 2004;
Short-Term Energy Outlook (Feb 2007)

*2006 is estimate

Figure 1: EIA's forecast of Malaysia's oil production and consumption

The depletion of fossil fuel does not only happen in Malaysia. It also happens to all oil producing country in the world. With the growing demand for energy consumption and the depletion of fossil fuel, renewable energy sources should be widely explored.

Present energy source is largely dependent on the fossil fuels. The usage of fossil fuels can caused global warming. Aside from that, the depletion of fossil fuel has caused more research to be done on more environmentally friendly solutions for the substitution of the current energy consumption. A significant amount of carbon dioxide emissions from the energy sector is mainly related to the usage of fossil fuels for the electricity generation.

In the Eighth Malaysian Plan, renewable energy was announced as the fifth fuel in the energy supply mix. Renewable energy is being targeted to be a significant contributor to the country total electricity and fuel supply. Greater effort are being undertaken to encourage the utilization of renewable energy sources such as biomass, biogas, solar and mini-hydro for energy generation.

Biomass has long been identified as one of the main energy substitution for fossil fuel. There are five major sectors contributing wastes to biomass energy in Malaysia: forestry (wood products), rubber cultivation, cocoa cultivation, sugar cane cultivation and oil palm cultivation. Biomass in Malaysia contributes about 14% of the approximately 340 million barrel of oil equivalent (boe) of energy used every year. According to Sumiani Yusoff (2004), biomass energy potential from palm oil was estimated at 250TJ. By the year of 2010, the biomass energy potential is expected to increase to 820TJ.

According to Bridgwater and Bridge (1996), pyrolysis is currently to be the most promosing thermochemical conversion technology for the production of pyrolysis oil. Fast pyrolysis utilizes biomass to produce a product that is used both as an energy source and a feedstock for chemical production. Products that can be obtained from pyrolysis are gas, liquid and char.

1.2 Problem Statement

Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures in which the biomass is rapidly heated in the absence of oxygen. Products from pyrolysis of biomass include residue chars, tars and volatile gaseous components. Biomass pyrolysis liquid products are commonly known as bio-oil and usually dark brown organic liquids.

Nevertheless, the potential for direct substitution of bio-oil for fossil fuels or other chemical feedstock maybe limited due to the high viscosity, high oxygen content and especially the thermal instability of bio-oil. Thus, upgrading the bio-oil is needed to give a desirable composition that can be used as fossil fuel substitution or chemical feedstock.

1.3 Objectives and Scope of Study

The main objectives of this project are:

i. To study on the methods available of upgrading the bio-oil in terms of the advantages and disadvantages of each methods.
ii. To do cost analysis for each of the technology.
iii. To do modeling for each of the technology using iCON process simulation.

The scope of study will be as following:

i. Research and literature review on theories and information on various related sources.
ii. Research on suitable method of upgrading bio-oil.
iii. Cost estimation of available method of upgrading bio-oil.
iv. Modeling using iCON simulation.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass

Biomass is one of the oldest and most well-establish energy sources in the world. Biomass is a renewable resource which means that biomass is part of the resources occurring naturally in the environment. Biomass is sustainable. The green plants from which biomass fuels are derived fix carbon dioxide as they grow, so their use does not add to the levels of atmospheric carbon.

One of the main local biomass resources in Southeast Asia is palm oil waste (including palm oil empty fruit bunch, fiber and shell). The demand for palm oil is increasing because of its use in biofuels. In the third outline Malaysian Perspective Plan, it stated that global production went from 4.5 million tons in 1980 to 20.9 million tons in 2000. About 9.9 million tones of palm oil wastes are generated every year in Malaysia alone and this is increasing at 5% annually.

2.2 Bio-Oil

Bio-oil is a dark, viscous liquid with the same elemental composition of biomass. Bio-oil is made up of many different oxygenated organic compounds and will not mix with traditional petroleum fuels. Crude bio-oil can be used in home heating and large-scale electricity generation, or refined into more efficient fuels and certain industrial chemicals. Energy produced with bio-oil is also cleaner than fossil fuel-generated energy. During combustion in a gas turbine, bio-oil releases 50% fewer nitrogen oxides.

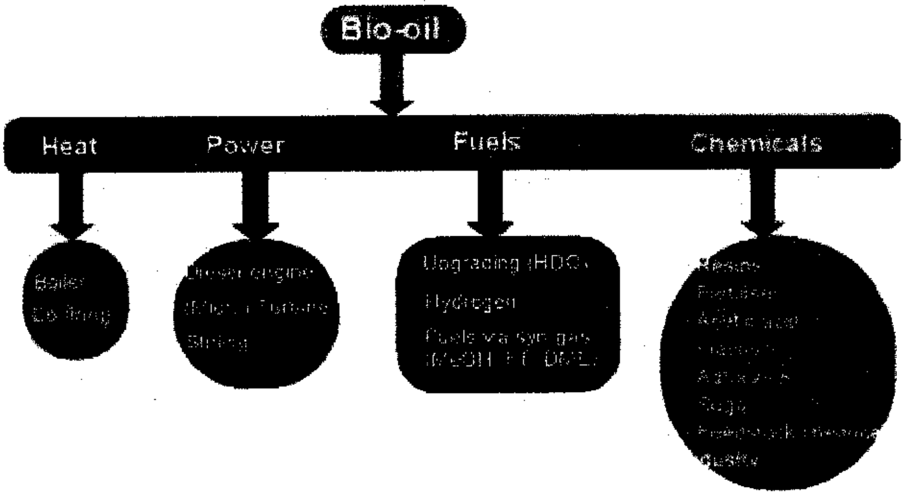


Figure 2: Application of bio-oil

Figure 3: Bio-oil

2.3 Pyrolysis

Pyrolysis dates back to at least ancient Egyptian times, when tar for caulking boats and certain embalming agents were made by pyrolysis. Pyrolysis processes have been improved and are now widely used with coke and charcoal production. In the 1980s, researchers found that the pyrolysis liquid yield could be increased by using fast pyrolysis where a biomass feedstock is heated at a rapid rate and the vapors produced are also condensed rapidly.

Pyrolysis is the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is presented that required for complete combustion. Another method to decompose biomass is gasification. Gasification decomposes biomass to syngas by carefully controlling the amount of oxygen present.

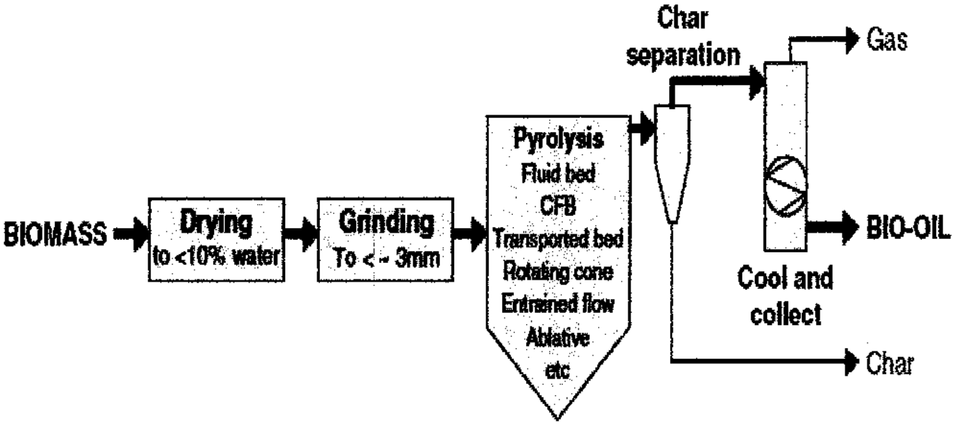


Figure 4: Brief overview of pyrolysis of bio-oil (Willis et. al., 2007)

In order to manufacture bio-oil in industrial scale, a number of steps must be followed:

1. Collecting Biomass

   Almost any type of biomass can be used in the fast pyrolysis process. In the Malaysia, palm oil empty fruit bunches (EFB) is the most commonly used because it is easy to find and abundant.
2. Drying

   Extra water in biomass source limits the pyrolysis reaction and causes lower yields of bio-oil. Biomass must be dried to less than 10% water.
3. Grinding

The surface area must be at the maximum in order to ensure the highest possible yield in most types of reactors. Thus, biomass should be ground to particles no larger than 3mm.

4. Pyrolyzing

   Among the types of reactor that are commonly used for pyrolyzing are bubbling fluid beds, circulating fluid beds and ablative pyrolysis.

5. Char separation

   Charcoal and gas are present after the reaction as byproducts in ratios of 25 and 5%, respectively. The char product can be separated at this point and used to drive the pyrolysis reaction further by burning it for heat to drive the forward reaction.

6. Cooling and collecting

   Rapid cooling of pyrolysis vapors emanating from the reactor is necessary to maximize fluid yield. Bio-oil can be collected and distributed for burning or further refinement and upgrading.

According to Dinesh Mohad (2008), the general changes that occurred during pyrolysis are specified as below:

1. Heat transfer from a heat source, to increase the temperature inside the fuel.
2. The initiation of primary pyrolysis reactions at this higher temperature releases volatile and forms char.
3. The flow of hot volatiles toward cooler solids results in heat transfer between hot volatiles and cooler unpyrolyzed fuel.
4. Condensation of some of the volatiles in the cooler parts of the fuel, followed by secondary reactions can produce tar.
5. Autocatalytic secondary pyrolysis reactions proceed while primary pyrolytic reactions simultaneously occur in competition.
6. Further thermal decomposition, reforming, water gas shift reactions, radicals recombination and dehydrations can also occur which are a function of the process's residence time/temperature/pressure profile.

