

OPTIMIZATION STUDY ON RECOVERY HYDROCARBONS
FROM PYROLYSIS OIL USING IONIC LIQUID

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A dissertation submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical Engineering
Unverisit Teknologi Malaysia

JULY 2012

To my beloved mother and father
谨以此献给含辛茹苦，我所爱的父母

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor, Professor Dr. Nor Aishah Saidina Amin, for her continuous guidance, advice and support throughout the period of completing my studying, and I have learned so many invaluable things from her. I only hope that a small part of her intuition, breadth of knowledge, and depth of understanding has rubbed off on me.

A special thanks to the CREG members and other technicians who have provided assistance at various occasions. Unfortunately, it is not possible to list all of them in this limited space. Their suggestions and tips are useful indeed. Thanks for them, I can spend and enjoy this good time in the laboratory.

Also should thanks to all the lecturers in my courses study. These courses really help me to understand this subject in different view, and will be useful for my further career.

Finally, I would like to extend special word of appreciation to the most important persons in my life: my dear parents, for their endless love and selfless support.

ABSTRACT

Energy crisis is a global issue because of fossil oil shortage. Biomass energy is a potential succedaneum for solving this problem, and fast pyrolysis is a effective route to convert biomass to liquid product. However the quality of pyrolysis oils is still a serious bottleneck for it service as transport fuel. Thus many study focused on how to improve it with physical or chemical methods. In this study, ionic liquid (1-butyl-3-methylimidazolium chloride, [BMIm]Cl) was used to separate hydrocarbon and improve the content in simulated pyrolysis oils which consisted some typical components. The optimization procedure was based on the Back Propagation (BP) Artificial Neural Network (ANN) modeling with Genetic Algorithm (GA). It was found that the hydrocarbon yield and content was increasing when oils to [BMIm]Cl ratio decreased, and the extraction system can be reached to equilibrium in a short time. Optimal condition was set as which extraction and holding time were at 20 and 6 minutes and oils to [BMIm]Cl ratio at 1.2 : 1, and hydrocarbon yield and content were 61.41% and 80.21% respectively as result. Finally, [BMIm]Cl is recycled by water extraction from waste. Comparing with original [BMIm]Cl, the result shows that hydrocarbons upgrading performance using recycled [BMIm]Cl is still acceptable.

ABSTRAK

Krisis tenaga adalah isu global disebabkan oleh faktor kekurangan minyak fosil. Bagi menyelesaikan permasalahan ini, tenaga biojisim adalah bahan alternatif yang berpotensi dan pirolisis secara pantas adalah satu kaedah yang berkesan untuk menukar biojisim kepada produk cecair. Walau bagaimanapun, kualiti minyak pirolisis masih dalam tahap yang kritikal untuk digunakan sebagai bahan api untuk segala jenis pengangkutan. Oleh itu, terdapat banyak kajian hanya memberi tumpuan kepada bagaimana untuk meningkatkan kualitinya dengan menggunakan kaedah fizikal atau kimia. Dalam kajian ini, cecair ionik (1-butyl-3-methylimidazolium klorida, [BMIm]Cl) telah digunakan untuk memisahkan hidrokarbon dan seterusnya memperbaiki kandungan dalam minyak simulasi pirolisis yang mana ia terdiri daripada beberapa komponen. Seterusnya, kaedah pengoptimuman dijalankan berdasarkan model propagasi bersama dengan Algoritma Genetik (GA). Daripada keputusan didapati, hasil hidrokarbon dan kandungan telah meningkat apabila minyak kepada nisbah cecair ionik menurun, dan sistem pengekstrakan boleh dicapai ke keseimbangan dalam masa yang singkat. Tahap optimum bagi masa pengestrakan dan masa pegangan adalah pada 20 dan 6 minit. Seterusnya, nisbah minyak kepada cecair ionik adalah pada kadar 1.2: 1 dan hasil dan kandungan hidrokarbon setiap satunya adalah bersamaan dengan 61.41% dan 80.21%. Akhir sekali, kajian terhadap cecair ionik yang dikitar semula dari sisa telah dilakukan. Dengan perbandingan dengan [BMIm]Cl yang asal, keputusan menunjukkan prestasi cecair ionik yang dikitar semula masih boleh diterima.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variance
ANN	-	Artificial Neural Network
[BMIm]Cl	-	1-butyl-3-methylimidazolium chloride
BP	-	Back propagation
CCD	-	Central composite design
d.f.	-	Degree of freedom
F	-	F calculated
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transform Infrared Spectroscopy
GA	-	Genetic Algorithm
GC	-	Gas Chromatograph
GC-MS	-	Gas Chromatograph Mass Spectrometric
IL	-	Ionic liquid
Mean Sq.	-	Mean square
MIV	-	Mean impact value
MSE	-	Mean square error
RSM	-	Response surface methodology
Sum Sq.	-	Sum of square

