OPTIMIZATION STUDY ON RECOVERY HYDROCARBONS FROM PYROLYSIS OIL USING IONIC LIQUID

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To my beloved mother and father

谨以此献给含辛茹苦，我所爱的父母

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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 equillibrium 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%).

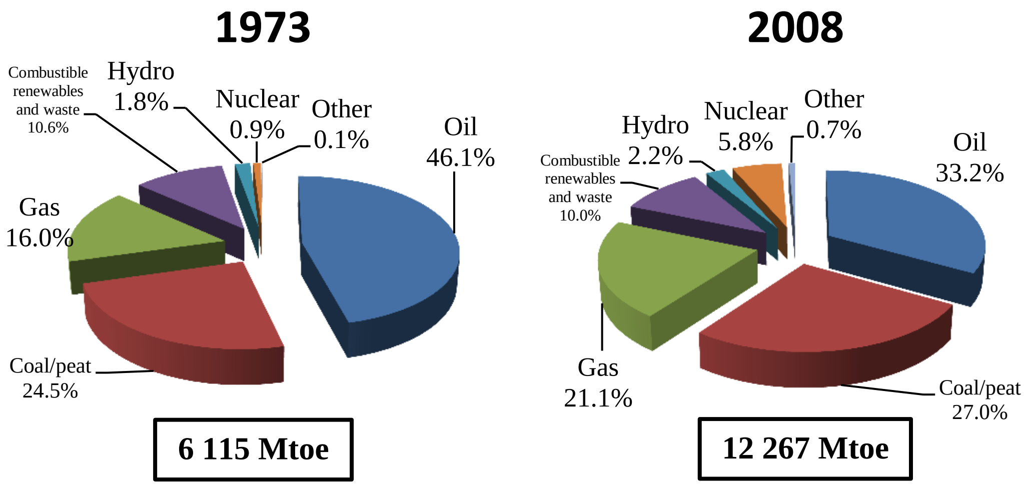


Figure 1.1: 1973 and 2008 fuel shares of TPES [1]

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.

CO_2 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 *CO_2 Emissions from Fuel Combustion Highlights (2010 Edition)* by International Energy Agency (IEA) [3] showed that CO_2 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 CO_2 from energy is 83% in Annex I countries (i.e., Australia, Austria, Belarus, and 38 other countries and

