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EFFECT OF ACTIVATION TEMPERATURE AND $ZnCl_2$ CONCENTRATION FOR MERCURY ADSORPTION IN NATURAL GAS BY ACTIVATED COCONUT CARBONS

PENGARUH TEMPERATUR AKTIVASI DAN KONSENTRASI $ZnCl_2$ TERHADAP PENYERAPAN MERKURI DALAM GAS BUMI OLEH KARBON TEMPURUNG KELAPA YANG TERAKTIVASI

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ABSTRAK

Elemen merkuri yang terkandung dalam gas bumi telah menjadi perhatian serius dari sisi lingkungan karena sifat volatilitas dan toksisitasnya yang tinggi. Penyerapan dengan carbon yang teraktivasi merupakan suatu metode mengontrol merkuri yang efektif. Kandungan merkuri dalam gas bumi harus dihilangkan untuk mencegah terjadinya kerusakan peralatan dalam plan pengolahan gas dan sistem jaringan pipa transmisi. Penelitian ini menggambarkan proses eliminasi merkuri yang terkandung dalam gas bumi dengan menggunakan karbon aktif dari tempurung kelapa yang diimpregnasi dengan $ZnCl_{2.}$ Temperatur aktivasi dan konsentrasi larutan $ZnCl_2$ merupakan variable yang dapat mempengaruhi kapasitas penyerapan merkuri. Karbon aktif dibuat dari kulit tempurung kelapa dan diaktivasi pada temperature 600, 700 and 800^oC dalam aliran konstan nitrogen. Pengaruh temperatur aktivasi dan konsentrasi larutan $ZnCl_2$ terhadap penyerapan merkuri oleh adsorben menunjukkan bahwa kemampuan adsorpsi adsorben telah dipengaruhi oleh temperature aktivasi hingga mencapai temperature optimumnya 700^oC. Kemampuan adsorpsi meningkat dengan meningkatnya konsentrasi larutan $ZnCl_2$ dan penyerapan optimum pada konsentrasi $ZnCl_2$7%. Hasil menunjukkan bahwa penyerapan merkuri oleh carbon teraktivasi yang terimpregnasi klor sangat signifikan dan diperoleh temperature aktivasi optimumnya. Kesimpulan akhir diperoleh temperature aktivasi optimum 700^oC dan 7% $ZnCl_2$ sebagai konsentrasi impregnasi yang dapat menyerap merkuri secara maksimal.

Kata Kunci: aktivasi, penyerapan merkuri, gas bumi, karbon tempurung kelapa teraktivasi

ABSTRACT

Elemental mercury from natural gas has increasingly become an environmental concern due to its high volatility and toxicity. Activated carbon adsorption is an effective mercury control method. Mercury content in natural gas should be removed to avoid equipment damage in the gas processing plant or the pipeline transmission system. This research describes the process of mercury removal from natural gas by coconut active carbon impregnated with $ZnCl_2$*. Activation temperature and* $ZnCl_2$ *solution concentration are significant affect the mercury adsorption capacity. Charcoal was prepared from coconut shell and activated at 500, 700 and 900*^oC *in constant flow of nitrogen. The effect of activation temperature and* $ZnCl_2$ *concentration for mercury adsorption on adsorbent show that the adsorption ability of adsorbent is affected by increasing activation temperature up to an optimum temperature of 700*^oC*. Ability of adsorption increases with increasing* $ZnCl_2$ *concentration and mercury adsorption was optimum at 7% concentration of* $ZnCl_2$*. The results indicated that the adsorption capacity of mercury in natural gas by activated carbon-impregnated*

chlor is very significant. The conclusion of this paper is that optimum activation temperature 700°C and 7% $ZnCl_2$ impregnated on adsorbent can improve the mercury adsorption in natural gas.
Keywords: *activation, mercury adsorption, natural gas, activated coconut carbon*