Pyrolysis is divided into two which is fast/flash pyrolysis and slow pyrolysis. The differences of each reaction are according to the following table:

Types of Pyrolysis / Characteristics	**Fast Pyrolysis**	**Slow Pyrolysis**
Definition	Rapid thermal decomposition of organic compound in the absence of oxygen to produce liquids, char and gas. The method is the most suitable to produce bio-oil from palm oil waste.	Slow thermal decomposition of organic compound in the absence of oxygen to produce liquids, char and gas.
Feedstock	Dry, <10%	Moderate
Residence time	Short residence time, <2s	Longer residence time, >3s
Size of particles	Small particles, <3mm	Moderate, >4mm
Operating temperature	Moderate, 300 - 500°C	Low moderate temperature, <300°C
Yield	Oil: 60 – 70% Char: 12 – 14% Gas: 13 – 25%	Oil: 30% Char: 35% Gas: 35%

Table 1: Comparison between fast pyrolysis and slow pyrolysis (Dinesh Mohan, 2004)

Over the last few decades, fundamental research on fast or flash pyrolysis has shown that high yield of primary, nonequilibrium liquids and gases, including valuable chemicals, chemical intermediates, petrochemiclas and fuels could be obtained from carbonaceous feedstocks. Thus, the lower value solid char from traditional slow pyrolysis can be replaced by higher-value fuel gas, fuel oil or chemicals from fast pyrolysis.

Pyrolysis and high pressure liquefaction (HPL) of biomass are two main thermochemical conversion methods used for the production of bio-oils. However, the HPL process has been superseded by the fast pyrolysis method. Adjaye et. al. in their research mentioned that both bio-oil types are corrosive, polar, viscous and thermally unstable. There are also a number of differences between the bio-oils obtained from both thermochemical conversion.

Parameters	**Pyrolysis**	**HPL**
Oxygen Content	40 – 50 wt%	9 – 25 wt%
Water Content	20 – 50 wt%	1 – 25 wt%
Bio-Oil Yields	70 – 80 wt%	30 wt%

Table 2: Properties comparison between bio-oil obtained from pyrolysis and HPL (Adjaye et. al., 1995)

On account of these low yields, production of HPL method received limited attention. Thus, production of bio-oil by pyrolysis is widely used and researched. However, this property alongside with its unstable nature has made the direct use of bio-oils as conventional fuel impossible, except for boilers or as turbine fuel. Hence, bio-oils need to be upgraded. There are many upgrading methods that have been done recently such as hydrodeoxygenation, emulsification, esterification and catalytic cracking.

2.4 Components of Bio-Oil

Zhang Qi et al. (2006) stated that bio-oils are multi-components mixtures of different size molecules derived from depolymerization and fragmentation of cellulose, hemicelluloses and lignin. However, the compositions of the bio-oils are different depending on the feedstock that is used. The basic and elemental composition of bio-oil and petroleum derived fuel are as shown in Table 2.

Physical Properties	**Bio-Oil**	**Heavy Fuel Oil**
Moisture content (wt%)	15 – 30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental 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
Higher Heating Value (MJ/kg)	16 – 19	40
Viscosity (at 50°C) (cP)	40 – 100	180
Solids (wt%)	0.2 – 1	1
Distillation residue (wt%)	Up to 50	1

Table 3: Typical properties of pyrolysis bio-oil and heavy fuel oil

2.4.1 Water Content

Bio-oil 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 at the same time reduces the viscosity and enhances the fluidity which is good for atomization and combustion of bio-oil in the engine.

2.4.2 Oxygen Content

The oxygen content of bio-oil is usually 35 – 40 wt%. High oxygen content leads to lower energy density than the conventional fossil fuel by 50%. Strong acidity of bio-oil makes them extremely unstable. Slow heating will induce polymerization of some reactive components and bio-oils start boiling below 100°C, while stopping at 250 - 280°C leaving 35 – 50 wt% of solid residues. Therefore, bio-oil cannot be used in the instance of complete evaporation before combustion.

2.4.3 Viscosity

The viscosities of the bio-oils depend on the types of the feedstock and ranging from 40 – 100 cP. Boucher et al tested bio-oil performance by adding methanol and it reduces the density and viscosity and increased with the limitation of a lowered flash point.

2.4.4 Acidity

Bio-oil contains considerable amounts of carboxylic acids such as acetic and formic acids. The acidity of bio-oil also depends on the feedstock and ranging from pH values of 2 – 3. Acidity makes bio-oil very corrosive and extremely severe at elevated temperature which imposes more requirements on construction materials of the vessels and the upgrading process before using bio-oil as transport fuel.

2.4.5 Ash Content

The presence of ash can caused erosion, corrosion and kicking problems in engines and the valve and may even deterioration when the ash content is higher than 0.1 wt%.

2.5 Environmental Issues

Before any commercial success could happen, scientists must consider a few items such as:

1. Scale-up from smaller model used now.
2. Reducing overhead costs.
3. Setting industry-wide product quality standards.
4. Encourage developers and investors.
5. Disseminate information to the public.
6. Address environmental and safety issues in handling and storage.

The environmentalist has been debating whether bio-oil is safe or otherwise for quite a time. Even though the fuel is renewable, it does not guarantee that is safe to the environment. Potential of bio-oil leaks, spills and human/environmental exposure could happen.

A group of scientists as Aston University (UK), the German Institute for Wood Chemistry and CIRAD France initiated the BioTox Project. The aims for this project were to identify the ideal operating conditions whereby reactors will avoid or minimize the formation of toxic products, to produce a standardized Material Safety Data Sheet (MSDS) outlining toxicity prevention procedures and to explore the potential toxicity of bio-oil products in order to minimize their formation in the future.

The conclusions on properties of bio-oil from the BioTox project are:

1. Not explosive.
2. Non-toxic (tested on rats) when orally ingested.
3. Low Polycylic Aromatics Hydrocarbon (PAHs are known as carcinogens) concentration – below 10 pars per million.
4. Small fertilizing effects on water.
5. Eutrophication limited, however, due to low nitrogen concentration.
6. Negligible toxicity for small aquatic animals.
7. Biodegradability better than most mineral oil products.
8. Similar toxicities for different biomass sources, reactor types.
9. Mutagenic.

However, despite this report, the public still fears over adapting to unknown fuel source. Most problematic is the discovery of bio-oil's role as a mutagen which alter the DNA of organisms and most commonly known as their role as carcinogenic agents. Bio-oil's mutagenicity may be due to the presence of suspected carcinogens formaldehyde and acetaldehyde, in addition to small concentrations of PAHs.

CHAPTER 3

METHODOLOGY

3.1 Project Activities

This project will be a research study. The project will be done by the following methods:

1. Identifying technology available for upgrading bio-oil.
2. Extensive research will be done by analyzing relevant journals and obtaining information from applicable books.
3. Comparing results and findings from journals.
4. Obtaining estimated cost analysis for each technology.

3.2 Progress of Project Work

The Gantt chart for Semester II of Final Year Project is as per attachment.

CHAPTER 4

RESULTS AND DISCUSSION

The following chapter will discuss on the technology that have been identified which are hydrotreatment, emulsification, catalytic cracking and steam reforming.

4.1 Hydrotreatment

Liquefied biomass or bio-oil usually contains in abundance oxygen-containing molecules that need to be removed to improve for example the stability of the liquids. A hydrotreating process, hydrodeoxygenation (HDO) is used most commonly for the purpose in industrial applications. HDO is a hydrogenolysis process of removing oxygenated compounds from the fast pyrolysis derived bio-oil using commercial hydrotreating catalyst in the form of water. HDO is similar to hydrodesulfurization (HSO) process in oil refining relying upon presulfided catalysts such as $CoMo/Al_2O_3$ and $NiMO/Al_2O_3$. However, the effectiveness of HDO treatment is strongly dependent on the composition of biomass (Outi Krause, 2008).

Zhang et al. (2004) in their research discovered that the bio-oil obtained from the fast pyrolysis has poor miscibility with hydrocarbon fuels but dissolved well in methanol because of the large amount hydroxyl groups. Thus, upgrading of bio-oil is done by hydrotreatment.

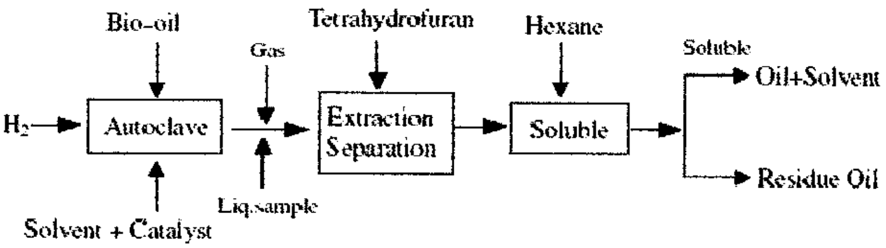


Figure 4: Diagram of upgrading pyrolytic bio-oil

Hydrotreatment was conducted in a 500ml autoclave with magnetically driven stirrer and water cooling coil. For each run, the autoclave was filled with tetralin (as a hydrogen donor solvent), bio-oil and catalyst. After the air was displaced, the cold H_2 pressure was then raised to a prefixed value of 2MPa and optimum temperature of 360°C with heating rate of 10°/min. The reaction mass was then quenched using an internal cooling coil when the run came to an end.

At a lower temperature, conversion and oil yield both were very low but increased rapidly with reaction temperature. However, after the optimum temperature, they did not show any further significant change. The cold hydrogen pressure did not affect much of the gas production. This is because tetralin is a good hydrogen donor that transferred the hydrogen from the gas phase in active form to the radical fragments for their stabilization.

From their research, they have found that the oxygen content was reduced from 41.8% of the crude oil to 3% of the upgraded one and the upgraded bio-oil was oil soluble for the dehydroxy.

The estimated cost analysis is as per Table 4.

No.	Items	Quantity Per Run	Price (USD)
1.	Bio-oil	Unavailable	Unavailable
2.	Co-Mo-P/γ-Al_2O_3 catalyst	Unavailable	Unavailable
3.	Tetralin	Unavailable	Unavailable
4.	Hydrogen	Unavailable	Unavailable
	TOTAL		Unavailable

Table 4: Estimated cost analysis for hydrotreatment using autoclave and tetralin as solvent.

Assumptions:

1. The estimated cost analysis is done as per ten runs of the experiment.
2. The price for materials is obtained on the year of 2009.
3. Price for bio-oil is USD0.55/gal. Price is obtained from Cole Hill Associates.