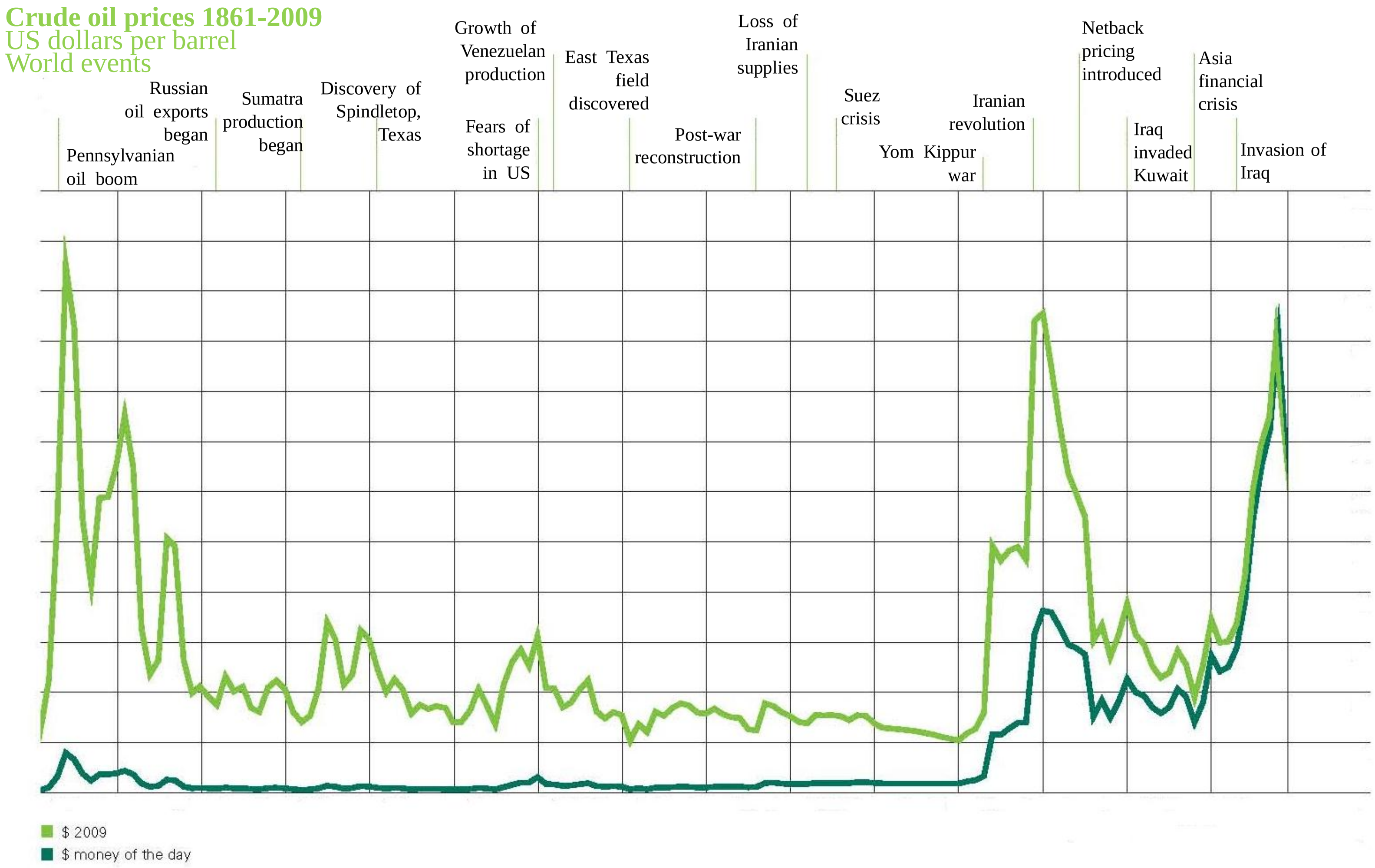


Figure 1.2: Crude oil prices from 1861 to 2009 [2]

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).

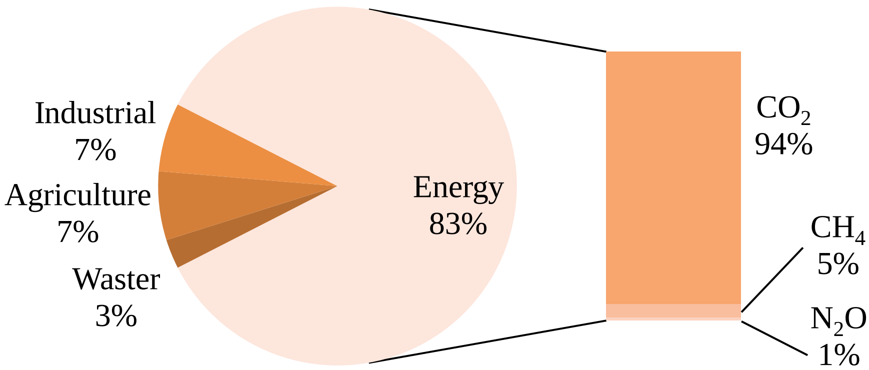
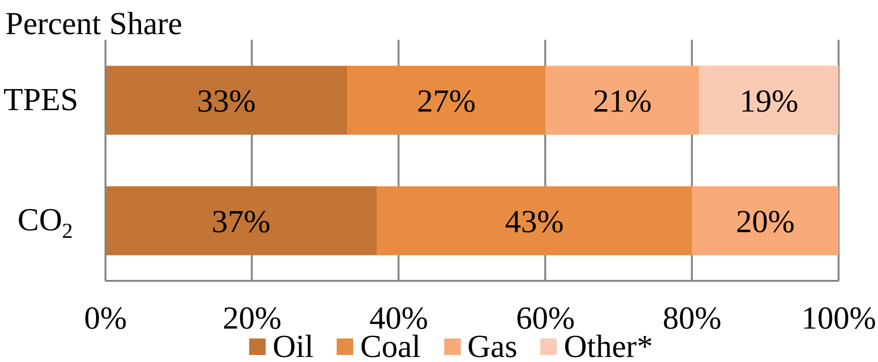