I. INTRODUCTION

Mercury (Hg^{2+}) is heavy metal in environmental. Mercury content is found in natural gas as a trace element. The increased concern by environmentalist and government on the effect of heavy metals and attempt to protect public health gave rise to a lot of research in the development of advance technology to remove heavy metals from the natural gas as fuels. The metal adsorption is development of advance technology to remove of mercury in natural gas and the adsorption ability of a powdered activated carbon (PAC) is derived from coconut shell. It was a more economic and effective adsorbent for the control of Hg(II) ion in the natural gas industry (Zabihi & Ahmadpour 2009). Mercury can be removed from the natural gas through activated carbons. Activated carbon adsorption is an effective mercury control method but there are cost limits. Coconut charcoal may act as a low-cost sorbent used for controlling mercury levels. In the natural gas processing industry, activated carbon is frequently employed for the removal of mercury to protect aluminum heat exchangers and for a safe working environment at the plant. Various types of activated carbons were developed from organic sewage sludge (SS) using H_2SO_4, H_3PO_4 and $ZnCl_2$ as chemical activation reagents, and the removal of Hg(II) from aqueous solution by these carbons was effectively demonstrated (Zhang *et al.* 2005). Mercury in water can be removed by using adsorption processes such as activated carbon that is impregnated with zinc chloride ($ZnCl_2$), which has been done by *Zeng* at al in 2003. That experiment showed that chloride impregnation with $ZnCl_2$ solution significantly enhanced the adsorptive capacity for mercury.

Ademiluyi and David in 2012 had done research of heavy metals adsorption about the effect of chemical activation on the adsorption of metals ions Cr^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} using bamboo, coconut shell and palm kernel shell was investigated. Bamboo, coconut shell and palm kernel shell activated at 800°C using six activating agents. The highest metal ions adsorbed were obtained from bamboo activated with HNO_3 (Ademiluyi *et al.* 2010). Similarly, in the work of Ramírez Zamora *et al.*, petroleum coke was activated with $ZnCl_2$ and preparation of activated carbon from Neem Husk by chemical activation with $ZnCl_2$ has investigated by Alau K *et al.* The degree of physicochemical alteration was significantly different for the three carbons obtained after activation with three chemicals. Activated carbon activated with H_3PO_4 being the strongest was able to adsorb mercury.

Mercury content in the natural gas should be removed to avoid damaging equipment in the gas processing plant or the pipeline transmission system from mercury amalgamation and embrittlement of aluminium (Crippen & Chao1997). Mercury can be removed by using adsorption processes such as activated carbon impregnated with chlor (Yan & Ling 2003), iodine or sulfur (John & Radisav 1997, Behrooz & Robert 2002). Activated carbons can be made from a wide variety of products and are made from 100% natural products such as hardwoods, coconut shells, and bamboo. In this paper, activated carbons were made from coconut shells. Furthermore, the coconut shells beenwas modified by physical and chemical treatment. Surface modification of a carbon adsorbent with a strong oxidizing agent, generates more adsorption sites on its solid surface for metal adsorption (Sandhya & Tonni 2004). The adsorbents are made up of coconut shell (*Cocos nucifera* L.), an agricultural waste from local coconut industries. Surface modifications of it with activator agents, such as Zinc Chloride respectively, are also conducted to improve removal performance. Physical and chemical properties of coconut active carbon and modified activated carbon were analyzed to investigate the effect of adsorbate properties and temperature activation on activated carbon adsorption performance (Li *et al.* 2012). Mercury adsorption was tested by zinc chloride impregnated activated carbon, which used $ZnCl_2$ solution. In order to increase the utilization of activated carbon, many efforts have been made to increase these functional groups by modifying with compounds of chlorine (Hu *et al.* 2009). The effects of activation temperature and $ZnCl_2$ activator concentration on adsorbent were studied.

II. METHODOLOGY

In this paper, the adsorptive potential of a modified activated carbon using $ZnCl_2$ for mercury vapor was investigated both in a laboratory and in the gas demonstration. Their pore structure and surface chemical properties were characterized by Iodine number, BET and SEM-ADX (Tan *et al.* 2011). Textural characteristics of samples were determined by nitrogen (N2) adsorption with an accelerated surface area was calculated from the isotherms by using the Brunauer - Emmett-Teller (BET) equation (Brunauer *et al.* 1938). The pore volume was found from the amount of N2 adsorbed at a relative pressure of 0.99. The average pore diameter was calculated from three times of the pore volume over the BET surface area.