4. Price for Co-Mo-P/γ-Al_2O_3 catalyst is unavailable due to pending quotation from the supplier.
5. Price for carbon dioxide is USD30/ton. Price is obtained from *www.business.timesonline.co.uk*.
6. Price for tetralin is USD282.67/gm.
7. Price for hydrogen is USD2.47/gal. Price is obtained from Global Hydrogen Inc.

Pindoria et al. (1998) have done research on direct hydrotreatment by using a two-stage fixed bed reactor. The feedstock for this experiment is Eucalyptus sawdust. The reactor for the pyrolysis consists of a single tubular pressure vessel that allows an operation of maximum pressure of 100bar at 850°C. Hydrocracking without catalysts was operated in the first stage and catalytic hydrotreatment was operative in the second stage.

The catalyst for this research is H-ZSM-5. The catalyst was introduced into the reactor and was held in place by a wire mesh plug fitted at the bottom of the reactor tube. The system was purged with helium, the tar trap below the reactor immersed in liquid nitrogen and the catalytic stage heated to desired temperature. After a run, the reactor was cooled down to room temperature; the tar trap and the reactor were washed with a mixture of chloroform and methanol to recover all tar and oil. The catalyst was removed from the reactor, washed with a mixture of chloroform and methanol and left it to dry before being introduced back into the reactor for the second run.

The following conclusions were obtained from their research:

1. The optimum temperature and pressure is 300°C and 10 bar respectively. The liquid product that was obtained was 27.1%.
2. The uptake of sample-derived material by the catalyst bed appeared to be decreasing with the extended use of catalyst. However, the drop in sample uptake by the catalyst bed upon re-use did not resulted in the production of more liquid product but in an increase of light volatile.
3. The hydroprocess process produced more water and complicated the bio-oil with many impurities.

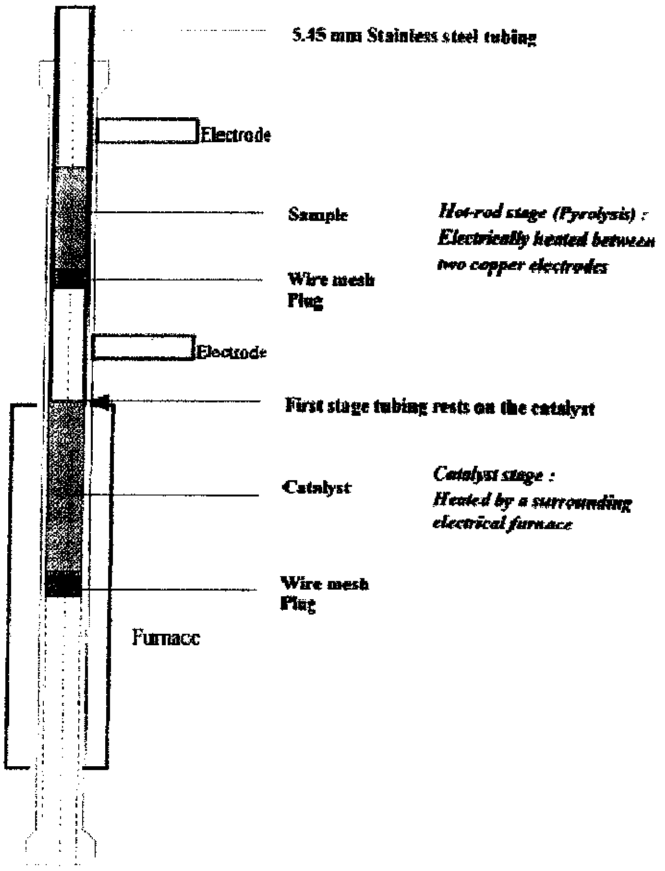


Figure 5: First and second stage positions in the reactor tubing

The estimated cost analysis as per Table 5 below:

No.	Items	Quantity Per Run	Price (USD)
1.	Sawdust	50 mg	~0.01
2.	H-ZSM-5 catalyst	5gm	0.20
3.	Helium	100ml	5.00
4.	Chloroform	40ml	3.20
5.	Methanol	10ml	0.43
	TOTAL		**8.84**

Table 5: Estimated cost analysis for hydrotreatment using two-stage fixed bed reactor

Assumptions:

1. The estimated cost analysis is done as per ten runs of the experiment.

2. The price for materials is obtained on the year of 2009.
3. Price for sawdust is USD30/ton. Price is obtained from www.recycle.net.
4. Price for H-ZSM-5 is USD300/kg. Price is obtained from Zeolyst Inc.
5. Price for methanol is USD16.14/gal. Price is obtained from www.methanex.com.
6. Price for chloroform is USD540/ton. Price is obtained from www.icis.com.
7. Price for helium is USD5.00/litre. Price is obtained from www.eurekalert.org.

4.2 Emulsification

Ikura et al. (2002) stated that although modified diesel engines and gas turbines are being developed, the entry of bio-oils into a market place as a diesel substitute or extender would be much easier if the bio-oils could be directly used as fuel in existing diesel engines without modifications.

Emulsification is regarded as the simplest way to use bio-oil as a transport fuel. It is done by combining directly bio-oil with diesel. Although the bio-oils are immiscible with hydrocarbons, they can be emulsified by the aid of a surfactant. Physical properties of emulsions would be more similar to the diesel than of the bio-oil itself. Furthermore, the negative effects of ash and char would be less because of dilution by diesel.

The experiment is done by using a continuous bench-scale emulsifier. Surfactants used are equal amounts of Hypermer B246SF and Hypermer 2234, diluted with methanol at a ratio of 5:2. Surfactants, bio-oil and diesel are pumped separately into the emulsifier. The methanol-diluted surfactant is fed by syringe pump and bio-oil and diesel are fed by peristaltic pumps. The emulsifying mixer is powered by a variable speed DC motor connected to digital power meter.

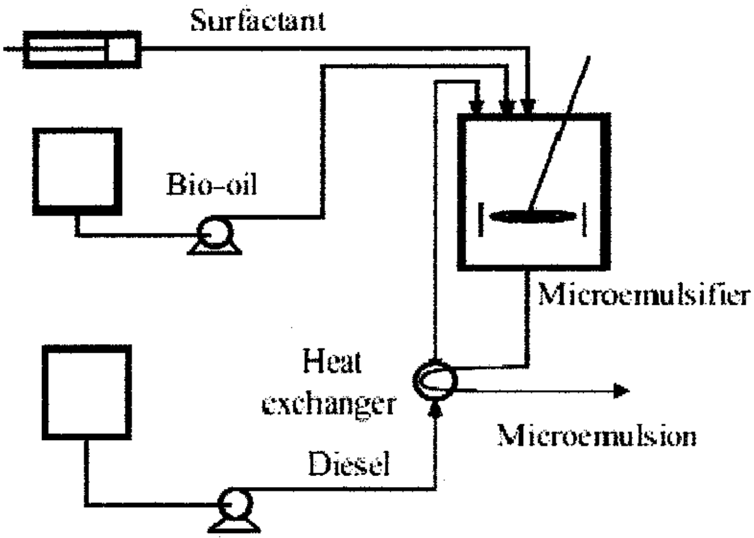


Figure 6: Continuous bench-scale emulsifier

The experiment was done with the following variables range:

1. Bio-oil concentration 10 – 30 wt%.
2. Surfactant concentration (wt% of bio-oil) 1% and 5%.
3. Residence time of 5 and 20 min.
4. Motor speed of 800 and 1740 rpm.
5. Temperature of 50 – 70°C.

After the mixing vessel was filled, the process was allowed to continue for three residence times before it was assumed to reach a steady state and a 1-l sample was withdrawn.

ASTM D665A tests were done. AISI steel rods were kept in samples and water at 60°C for 24h. The weight losses for the test rods are calculated. From the test, they have found that emulsions still can cause the bio-oil to be corrosive even though the corrosivity of emulsion fuels is about half of the bio-oil alone.

Ikura et al also did the cost analysis for producing zero stratification emulsions. They have assumed that the price for Hypermers is USD6.35/kg and USD0.07/kWh for electricity. They have concluded that the surfactant cost is the dominant factor and overshadowed the power cost. The costs of producing emulsions with zero stratification are:

1. 2.5cents/L for 10% emulsion.
2. 3.4cents/L for 20% emulsion.
3. 4.1cents/L for 30%emulsion.

Thus, the total estimated cost for emulsification is as Table 6.

Emulsions	**Price (USD/L)**			
	Hypermer Surfactant	**Bio-oil**	**Diesel**	**Total**
10%	0.025	0.015	0.617	**0.657**
20%	0.034	0.029	0.549	**0.612**
30%	0.041	0.044	0.480	**0.565**

Table 6: Total estimated cost for emulsification of different percentage

Assumptions:

1. The price for materials is obtained on the year of 2009.
2. Price for bio-oil is USD0.55/gal. Price is obtained from Cole Hill Associates. However, the stated cost is only referring to production cost provided by Cole Hill Associates. The trade or retail cost is unknown.
3. Diesel costs is USD0.69/L. This diesel cost is as per current diesel price in Malaysia.

4.3 Catalytic Cracking

Before fast pyrolysis, bio-oil is produced from high pressure liquefaction (HPL). In HPL, the bio-oil is produced from using a number of catalysts such as H-ZSM-5 and typical hydrotreating catalysts (J.D.Adjaye, 1995).

The bio-oil obtained from HPL is generally contained lower water contents and oxygen contents compared to fast pyrolysis oil. Thus, a lot of studies of upgrading bio-oil have been done by using the stated catalysts especially by using H-ZSM-5. However, the bio-oil obtained from HPL has lower yield compared to fast pyrolysis oil.

The upgrading of fast pyrolysis bio-oil was studied with different catalysts in a fixed bed micro-reactor by Adjaye et al (1995). H-ZSM-5, silicatate, H-modernite, H-Y and silica-alumina were the catalysts that were for the upgrading of bio-oil. Bio-oil was obtained fro ENSYN Technologies Inc.

