

Aplikasi Green Inhibitor dari Campuran Ekstrak Gambir Sebagai Anti Kerak Pada Instalasi Pipa Pembangkit Listrik Tenaga Uap (PLTU)

PROF. SUHARSO, PH.D.

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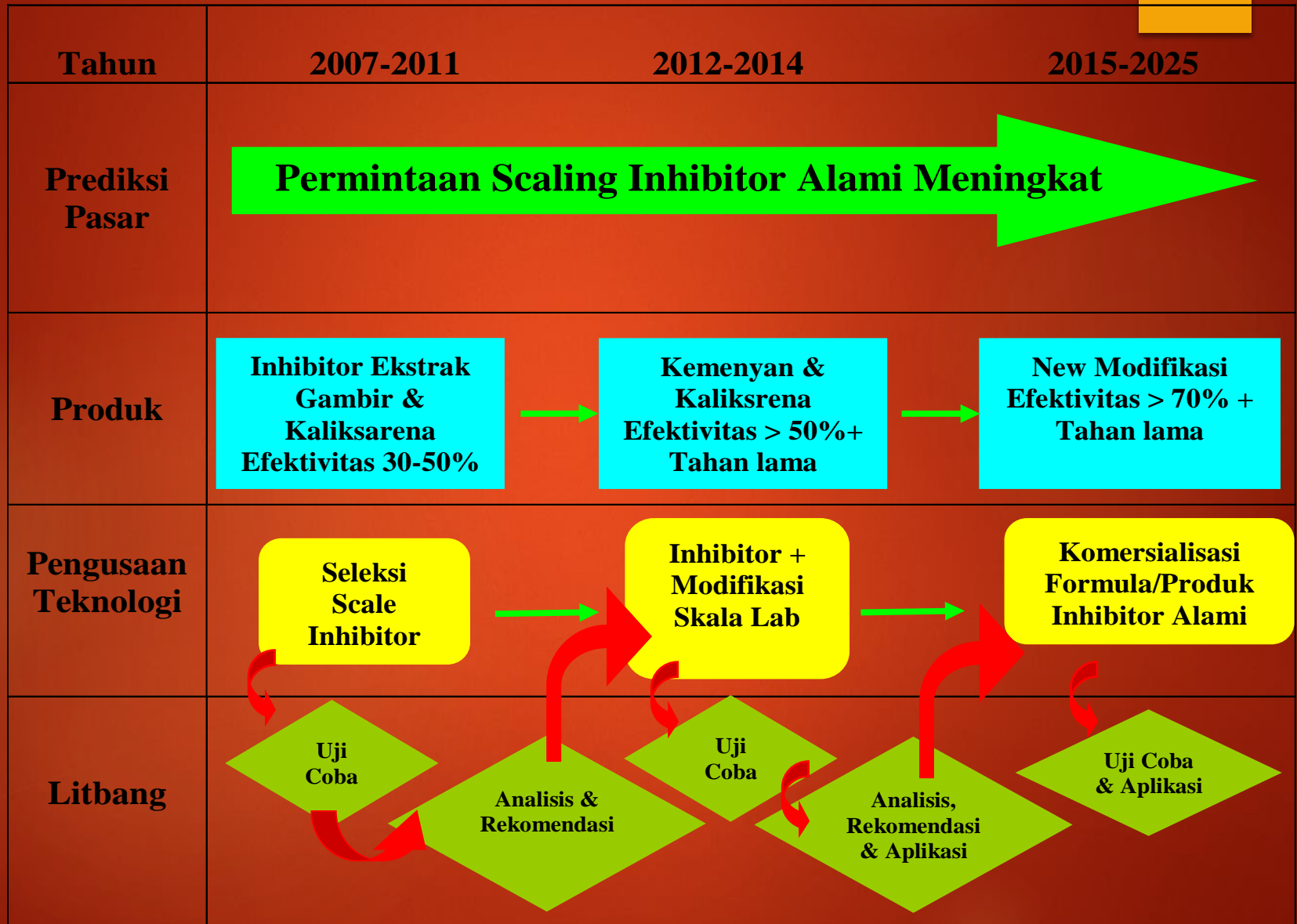
