

PROCEEDING BOOK I



CHEMMPRO 2014

MINERAL AND MATERIAL PROCESSING

International Seminar on Chemical Engineering
in conjunction with

Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) 2014

"Minerals and Materials Processing Toward Sustainable Development"

Bandung, Indonesia

30 - 31 October 2014

Organized by :

Department of Chemical Engineering
Faculty of Industrial Technology
Institut Teknologi Bandung

Supported by :



Sponsored by :



Badak LNG
A World Class Energy Company



PT FREEPORT INDONESIA
Affiliate of Freeport-McMoRan



ISSN 2354-5917



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

PREFACE

International Seminar on Chemical Engineering in conjunction with Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) was held at East Hall, Institut Teknologi Bandung during 30 – 31 October 2014. This international conference had a theme of “Mineral and Material Processing” which was applicable with the enactment of Law No.4 of 2009 on Mineral and Coal Mining where the ban on the export of unprocessed minerals has been applied since January 2014. Chemical engineers hold a significant role in this area, especially to develop and implement appropriate processing technologies to the mineral resources, which also should considering the sustainable development.

There were five plenary lectures in this two-days conferences, with theme “Sustainable Mineral and Metal Processing” and “The Advancement of Chemical Engineering Technology” along with plenary discussion about “Overcome the Challenges in Indonesia’s Mineral and Materials Processing Industry”. This proceeding comprises the summary of these outstanding speech and the collected papers that has been presented in the parallel sessions. These papers are divided into several general themes: mineral processing, material processing, material refining and recovery, advance materials, nanotechnology, catalyst, polymers, and others.

The international conference provides an opportunity to publicize research works which done or in ongoing ones in many research institution and showcase their latest advancement and technologies. We have expectation in this occasion is not only a good place to exchange and discuss the progress of their research in chemical engineering that applicable to material and mineral processing, but also a venue to collect and to disseminate the most updated technologies and the researches of regional issue and public interest in order to contribute to the community and to draw support from the industrial and the governmental sectors.

We would like to grateful to all participants and sponsors who has contributed to the conference, to the organizing committee for their commitment in their busy days so that the conference is possible to be held and conducted successfully.

Thank you,

Dr. Dendy Adityawarman
Conference Chairman



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

TABLE OF CONTENT

PREFACE	i
TABLE OF CONTENT	ii
COMMITTEE	xi
PROGRAM	xii
KEYNOTE PRESENTATION	1
• Development of Solar Thermal Reactors for Materials Production by Ben Ekman, Prof. Geoffrey Brooks & Assoc. Prof. M. Akbar Rhamdhani	1
• Metals from Urban Ores: Opportunities, Challenges, and Technology Development by Assoc. Prof M. Akbar Rhamdhani	7
• Minerals and Materials Processing and The Challenges by Drs. R. Edi Prasodjo, M.Sc.	15
• Peran Teknologi Proses Dalam Pertambangan dan Perkembangannya di Indonesia by Ir. Hendra Santika, MM	23
• Throughput Prediction Model Development at Batu Hijau – PT Newmont Nusa Tenggara by Martiono Hadiano, Dinar Aryasena, Fattih Wirfiyata.....	29
• Direct Nickel Process – Breakthrough Technology by Graham Brock	41
• Use of Phase Diagrams for Designing Recovery Processes for Minerals and Materials by Prof. Ka Ming NG.....	51
• Assembly of Fine Particles Synthesized from the Gas-Phase by Assoc. Prof Wuled Lenggoro	59
• Shape Selectivity of MFI type Core-Shell Zeolite Catalysts by Assist. Prof. Manabu Miyamoto	75
PAPERS	89



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

BOOK I

ADVANCED MATERIAL

Code	Title	Authors	Page
AM.01	Key Parameters to Optimize an Autoclave Technology Application for Advanced Composite Materials Processing	Handoko Subawi	91
AM.02	Effect of Bentonite Addition on Geopolymer Concrete from Geothermal Silica	Himawan Tri Bayu Murti Petrus, Joshepine Hulu, Elsa Malinda, Rizal Agung Prakosa	103
AM.03	Effect of Clay as The Catalyst in The Palm Oil Glycerolysis Process	Siti Mujdalipah, Ani Suryani, Ika Amalia K, Dewi Cakrawati	117
AM.04	The Utilization of Mineral in Crude Glycerol Purification	Siti Mujdalipah, Yatti Sugiarti, Puji Rahma N	125
AM.06	Modified Natural Zeolites for Ethanol Purification	Chandra Wahyu Purnomo, Indra Perdana, P. Sumardi	133
AM.07	Preparation of Heat-Resistant Insulator Material Advanced from Raw Materials of Silica Sand at Atmospheric Pressure	Poerwadi Bambang, Agustina Diah P, Meidiana Christia, Indahyanti Ellya	139
AM.08	Getting Capsaicin Extract from Chili Powder that Has Quality and Optimum Yield by Using The Solvent Extraction and Microwave Solvent Extraction Method	Achmad Ferdiansyah and Mahfud	147
AM.10	Utilization of Fly Ash from Coal Fired Power Plant for Zeolite Synthesis	Amelia Panca, Devina Jonathan, Dwiwahju Sasongko, Winny Wulandari	153
AM.11	Development of Silica Membrane by Sol-Gel Method for Separation of Acetic Acid and Water by Pervaporation	Samuel P. Kusumocahyo and Masao Sudoh	157
AM.12	Titanium Silicon Carbide Formation Mechanism	Solihin	171
AM.13	The Effect of Ultrasonic Radiation on Preparation Zeolite Catalyst from Natural Mineral	Widayat, H Susanto and H Satriadi	177