The experimental data were obtained at atmospheric pressure in a continuous downflow mode using a fixed bed micro-reactor. The reactor was operated at 1.8 or $3.6h^{-1}$ and a temperature range of 290 – 410°C. The reactor was first loaded with 2 g (for 3.6 h^{-1}) or 4 g for ($1.8h^{-1}$) catalyst supported on a plug of glass wool and another plug of glass wool was placed above the catalyst bed. The reaction temperature was brought to the desired value in a stream of argon flowing at 21/h. When the desired temperature is reached, the argon flow was stopped and the bio-oil was fed to the reactor by a micro-metering pump.

In the upper section above the glass wool, some of the bio-oil components readily reacted to form which will be deposited on the inner walls of the reactor. The rest of the oil will be vaporized. The vapors then flowed through the glass wool into the catalyst bed where the main reactions occurred. A run will lasted for 30 minutes. The reaction products will be separated into liquid and gas product. The liquid product can be obtained in two forms which are either single homogeneous or in a two layers of organic and aqueous layer.

If a single homogenous product is obtained, the liquid product will then undergone distillation under operating condition of 200°C, vacuum pressure of 172Pa and heating rate of 40°C. The vacuum distillation of the liquid products will produced two fractions which are volatile (distillate) and non-volatile (residue) components.

If the liquid product exists in a two layered form, the organic fraction will be separated from the aqueous fraction by micro pipette and distilled at 200°C and vacuum pressure of 172Pa. Two fractions also obtained: volatile (distillate) and non-volatile (residue). The procedure is simplified to a flow diagram as per Figure 6 below:

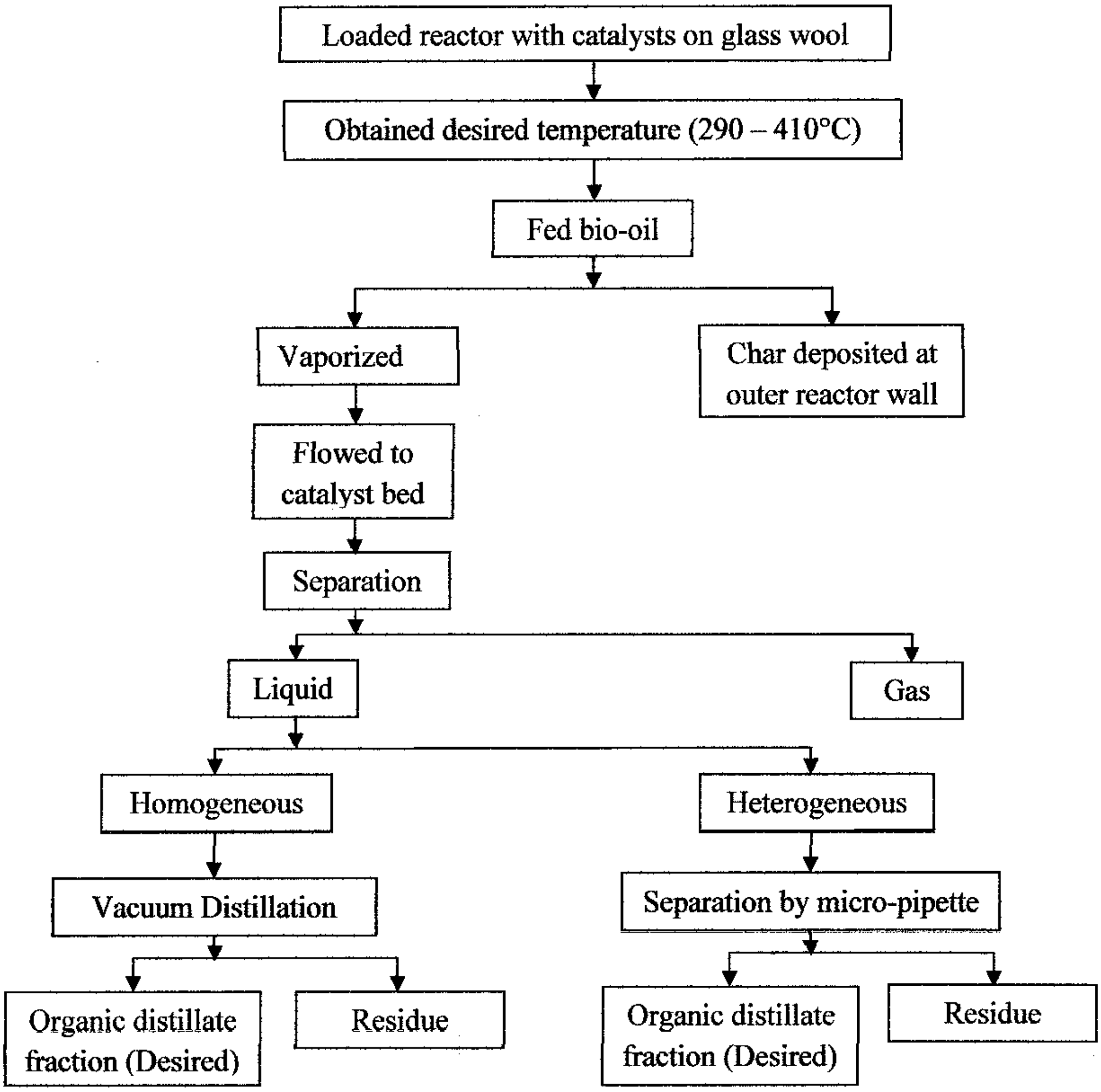


Figure 7: Simplified diagram for experimental setup

From their research, they have concluded that the bio-oil can be upgraded to produce organic distillate fraction with the catalysts studied. For the catalysts' performances, H-ZSM-5 and H-modernite were responsible for producing higher amounts of aromatic hydrocarbons than aliphatic hydrocarbons. Aside from that, H-ZSM-5 and H-modernite were more selective for aromatic hydrocarbons within the gasoline boiling point range. The acidic zeolite catalysts were most effective in converting the bio-oil to hydrocarbons than the less acidic silica-alumina and non-acidic silicalite. However, the yield of coke is considerably high, which is ranging from 5 wt% to 25 wt%.

The estimated cost analysis as per Table 7 below:

No.	Items	Quantity Per Run	Price (USD)
1.	Bio-oil	2000mL	0.29
2.	H-ZSM-5 catalyst	6g	0.54
3.	Silicatate	6g	0.54
4.	H-modernite	6g	0.54
5.	H-Y	6g	0.54
6.	Silica-alumina	6g	0.54
	TOTAL		**2.99**

Table 7: Estimated cost analysis for hydrotreatment using two-stage fixed bed reactor

Assumptions:

1. The price for materials is obtained on the year of 2009.
2. Price for bio-oil is USD0.145/L. Price is obtained from Cole Hill Associates. However, the stated cost is only referring to production cost provided by Cole Hill Associates. The trade or retail cost is unknown.
3. Price for the catalyst is USD 90/kg. Price is obtained from Zeolyst Inc.

4.4 Steam Reforming

Hydrogen is an important raw material widely used in the production of chemicals and power generation. It is typically produced by reforming of fossil fuels such as natural gas, naphtha or gasification of coal. These days, hydrogen production from renewable energy such as wind, biomass and solar energy is expected to partially replace fossil fuel sources. Steam reforming of pyrolysis oil is one of the promising routes of hydrogen production from renewable sources. Bio-oil can be converted to hydrogen via catalytic steam reforming over a metal-based catalyst.

The overall steam reforming of bio-oil can be systematically expressed by the reaction,

$$C_nH_mO_k + (2n-k)H_2O \rightarrow nCO_2 + (2n + m/2 - k)H_2$$ (Dingneng Wang, 1998)

Kinoshita et al *(2003) in their research stated that the procedure of steam reforming for* bio-oil is:

1. Bio-oil is mixed with steam and fed to a pressurized, fluidized bed absorbing reactor containing CaO sorbent and reforming catalyst (as needed).
2. The hydrogen-rich gas exiting the absorbing reactor is cooled through heat recovery and then purified into fuel-grade H_2 using pressure-swing adsorption (PSA).

4.4.1 Steam Reforming Modeling using iCON

Steam reforming modeling has been done by using iCON simulation. The purpose of this modeling is to obtain optimum operating conditions for steam reforming of bio-oil. Among the variables that were investigated are:

1. Operating temperature ranging from 500 to 800 °C.
2. Operating pressure ranging from 5 bar to 20 bar.
3. Steam to carbon ratio (S/C) ranging from 1.5 to 5.0

Among the assumptions made in this simulation are:

1. Bio-oil contains complex composition. For the purpose of this modeling, dextrose ($C_6H_{12}O_6$), a form of glucose is chosen to model the chemically complex bio-oil.
2. The feed for bio-oil is fixed at 10 kg/hr.
3. The reactor is modeled by using 10% conversion.

The stoichiometry of the overall process is,

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$$

All the data from the iCON simulation can be found in the Appendix B.

From Figure 8, we can see that as temperature increased, the composition of hydrogen also increased. However, as pressure increased, the composition of hydrogen decreased. The same trend can be observed for different S/C ratio as shown in Figure 9 to Figure 12. From the simulation, the optimum conditions would be operating temperature of 800°C and operating pressure of 5 bar.

At the optimum operating conditions, S/C ratio of 5.0 will give more hydrogen produced compared to other ratios as can be seen in Figure 13.