LIST OF SYMBOLS

b	-	Bias
V	-	Volume
I	-	Relative importance
R^2	-	Correlation coefficient
W	-	Weight
X	-	Variable
X_1	-	Extraction time (min)
X_2	-	Holding time (min)
X_3	-	Oils : IL ratio (V/V)
Y	-	Response
Y_1	-	Yield, %
Y_2	-	Hydrocarbon yield, %
Y_3	-	Hydrocarbon content, %

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CHAPTER 1

INTRODUCTION

1.1 Background

Energy sources transcend the boundaries between national security, economic policy and environmental issue. With the increasing productivity and improving technology, energy plays an important role in this modern society. This is especially significant after World War II, when the world economics developed rapidly, driving the sharp increment in energy consumption, particularly fossil fuels. The fossil fuels (include coal, oil and natural gas) remain the dominant energy source in the energy consumption market all around the world. Figure 1.1 showed the total primary energy supply (TPES) by fuels in 1973 and 2008 [1]. Though many governments are placing increased emphasis on the usage of other renewable energy such as biomass, wind, solar etc., fossil fuels sustained its dominancy in world energy consumption. The amount of new energy supply had increased in the past thirty years, but fossil fuel remained the largest supplier (>80%).

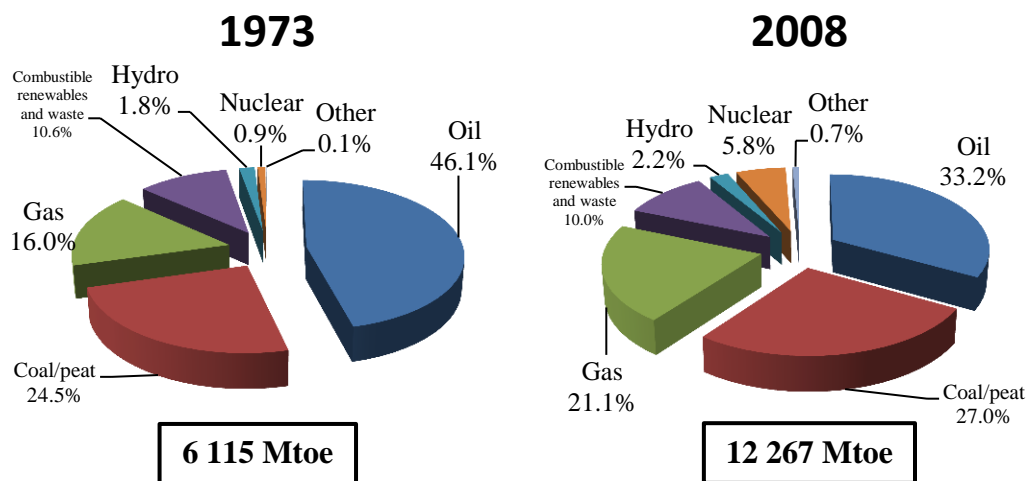


Figure 1.1: 1973 and 2008 fuel shares of TPES [1]