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Code	Title	Authors	Page
AM.14	A Comparative Study of Zn-ZrO ₂ Nanocomposite Coatings Obtained by Direct and Pulsed Current Electrodeposition	Marsetio Noorprajuda and Asep Ridwan Setiawan	187
AM.15	Preparation of Carbon-Based Strong Acid Catalyst by Hydrothermal Carbonization and It's Performance on Corn Starch Hydrolysis	Iryanti Fatyasari Nata, Chairul Irawan, Primata Mardina and Cheng-Kang Lee	201
AM.16	Evaluation of Erosion Resistance and Microhardness of Ni-ZrO ₂ Nano-composite Coating Fabricated by DC Electrodeposition	Jodie Ridha Arrozak, Asep Ridwan Setiawan	213

CATALYST

Code	Title	Authors	Page
CT.02	Preparation and Testing of Cu/ZnO Catalyst for Methanol Synthesis	Yusi Prasetyaningsih, Hendriyana, Subagjo	223
CT.03	Preparation of a Hydrocracking Catalyst by Combining The Components of Zeolite Y from Kaolin, Amorphous Silica Alumina and NiMo Active Metals	Endang Sri Rahayu, Subagjo, Tjokorde Walmiki Samadhi, Melia Laniwati Gunawan	235
CT.04	Characterization and Activation of Cement Kiln Dust as Heterogeneous Catalyst for Biodiesel Transesterification Process	Wahyudin, Joelianingsih, Hiroshi Nabetani, Nanik Purwanti, and Armansyah H. Tambunan	245
CT.05	Measurement of SO ₂ Adsorption Capacity of CuO/γ-Al ₂ O ₃ Prepared using Dry Impregnation	Yuono, David Bahrin, Subagjo and Herri Susanto	255

INDUSTRY

Code	Title	Authors	Page
IN.03	Experience Shared in Managing Cooling Water Treatment for 30 th Years Old Ammonia Plant	Rahayu Ginanjar Siwi, Iswahyudi Mertosono, Rahadiyan Dewangga	263



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

MATERIAL PROCESSING

Code	Title	Authors	Page
MAP.01	Degradation of Chitosan to Make a Medically Standard of Oligochitosan	Noor Anis Kundari, Kartika Cahyani, Maria Christina Prihatiningsih, and Bangun Wasito	277
MAP.02	Hot Corrosion of Aluminide Coated Ti-Al-Cr-Nb-Zr-Y Intermetallic Alloys	Ahmad Fauzi, Djoko H. Prajitno, and Eddy Agus Basuki	291
MAP.03	Microstructural Evolution and Oxidation Behavior of Fe-Ni-Al Alloys at High Temperatures	Cholidah Akbar Fitriani and Eddy Agus Basuki	301
MAP.04	Prediction of Al ₂ O ₃ Ceramic Mechanical Structure by Adding Aditive and Sintering Temperature Processed by Neural Network	Moh Ilfan Jauhari, Zulkifli , Detak Yan Pratama	309
MAP.05	Corrosion Database Development	Muh Ashadi Cangara, Tjokorde Walmiki Samadhi, Isdiriyani Nurdin & Hary Devianto	321
MAP.06	The Effect of Tannin on Carbon Steel Corrosion in Nitric Acid Solutions	Anna Sonya Asoka, Listiani Artha, Isdiriyani Nurdin, and Hary Devianto	331

MINERAL PROCESSING

Code	Title	Authors	Page
MIP.01	The Study of Coal Ratio Effect on Smelting Processes of Carbonat Type of Copper Ore Using Mini Blast Furnace (MBF)	Pintowantoro, Sungging and Abdul, Fakhreza	343
MIP.02	Modelling and Simulation of Coal Gasification Using ASPEN PLUS	Daniel Prasetyo, Dwiwahju Sasongko, and Winny Wulandari	355
MIP.04	Process modelling of two-steps dimethyl ether synthesis from Berau coal by indirect coal liquefaction	Abdurrahman Fadhil Halim Luthan, Dwiwahju Sasongko, and Winny Wulandari	375
MIP.07	Separation of Cobalt and Nickel by Solvent Extraction using Cyanex 272 and Nickel Stripping Behavior under Variations of Temperature and Volume Ratio of Aqueous to Organic Solution	F. Syarifah, S. Purwadaria, M.Z. Mubarak	393



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Code	Title	Authors	Page
MIP.08	Treatment of Artificial Gold Preg-Robbing Ore by Blinding Agent and Its Synergistic Effect With Resin-in-Leach for Improving Gold and Silver Recoveries	M.Z. Mubarok and P.S. Irianto	407
MIP.09	Effects of Burner Rearrangement on Fuel Consumption in A Steel Stock Reheating Furnace	Irawan. A and Bindar. Y	423
MIP.10	Reduction of Nickel Laterite Ore from South East Sulawesi	Solihin	431
MIP.13	Coal Processing and Recycling Technology for Foundry Cokes and Carbon Raiser Production and Its Application for Metallic Mineral Reduction	Anggoro Tri Mursito, Dina Syazwani, Alia Najiah, Aditya Wibawa and Bagus Dinda Erlangga	437