Figure 1.3: Greenhouse gas emissions in Annex I countries, 2008 [2]



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

Figure 1.4: World TPES and CO_2 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.

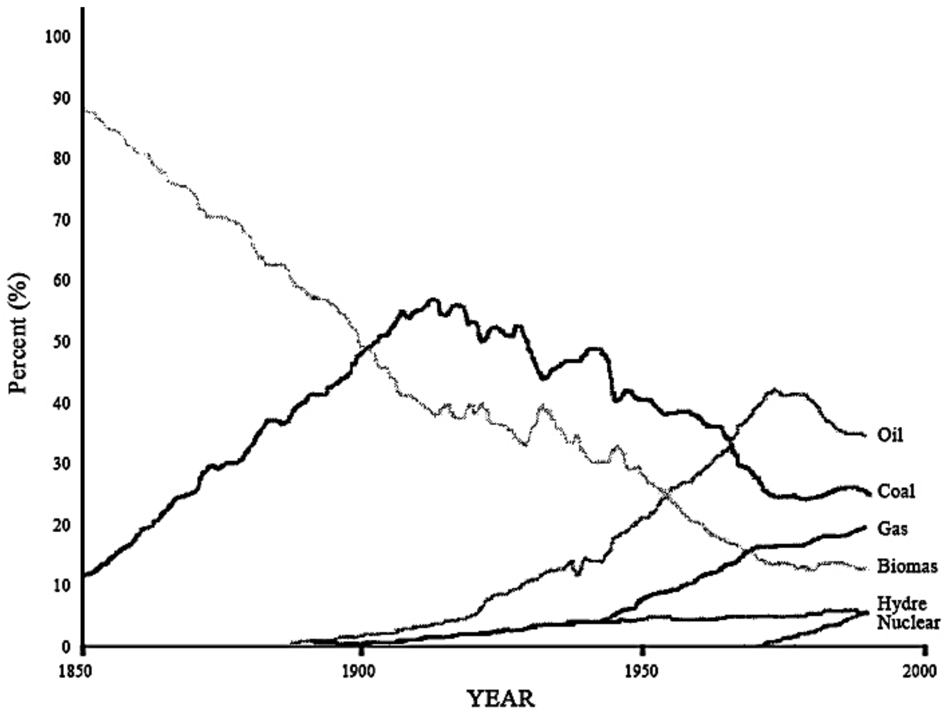


Figure 1.5: The position of biomass in the history from 1850 to 2000 [4]