Reports estimated the reserves of total oil resources to be 1333.1 thousand million barrels at the end of 2009 [2]. As this limited quantity of the non-renewable energy is drying up, the world is alarmed with energy shortage problem, thus inserting, the rising trend in current crude oil price (See Figure 1.2), as well as future price prediction. In May 2008, the price of crude oil was closed to US\$ 140 in New York Mercantile Exchange (NYMEX). The high price of oil manipulates the direction of economic policy by governments. Besides establishing energy reserves systems, many authorities encourage the development of renewable energy thus securing the national energy security.

CO₂ is one of the most significant greenhouse gases which contribute to global warming, and most climate scientists agree that, this will cause major adverse effects for the environment. The data released from *CO₂ Emissions from Fuel Combustion Highlights (2010 Edition)* by International Energy Agency (IEA) [3] showed that CO₂ emissions from the combustion of coal, oil, gas was 12.6 Gt, 10.8 Gt, and 5.8 Gt respectively in 2008. The percentage of CO₂ from energy is 83% in Annex I countries (i.e., Australia, Austria, Belarus, and 38 other countries and

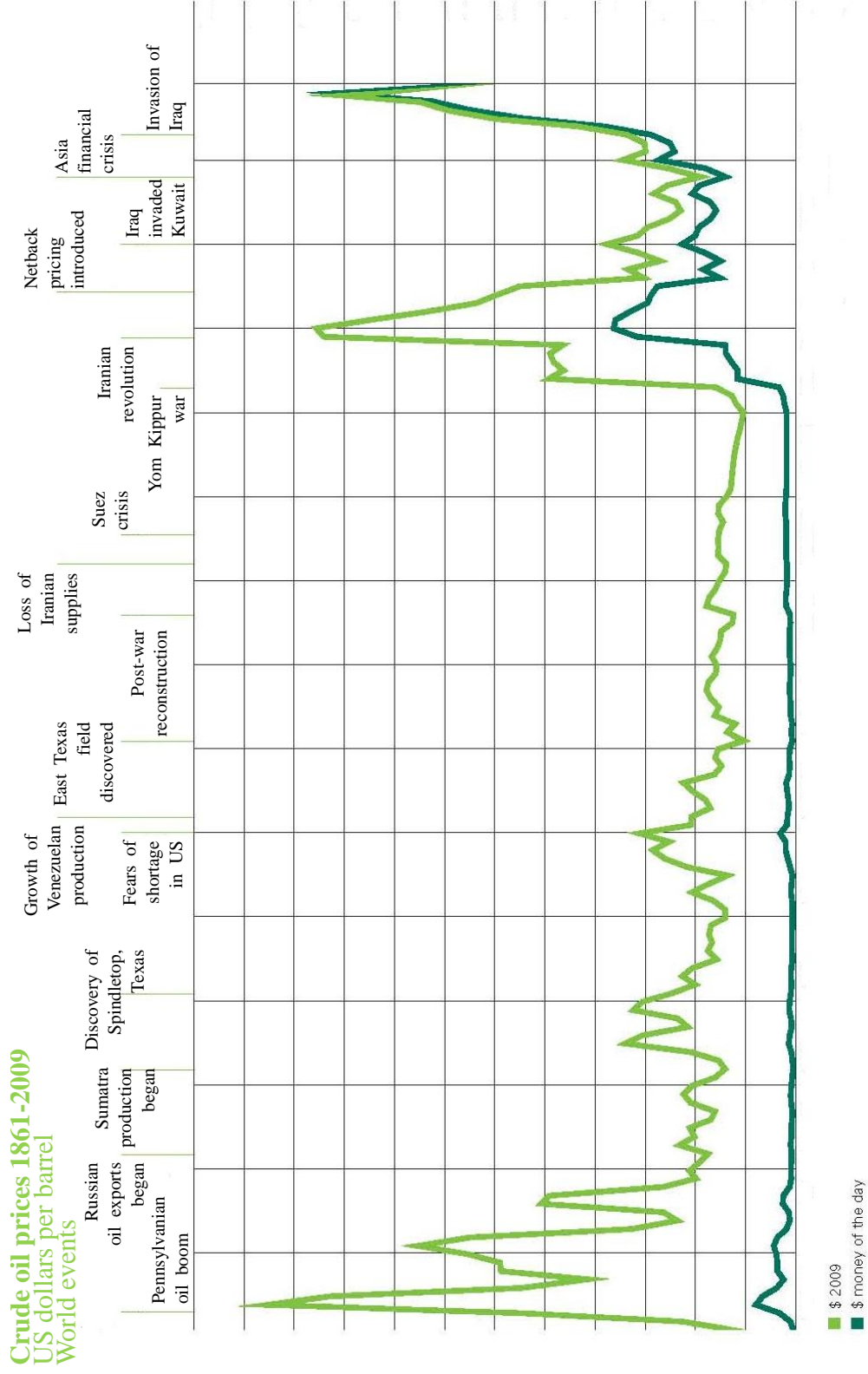


Figure 1.2: Crude oil prices from 1861 to 2009 [2]

organizations, which participated in the 1992 UN Framework Convention on Climate Change (UNFCCC), and the proportion is mostly from fossil fuel, when the TPES is just 81% of them (See Figure 1.3 and 1.4).

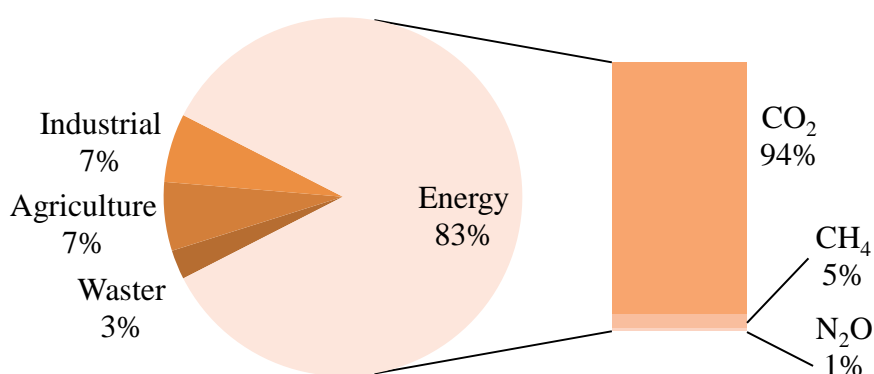
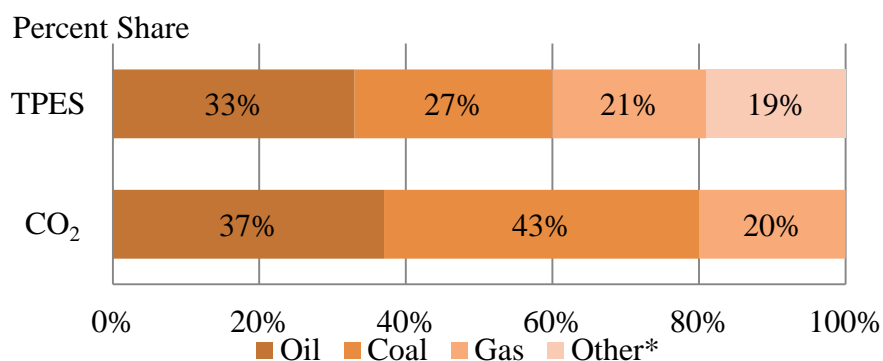


Figure 1.3: Greenhouse gas emissions in Annex I countries, 2008 [2]



* Other includes nuclear, hydro, geothermal, solar, tide, wind, combustible renewables and waste.