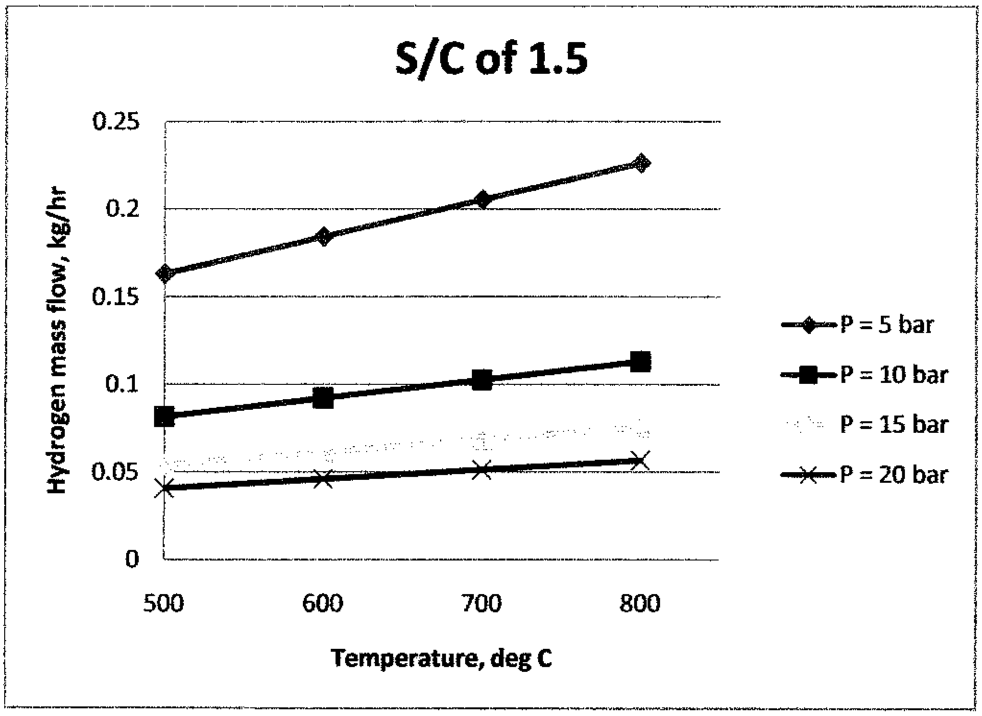


Figure 8: Graph of hydrogen composition for steam and carbon ratio of 1.5

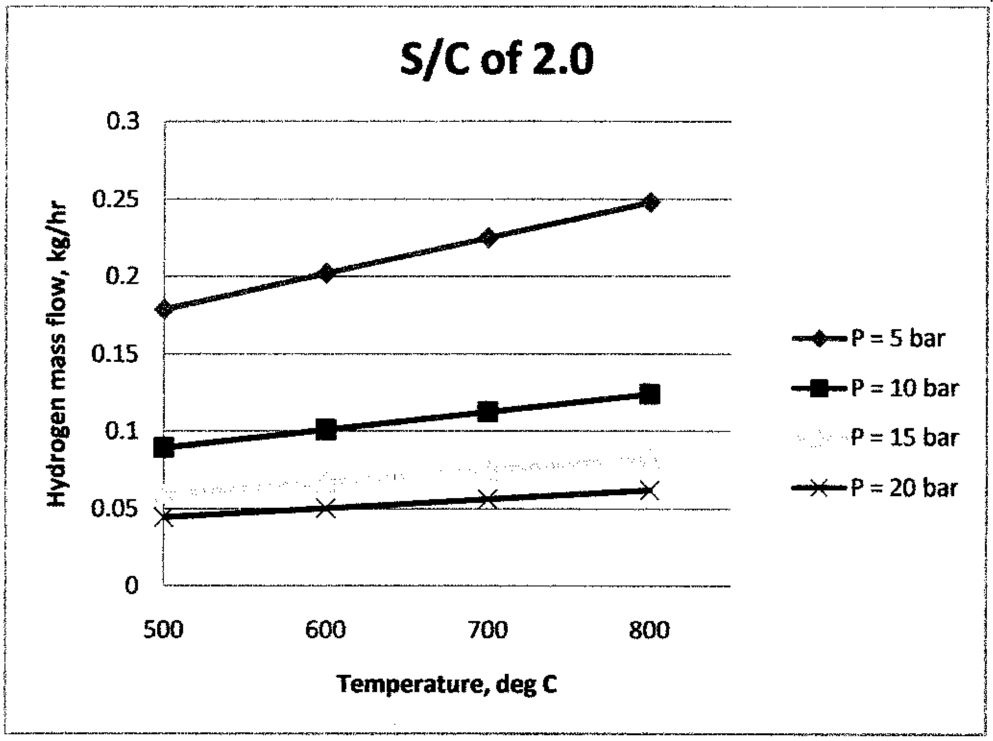


Figure 9: Graph of hydrogen composition for steam and carbon ratio of 2.0

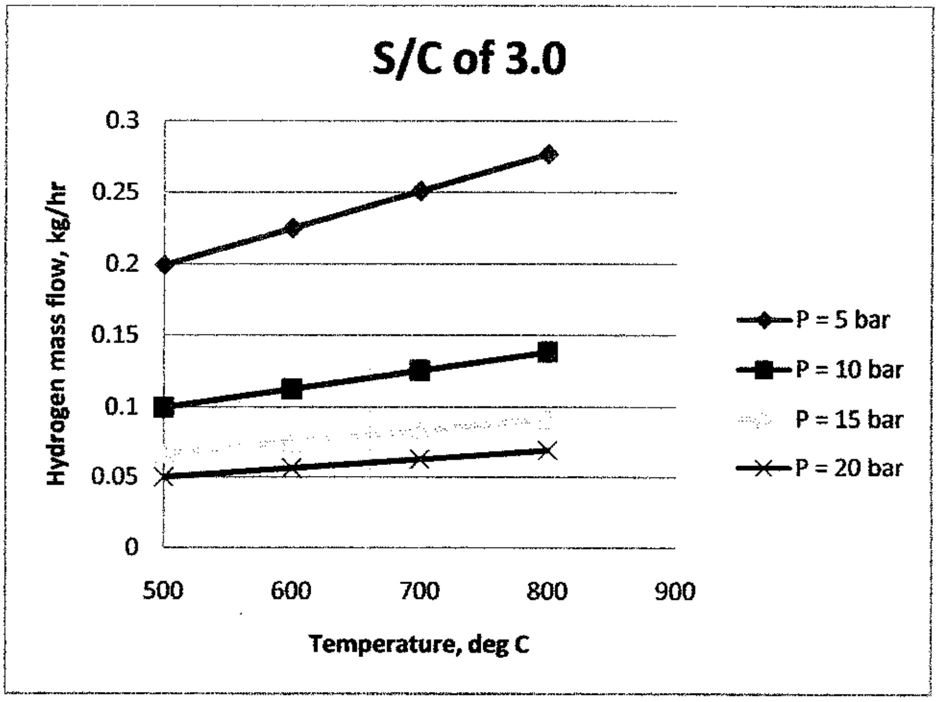


Figure 10: Graph of hydrogen composition for steam and carbon ratio of 3.0

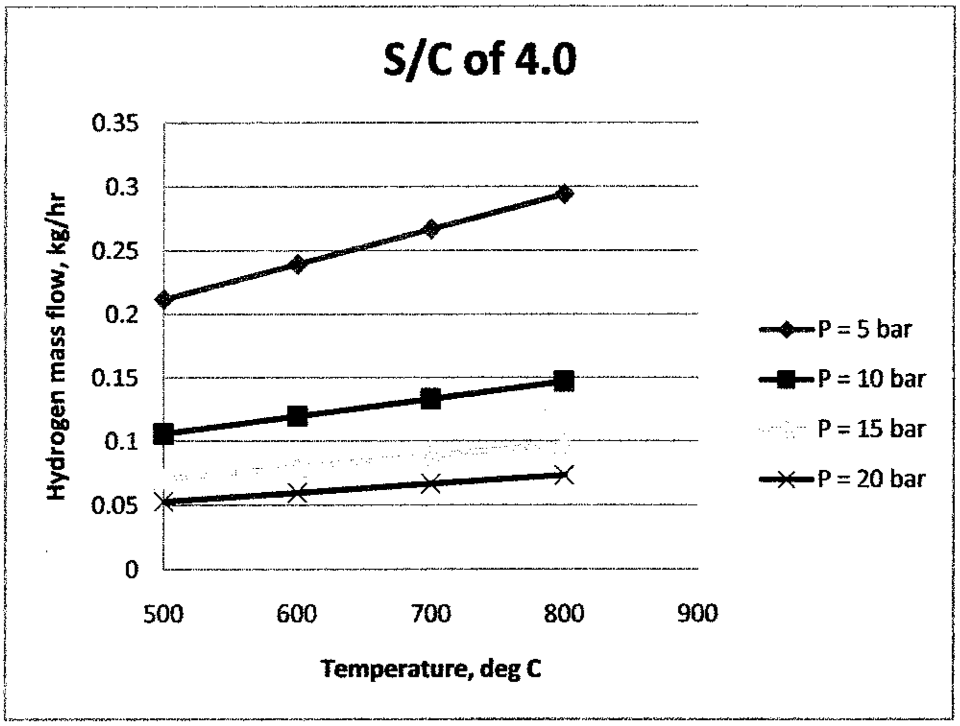


Figure 11: Graph of hydrogen composition for steam and carbon ratio of 4.0

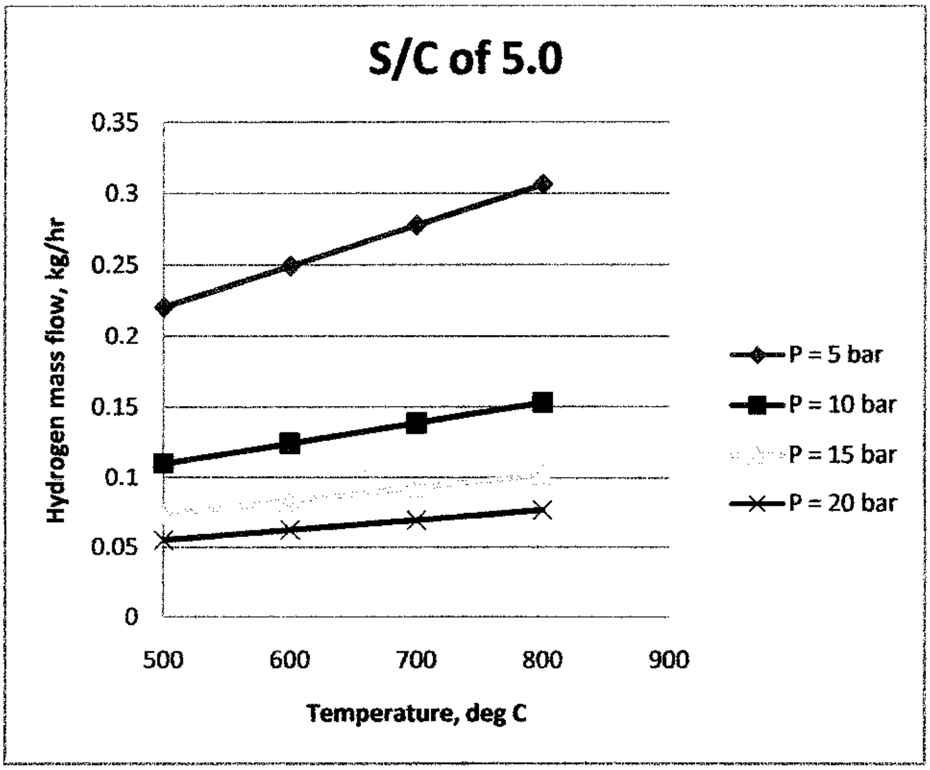


Figure 12: Graph of hydrogen composition for steam and carbon ratio of 5.0

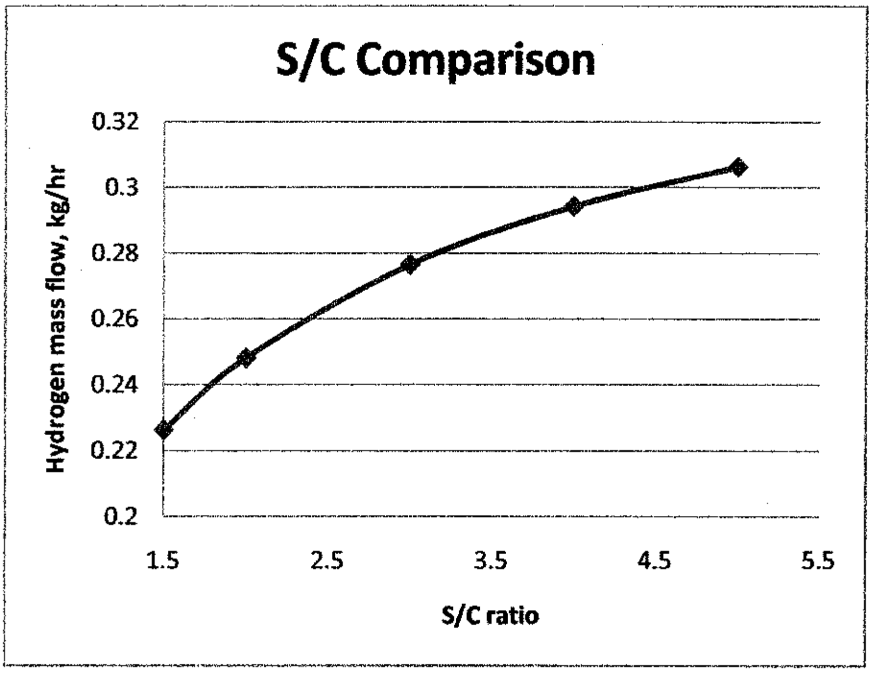


Figure 13: Graph of hydrogen mass flow for different S/C ratio

From the calculation, the highest yield for hydrogen that can be obtained is only 3.06% which is considerably low. This is because the conversion for the reaction is only 10%. Higher conversion will caused more by-product, carbon dioxide, to be produced. Thus, the conversion needed to be as low as possible.

The estimated cost analysis for the optimum operating conditions is as per Table 7 below:

No.	Items	Quantity Per Run	Price (USD)
1.	Bio-oil	649 L	94.16
2.	Water	0.05 m^3	~0.01
	TOTAL		**94.17**

Table 8: Estimated material cost analysis for steam reforming

Assumptions:

1. The price for materials is obtained on the year of 2009.

2. Price for bio-oil is USD0.145/L. Price is obtained from Cole Hill Associates. However, the stated cost is only referring to production cost provided by Cole Hill Associates. The trade or retail cost is unknown.
3. The price for water is taken from *Kementerian Tenaga, Teknologi Hijau dan Air*. It is assumed that the research will be done on a laboratory scale. Thus, the price water is, 0.18 USD/m^3.
4. The price for catalyst or absorbent is neglected because there is no fix catalyst used in this simulation.

CHAPTER 5

CONCLUSION

The first objective of this project is to study on the methods available of upgrading the bio-oil in terms of the advantages and disadvantages of each method. For the purpose of this project, the methods have been studied are hydrotreatment, emulsification, catalytic cracking and esterification. The following are the advantages and disadvantages of both methods:

Technology	**Advantages**	**Disadvantages**
Hydrotreatment	1. Can reduced oxygen content which ultimately makes the upgraded bio-oil to become more stable.	1. For catalytic hydrotreatment, if the catalyst is regenerate, the yield would be lower. Thus more cost in catalyst is needed. 2. Hydro-treating process needs complicated equipment.