1.2 Problem Statement

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

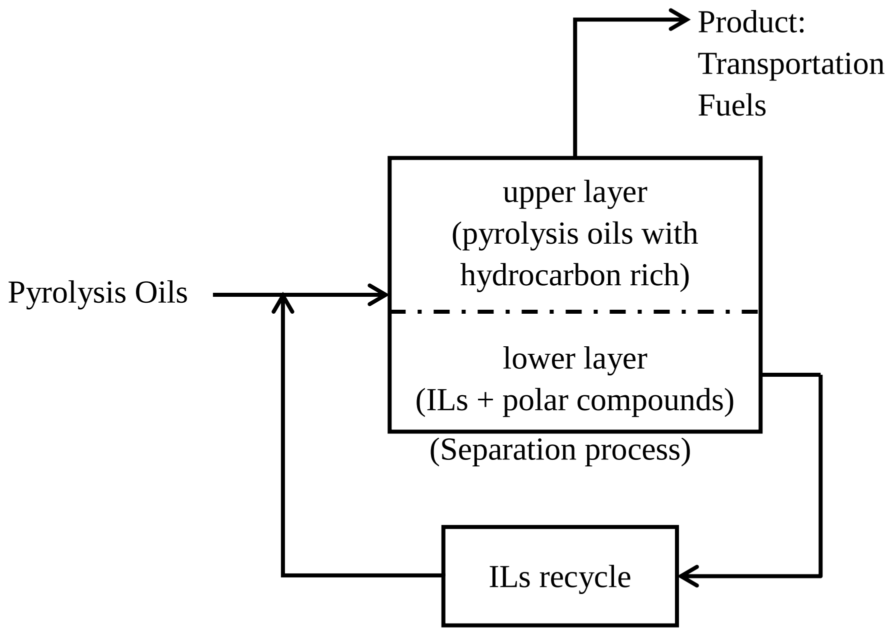


Figure 1.6: Blueprint of study

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.

REFERENCES

[1] International Energy Agency. *2010 Key World Energy Statistic*. [Brochure]. Paris, France: Soregraph. 2010

[2] British Petroleum. *BP Statistical Review of World Energy June 2010*. [Brochure]. London, UK: Beacon Press. 2010

[3] International Energy Agency. *CO_2 Emissions from Fuel Combustion Highlights (2010 Edition)*. Paris, France: Soregraph. 2010

[4] Wang, Q. *Research on Production and Utilization of Bio-oil from Biomass Fast Pyrolysis*. Doctor. Zhejiang University, Hangzhou, P.R.China; 2008

[5] Liu, Y. H., Zhu, L. L., Sun, X. Q. and Chen, J. Toward Greener Separations of Rare Earths: Bifunctional Ionic Liquid Extractants in Biodiesel. *AIChE Journal*. 2010. 56 (9): 2338 – 2346.

[6] Czernik, S. and Bridgwater, A. V. Overview of Applications of Biomass Fast Pyrolysis Oil. *Energy Fuels*. 2004. 18 (2): 590 – 598.

[7] Lu, Q., Li, W. Z. and Zhu, X. F. Overview of fuel properties of biomass fast pyrolysis oils. *Energy Conversion and Management*. 2009. 50 (5): 1376 – 1383.

[8] Huber, G. W., Iborra, S. and Corma, A. Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chemical. Reviews*. 2006. 106 (9): 4044 – 4098.

[9] Oasmaa, A. Testing Standard Methods. In: Bridgwater, A. V. ed. *Fast Pyrolysis of Biomass: A Handbook*. UK: CPL Press. 70; 2003.

[10] Meier, D., Oasmaa, A. and Peacocke, G. V. C. Properties of Fast Pyrolysis Liquids: Status of Test Methods. In: Bridgwater, A. V. ed. *Fast Pyrolysis of Biomass: A Handbook*. UK: CPL Press. 82; 2003.

[11] Diebold, J. P. A Review of the Toxicity of Biomass Pyrolysis Liquids Formed at Low Temperature. In: Bridgwater , A. V. ed. *Fast Pyrolysis of Biomass: A Handbook*. UK: CPL Press. 140 – 145; 2003.

[12] Bridgwater, A. V. An Introduction to Fast Pyrolysis of Biomass for Fuels and Chemicals. In: Bridgwater, A. V. ed. *Fast Pyrolysis of Biomass: A Handbook*. UK: CPL Press. 9; 2003.

[13] Zheng, J. L. and Wei, Q. Improving the Quality of Fast Pyrolysis Bio-oil by Reduced Pressure Distillation. *Biomass and Bioenergy*. 2011. 35 (5): 1804 – 1810.

[14] Sandvig, E., Walling, G., Daugaard, D. E., Pletka, R. J., Radlein, D., Johnson, W. and Brown, R. C. The Prospects for Integrating Fast Pyrolysis into Biomass Power Systems. *The Journal of International Journal of Power and Energy Systems*. 2004. 24 (3): 228 – 238.