Figure 1.4: World TPES and CO₂ emissions: share by fuels in 2008 [2]

The biomass potential, a renewable energy source, is one of the earliest sources of energy in human history. One typical example is the use of burning wood for cooking. Figure 1.5 showed the important role played by biomass energy before coal became the dominant energy source consumed in 1900s. This was replaced by

the consumption of oil in 1970s as the dominant energy source, with gas consumption ranked at the third position gas at the same time [4]. Nevertheless, biomass are still the forth energy resources. Considering the current environmental issues, the spreading energy shortage problems and the increasing price of fossil fuels, biomass may reclaim its significant position as the most important renewable energy source in the near future.

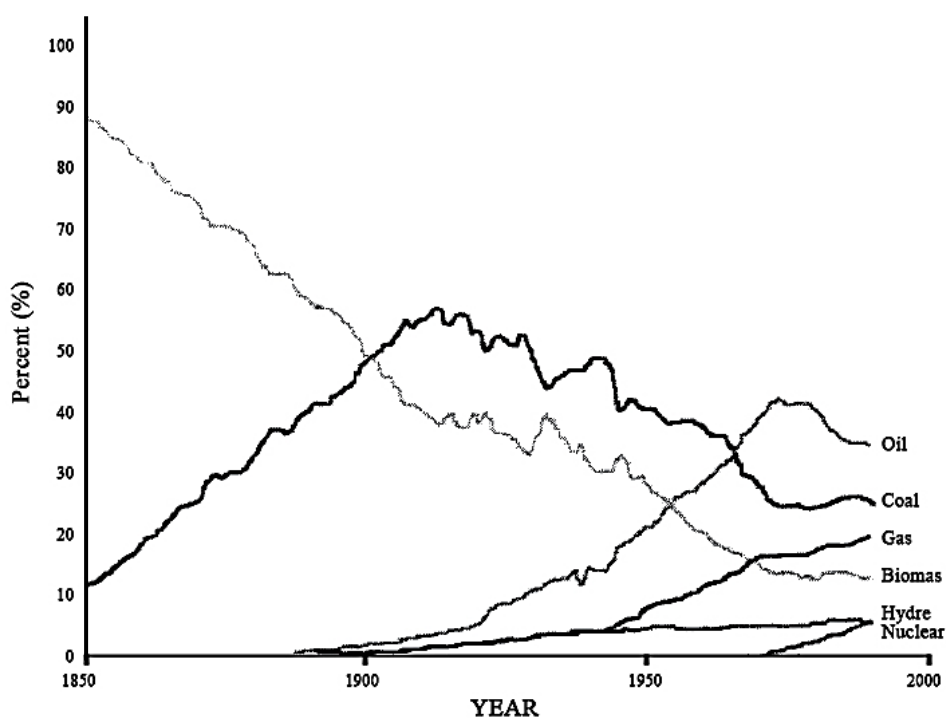


Figure 1.5: The position of biomass in the history from 1850 to 2000 [4]

1.2 Problem Statement

The study will attempt to produce transportation fuels from pyrolysis oils. The blueprint was shown in Figure 1.6.