Emulsifications	1. There is no redundant chemical transformation.	1. High cost and high energy consumption. 2. May caused corrosiveness to engines if used for a long period.
Catalytic cracking	1. Cheaper route by converting oxygenated feedstocks to lighter fractions.	1. High coking (8 – 25 wt%). 2. Poor quality of fuels.
Steam reforming	1. Can produced hydrogen with lower coke formation.	1. Complicated techniques that needed absorbing and desorbing reactors.

Table 9: Comparison between the technologies of upgrading bio-oil

The estimated costs for each of the technology are as follow:

Technology	**Estimated Cost per Run(USD)**
Hydrotreatment	8.84
Emulsifications	10% Emulsion: 0.657 20% Emulsion: 0.612 30% Emulsion: 0.565
Catalytic cracking	2.99
Steam reforming	94.17

Table 10: Comparison of estimated material costs

For the time being, only the steam reforming technology can be modeled by using iCON process simulation. From the simulation, the optimum conditions for steam reforming is operating pressure of 5 bar, operating temperature of 800 °C and steam and carbon (S/C) ratio of 5. The maximum hydrogen yield is 3.06%.

5.1 Recommendation for Future Work

The following are the recommendation for the future work:

1. A detailed and complete cost analysis must be done to determine the feasibility of each of the technology.
2. iCON simulation must be done for each of the technology.

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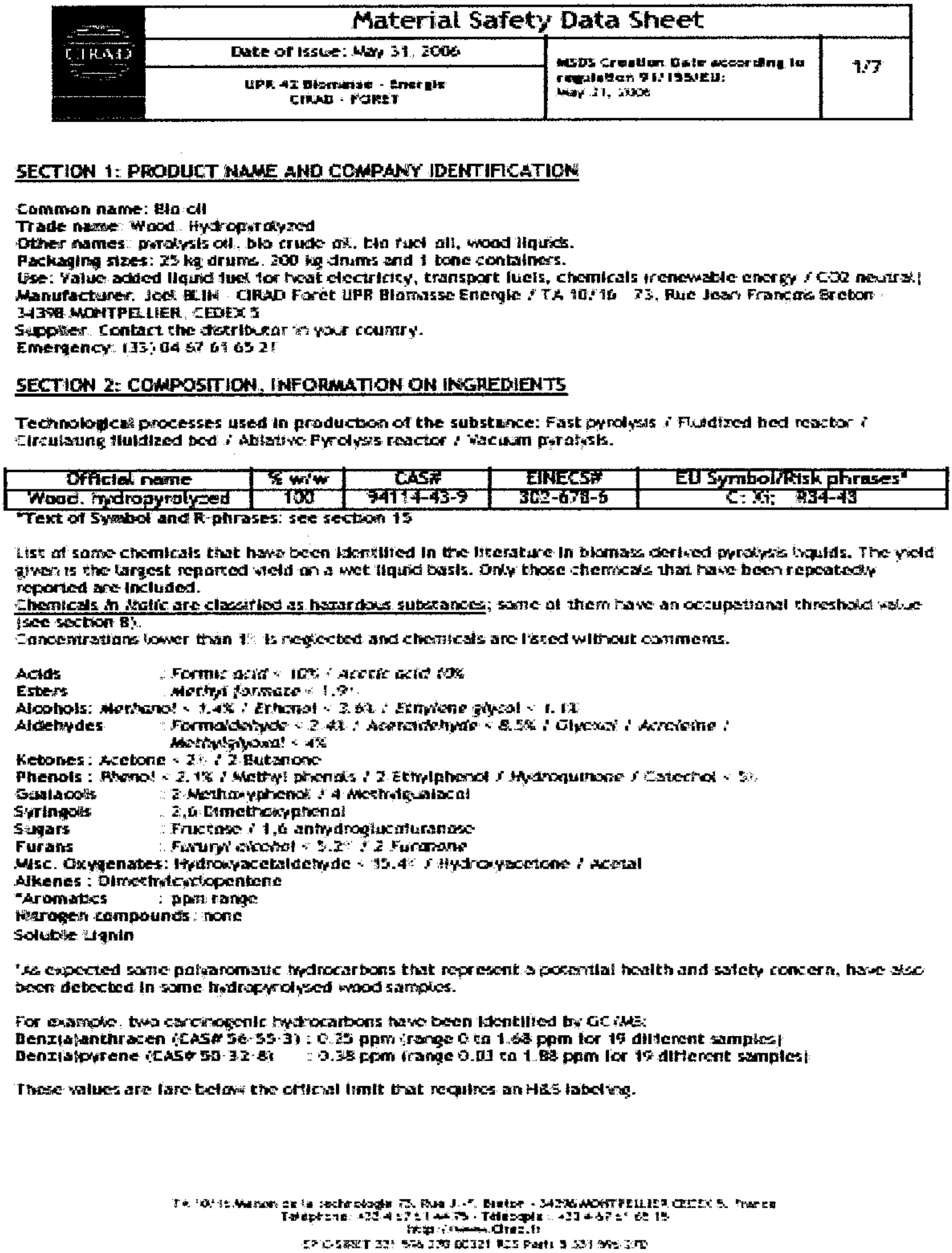
APPENDIX A



CIRAD	Material Safety Data Sheet		
	Date of issue: May 31, 2006	MSDS Creation Date according to regulation 91/155/EU: May 31, 2006	1/7
	UPR 42 Biomasse - Energie CIRAD - FORET		

SECTION 1: PRODUCT NAME AND COMPANY IDENTIFICATION

Common name: Bio oil
Trade name: Wood, Hydropyrolyzed
Other names: pyrolysis oil, bio crude oil, bio fuel oil, wood liquids.
Packaging sizes: 25 kg drums, 200 kg drums and 1 tone containers.
Use: Value added liquid fuel for heat electricity, transport fuels, chemicals (renewable energy / CO2 neutral)
Manufacturer: Joël BLIN - CIRAD Forêt UPR Biomasse Energie / TA 10/16 - 73, Rue Jean François Breton - 34398 MONTPELLIER, CEDEX 5
Supplier: Contact the distributor in your country.
Emergency: (33) 04 67 61 65 21

SECTION 2: COMPOSITION, INFORMATION ON INGREDIENTS

Technological processes used in production of the substance: Fast pyrolysis / Fluidized bed reactor / Circulating fluidized bed / Ablative Pyrolysis reactor / Vacuum pyrolysis.