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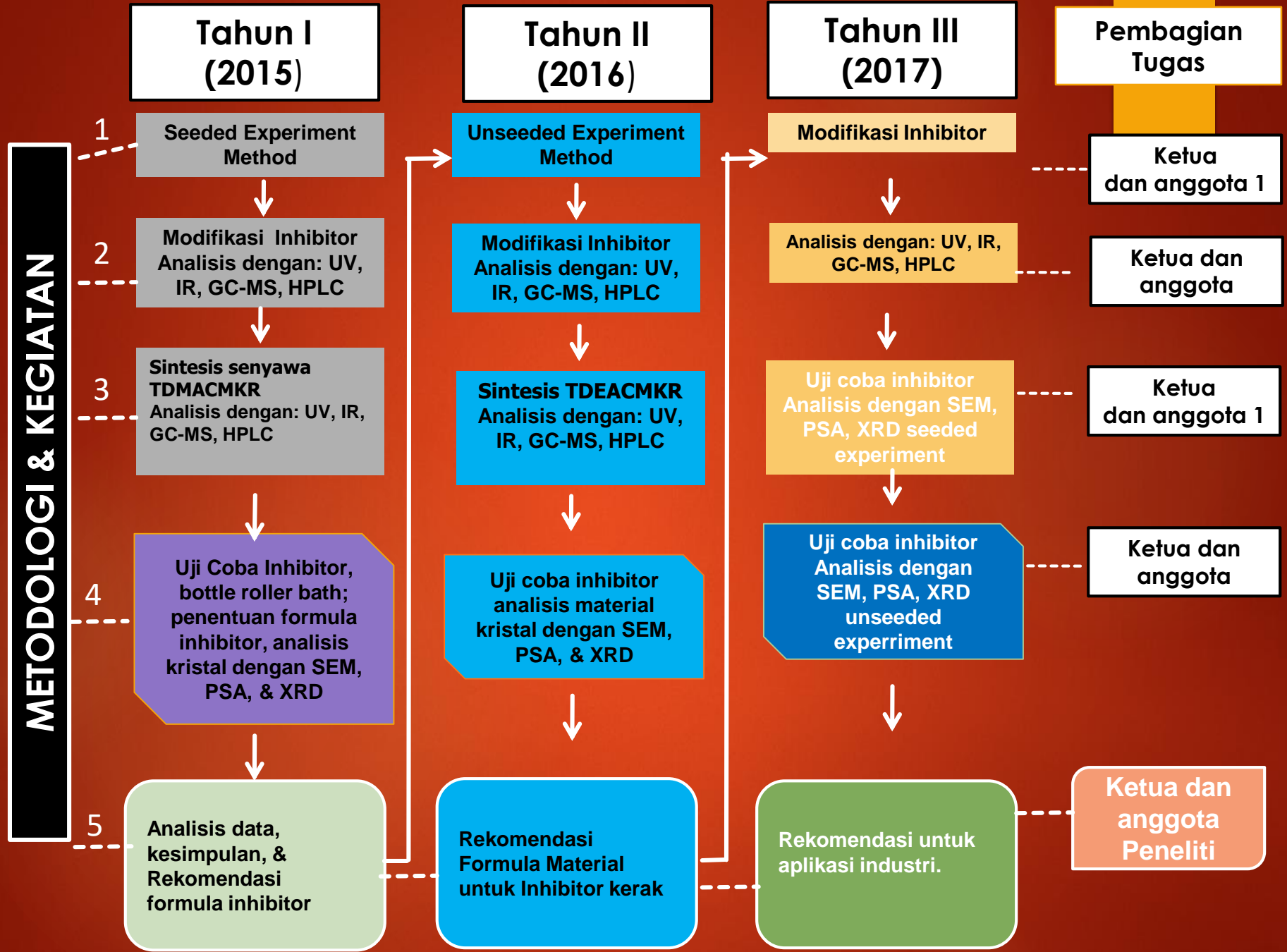
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Inhibition of calcium carbonate (CaCO_3) scale formation by calix [4] resorcinarene compounds