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

BOOK II

MATERIAL RECOVERY

Code	Title	Authors	Page
MRY.01	Separation of Heavy Metals Cu and Cd from Synthetic Metal Solution and Industrial Wastewater by Using <i>Chlorella Vulgaris</i> Biomass and <i>Chlorella Vulgaris</i> Biomass as Immobilization Adsorbent	Sri Rachmania Juliastuti, Otta Richard, Bena Pinem and Taufiq Fajar Sani	449
MRY.02	Dynamic Process Simulation of BOG Handling on LNG Storage Facility	Tri Partono Adhi, Moch. Syahrir Isdiawan B., and Budianto Setiawan W.	459
MRY.03	Experiment and Correlation of CO ₂ Solubility in Electrolyte Solution of K ₂ CO ₃ -(Mdea+Dea)-H ₂ O	Saidah Altway, Kuswandi, Iqwal Zulfetra, Firda Nuharani	477
MRY.04	Effect of Li/Mn Mole Ratio of Lithium Manganese Oxide on Lithium Recovery Process from Geothermal Fluid Lumpur Sidoarjo	Lukman Noerochim , Gita Akbar Satriawangsa, and Amien Widodo	493
MRY.05	Co-Pyrolysis of Low Rank Coal and Oil Palm Empty Fruit Bunch	Siti Zullaikah, Mardiah, M. Rachimoellah & Binti Mualifatul Rosydh	505
MRY.06	Removal of Cod, Tom, and Phospate Removal from Laundry Wastewater by Coal Fly Ash Modified	Chairul Irawan, Aditya Nugroho, and Agus Riyadi	513
MRY.07	Utilization of Fly Ash in Solidification Processes of Drinking Water Purification Installation Mud (IPAM)	Didik Bambang S	523

NANOPARTICLE

Code	Title	Authors	Page
NP.02	Controlled Corrosion for Nanoparticles	Leksy Teken Lita, Isdiriyani Nurdin, and Winny Wulandari	531



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

NANOTECHNOLOGY

Code	Title	Authors	Page
NT.01	Synthesis of Nanocrystalline SrTiO ₃ by Polystyrene Assisted Spray Pyrolysis Method and Its Application For Water-Splitting Process	Ferry Iskandar and Raymond Tanumiharja	535
NT.02	Characterization of Chitosan Alginate Nanoparticles as Drug Delivery Systems Using Spray Drying Method	Mas Gunawan Haryanto, Qismet Qusdinar, Ajeng Risalina, Muhammad Rizky Fadhilah, Jayanudin	545
NT.03	Catalytic Performance of Fe ₃ O ₄ Nanoparticles Prepared by Co-precipitation in Oxidation of Methylene Blue and Rhodamine B by H ₂ O ₂	Fauziatul Fajarah and Sutrisno	553

POLYMER

Code	Title	Authors	Page
PL.01	Novel Biocompatible Hydrogel For Lower Critical Solution Temperature (LCST) Near Body Temperature	A. Z. Abidin and H.P.R.Graha	563
PL.02	Performance Test of Spray Dryer Design for Natural Rubber Powder Production Using CFD Simulation	A. Z. Abidin, Y. Bindar dan A. Vachlepi	579
PL.04	Improving of Poly(L-Lactic Acid) Properties by Solution Blending of Biodegradable Polymers	Rizki Insyani, Hyung W. Lee, IGBN Makertiharta, and Johnner P. Sitompul	603
PL.05	Synthesis and Properties of Poly(ionic liquid)s from Substituted Acetylene Monomers	Edy Marwanta, Masahiro Teraguchi, Takashi Kaneko, and Toshiki Aoki	613
PL.06	Kinetics Study of Alkyd Resin Synthesis from Glycerol and Adipic Acid Modified with Rubber Seed Oil	Desi Nurandini, Rochmadi, and Bardi Murachman	617
PL.09	Chemical Synthesis of Polylactides And Evaluation of Their Biodegradability	Rofiq Sunaryanto, Edy Marwanta, Hardaning Pranamuda and Tarwadi	627



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

OTHERS

Code	Title	Authors	Page
OT.01	Influence Temperature and Holding Time of Torrefaction to Energy Content of Oil Palm Empty Fruit Bunches	Irawan. A, Anggraeni. N.D, and Kurniawan.P	635
OT.03	Antioxidants Extraction from Physalis angulata Fruit using Subcritical Water Extraction	Ratna Frida Susanti, Kennedy, and Ashianti Stenny Winata	643
OT.04	Effect Pericarp Extract Of The Mangosteen For Oxidation Stability Of Palm Oil, Jatropha Oil And Soybean Oil Biodiesel	Tirto Prakoso, Addin Akbar	657
OT.05	Bleed water treatment using non-thermal plasma method	Anto Tri Sugiarto, Rini Permanawati, and Tirto Prakoso	665
OT.06	Bio-Char Production in A Two Chamber Pyrolysis Furnace From Biomass of Breadfruit Tree	Zen Zen Muttakin, Hasan Hidayattuloh, and Yazid Bindar	675
OT.07	Preparation and Characterization of Pd/ α -Al ₂ O ₃ Membrane for Hydrogen Separation	Galih Okta, Ramavi Akbar, Yogi Wibisono Budhi, Irwan Noezar, Manabu Miyamoto, and Shigeyuki Uemiya	695
OT.08	Dynamic Behavior of Hydrogen Permeation through Pd/ α -Al ₂ O ₃ Membrane during Natural Hot-run Start-up	Ramavi Akbar, Galih Okta, Yogi Wibisono Budhi, Irwan Noezar, Manabu Miyamoto, and Shigeyuki Uemiya	713
OT.09	Optimization in Eugenol Production from Clove Oil with Saponification – Netralization Process by using Surface Response Methods	Widayat, Bambang Cahyono, Hadiyanto and Ngadiwiyana	729
OT.11	Optimizing Jatropha press cake detoxification to reduce production cost in Jatropha biorefinery	Dianika Lestari, M. Insanu, Widyarani, Susan C.M. Wittevan Dijk, Wilhelmus J. Mulder, Johan P.M. Sanders, Marieke E. Bruins	741
OT.12	Optimization and Kinetic Modelling of The Enzymatic Hydrolysis of Oil Palm Empty Fruit Bunch Using Crude Fungal Xylanase	Efri Mardawati, Ronny Purwadi, MTAP Kresnowati, and Tjandra Setiadi	755