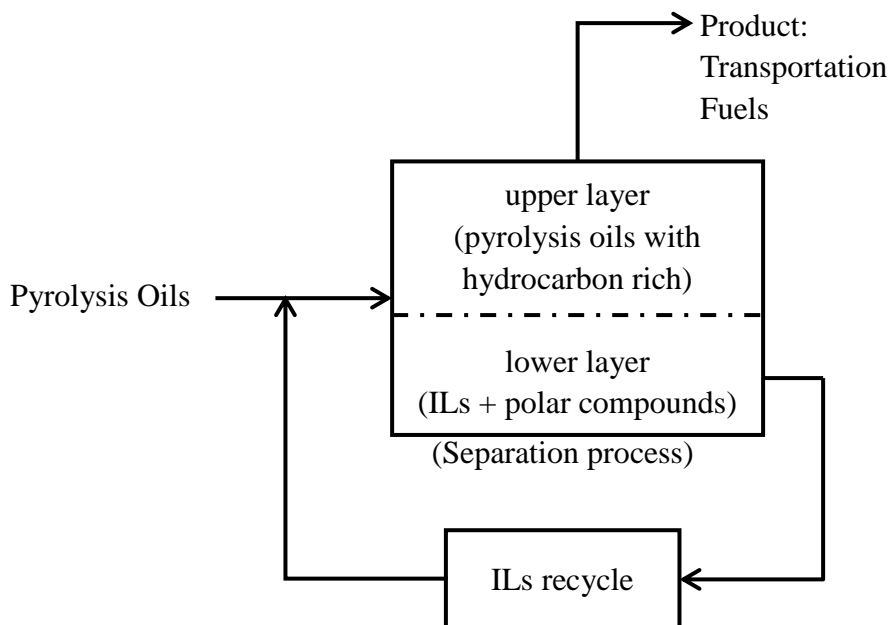


Figure 1.6: Blueprint of study

The pyrolysis oils, which consist of fatty acid methyl ester (FAME), hydrocarbon and acids, are production from fast pyrolysis in previous studies. In this study, Ionic liquids (ILs) will be used as the solvent to separate hydrocarbon from other main components in pyrolysis oils because of its strong polarity. ILs will be recycled for the separation processes to reduce operating cost.

1.3 Objective

The objectives of this study include:

- i. To determine the approach to upgrade hydrocarbon content in pyrolysis oil using separation with ionic liquid (1-butyl-3-methylimidazolium

chloride, [BMIm]Cl) with different extraction time, holding time and oil to ionic liquid ratio;

- ii. To study the performance of recycle [BMIm]Cl for upgrading pyrolysis oil;
- iii. To develop the mathematical model using Artificial Neural Network (ANN) method and determine optimal operation conditions using Genetic Algorithm (GA) method.

1.4 Scopes

The scopes of this research are listed in the following:

- i. Separation study: the scopes of separation study include the following aspects:
 - a) To determine the different performance of upgrading hydrocarbons content in the simulated pyrolysis oils using [BMIm]Cl with Central Composition Design(CCD) at different extraction time, holding time and oil : ionic liquid ratio by volume;
 - b) To determine the upgrading performance which influence by the water content (no water content, 10%, 20% and 30% by volume) in the simulated pyrolysis oils;

- c) To attempt the approach to recovery [BMIm]Cl using water extraction, and determine the upgrading performance using recovery [BMIm]Cl;
- ii. Model study: to establish a mathematical model (quadratic and ANN), and determine which one has a better fitting and predicted performance for this case;
- iii. Optimization study: based on ANN model, to calculate the optimal conditions using GA, and make a confirmation using experiment.

1.5 Significance

It is significant to develop energy from biomass for decreasing the dependent on energy from fossil fuels. It not only can help to solve the energy crisis and energy security with the diversity of energy resources, but to decrease the tension for environmental requirements as well. It is potential to be used as transportation fuels from pyrolysis oils, and had a large of achievements in this field, but it is still not economic and less competitive compared with petroleum diesel nowadays. It is necessary to increase the quality of pyrolysis oils as transportation fuels, and decrease the total cost to obtain these high quality pyrolysis oils with some new technology.

1.6 Innovation

ILs will be employed to separate hydrocarbon from pyrolysis oils in this study. As green chemical solvents, ILs are used not only in chemical reaction and electrochemistry application, but in catalysts and other fields as well. ILs had been applied in extraction, gasoline desulfurization studies, rare earths extractions [5], and other fields such as heavy oils, essential oils, and biofuels etc. However, the study in pyrolysis oils separation process with ILs was still limited.

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