[15] Moens, L., Black, S. K., Myers, M. D. and Czernik, S. Study of the Neutralization and Stabilization of a Mixed Hardwood Bio-Oil. *Energy Fuels*. 2009. 23 (5): 2695–2699.

[16] Guo, Z. G., Wang, S. R., Zhu, Y. Y., Luo, Z. Y. and Cen, K. F. Separation of Acid Compound for Refining Biomass Pyrolysis Oil, *Journal of Fuel Chemistry and Technology*. 2009. 37 (1): 49-52.

[17] Luik, H., Johannes, I., Palu, V., Luik, L. and Kruusement, K. Transformations of Biomass Internal Oxygen at Varied Pyrolysis Conditions. *Journal of Analytical and Applied Pyrolysis*. 2007. 79 (1-2): 121 – 127.

[18] Zheng, F. X., Liu, W. J., Jiang, H., Yu, H. Q., Zeng, R. J. and Guo, Q. X. Separation of Phthalate Esters from Bio-oil Derived from Rice Hush by a Basification-Acidification Process and Column Chromatography. *Bioresource Technology*. 2011. 102 (2): 1982 – 1987.

[19] Naik, S., Goud, V. V., Rout, P. K. and Dalai, A. K. Supercritical CO_2 Fractionation of Bio-oil Produced from Wheat–Hemlock Biomass. *Bioresource Technology*. 2010. 101 (19): 7605 – 7613.

[20] Patel, R. N., Bandyopadhyay, S. and Ganesh, A. Extraction of Cardanol and Phenol from Bio-oils Obtained through Vacuum Pyrolysis of Biomass Using Supercritical Fluid Extraction. *Energy*. 2011. 36 (3): 1535 – 1542.

[21] Ba, T., Chaala, A., Garcia-Perez, M. and Roys, C. Colloidal Properties of Bio-oils Obtained by Vacuum Pyrolysis of Softwood Bark. Storage Stability. *Energy Fuels*. 2004. 18 (1): 188 – 201.

[22] Ikura, M., Stanciulescu, M. and Hogan, E. Emulsification of Pyrolysis Derived Bio-oil in Diesel Fuel. *Biomass and Bioenergy*. 2003. 24 (3): 221 – 232.

[23] Hyötyläinen, T., Andersson, T., Jussila, M., Wiedmer, S. K., Rautiainen, M. and Riekkola, M. L. Determination of Phenols in Pyrolysis Oil by On-line Coupled Microporous Membrane Liquid-Liquid Extraction and Multidimensional Liquid. *Journal of Separation Science*. 2001. 24 (7): 544 – 550.

[24] Ye, T. X., Zhang, Y. H., Liu, J. H. and Zhang, Z. L. Synthesis of the Ionic Liquid of Alkyl Imidazolium Borofluoride and Properties of Solvent. *Journal of the University of Petroleum, China*. 2004. 28 (4): 105 – 111.

[25] Hayyan, M., Mjalli, F. S., Hashim, M. A. and AlNashef, I. M. A Novel Technique for Separating Glycerine from Palm Oil-based Biodiesel Using Ionic Liquids. *Fuel Processing Technology*. 2010. 91 (1): 116 – 120.

[26] Wilkes, J. S. A Short History of Ionic Liquid – from Molten Salts to Neoteric Solvents. *Green Chemistry*, 2002.4: 73 – 80.

[27] Welton, T. Room-Temperature Ionic Liquid. Solvents for Synthesis and Catalysis. *Chemical Review*. 1999. 99 (8): 2071 – 2084.

[28] Wasserscheid, P. and Keim, W. Ionic Liquid New "Solutions" for Transition Metal Catalysis. *Angewandte Chemie International Edition*. 2002. 39 (21): 3773 – 3789.