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Code	Title	Authors	Page
OT.13	Freshwater Phytoplankton as Potential Heavy metal Biosorbent and its Natural Aquatic Physico-Chemical Characteristics: A Study Case on Situ Rawa Kalong-Depok	Awalina, Fachmijany Sulawesty, Eka Oktariani, Tjandra Chrismadha, Ika Atman Satya, Eki Naidida and Tjandra Setiadi	769
OT.14	Production of Crude Cellulase with Mahogany Substrate by Aspergillus Niger for Biodeinking Newspaper Waste	Yanty Maryanty, Kristina Widjayanti, Sri Rulianah, Firmandana Krisna, Titik Endahwati, Meiliefiana, Windra Putri Juwita	785
OT.15	Modelling and Simulation of Pilot-Scale Reverse Flow Reactor for Oxidation of Gasoline Vapor	Fuji Permata Sari and Yogi Wibisono Budhi	797
OT.16	Stability of Candle Nut Biodiesel Blends with Petro-Diesel in High and Low Sulphur Content	Tirto Prakoso, Meiti Pratiwi, and Tatang H. Soerawidjaja	809



October 30th - 31st 2014, Bandung, Indonesia

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

COMMITTEE

Organizing committee:

Chairman	: Dr. Dendy Adityawarman
Secretary	: Dr. Dianika Lestari Dr. MTAP Kresnowati
Treasury	: Dr. Tirto Prakoso Dr. Melia Laniwati G.
Program and Papers	: Dr. Winny Wulandari Dr. IDG A. Putrawan Dr. IGBN Makertiharta Dr. Yogi Wibisono Budhi
Information and Publication	: Dr. Antonius Indarto Dr. CB. Rasrendra Dr. Ardiyan Harimawan
Logistic	: Dr. Johnner Sitompul Dr. Harry Devianto Pri Januar Gusnawan, ST, MT

Steering Committee:

Prof. Dr. Herri Susanto (ITB)
Dr. Tatang Hernas Soerawidjaja (ITB)
Dr. Tjokorde Walmiki Samadhi (ITB)
Dr. Subago (ITB)
Dr. Zulfiadi (ITB)
Prof. Johny Wahyuadi (UI)
Dr. Mubiar Purwasasmita (ITB)
Dr. Soemantri Widagdo
Ir. Martiono Hadiano (Newmont Indonesia)
Ir. Tato Miraza (ANTAM)
Dr. Ir. Rozik B. Soetjipto (Freeport Indonesia)

International Advisory Committee:

Prof. Dr. Tjandra Setiadi (ITB)
Prof. Geoffrey Brooks (Swinburne University)
Prof. Dr. Norikazu Nishiyama (Osaka)
Dr. Wuled Lenggoro (TUAT)
Prof. Mikrajuddin Abdullah (ITB)
Dr. Ferry Iskandar (ITB)
Prof. Dr. Ir. Rochim Suratman (ITB)



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Optimization in Eugenol Production from Clove Oil with Saponification – Neutralization Process by using Response Surface Methods

Widayat,^{1,3} Bambang Cahyono², Hadiyanto^{1,3} and Ngadiwiyan²

¹Chemical Engineering Department, Diponegoro University, Indonesia

²Chemistry Department, Diponegoro University, Indonesia

³Center of Biomass and Renewable Energy (CBIOR) Center of Research and Service
Diponegoro University (CORES DU) Indonesia

Email : yayat_99@yahoo.com

Abstract: The objective of this research was to obtain optimum condition in eugenol production from clove oil with response surface methods. Clove oil was founded from essential oil cluster in Batang district Central Java. The eugenol was produced with saponification and neutralization process. Eugenol was obtained with vacuum distillation. Eugenol concentration was analyzed with gas chromatography. In this research, the variable was studied are temperature and ratio of sodium hydroxide to clove oil and yield of eugenol as response variable. So the results was obtain in minimum condition with yield of eugenol 39.17% at $X_1 = -0,0109$ and $X_2 = 0.3095$ with determinant coefficient 0.764.

Keywords: *eugenol, clove oil, saponification –neutralization process, yield of eugenol, and surface response methods (SRM)*

1. Introduction

Batang Regency, Central Java, is one of the producers of clove oil in Indonesia with production 250 tons in 2011[1]. Clove oil is kind of essential oil that can be obtained from clove plant (*Eugenia caryophyllata Thunb*), in some part like leaves, flower, and stem. The quality of cloves oil analysed by amount of phenol, especially eugenol[2,3]. The problem in clove oil eugenol contents is under SNI standard. The Small Medium Entrepreneurship (SME) in Batang Regency produce clove oil that eugenol contents is 80% and sometime under 80%[1,4].

Eugenol or Phenol, 2-methoxy-4-(2-propenyl) is main component of clove oil, colourless, has spicy taste and special odour so it used for fragrance and flavour industry. Eugenol can use as antiseptic, eugenol used for pharmacy industry. β -Caryophyllene is impurities that cause decrease clove oil quality[4]. According to USP (United States Pharmacopeia) standard, eugenol product must have purity more than 98 %. Clove oil with purity under 70% priced Rp 120.000,00/kg[5]. So eugenol with purity 98 % priced 500.000/kg. Because of that, further



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

step must be done to obtain clove oil with eugenol purity more than 98% in order to clove oil has higher economic value.

The main problems faced by the SME in Batang District are low product quality due to availability of eugenol and darkness of colour[5]. The solution of this problem has been attempted by several researches by using chelating agent. The chelating agents that used for increasing eugenol contents in clove oil as citric acid and sodium EDTA[1,4,6-8]. Commonly, this process can be increase eugenol contents from 78% to 80%. In the other process that use for eugenol purification as saponification and distillation, fractionation. Anny (2002), Sukarsono and workers (2003) used saponification and distillation. Sodium hydroxide react with clove oil and neutralized by adding sulphuric acid or hydrochloride acid. The product then separated with decantation and distillation process. Eugenol contents on product has eugenol purity 82,6 % (minimum)[9-10]. Widayat and workers (2013, 2014) done experiments and simulation about clove oil purification. They use fractional distillation process at vacuum pressure. The product has purity of eugenol from 93 % up to 97 % [11-12]. This process has not been applied yet for eugenol with low purity that produced by small industry in Batang Regency. Therefore, the objective of this research is doing optimization of eugenol purification from clove oil using neutralization process and fractional distillation with Response Surface Methodology (RSM).