Official name	% w/w	CAS#	EINECS#	EU Symbol/Risk phrases*
Wood, hydropyrolyzed	100	94114-43-9	302-678-6	C; Xi; R34-43

*Text of Symbol and R-phrases: see section 15

List of some chemicals that have been identified in the literature in biomass derived pyrolysis liquids. The yield given is the largest reported yield on a wet liquid basis. Only those chemicals that have been repeatedly reported are included.
Chemicals in *italic* are classified as hazardous substances; some of them have an occupational threshold value (see section 8).
Concentrations lower than 1% is neglected and chemicals are listed without comments.

Acids : *Formic acid* < 10% / *acetic acid 10%*
Esters : *Methyl formate* < 1.9%
Alcohols: *Methanol* < 1.4% / *Ethanol* < 3.6% / *Ethylene glycol* < 1.1%
Aldehydes : *Formaldehyde* < 2.4% / *Acetaldehyde* < 8.5% / *Glyoxal* / *Acroleine* / *Methylglyoxal* < 4%
Ketones : Acetone < 2% / 2 Butanone
Phenols : *Phenol* < 2.1% / Methyl phenols / 2 Ethylphenol / *Hydroquinone* / *Catechol* < 5%
Guaiacols : 2 Methoxyphenol / 4 Methylguaiacol
Syringols : 2,6 Dimethoxyphenol
Sugars : Fructose / 1,6 anhydroglucofuranose
Furans : *Furfuryl alcohol* < 5.2% / 2 *Furanone*
Misc. Oxygenates: Hydroxyacetaldehyde < 15.4% / Hydroxyacetone / Acetal
Alkenes : Dimethylcyclopentene
***Aromatics** : ppm range
Nitrogen compounds : none
Soluble Lignin

*As expected some polyaromatic hydrocarbons that represent a potential health and safety concern, have also been detected in some hydropyrolysed wood samples.

For example, two carcinogenic hydrocarbons have been identified by GC/MS:
Benz(a)anthracen (CAS# 56-55-3) : 0.25 ppm (range 0 to 1.68 ppm for 19 different samples)
Benz(a)pyrene (CAS# 50-32-8) : 0.38 ppm (range 0.03 to 1.88 ppm for 19 different samples)

These values are fare below the official limit that requires an H&S labeling.

SECTION 3: HAZARD IDENTIFICATION

Fire and explosion hazard:

- Flammable liquid at extremely high temperatures.
- Slow evaporation rate.
- Not an explosive when subjected to heat or shock.

Health hazard:
Primary routes of exposure: skin contact, eye contact, ingestion.

- **Eyes**: Corrosive, causes burns, severe corneal injury.
- **Skin**: Corrosive, causes burns or strong irritation.
- **Ingestion**: Causes burns to mouth, oesophagus and gastrointestinal tract if swallowed.
- **Inhalation**: Causes irritation to the respiratory tract.

SECTION 4: FIRST AID MEASURES

Eyes:
Immediately flush eyes with plenty of tepid water for at least 15 minutes, occasionally lifting the upper and lower lids.
Any contact lens must be removed. Get medical attention even if the injury appears to be mild.

Skin contact:
Remove all contaminated clothing immediately and wash affected skin area with soap and water.

Ingestion:
First immediately rinse your mouth several times with water. Should the product be swallowed administer 2-3 glasses of water for dilution.
Do not induce vomiting. Stay calm and seek medical advice.

Inhalation:
If eye, nose or throat irritation from dust or mists develops, move to fresh air until symptoms disappear.

Generalities:
Give nothing by mouth to an unconscious person.
If breathing is irregular or has stopped, give artificial respiration.
In all cases of doubt or if symptoms persists, seek medical attention and show this sheet to the doctor.

Antidote:
No specific antidote exists. The product is acidic (pH 2 -3) and is partly soluble in water. Treat symptomatically.

SECTION 5: FIRE FIGHTING MEASURES

Extinguishing media:
Water, carbon dioxide, foam, dry powder.
Use water spray to cool product containers and tanks near the fire.

Special exposure hazards in a fire:
Do not inhale smoke from the fire. Wear self-contained breathing apparatus and full protective clothing.
Explosion risk due to pressure increase into containers placed near a fire.
The heat may melt the containers allowing the content to mix with extinguishing water.

SECTION 6: ACCIDENTAL RELEASE MEASURES

Personal precautions: evacuate people upwind from the spill area.
Environmental precautions: do not allow the product to enter drains or surface water.

Methods for cleaning up:
To handle spills, the following preliminary advices are given.

- **Small quantities (< 1000 ml)**

  The suggested actions for such spillage are:
  Wear rubber gloves and suitable eye and face protection. If there is an inadequate ventilation, a suitable organic vapours filter mask or NIOSH approved respirator must be worn. Cover contaminated area with an inert adsorbent e.g. vermiculite, sawdust. Take up the used adsorbent and place it in a container for disposal or incineration.

- **Large quantities (> 1000 ml)**

  For spillage of significant quantities first evacuate rapidly workers present in the area and then take the same actions as described above.

SECTION 7: HANDLING AND STORAGE

Handling
Combustible.
Keep away from sources of ignition. Take precautionary measures (e.g. earthing) against electrostatic discharges.
When transferring the product and opening containers, avoid inhalation of vapours or gases. Ensure good ventilation when handling the product.
During tank cleaning operations follow special instructions provided by the manufacturer.

Storage
The product must be stored in containers suitable for combustible liquids and resistant to acids. Keep containers tightly closed at temperatures below 25°C in a well ventilated area. The product contains compounds that may either consume oxygen creating an under-pressure in the container; or may emit vapours that create an overpressure in the container.

Recommended storage materials: acid-proof steel, plastics (PETE, PP, HDPE). Filled containers may be gently heated to not more than 50°C before use for transfer of contents.

SECTION 8: EXPOSURE CONTROLS, PERSONAL PROTECTION

Engineering controls

Provide local and general exhaust ventilation to effectively remove and prevent vapors and mists generated from the handling of this product. Ensure that eyewash station and safety showers are proximal to the workplace location.

Personal protective equipment:

Eyes/Face
Wear safety glasses, chemical goggles if splashing is possible, or to prevent eye irritation from heated vapours or mists.

Skin/Hands/Feet
Wear chemically resistant gloves (nitrile gloves or thermally insulated gloves when handling hot products) and footwear with good traction to avoid slipping.
If splashing or contact with hot material is possible, consider the need for use of an impervious overcoat. Remove contaminated clothing and clean before reuse.

Fire resistant or natural fibre clothing is recommended.

Respiratory
If ventilation is not sufficient to effectively prevent aerosols or vapours, or if airborne concentrations are above the applicable exposure limits, use a NIOSH approved organic vapour cartridge respirator. Air supplied breathing apparatus must be used when airborne concentration may exceed the limits of the air purifying respirator used.

General
Personal protective equipment (**PPE**) should not be considered a long-term solution to exposure control. Consult a competent industrial hygiene resource, the PPE manufacturer's recommendation, and/or applicable regulations to determine hazard potential and ensure adequate protection.
Threshold Limit Values (MAK-values) of some chemicals listed in section 1.

Chemical name	CAS#	MAK-values in ppm or ml/m3
Acetaldehyde	75-07-0	50.0
Acetone	67-64-1	500.0
Formic acid	64-18-6	5.0
Acetic acid	64-19-7	10.0
Methanol	67-56-1	200.0
Formaldehyde	50-00-0	0.3
Furfuryl alcohol	98-00-0	10.0

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of the product may vary according to the used raw material, the manufacturing technology and the delivered batch.
The data below is representative of a typical bio-oil made from wood.

Colour	Dark brown viscous liquid
Odour	Strong characteristic, smoky
Density	Close to 1.2 kg/l
Water content	25 %
Water insoluble	20 % (pyrolytic lignin)
Log Pow	No data available
Viscosity-kinematics, cSt	225 at 20°C; 30 at 50°C
Surface tension, mN/m	29.2
pH	2.5
Flash point	Data is unreliable ranging from 40°C to over 110°C
Initial boiling point	< 100°C (beginning of the distillation)
Explosive properties	*Not heat or shock explosive*
Vapour pressure	Approximately 5 kPa at 38°C
Pour point	-20°C
Auto ignition temperature	About 500°C
Miscible with:	Acetone, methanol, ethanol
Not miscible with:	Hydrocarbons; water above 50% weight concentration

SECTION 10: STABILITY AND REACTIVITY

Chemical stability: stable under normal conditions of use and storage.

Chemical stability: conditions to avoid
Heating above 100°C: polymerization may occur with release of harmful or toxic fumes (carbon monoxide, carbon dioxide, formic acid, formaldehyde, methanol, acetaldehyde, acroleine and other organic compounds).

Corrosivity: reacts with mild steel and impure copper due to high acidity.

SECTION 11: TOXICOLOGICAL INFORMATION

The test results given below are based on one selected representative sample.

This sample has been obtained under well known operating conditions: temperature of 500°C; fluidized bed system; softwood.