[29] Dupont, J., de Souza, R. F. and Suarez, P. A. Ionic Liquid (Molten Salt) Phase Organometallic Catalysis. *Chemical Review*. 2002. 102 (10): 3667 – 2692.

[30] Brennecke, J. F. and Maginn, E. J. Ionic Liquids: Innovative Fluids for Chemical Processing. *AIChE Journal*. 2001. 47 (11): 2384 – 2389.

[31] Xiang, X. Y. *Desulfurization of Gasoline by Extraction with [Bmim]*BF_4 *Ionic Liquids*. Master of Engineering. Huaqiao University, Xiamen, P.R.China; 2007

[32] Pei, Y. C. *Studies on the Separation Performance of Ionic Liquids and Their Interactions with Solutes*. Doctor. Lanzhou University, Lanzhou, P.R.China; 2008

[33] Walden, P. and Bull. Acad. *Imper. Scl.* (St. Petersburg). 1914. 1800.

[34] Hurley, F. H. and Wier, T. P. Electrodeposotion of Metals from Fused Quaternary Ammonium Salts. *Journal of The Electrochemical Society*. 1951. 98 (5): 203 – 206.

[35] Chum, H. L., Koch, V. R., Miller, L. L. and Osteryoung, R. A. Electrochemical Scrutiny of Organometallic iron Complexes and Hexamethylbenzene in A Room temperature Molten Salt. *Journal of the American Chemical Society.* 1975. 97 (11): 3264 – 3265.

[36] Wilkes, J. S., Levisky, J. A., Wilson, R. A. and Hussey, C. L. Dialkylimidazolium Chloroaluminate Melts: A New Class of Room-temperature Ionic Liquids for Electrochemistry Spectroscopy and Synthesis. *Inorganic Chemistry.* 1982. 21 (3): 1263 – 1264.

[37] Laher, T. M. and Hussey, C. L. Copper(I) and Copper(II) Chloro Complexes in the Basic Aluminum Chloride-1-Methyl-3-Ethylimidazolium Chloride Ionic Liquid. *Inorganic Chemistry*. 1983. 22 (22): 3247 – 3251.

[38] Wilkes, J. S. and Zaworotko, M. J. Air and Water Stable 1-Ethyl-3-Methylimidazolium Based Ionic Liquids. *Journal of the Chemical Society*, *Chemical Communications*. 1992. 13: 965 – 967.

[39] Marciniak, A. Activity Coefficients at Infinite Dilution and Physicochemical Properties for Organic Solutes and Water in the Ionic Liquid 1-(3-Hydroxypropyl)Pyridiniumbis(Trifluoromethylsulfonyl) -Amide. *The Journal of Chemical Thermodynamics*. 2011. 43 (10): 1446 – 1452.

[40] Domańska U., Redhib, G. G. and Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-1-Methylpyrrolidinium Trifluoromethanesulfonate Using GLC. *Fluid Phase Equilibria*. 2009. 278 (1-2): 97 – 102.

[41] Zhu, J. Q., Chen, J. and Fei, W. Y. Separation of Aromatic Hydrocarbons and Olefins from Paraffins Using New Ionic Liquids. *Journal of Chemical Industry and Engineering (China)*. 2004. 55 (12): 2091 – 2094.

[42] Yu, Y. M., Zhang, Y. F. and Zhu, D. X. Research on Solubility of the Compositions of Fuel Oil in Imidazolium-Based Ionic Liquids. *Journal of Northeast Normal University (Natural Science Edition)*. 2009. 41 (2): 121 – 125.

[43] Box, G. E. P. and Wilson, K. B. On the Experimental Attainment of Optimum Conditions. *Journal of the Royal Statistical Society. Series B (Methodological)*.1951. 13 (1): 1 – 45.