2. Methodology

Materials and Equipments

Materials that used in this study were obtained from clove oil essential oils Cluster Batang District. The clove oil has eugenol contents 80% [1,4]. Sodium hydroxide and hydrochloride acid have technical specification that found in chemical shop in Semarang. Aquadest or distilled water obtained from Laboratory in the Department of Chemical Engineering. The equipment used saponification process like presented in Figure 1. A beaker glass 500 ml used as reactor and magnetic stirrer used for heating and stirring. Figure 2 is a equipment that used for distillation. The distillation was operated in vacuum pressure that obtained with vacuum pump. Distillation column used packing system.

Research Design

The experimental design used is Response Surface Methodology (RSM) as described in Table 1 with two variables: operation temperature and the ratio of clove oil to sodium hydroxide (NaOH). Experiment process were performed on a laboratory scale and batch processes. The operating conditions used are as follows;

a. Fixed Variables

- ✓ Clove oil volume (ml) : 150
- ✓ Materials : clove oil
- ✓ Operational time : 45 minute

b. Experimental variables:

- Temperature : (-1) : (40) and (+1) (60) °C
- Ratio NaOH/Clove oil (v/v) : (-1) (2,5) and (+1) (3,5)



Figure 1 Saponification and Neutralization equipments

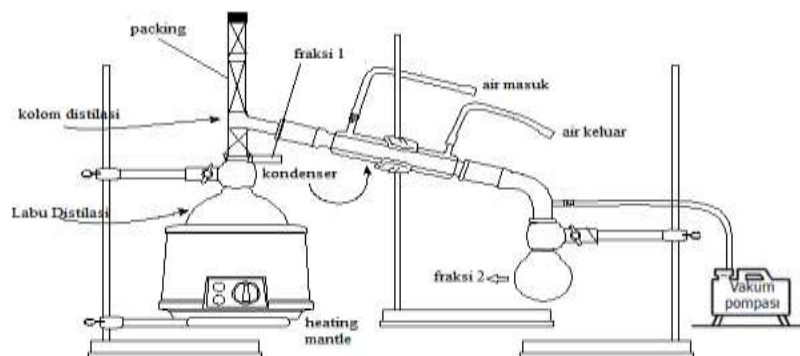


Figure 2 Vacuum Distillation equipment

Procedure

The experiments start with oil density measurement, so by determination of specific volume which desired, will be known the requirement of clove leaf oil weight. For each experiment clove oil has been purified first using citric acid[4]. 150 ml of clove oil and put in a flask and NaOH was added with ratios of variables. Saponification reaction time is 45 minutes, and then performed decantation for 1 day. Solids or soaps which formed is then neutralized with hydrochloride acid and reacted for 5 minutes. Decantation process is then



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

performed for 15 minutes. Then the eugenol product is distilled (Figure 2) for 1.5 hours. The final product is collected in a sample. The final product was measured and the volume and refractive index. The products were also analyzed by gas chromatography concentration.

Table 1 Variable Central Composite Design for Experiment

Run	Block	X ₁	X ₂	Y
1	1	-1	-1	Y ₁
2	1	-1	+1	Y ₂
3	1	+1	-1	Y ₃
4	1	+1	+1	Y ₄
5	1	0	0	Y ₅
6	2	0	-1,424	Y ₆
7	2	0	+1,424	Y ₇
8	2	-1,424	0	Y ₈
9	2	+1,424	0	Y ₉
10	2	0	0	Y ₁₀

Where:

X₁ = Coding for variable ratio oil to NaOH

X₂ = Coding for temperature variable

Y = Yield

Data Analysis

The responses in this research are density, viscosity and eugenol concentration. The eugenol concentration was analyzed by gas chromatography that did in Malang Polytechnic Laboratory. The liquid product was analysed by using gas chromatography (HP 5890, with HP 608 column) with FID detector. The operating condition used helium as gas carries with flow rate of 20 ml/minute, temperature of 100-200°C with temperature gradient 5°/minute and initial time 5 minute. Detector temperature is 275°C. The product was analysed with internal standard methods.

6 µL eugenol standard solutions was added with internal standard (benzyl alcohol) 6 µL and 1 ml of solvent. The solution injected on GC equipment and did triple runs. The response detector was calculated with sample area divided internal standard area. This parameter was averaged and used for eugenol concentration calculation. Eugenol concentration was used for calculation of yield of eugenol with equation 1. The data were processed using Statistica software.



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

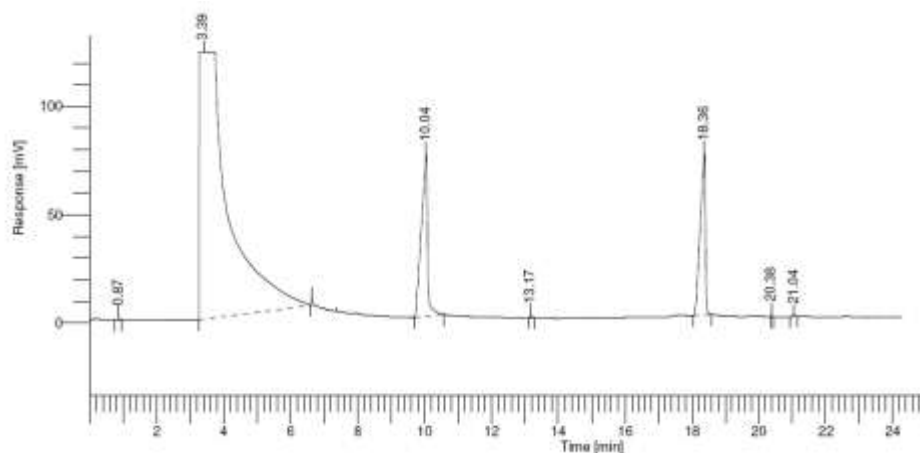
International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

$$\text{Yield (\%)} = \frac{\text{weight of eugenol}}{\text{weight of clove oil}} \times 100 \quad (1)$$