The experiment was carried out in the Physical Chemistry Laboratory and The Gas Demonstration System Plant of Gas Technology Unit, PPPTMGB ”LEMIGAS” Jakarta.

A. Sample Preparation

Activated coconut carbon that has 70 mesh size was prepared from coconut shell by physical activation in a stainless steel reactor with temperature range of 500 – 900 ^oC. Nitrogen was passs through a preheater at the temperature 250-300^oC. The products were washed sequentially with 0.5 N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters. Activated coconut carbons were treated by impregnation with activator agent of $ZnCl_2$ solution in the a concentration range of 0, 3, 5 and 7 % (w/v) for 24 hours. Impregnated activated coconut carbons were dried in an oven at 90^oC, cooled down to room temperature and then stored in desiccators for future use.

B. Sample Characterisation

Characterization of the activated carbons includes Iodine Number with standard method of ASTM D 4607-94, BET surface area was calculated based on N_2 adsorption isotherm by using the Brunauer-Emmett-Teller (BET) equation (Brunauer *et al.* 1938). The average BET surface area, pore diameter and total volume pore was calculated three times (triple calculations). The textural characteristics of the untreated and $ZnCl_2$-impregnated activated carbons was analyzed by SEM-ADX. The analysis of this data is provided in Figure 4.

3. Mercury Vapor Adsorption in Natural Gas

The experiment of mercury vapor adsorption in natural gas is described in a schematic diagram shown in Fig 1. The working principle of this mercury removal equipment is to pass the natural gas containing mercury vapor at known concentration through an adsorbent. An amount of mercury is adsorbed and the remaining mercury in the natural gas will be adsorbed by $KMnO_4$ solution. The solution is then analyzed by a Lumex mercury analyzer. The volume of the flowing gas is measured by wet test meter equipment. Measurement of

Table 1
Natural Gas Composition

	Analysis	Methode	Unit	Result (%)
1	Composition	GPA2261	% mol	
	Nitrogen			0,3130
	Carbondioxide			0,3897
	Methane			81,7099
	Ethane			8,6269
	Propane			5,2151
	iso-Butane			1,1026
	N-Butane			1,2338
	iso-Pentane			0,4217
	N-Pentane			0,2541
	Hexane plus			0,1879
2.	Sulphur compound:			
	Hydrogen Sulfide (H_2S)		ppm	3,06
	Mercaptane (RSH)	ASTM D 2385	ppm	1,75
	Carbonyl Sulfide (COS)		ppb	15,61
3.	Mercury	ISO 6978	ug/m^3	0,37
4.	Water Contain	ASTMD 1142	Lb/Mmscf	7,72
5.	Gross Heating Value (GHV)		Btu/ft^3	1034,9986
	Net Heating Value (GHV)	GPA2172		934,3538
	Compressibility factor (Z)			0,9975

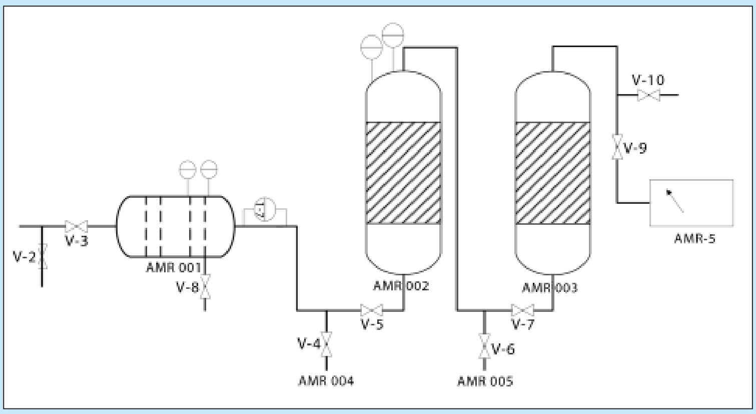

Figure 1
Schematic diagram of Mercury Adsorption

standard mercury and mercury sample is made in an Outlet Adsorber (AWWA 1975). The natural gas is flown through mercury stainless steel reactor adsorber at a temperature of 32°C. The gas from the outlet of the mercury cylinder is put into a mercury solution ($KMnO_4 + H_2SO_4$), and the mercury concentration is in the solution is analyzed by a *Mercury Analyzer* (Lumex 91), measured in µg/m^3.