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ABSTRACT

Inhibition effect of tetrakis((dimethylamino)methyl)C-methyl calix [4] resorcinarene (TDMACMKR) compound on calcium carbonate (CaCO_3) scale formation has been studied using seeded experiment and bottle roller bath method. The effect of the addition TDMACMKR as inhibitor on CaCO_3 scale formation was analyzed by measuring the weight of precipitation of CaCO_3 formed. The morphology and particle size distribution of obtained CaCO_3 crystals caused by the addition of TDMACMKR were analyzed by scanning electron microscopy (SEM), and particle size analyzer. The data obtained show that the TDMACMKR inhibits formation of CaCO_3 scale at various inhibitor concentrations added.

Keywords: Calix [4] resorcinarene; Scale inhibitor; Calcium carbonate

1. Introduction

One of the most serious problems encountered in some industrial processes such as oil and gas, chemical industry, power generation, and geothermal industry is the formation of scale (undesired crystal growth) on surface of industrial equipment [1–6]. This scaling impact on the efficiency of the equipment, and because of this, for example, the Indonesian Oil Company (PT PERTAMINA) has spent US\$ 6–7 million to renew every pipeline at the Geothermal Industry every 10 y [7].

A widespread method used to reduce the impact of scale formation is to add an inhibitor. Selection of an appropriate inhibitor can provide a cheap and effective reduction in scale formation, as low concentrations can have a large impact on acryl growth. Research into scale inhibitors is driven by the strong industrial need for effective inhibitors [8–11].

In this report, the calix [4] resorcinarene (TDMACMKR) compound was synthesized and reported previously [12], and tested as an inhibitor of CaCO_3 precipitation. TDMACMKR was selected for investigation as it combines O-donor groups, with amine functional groups. While most inhibitors studied to date involve O-donor groups, such as carboxylates and phenolates, there are relatively few report where these groups are used alongside amine functional groups. Another reason the use of TDMACMKR as the inhibitor of CaCO_3 precipitation is the existence of amine group classified as a hard bases and the cation of Ca^{2+} classified as a hard acid. According to Person's hard soft acid base (HSAB) theory, the hard bases are more likely to pair up with the hard acids. Therefore, the existence of amine groups in TDMACMKR will inhibit growth rate of the CaCO_3 crystals. Previous studies of this compound focused on its use an adsorbent to bind the heavy metal ions [12–19].

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Kemenyan (*Styrax benzoin* Dryand) extract as green inhibitor of calcium carbonate (CaCO_3) crystallization

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ABSTRACT

To study the effect of Kemenyan extract from *Styrax benzoin* Dryand resin as green inhibitor on calcium carbonate (CaCO_3) scale formation, experiment has been carried out using a bottle roller bath method at temperature of 80°C and at various growth solutions from 0.050 to 0.100 M. The extraction result of the Kemenyan was characterized using Fourier transform infrared spectroscopy to identify functional groups found in the Kemenyan extract. The morphology of CaCO_3 crystal obtained was analyzed using SEM and the particle size distributions of the CaCO_3 crystals produced were measured by a particle size analyzer. The result of the experiment showed that Kemenyan extract can be used as a green inhibitor of calcium carbonate scale formation. The presence of Kemenyan extracts in the various growth solutions of CaCO_3 0.050, 0.075, and 0.100 M gives percentage of inhibition ability from 12% to 77% in inhibiting the formation of the CaCO_3 scale. The ability of the Kemenyan extract to inhibit the growth rate of CaCO_3 crystallization depends on amount of the inhibitor concentration added and the growth solution concentration as a crystal growth media under these experiment conditions.

Keywords: Kemenyan extract; CaCO_3 crystal; Green inhibitor

AQ1

1. Introduction

Use of additives in inhibiting the inorganic material scale formation is used more increasingly in many industries involving salt water in cooling system of boiler. The additives are utilized because of simple and economic application. Additives are able to change a crystal morphology [1], to inhibit or as inhibitor of crystal formation [2], or both. Therefore, negative effect of the inorganic material scale formation can be controlled earlier. Because of these negative impacts, Indonesian Oil Company (Pertamina) has spent US\$ 6–7 million to renew every pipeline at the Pertamina Geothermal Power Plant every 10 years [3].

Nevertheless, the use of scale inhibitor containing compounds of sulfonate and phosphonate polymer more to inhibit the inorganic material scale formation in several industries in Indonesia such as steam power plant (PLN/ Indonesian Electricity Company) and geothermal power plant (Pertamina Geothermal Power Plant) is not environmentally friendly. The majority of industrial wastes are thrown away into aquatic environments. Of course, the use of these compounds causes environmental contamination and affects ecological equilibrium in the aquatic environments.