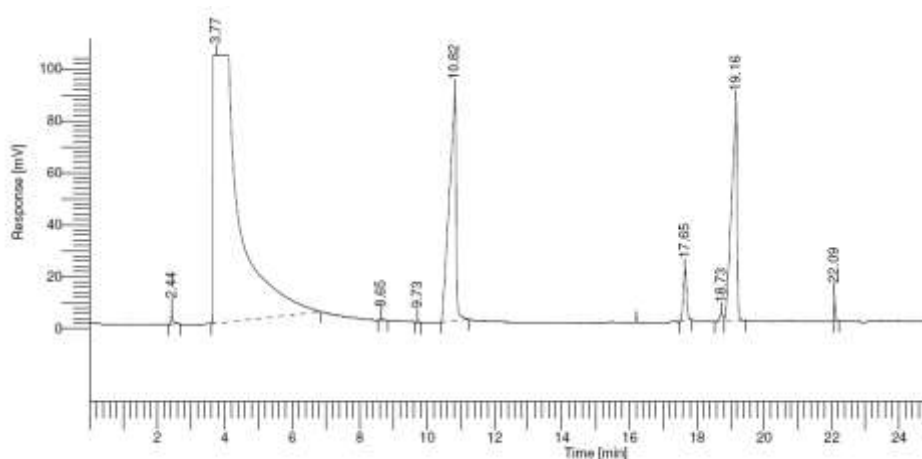
3. Result and Discussion

Chromatography Analysis

The results of qualitative and quantitative analysis for eugenol and benzyl alcohol were presented in Fig. 3. Fig. 3 shows chromatogram for methanol as solvent, benzyl alcohol and eugenol with retention time of 3.39; 10.04 and 18.36 minute, respectively. The eugenol contents in product varied 75.10 – 96.00%. If compared with Widayat (2013, 2014) that eugenol produced with fractionation process, this products have eugenol contents less than product from fraction process. The eugenol contents in eugenol product that produce with fractionation distillation process is 76.5-98.93%[12,13]. Figure 3.a. is a chromatogram for eugenol and internal standard and figure 3.b. for product sample. The both chromatogram in figure 3 don't different. Retention time in sample product just shift, but all components shift too.



a. Eugenol and internal standards



b. Sample with internal standard

Figure 3. Chromatogram of eugenol

Response Surface Methods Analysis

The results of statistic analysis include mathematical model, t test, analysis of variance, pareto analysis and validation of mathematical model. Polynomial equations to mathematical model the surface response methods follow:

$$Y = X_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad (2)$$

Where:

Y = predicted response

β_1, β_2 = linear coefficient for 1, 2 variable

β_{11}, β_{22} = squared term coefficient for 1,2 variable

β_{12} = interactions variable coefficient

X_1, X_2 = non dimensional number of independent variables

The results of analysis regression for equation 2 like presented in equation 3.

$$Y = 34.4639 - 0.5886 X_1 + 19.6363 X_1^2 - 5.6989 X_2 + 9.2652 X_2^2 + 3.2853 X_1 X_2 \quad (3)$$

In 3 equations, shown that the value of each of the linear variables X_1 and X_2 is negative and quadratic and interaction variables are positive. The negative value can be explained that if ratio oil to NaOH (X_1) and temperature (X_2) increase can cause reduce yield of eugenol (for X_1 and $X_2 > 0$). However, the interaction between the variables of temperature and the addition of NaOH or $X_1 X_2$, and quadratic variable of X_1 and X_2 are positive which means that increase the value can increase yield of eugenol. If the reduction of eugenol yield any increase in single variable compared with quadratic variable, showed that the increase in



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

yield caused by the quadratic variable is greater than a single variable. Increasing quadratic variable is 33.36 times larger than the single variable (X_1) and 1.63 times for X_2 variable. This is showed that single variable (X_1) not yet effect in yield of eugenol.

In Table 2 contains the coefficients, their standard errors, test statistic (t), p-values and 95% confidence interval for each predictor variable. For this table shown 3 equations is a multivariate regression.

Table 2. Regression analysis result

Parameters	Regression	Std.Err.	t(3)	p	-95.%	+95.%
Mean/Interc.	34.4639	11.0747	3.1119	0.0528	-0.7808	69.7085
Blocking	-5.5849	4.9528	-1.1276	0.3415	-21.3468	10.1770
X_1	-0.5886	5.5374	-0.1063	0.9221	-18.2109	17.0337
X_1^2	19.6363	7.3252	2.6806	0.0750	-3.6759	42.9485
X_2	-5.6989	5.5374	-1.0292	0.3791	-23.3212	11.9235
X_2^2	9.2652	7.3252	1.2648	0.2952	-14.0470	32.5773
X_1X_2	3.2853	7.8310	0.4195	0.7031	-21.6365	28.2070

Variance of mathematical model was analyzed and the results presented in Table 3. Table 3 can be used to determine whether the independent variables simultaneously significant effect on the dependent variable. The degree of confidence that is used is 0.05[13-14]. The parameters have F value more than p for all parameters except X_1 quadratic variable and interaction variable. X_1 quadratic variable has F value = 0.0113 p=0.9221 and and interaction variable X_1 and X_2 parameter has F=0.1759 and p= 0.2953. The results of variance analysis support the t-test in Table 2 for X_1 and X_2 variable (single variable). It also shows that the mathematical model already in optimum condition (maximum / minimum) no stripes ascend and mathematical model can use in optimization.