- **LD50 (oral, rat)**: >2000 mg/kg/body weight
- **7-days oral, gavage, rats**: At 150 mg/kg/body weight, there were no clinical signs of toxicity, a slight reduction in the body weight gain of the females and no effect on food consumption. No macroscopic abnormalities were observed.
- **Acute dermal toxicity**: Test not performed as the product is corrosive.
- **Dermal Irritation** (rabbit): Corrosive
- **Eye Irritation** (not done for ethical reason): Corrosive
- **Inhalation**: Avoid inhalation as the product may contain hazardous substances depending on the manufacture process and temperature.
- **Skin sensitization** (LLNA, mice): Moderate sensitizer
- **Mutagenic tests**:
  1. *Ames test (Salmonella typhimurium)*: Positive, the product is mutagenic in this test.
  2. *Bone marrow micronucleus test by oral route gavage in mice*: Negative
  3. *Micronucleus test in L5178 TK mouse lymphoma cells*: Light mutagenic activity
- **Teratogenicity**: No known or listed teratogenic effects.
- **Reproductive effects**: No information available.
- **Neurotoxicity**: No information available.
- The product contains traces of substances classified as **carcinogenic** (e.g. formaldehyde, acetaldehyde, and furfural).

SECTION 12: ECOLOGICAL INFORMATION

- **Biodegradation** (Modified Sturm Test): The product biodegrades rapidly at percentages between 32 and 50%. Low biodegradation under anaerobic conditions.
- **Algal growth test**: At low concentration the product has a small fertilizing effect. At higher concentration, algal growth is slightly inhibited. From 0 to 72 hours the NOEL was > 100 mg/l.
- **EC50 (Acute toxicity to Daphnia Magna)**: > 100 mg/l

The potential to contribute to eutrophisation should be small due to the very low nitrogen, and very low minerals content of the product.
The product is not likely to bioaccumulation as most of components are highly soluble in water and/or biodegrade rapidly.

Waste treatment organisms: Large quantities may increase the pH value.

SECTION 13: DISPOSAL CONSIDERATIONS

Product waste is classified as **hazardous waste.**

European waste catalogue number: 13 07 03* Other Fuels (including mixture)
Do not allow this product to reach drains or ground water.
Follow national and municipal regulations obtained from local authorities.

SECTION 14: TRANSPORT INFORMATION

The information given below is provided to assist in documentation. See also *Section 16, 1)*

ADR/RID:	UN Number:	UN 2924
	Labels:	6 + 8 + 11
	Proper shipping name:	FLAMMABLE LIQUID, CORROSIVE, N.O.S. Wood distillate
	Risk Code	30
	Packaging group:	III
IMDG:	UN Number:	UN 2924
	Labels:	6 + 8 + 11
	Proper shipping name:	FLAMMABLE LIQUID, CORROSIVE, N.O.S Wood distillate
	EmS:	3-07
	Packaging group:	III
IATA:	UN Number:	UN 2924
	Labels:	6 + 8 + 11
	Proper shipping name:	FLAMMABLE LIQUID, CORROSIVE, N.O.S. Wood distillate
	Class:	3
	Packaging group:	III

SECTION 15: REGULATORY INFORMATION

European labeling: Wood, hydropyrolysed.

Symbol C: Corrosive

R 34: Causes burns.
R 43: May cause sensitization by skin contact.
S 26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 23: Do not breathes vapours.
S 37/39: Wear suitable gloves and eye protection.
S 45: In case of accident or if you feel unwell, seek medical advice immediately and show the product label or MSDS.

SECTION 16: OTHER INFORMATION

1) Transport Report

Transport, storage and handling of biomass derived fast pyrolysis liquid. Compliance with all international modes of transport.
EU Contract Nr NNE5 - 2001 - 00744 - Biotox
Web site: www.pyne.co.uk

2) Technical Report

A guide to physical property characterization of biomass derived fast pyrolysis liquids.
VTT Publications, Author: Anja Oasmaa & Cordner Peacocke.
Web site: www.vtt.fi

3) Technical Report

An assessment of bio-oil toxicity for safe handling and transportation.
Project Co-ordinator: Centre de Coopération Internationale en Recherche Agronomique pour le Développement (**Cirad**)
Web site:

- europa.eu.int/comm./energy/res/sector/doc/bioenergy/biotox_publishable_repport.pdf
- www.pyne.co.uk

The information contained herein is accurate to the best of our knowledge. We do not suggest or guarantee that any hazards listed herein are the only ones that exist.

CIRAD-Forêt, Aston University and the Institute for Wood Chemistry make no warranty of any kind, express or implied, concerning the safe use of this material in your process or in combination with other substances.

Users must meet all applicable safety and health standards to ensure proper use and disposal of these materials.

APPENDIX B

Data from iCON simulation for steam reforming.

Pressure, P = 5 bar and S/C ratio = 1.5

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.1631	1.5479	1.6307
600	0.1842	1.7481	1.8416
700	0.2052	1.9483	2.0525
800	0.2263	2.1486	2.2634

Pressure, P = 10 bar and S/C ratio = 1.5

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0815	0.7740	0.8153
600	0.0921	0.8741	0.9208
700	0.1026	0.9742	1.0262
800	0.1132	1.0743	1.1317

Pressure, P = 15 bar and S/C ratio = 1.5

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0544	0.5160	0.5436
600	0.0614	0.5827	0.6139
700	0.0684	0.6494	0.6842
800	0.0754	0.7162	0.7545

Pressure, P = 20 bar and S/C ratio = 1.5

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0408	1.0022	0.4077
600	0.0460	1.1318	0.4604
700	0.0513	1.2615	0.5131
800	0.0566	1.3911	0.5659

Pressure, P = 5 bar and S/C ratio = 2.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.1788	1.6971	1.7878
600	0.2019	1.9166	2.0190
700	0.2250	2.1361	2.2503
800	0.2482	2.3556	2.4815

Pressure, P = 10 bar and S/C ratio = 2.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0894	0.8485	0.8939
600	0.1010	0.9583	1.0095
700	0.1125	1.0680	1.1251
800	0.1241	1.1778	1.2408

Pressure, P = 15 bar and S/C ratio = 2.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0596	0.5657	0.5959
600	0.0673	0.6389	0.6730
700	0.0750	0.7120	0.7501
800	0.0827	0.7852	0.8272

Pressure, P = 20 bar and S/C ratio = 2.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0447	0.4243	0.4470
600	0.0505	0.4791	0.5048
700	0.0563	0.5340	0.5626
800	0.0620	0.5889	0.6204

Pressure, P = 5 bar and S/C ratio = 3.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.1992	1.8913	1.9924
600	0.2250	2.1359	2.2501
700	0.2508	2.3805	2.5078
800	0.2766	2.6252	2.7655

Pressure, P = 10 bar and S/C ratio = 3.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0996	0.9457	0.9962
600	0.1125	1.0680	1.1251
700	0.1254	1.1903	1.2539
800	0.1383	1.3126	1.3828

Pressure, P = 15 bar and S/C ratio = 3.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0664	0.6304	0.6641
600	0.0750	0.7120	0.7500
700	0.0836	0.7935	0.8359
800	0.0922	0.8751	0.9218

Pressure, P = 20 bar and S/C ratio = 3.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0498	0.4728	0.4981
600	0.0563	0.5340	0.5625
700	0.0627	0.5951	0.6270
800	0.0691	0.6563	0.6914

Pressure, P = 5 bar and S/C ratio = 4.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.2120	2.0122	2.1198
600	0.2394	2.2725	2.3939
700	0.2668	2.5327	2.6681
800	0.2942	2.7930	2.9423

Pressure, P = 10 bar and S/C ratio = 4.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.1060	1.0061	1.0599
600	0.1197	1.1362	1.1970
700	0.1334	1.2664	1.3341
800	0.1471	1.3965	1.4711

Pressure, P = 15 bar and S/C ratio = 4.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0707	0.6707	0.7066
600	0.0798	0.7575	0.7980
700	0.0889	0.8442	0.8894
800	0.0981	0.9310	0.9808

Pressure, P = 20 bar and S/C ratio = 4.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0530	0.5030	0.5299
600	0.0598	0.5681	0.5985
700	0.0667	0.6332	0.6670
800	0.0736	0.6982	0.7356

Pressure, P = 5 bar and S/C ratio = 5.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.2207	2.0947	2.2067
600	0.2492	2.3656	2.4921
700	0.2778	2.6365	2.7775
800	0.3063	2.9075	3.0629

Pressure, P = 10 bar and S/C ratio = 5.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.1103	1.0473	1.1033
600	0.1246	1.1828	1.2460
700	0.1389	1.3183	1.3888
800	0.1531	1.4537	1.5315

Pressure, P = 15 bar and S/C ratio = 5.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0736	0.6982	0.7356
600	0.0831	0.7885	0.8307
700	0.0926	0.8788	0.9258
800	0.1021	0.9692	1.0210

Pressure, P = 20 bar and S/C ratio = 5.0

Temperature, °C	H_2 Mass Flow, kg/hr	CO_2 Mass Flow, kg/hr	H_2 Yield, %
500	0.0552	0.5237	0.5517
600	0.0623	0.5914	0.6230
700	0.0694	0.6591	0.6944
800	0.0766	0.7269	0.7657

PETRONAS

GANTT CHART FOR FYP II

No	Task	JAN		FEBRUARY				MARCH			MID-SEM BREAK	APRIL					MAY				JUNE	
		1	2	3	4	5	6	7	8	9		10	11	12	13	14	15	16	17	18	19	20
1	Continuation of Project Work	■	■	■	■	■	■	■	■	■	▨	■	■	■	■							
2	Submission of Progress Report I				■						▨											
3	Submission of Progress Report II										▨	■										
4	Preparation for Poster Exhibition									■	▨	■										
5	Poster Exhibition										▨		■									
6	Submission of Final Report										▨					■						
7	Preparation for Oral Presentation										▨						■	■	■			
8	Final Oral Presentation										▨									■	■	
9	Submission of Hardbound Copies										▨											■

■ Milestone set by the FYP Committee
■ Progress Work