Thus, the use of a green inhibitor which is environmentally friendly and economic in inhibiting the inorganic material scale formation is a main choice for recently used inhibitors applied widely by industries containing chemical compounds such as organophosphate and organophosphonate

AQ2

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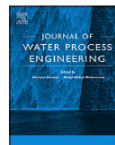
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Modification of Gambier extracts as green inhibitor of calcium carbonate (CaCO₃) scale formation



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ABSTRACT

The addition of the Gambier extract (*Uncaria gambier* Roxb leaves) modification (Gambier:benzoic acid: citric acid:2:1:2) as a green inhibitor on the formation of CaCO₃ scale at various concentrations was carried out using a seeded experiment method. The experiments were performed with observing the precipitation change of the CaCO₃ crystals growth obtained. In order to prove the efficiency of the inhibitor in inhibiting the formation of the CaCO₃ crystals, the changes of the crystal morphology were investigated by scanning electron microscopy (SEM) and the changes of the crystal size distribution were analyzed by particle size analyzer (PSA). The research results showed that the Gambier extract modification was able to inhibit the formation of the CaCO₃ scale indicated with the morphology change of the CaCO₃ crystals and smaller crystal size distribution after the addition of this inhibitor.

1. Introduction

Scale formation causes a serious issue encountered by many industries in Indonesia and other countries such as; the industry of oil or gas production, water transport, power generation, and batch precipitation [1–6]. Faced with this issue; PT Pertamina Geothermal Energy (PGE) which is one of subsidiary of Indonesian Oil Company (PT. Pertamina) has spent US\$ 6–7 million to rejuvenate the pipe installation of the Geothermal Energy Industry for 10 years. In order to solve this problem, several researchers studied many additives to prevent the scale formation or to modify the crystal morphology [7–12]. The addition of the additive in a growth solution of the scale formation is looked a cheaper method and an effective enough to inhibit the scale formation of an inorganic material.

Gambier extract from *Uncaria gambier* Roxb leaves was reported as a green inhibitor of CaCO₃ scale formation [13]. Nevertheless, the Gambier extract has several problems, such as; it is easily moldy and cannot be stored for a long time. In order to control these problems, the Gambier extract was mixed with citric and benzoic acid. Previous research reported that the citric and benzoic acid can play a role as an inhibitor also to inhibit the scale formation [14–16]. In addition, these mixtures are potential as a green inhibitor of the scale formation because they have some chemical compounds such as tannic acid, catechin, and quercetin [13] which are effective inhibitors of scale formation of CaCO₃ beside the citric and benzoic acid. Other advan-

tages of these mixtures are cheaper and they can be applied as a green inhibitor like other materials which have been used previously [17–27] to keep our environment.

The effects of the Gambier extract modification as the inhibitor of CaCO₃ scale formation at various concentrations from 0 to 300 ppm on the precipitation rate of calcium carbonate was observed at temperature of 80 °C and at a growth solution of 0.1, 0.3 and 0.6 M under seeded experiment. The seeded experiments were applied by previous researchers to investigate the inhibition of the calcite crystal growth with using phosphonates additive and they monitored the rate of crystallization by measuring the concentration of calcium ion as a function of time [28]. In this experiment, the rate precipitation of the calcium carbonate seed crystals was monitored by weighing the amount of the calcium carbonate precipitated as function of time [13]. The precipitation obtained was characterized using scanning electron microscopy and particle size distribution to give an overview of its composition, size and morphology of the CaCO₃ crystals was analyzed by particle size analyzer.

2. Experimental procedure

2.1. Preparation of Gambier extract modification

Preparation of Gambier extract modification was made with the ratio of 2:1:2 (Gambier:benzoic acid: citric acid). The benzoic and citric

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Synthesis of new material from calix[4]resorcinarene-chitosan hybrid

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ABSTRACT

Synthesis of new calix[4]resorcinarene-chitosan hybrid using vanillin as raw material has been conducted. The synthesis was carried out in four steps i.e. (1) alkylation of vanillin, (2) HCl-catalyzed condensation allyl vanillin with resorcinol, (3) chloromethylation of C-4-allyloxy-3-methoxyphenylcalix[4]resorcinarene with paraformaldehyde and HCl in the presence of ZnCl₂ to yield tetrakis-chloromethyl-C-4-allyloxy-3-methoxyphenylcalix[4]resorcinarene, and (4) reaction of tetrakis-chloromethyl-C-4-allyloxy-3-methoxyphenylcalix[4]resorcinarene with chitosan to yield calixarene-chitosan hybrid. Structure elucidation of products were performed using FT-IR, ¹H-NMR, ¹³C-NMR, GC-MS, XRD, and SEM. The product of calixarenes-chitosan hybrid was obtained as dark red solid with m.p. > 300 °C in 78% yield.