Table 3 Analysis of variance(ANOVA)

Parameter	SS	df	MS	F	p
Blocks	311.911	1	311.911	1.2716	0.3415
X_1	2.771	1	2.771	0.0113	0.9221
X_1^2	1762.671	1	1762.671	7.1858	0.0750
X_2	259.816	1	259.816	1.0592	0.3791
X_2^2	392.427	1	392.427	1.5998	0.2953
X_1X_2	43.172	1	43.172	0.1759	0.7031
Error	735.896	3	245.299		
Total SS	3120.280	9			



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

Pareto diagram can assist in efforts on the most important on process[13-14]. Pareto diagram in this study are presented in Figure 4. Figure 4 show that a linear variable X_2 has the smallest value. So this variable can be neglected or not effect in this process. The all variable have histogram don't cross the line $p = 0.05$. Pareto chart show quadratic variable of X_2^2 has a histogram near with line $p = 0.05$. This was shown a quadratic variable X_2^2 has the most effect in eugenol yield. This condition can be increase for obtain optimum condition.

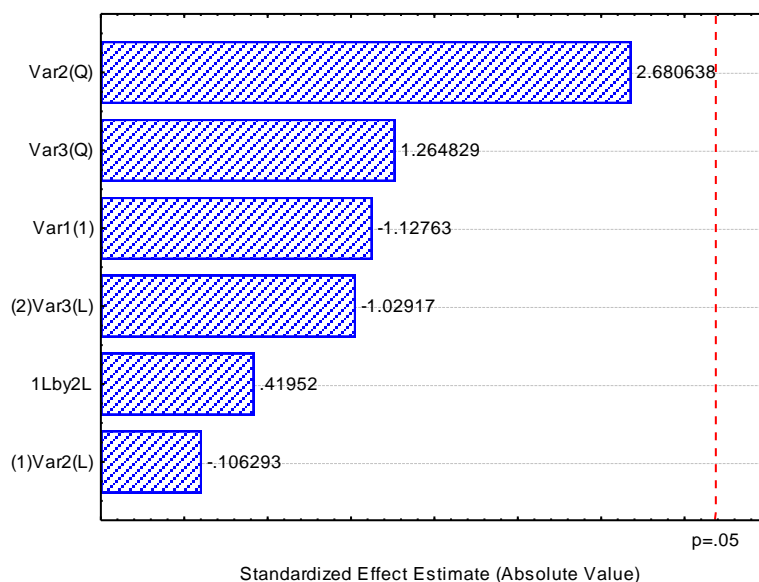


Figure 4 Parreto Diagram

The optimum conditions can be seen in Figure 5. Figure 5 is a surface response graph that consists of x and y axis as independent variable (X_1 and X_2) and z-axis as dependent variable or yield of eugenol (Y). In surface contours figuring in colour areas, so it can be seen profile graph. Figure 4 has the form a minimum point. This is shown the type of optimization process is already minimized.

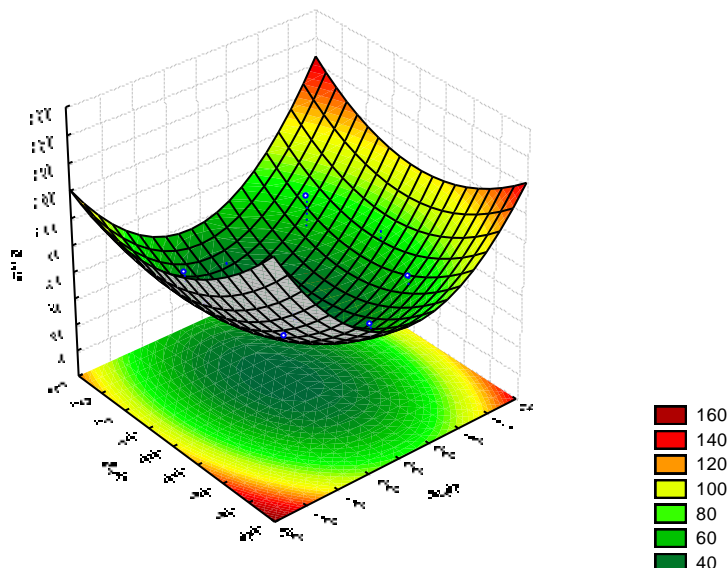


Figure 5 Countour Graphics of optimization results material ratio and temperature

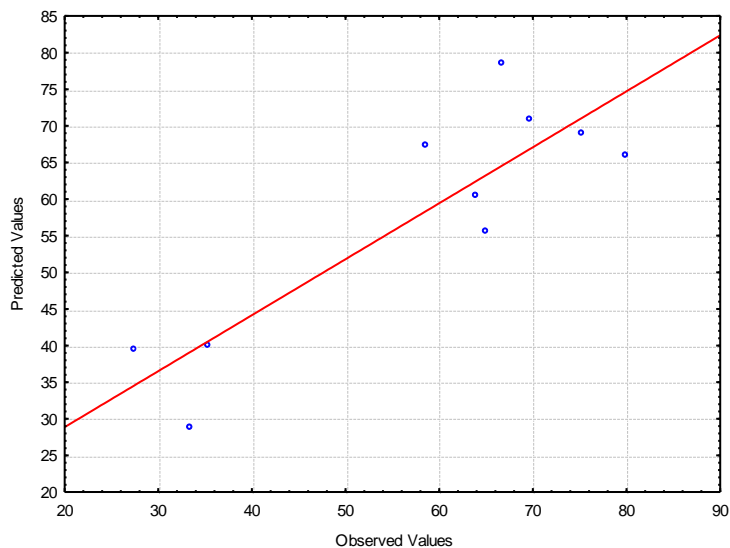


Figure 6 Model validation with experimental data

Mathematical model in equations 3 was validated with experiments data. The result of this analysis presented in Figure 6. Mathematical model is less valid because the experimental data coincide with the results of the calculation very little. The coefficient determination obtain $R^2=0.764$. This value is more than 0.7, so mathematical model can be used in optimization process can be follow to obtain optimum condition.