The experiment of Mercury adsorption was carried out by using 40 kg activated coconut carbons. The natural gas as a sample and the operation conditions were natural gas pressure of 100 psig, temperature 32°C, and flow 50 Cuft/hour. Mercury standard solution was known 14570 µg/m^3. The natural gas concentration that was used on performance test was dry gas. It had flown to the system via a vessel/cylinder that contained standard mercury. The characteristics of natural gas is showed in Table 1.

Natural gas composition above was resulted from analysis of the natural gas sample by using a gas chromatography instrument with series number GC-NGA HP 6890 with a TCD detector. The composition analysis was done by GPA 2261-00 methods and the heating value calculated with GPA 2172:2009. The mercury concentration was analyzed by using ISO 6978 standard and mercury analyzer.

III. RESULT AND DISCUSSION

This paper discusses the results of this research on mercury adsorbent characteristics. The experiment has data on the effect of temperature activation and $ZnCl_2$ concentration. The laboratory testing of the adsorbent involved iodine number, BET surface area and optimum adsorption of mercury.

The iodine number is the most fundamental parameter used in characterizing activated carbon. It is a measure of activity level and the micropore content of the activated carbon (higher number indicates higher degree of activation (Activated carbon 2012). This result showes that ability of the activated coconut carbons is different at the low (500°C) and the high temperature (700°C). Furthermore, the difference in the iodine number in the temperature range due the existence of the suitable temperature for the mercury adsorption. Iodine number is the ability of the adsorbent to adsorp the adsorbat. When the activation temperature is at 700°C, the adsorption reached the highest level, due to the increasing physical adsorption ability, as a result of increasing the surface area and total volume pore on the adsorbent. At 900°C, mercury adsorption was lower than that at 700°C due to desorption making physical adsorption decrease, so that the total adsorption decreased (Figure 2). Decreasing of iodine number related with decreasing of mercury adsorption and its reverse. That is indicating a typical physisorption mechanism due to van der waals forces between the adsorbate and the adsorbent. Heating of adsorbent will produce some new pore and increasing of its surface area.

Impregnation with $ZnCl_2$ concentration 3% up to 7% showes that the iodine number of adsorbent significantly increased (Figure 3). That means $ZnCl_2$ impregnation actually decreased both the BET surface area and the total pore volume of the activated carbons samples due to the blockage of internal porosity by incorporated $ZnCl_2$ molecules. Impregnation at a higher temperature promotes a more uniform distribution of Chlor on the adsorbent pore structure.

The iodine number result for untreated $ZnCl_2$ was lower than impregnated $ZnCl_2$. The average pore size of the activated carbon also increased when increasing the $ZnCl_2$

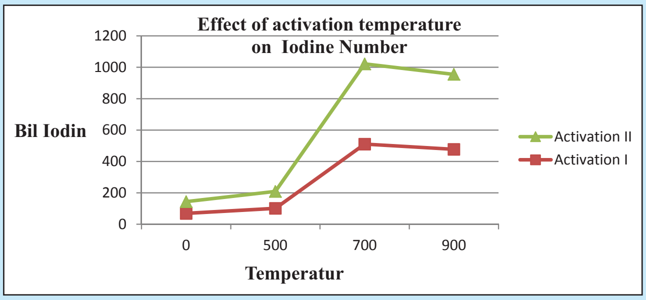

Figure 2
Iodine Number and Activation Temperature

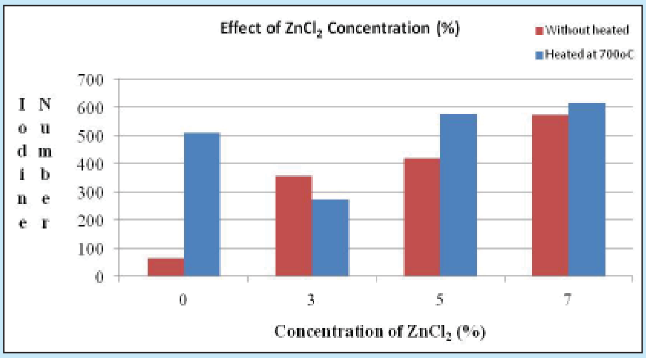

Figure 3
Effect of $ZnCl_2$ Concentration (%) for Iodine Number

solution concentration. That means the adsorbent is blocking micropores, resulting in a drop in specific surface area and total pore volume. The iodine number result for non activator and with activator is shown in Table 2.