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1. Introduction

Calixarene has attracted the attention of scientists since it was first introduced in 1978¹ because it can be utilized in various fields. Calixarene has been studied its use for various purposes, including: sunscreen,² extraction,³ inhibitor of calcium carbonate^{4,5} and calcium sulphate⁶ scale formation, a stationary phase of HPLC,^{7,8} drug delivery,⁹ antioxidant and anti-toxoplasma,¹⁰ dye fibers,¹¹ biosensors,¹² and adsorbent^{13,14}. Calixarene is compound group of synthetic oligomer containing aromatic ring in a cyclic sequence linked by a methylene group¹. One derivate of this compound that has been studied is calix[4]resorcinarene.^{15,16,17} Calix[4]resorcinarene (Fig. 1) consists of 4 units of resorcinol in the form of cyclic linked by a methylene bridge. It can be synthesized by reaction of resorcinol with an aldehyde under acidic conditions.

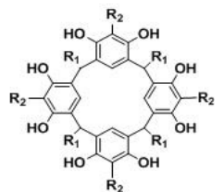


Fig. 1. Structure of calix[4]resorcinarene

A number of studies have shown that research developments of calixarene more focused on modifying the calixarene structure by adding a variety of new functional groups. Timmerman *et al.*, (1996)¹⁸ have been succes to synthesize and modify a wide variety of calix[4]resorcinarene by varying groups at R₁ and R₂. Groups at R₁ can be varied by using aldehyde different as the reagent forming of calix[4]resorcinarene. While groups at R₂ can be varied via electrophilic substitution reaction of calix[4]resorcinarene. Because a position between OH in the aromatic ring of resorcinol has high electron density so it is very reactive to the presence of an electrophilic.¹⁹

In this research, the new calixarene produced was derived from reaction between resorcinol and vanillin as a source of aldehyde functional group. In addition, modification of calixarene structure was performed by reacting chitosan with calix[4]resorcinarene at R₂ position formed a calix[4]resorcinarene-chitosan hybrid. Anggraini (2013)²⁰ has been successfully produced calix[4]resorcinarene-chitosan hybrid from chitosan and C-4-methoxycarbonilmethoxy-3-methoxyphenylcalix[4]resorcinarene through amide bond formation at R₁ group. The product has sufficiently low yield, which is 28%. In this research, the hybrid was synthesized through bond formation of secondary amine between the amine group of chitosan with chloromethyl group of tetrakis-chloromethyl-C-4-allyloxy-3-methoxyphenylcalix[4]resorcinarene at R₂ group. Cl atom on the alkyl halide is better leaving group than -OCH₃ at the carbonyl group, so the hybrid formation reactions in this research would be easier to happen and has a high yield.

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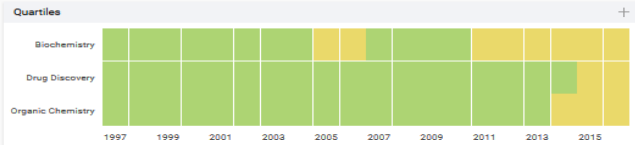
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permintaan paten : []
(54) Judul Invensi : []

**KOMPOSISI EKSTRAK GAMBIR (*Uncaria gambier* Roxb) DAN
KEMENYAN (*Styrax benzoin* Dryand) SEBAGAI INHIBITOR KERAK
KALSIUM KARBONAT**

mengajukan permintaan pemeriksaan substantif untuk
permintaan paten tersebut di atas.

bersama ini, saya/kami sampaikan :

[] biaya pemeriksaan substantif paten sebesar Rp. []
(.....)
[] biaya klaim yang belum dibayar buah @ Rp. []
sejumlah Rp.
(.....)
[] kekurangan-kekurangan lain yang rincian ringkasnya tersebut
dalam lampiran formulir ini. []

Yang mengajukan permintaan
UNTUK DAN ATAS NAMA LPPM UNILA,
DIREKTORAT JENDERAL HAK KEKAYAAN INTELEKTUAL



Parsono, Ph.D.) #

Invited Speaker

May 31, 2017

Dr. Suharso Suharso
University of Lampung
Indonesia

INVITATION LETTER

Dear Dr. Suharso Suharso,

On behalf of the conference committees, we are pleased to invite you to deliver an invited presentation for the Collaborative Conference on Crystal Growth (3CG), which will be held from 7 to 11, August 2017 at the Mövenpick Hotel Berlin, Berlin, Germany. Detailed information is available on: <http://emmmeeting.org/Europe/3cg/>.