[44] Hagan and Martin, T. *Neural Network Design*. Boston, U.S.A.: PWS Pub. 1996

[45] Demuth, H. and Beale, M. *Neural Network Toolbox for User with MATLAB* (Version 4). Natick, MA, U.S.A.: MathWorks, Inc. 2000

[46] Elmolla, E. S., Chaudhuri, Y. and Eltoukhy, M. M. The use of artificial neural network (ANN) for modeling of COD removal from antibioticaqueoussolution by the Fenton process. *Journal of Hazardous Materials*. 2010. 179 (1 – 3): 127 – 134.

[47] Yetilmezsoy, K. and Demirel, S. Artificial Neural Network (ANN) Approach for Modeling of Pb(II) Adsorption from Aqueous Solution by Antep Pistachio (Pistacia Vera L.) Shells. *Journal of Hazardous Materials*. 2008. 153: 1288 – 1300

[48] Zhuo, J. W. *Application of MATLAB in Mathematics Modeling*. Beijing. P.R.China: Beihang University Press. 2011

[49] The MathWorks. Inc. *Global Optimization Toolbox User's Guide* (R2011b). Natick, MA, U.S.A.: MathWorks, Inc. 2011

[50] Şenol, O. İ. *Hydrodeoxygenation of Aliphatic and Aromatic Oxygenates on Sulphided Catalysts for Production of Second Generation Biofuels*. Doctor of Science in Technology. Helsinki University of Technology; 2007

[51] Montgomery, D. C. *Design and Analysis of Experiments*. New York: John Wiley & Sons. 2001

[52] Clarke, G. M. and Kempson, R. E. *Introduction to the Design and Analysis of Experiments*. London: Arnold. 1997

[53] Cornell, J. A. *How to Apply Response Surface Methodology*. Milwaukee: American Society for Quality Control (ASQC). 1990

[54] Ahari, J. S., Sadeghi, M. T. and Pashneh, S. Z. Optimization of OCM Reaction Conditions over Na–W–Mn/SiO_2 Catalyst at Elevated Pressure. *Journal of Taiwan Institute of Chemical Engineers*. 2011. 42 (5): 751 – 759.

[55] Bhatti, M. S., Kapoor, D., Kalia, R. K., Reddy, A. S. and Thukral, A. K. RSM and ANN Modelling for Electrocoagulation of Copper from Simulated Wastewater: Multi Objective Optimization Using Genetic Algorithm Approach. *Desalination*. 2011. 274 (): 74 – 80.

[56] Istadi and Nor, A. S. A. A Hybrid Numerical Approach for Multi-responses Optimization of Process Parameters and Catalyst Compositions in CO_2-OCM Process over CaO-MnO/CeO_2 Catalyst. *Chemical Engineering Journal*. 2005. 106 (3): 213 – 227.

[57] Rudolf, N. C., Michael, R. F. Aitken. *ANOVA for the Behavioural Sciences Researcher*. Mahwah, New Jersey, UK: Lawrence Erlbaum Associates, Inc. 2006

[58] MathWorks. *Statistics Toolbox™ 7 User's Guide*. Natick, MA, USA: The MathWorks, Inc. 2010

[59] Xie, Z. H. *Statistical Analysis and Application: 40 Cases Study*. Beijing, P.R.China: Beihang University Press. 2010

[60] Garson, G. D. Interpreting Neural-Network Connection Weights. *AI Expert*. 1991. 6: 47–51.

[61] Xie, Z. H. *MATLAB Applications in Artificial Neural Network: 30 Cases*. Beijing, P.R.China: Beihang University Press. 2010

[62] Yetilmezsoy, K. and Demirel, S. Artificial Neural Network (ANN) Approach for Modeling of PB(II) Adsorption from Aqueous Solution by Antep Pistachio (Pistacia Vera L.) Shells. *Journal of Hazardous Materials.* 2008. 153 (3): 1288 – 1300.

[63] Gao, J. S., Wang, P., Dong, K., Wang, D. X. and Xu, C. M. The Simulation Calculation of Molecular Structure and IR Spectrum of Alkyllimidazolium Chloride Ionic Liquid. *Acta Petrolei Sinica (Petroleum Processing Section)*. 2006. 22 (1): 72 – 76.