Table 3 indicates that BET surface area and the total pore volume of the activated carbons samples without activator were higher than activator agent with concentration 7%. Activated carbon morphology is shown at Figure 4.

The experiment testing result of mercury adsorption onto activated coconut carbons indicated that performance of pilot plant adsorber mercury adsorption was satisfied. Mercury concentration was decreasing after the natural gas was flowing to the equipment system of adsorption mercury and was able to adsorb mercury vapor with efficiency 99,97% with natural gas pressure gas 100 psia, temperature 37^{o}C and natural gas flow 50 Cuft/jam.

The mechanism of chemisorption of mercury onto the Cl-impregnated activated carbons with reaction $ZnCl_2 + C_nH_xO_y \Rightarrow Zn + [Cl_2\text{-}C_nH_xO_y]$ where functional group Cl is very important to the process. Cl atoms which are created by $ZnCl_2$ impregnation, are involved by probably forming various complexes, for example $[HgCl]^+$, $[HgCl_2]$ and if more of the Cl concentration, the reaction result $[HgCl_4]^{2-}$. The results suggested that Cl-active carbon had excellent adsorption potential for elemental mercury even at a relative higher temperature, and the enhancing-effect was more obvious with increasing Cl content (Lau *et al.* 2012). There was an optimum $ZnCl_2$ concentration for impregnation. The increase of performance of adsorbent is probably due to the increase of active sites for mercury adsorption. The kind of Cl functional groups on the original and $ZnCl_2$-modified active carbon was found to be different, the latter is of the active site for mercury adsorption and oxidation, and for the former it is negligible. There is an optimum Cl content on the $ZnCl_2$-modified adsorbent carbon for mercury removal that could be formed during mercury sorption. These results demonstrate significant enhancement of activated coconut carbon reactivity with minimal treatment and are applicable to mercury removal in natural gas plant facilities.

Table 2
Iodine Number Result

No	Non $ZnCl_2$	$ZnCl_2$ 7%
1	525,0130	766,6200
2	542,6821	748,3425
3	495,3484	579,5988
4	535,7470	605,4288
5	438,1422	728,3951
6	426,6570	732,6871

Table 3
BET (Brunauer-Emmett-Teller) Result

NO	Activated Carbon	Surface Area BET (m^2/g)	Total Pore Volume (cc/g)	Mean of Radius Pore (Å)
1	Non ZnCl2 1	1096	0,5986	10,92
2	$ZnCl_2$ 7 % 1	1009	0,5431	10,77
3	Non ZnCl2 2	1093	0,5981	10,86
4	$ZnCl_2$ 7 % 2	928	0,4927	10,22
5	Non ZnCl2 3	1098	0,5990	10,98
6	$ZnCl_2$ 7 % 3	1012	0,5436	10,84

Figure 4
Morfology of activated coconut carbons surface area

IV. CONCLUSIONS

The effect of adsorbent activation temperature for adsorption of the mercury vapor from natural gas with activated coconut carbon is now much clearer. Adsorption by activated carbons, particularly those impregnated with chloride (Cl) is a technology that offers great potential for the removal of Hg^o from the natural gas. Chloride impregnation with 7% $ZnCl_2$ solution actually decreased both the BET surface area and the total pore volume of the activated carbons samples due to the blockage of micropores by incorporated chemicals. Zinc Chloride-impregnated activated coconut carbon showed that it significantly enhanced the adsorptive capacity for mercury.

The experiment of activation temperature variation can explain how temperature affects mercury adsorption performance. The treatment with $ZnCl_2$ impregnation on activated carbon have been effectively reducing the mercury content in natural gas.

Physical activation with optimum temperature 700°C of adsorbent will produce some new pore and increase of its surface area until reaching the optimum temperature. A decrease in the iodine number results in a decrease in mercury adsorption. Mercury adsorption in natural gas involves both physisorption and chemisorptions,

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