The 3CG 2017 aims to promote discussions and information exchange across the frontiers of research in the fields of crystal growth and engineering. International scientists with common professional interests in crystal research will unite in a virtual, friendly and informal atmosphere to share their experimental and/or theoretical expertise in the physical, chemical, and biological phenomena and processes related to the design, growth, and application of crystalline material.

We are hoping to attract some of the prominent researchers across the frontiers of crystal growth and you are certainly one of them. Looking forward to working with you at the 3CG 2017 and trust it will prove to be a scientifically stimulating experience.

Sincerely yours,



PD Dr. Mohamed Benyoucef
Local Organizing Committee Member,
Institute of Nanostructure Technologies and Analytics
University of Kassel
Heinrich-Plett-Str. 40,
34132 Kassel, Germany
Tel.: +49-561-804-4553
Email: m.benyoucef@physik.uni-kassel.de



EMN 3CG 2016
Collaborative Conference on Crystal Growth
September 4-8, 2016 San Sebastian, Spain

April 15, 2016

Dr. Suharso Suharso
Department of Chemistry
University of Lampung
Indonesia

Dear Dr. Suharso,

On behalf of the conference committees, we are pleased to invite you to deliver an invited talk for the Collaborative Conference on Crystal Growth (3CG), which will be held from 4 to 8, September 2016 at the NH Collection Aranzazu Hotel, San Sebastian, Spain. Detailed information is available on: <http://emn3cg.org/2016/>.

The 3CG 2016 aims to promote discussions and information exchange across the frontiers of research in the fields of crystal growth and engineering. International scientists with common professional interests in crystal research will unite in a virtual, friendly and informal atmosphere to share their experimental and/or theoretical expertise in the physical, chemical, and biological phenomena and processes related to the design, growth, and application of crystalline material.

We are hoping to attract some of the prominent researchers across the frontiers of crystal growth and you are certainly one of them. Looking forward to work with you at the 3CG 2016 and trust it will prove to be a scientifically stimulating experience.

Sincerely yours,



Dr. Yury Rakovich, General Chair
Materials Physics Center (CFM, CSIC-UPV/EHU),
Paseo Mammel de Lardizabal 5, 20018 DonostiaSan
Sebastian, Spain
Email: yury.rakovich@gmail.com



KEMENTERIAN RISET, TEKNOLOGI DAN PENDIDIKAN TINGGI
UNIVERSITAS ANDALAS
FAKULTAS MATEMATIKA DAN ILMU PENGETAHUAN ALAM
JURUSAN KIMIA

PANITIA SEMINAR NASIONAL KIMIA 2017
Kampus Unand Limau Manis, Padang-25163 Email: kimia@fmipa.unand.ac.id



No. : 167/UN16.03.5.1/PP/2017 Padang, 4 Juli 2017
Lamp. : 1 berkas
Hal : **Permohonan Pembicara Tamu (Invited Speaker)**

Yth. Bapak Prof. Suharso, Ph.D
Di tempat

Assalamu'alaikum Warrahmatullahi Wabarakatuh

Puji syukur kehadiran Allah SWT atas limpahan rahmat dan hidayah-Nya kepada kita semua, sehingga kita masih dalam keadaan sehat wal'afiat dan dapat melakukan aktivitas tanpa suatu halangan apapun. Sholawat dan salam semoga selalu tercurahkan kepada Rosululloh Muhammad SAW, keluarga, sahabat dan orang-orang yang selalu istiqomah dijalan-Nya.