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

In table 4, the critical value of dimensionless numbers for each variable. Critical dimensionless value obtained for X_1 (ratio clove oil to sodium hydroxide) is -0.0109 and X_2 (temperature) 0.3095. X_1 and X_2 critical value is substituted to equation 6 to obtained yield of eugenol. Yield of eugenol in minimum condition is 39.17%.

Table 4 Critical value results / optimization

Solution: minimum			
	Observed	Critical	Observed
X_1	-1.4142	-0.0109	1.4142
X_2	-1.4142	0.3095	1.4142

4. Conclusion

The Surface Response Method (SRM) employed for optimization and analysis of production and purification of eugenol from clove oil by using neutralization and fractionation distillation from process. In minimum condition of increasing surface was obtained yield of eugenol 39.17% at X_1 -0.0109 and X_2 0.3095. The mathematical coefficient determination model is 0.7642.

References

- [1] Widayat, Cahyono, B, Hadiyanto & Ngadiwiyono. “*Rancang Bangun dan Uji Alat Proses Peningkatan Minyak Cengkeh Pada Klaster Minyak Atsiri kabupaten Batang*”. Jurnal Ilmu Lingkungan Magister Ilmu Lingkungan Universitas Diponegoro Semarang Vol 9(2):57-61, 2011
- [2] Guenther E.. *Minyak Atsiri*, jilid 1. Jakarta Universitas Indonesia. 1987
- [3] Badan Standarisasi Nasional. Standar Nasional Indonesia Minyak Daun Cengkeh. SNI 06-2387-2006 2006.
- [4] Widayat, Cahyono B., Hadiyanto & Ngadiwiyana, *Improvement of Clove Oil Quality by Using Adsorption-distillation Process*, Research Journal of Applied Sciences, Engineering and Technology 7(18): 3867-3871 2014 Maxwell Scientific Organization,
- [5] Klaster Minyak Atsiri, *Profil Kluster Minyak Atsiri Kabupaten Batang Propinsi Jawa Tengah* 2011)
- [6] Marwati T, Rusli, M.S., Noor, E., and Mulyono, E., *Peningkatan Mutu Minyak Daun Cengkeh Melalui Proses Pemurnian*, Jurnal Pasca Panen (2) pp. 45-52 2005
- [7] Silviana, *Proses Pengkelatan Minyak Cengkeh dengan Asam Sitrat*, Jurnal Metana, Fakultas Teknik Universitas Diponegoro Semarang pp.16-20 2007
- [8] Ma'mun *Pemurnian Minyak Nilam Dan Minyak Daun Cengkeh Secara Kompleksometri*, Jurnal LITTRI, Vo. 4 No. 1 pp.36-42 2008



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014

-
- [9] Anny,Sri. *Pengolahan Lanjut Minyak Atsiri dan Penggunaannya Dalam Negeri*. Workshop Nasional Minyak Atsiri 30 Oktober 2002, Dirjen Industri Kecil Dagang Menengah, Depperindag
 - [10] Sukarsono, Dahroni, I., & Sucahyo, D.H., “Kajian Pemisahan Komponen – komponen dari Minyak Cengkeh”. Yogyakarta Puslitbang Teknologi Maju BATAN 2003
 - [11] Widayat, Haidar, M.H., Nurdiana, L., Cahyono B., Ngadiwiyan, & Satriadi, H, **Fractional Distillation of Clove Oil at Vacuum Pressure**, Proceeding International Seminar 2013 Faculty of Engineering University Muhammadiyah Purwokerto
 - [12] Widayat, Haidar, M.H., Nurdiana, L., Cahyono B., Ngadiwiyan, & Satriadi, H, **Proses Destilasi Vakum Pada Minyak Cengkeh Pada Tekanan Vakum: Simulasi Dan Eksperimen**, Proceeding Seminar Nasional Rekayasa Kimia dan Proses 2014 Jurusan Teknik kimia Fakultas Teknik UNDIP Semarang
 - [13] Box G.EP., Hunter J.S., & Hunter, W.G., Statistics For Experiments second edition John Wiley and Sons, New York 2005
 - [14] Lazic, Z, Statistics Experiments for Chemical engineering, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2004



October 30th - 31st 2014, Bandung, Indonesia

OTHERS
OT.09

International Seminar of Chemical Engineering in Minerals and Materials Processing
In conjunction with Seminar Teknik Kimia Soehadi Reksowardojo 2014



CHEMMPRO 2014
MINERAL AND MATERIAL PROCESSING

CERTIFICATE

is hereby presented to

Rad Widayat

Optimization in Eugenol Production from Clove Oil with Saponification - Neutralization Process by using Response Surface Methods

as

Paper Presenter

International Seminar on Chemical Engineering
in conjunction with

Seminar Teknik Kimia Soehadi Reksowardojo (STKSR) 2014

"Minerals and Materials Processing Toward Sustainable Development"

30-31 October, 2014 at East Hall, Institut Teknologi Bandung, Indonesia

Dr. Tjokorde Walmiki Samadhi
Chemical Engineering
Undergraduate Program Chairman



Dr. Dendy Adityawarman
CHEMMPRO 2014
MINERAL AND MATERIAL PROCESSING
Conference Chairman