Selubungan akan diselenggarakannya acara "Seminar Nasional Kimia (SNK 2017)" Jurusan Kimia FMIPA Universitas Andalas dengan tema **Green Chemistry dan Energi Terbarukan untuk Kehidupan Masa Depan**, maka kami panitia seminar bermaksud mengajukan permohonan kepada Bapak untuk menjadi Pembicara Tamu (*Invited Speaker*). Seminar ini akan dilaksanakan pada:

Hari/Tanggal : Senin/11 September 2017
Waktu : 07.30 - 17.00 WIB
Tempat : Hotel Axana Padang

Demikian permohonan ini kami sampaikan. Atas perhatian dan kesediaan Bapak kami ucapkan terima kasih.

Hormat kami,

Mengetahui,
Ketua Jurusan Kimia Unand

Dr. Afizal
NIP: 196002091987031004

Ketua Panitia

Dr. Upita Septiani
NIP: 197009171999032001

Buku

 GRAHA ILMU



Prof. Suharso, Ph.D.
Dr. Buhani, M.Si.

PENANGGULANGAN KERAK

EDISI 2

PENANGGULANGAN KERAK

EDISI 2

Permasalahan serius yang sering dijumpai pada sebagian besar peralatan industri yang melibatkan air garam adalah terjadinya penumpukan material anorganik pada dinding-dinding peralatan industri. Terakumulasinya endapan tersebut mengakibatkan terbentuknya kerak, dan kasus ini umum terjadi pada industri yang melibatkan air, seperti proses desalinasi dan ketel, industri minyak dan gas, serta industri kimia. Akibat penumpukan kerak tersebut umur sumur pipa pada industri panas bumi Pembangkit Listrik Tenaga Panas Bumi (PLTP) hanya berumur 10 tahun, kemudian harus dibuat baru dengan biaya 6-7 juta dolar per sumur. Hal tersebut mengakibatkan terjadinya inefisiensi pada industri dari sisi waktu, energi, dan biaya.

Buku ini menyajikan hasil-hasil penelitian terkait penanggulangan kerak, baik menggunakan senyawa hasil sintesis maupun ekstrak tanaman yang digunakan sebagai inhibitor dalam menghambat pertumbuhan kerak. Tentunya buku ini layak dibaca bagi para peneliti dan mahasiswa untuk menambah khasanah pengetahuan atau ingin lebih mendalami penelitian terkait penanggulangan kerak.



Prof. Suharso, Ph.D. adalah staf pengajar Jurusan Kimia FMIPA Universitas Lampung sejak 1995. Ia menyelesaikan pendidikan S1 di Jurusan Kimia FMIPA Universitas Lampung pada tahun yang sama. Tanpa melalui jenjang S2, ia menempuh jenjang S3 di School of Applied Chemistry, Curtin University of Technology Australia dalam bidang Crystal Growth (1998-2003). Sejak 2003, ia aktif dalam penelitian dan mendapatkan hibah penelitian dari Kementerian Pendidikan Nasional berupa Hibah Fundamental, Hibah Bersaing, Riset Unggulan Strategis Nasional, Hibah Kompetensi, dan Hibah IPTEK. Ia juga mendapatkan Insentif Riset Dasar dari Kementerian Riset dan Teknologi tahun 2007 dan 2008. Selain itu, ia juga mendapatkan penghargaan dari Kementerian Pendidikan Nasional sebanyak tiga kali berupa Insentif Publikasi Internasional atas karya-karyanya yang dipublikasikan pada Jurnal Internasional.



Dr. Buhani, M.Si. menyelesaikan pendidikan S1 pada Program Studi Pendidikan Kimia FKIP Universitas Lampung pada tahun 1992, menyelesaikan pendidikan S2 pada Jurusan Kimia FMIPA UGM pada tahun 1999, dan S3 pada Jurusan dan fakultas yang sama pada tahun 2010 di UGM. Setelah menamatkan pendidikan S2, penulis diangkat sebagai staf pengajar Jurusan Kimia FMIPA Universitas Lampung. Sejak lulus dari S2 tahun 1999 penulis aktif dalam sejumlah penelitian seperti Penelitian Dosen Muda, Hibah Fundamental, Hibah Bersaing, Hibah Strategis Nasional, Hibah Doktor, Riset Unggulan Strategis Nasional, dan Hibah Kompetensi. Dari hasil-hasil penelitian yang telah dilakukan, penulis mempublikasikannya pada jurnal-jurnal internasional, nasional terakreditasi, dan dalam sejumlah seminar nasional dan internasional.

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TERIMA KASIH KEPADA
KEMENRISTEKDIKTI &
LPPM UNILA

