

ORIGINAL ARTICLE

## A Study on the Estimation of Greenhouse Gas Using Oyster Shell Recycling for Paper Filler

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### Abstract

This study has conducted greenhouse gas emission reduction test as using Oyster-shells originated PCC paper filler compare to non-Oyster shells used PCC. This examination was estimated and calculated in accordance with both IPCC (Intergovernmental Panel on Climate Change) and World Business Council for Sustainable Development (WBSCD). The greenhouse gas emission reduction estimation result indicates that, when oyster shells are recycled and used as paper filler, it reduces 27.97 tCO<sub>2</sub> per 100 ton of oyster shells. It is greenhouse gas emission 44.27 tCO<sub>2</sub> from PCC production changed to carbon emission reduction when replaced with oyster shell. LNG greenhouse gas emission 16.3 tCO<sub>2</sub> in relation to the pre-treatment with oyster shell per 100 ton is also reflected. As a result, it is assumed that roughly 0.2797 tCO<sub>2</sub>/oyster shell-ton.

**Key words** : Oyster shell, Lime stone, Precipitated calcium carbonate, Calculation methodology, Greenhouse gas

### 1. Introduction

If oyster shells generated from the farming and processing processes are left alone, then microorganisms will proliferate due to the influence of flesh attached to the shells. As a result, those microorganisms might cause diseases with odor, leachate, etc. This environment pollution becomes a cause for pollution in the coastal fishing grounds, a management issue for public water and damage to natural landscape. Furthermore, it will have a negative impact on the image for those ocean tourist cities. Therefore, it is imperative to resolve this issue through an appropriate process. However, oyster shells cannot be transported via a general vehicle

since they are classified as a work site waste pursuant to the Waste Management Act. They should be transported only through those vehicles specially designed for transporting wastes. Thus, they become a cause for increasing the consigned process fee. In particular, the economic burden of fishermen is on the rise.

To produce high value-added products by recycling oyster shells, this study aimed to manufacture quicklime (CaO), slacked lime (Ca(OH)<sub>2</sub>), precipitated calcium carbonate (CaCO<sub>3</sub>) through calcination, hydration and carbon gasification reaction in order to produce high value-added products by recycling oyster shells and estimate reduction effect along with the review of calculation methodology for estimation of

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reducible greenhouse gas quantity by replacement effect for the original products after using them as a paper filler.

## 2. Materials and Methods

This study considered the case in which all of the oyster shells (308,277 tons as of 2011) generated in Korea from lime stone used in the paper mills were recycled and manufactured as a precipitated calcium carbonate that is a paper filler. In this regard, this study utilized the method of applying greenhouse gas emission generated from the lime production process as reduction quantity. (Korea maritime institute(KMI), 2002)

The process related to lime production stated in "the guideline on operation and management of greenhouse gas energy target (Ministry of Environment, June 2012)" for the estimation of greenhouse gas emission generated from the lime production process is as follows.<sup>7</sup> Lime is mainly used in refining of metals (aluminum, steel, copper, etc.), environment (flue gas desulfurization, softening, pH control, waste disposal, etc.) and construction (soil stabilization, asphalt additives, etc.). It mainly utilizes dolomite or dolomite limestone (lime stone whose magnesium carbonate accounts for at least 44

percent of its whole contents) as raw material and produces lime through the following reaction at 900 to 1,500 °C in kiln.

The firing facility in the lime production process is equivalent to the firing facility in the cement production process unit. In the general lime production process, a variety of firing facilities are used. These include long rotary kiln, preheater-rotary kiln, parallel flow regenerative kiln, annular shaft kiln, etc.

Greenhouse gas emission in the lime production process is conducted mainly in the firing process. More specifically, it can be sub-divided into process emission related to firing reaction of lime stone and combustion activity of fuel (fossil fuel and waste fuel are included) within the firing facility. Greenhouse gas emission quantity per quicklime production quantity (BM, Bench-Ma) can be estimated through the following equation.(National Institute of Environmental Research(NIER), 2007; Lee, 2012)

It is possible to reduce lime stone consumption by reaching the maximum yield of gemstone for lime stone with the optimized mining technique (blasting and drilling) and continuing to use by reducing the fuel consumption as much as possible in the production process from gemstone for kiln to finished

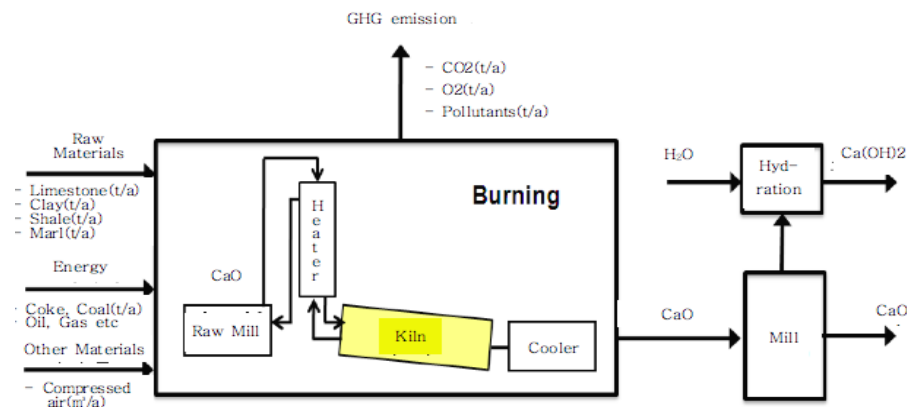


Fig. 1. Mass balance in burning system.

**Table 1.** The calculation methodology for greenhouse gas emission in lime manufacturing process

Level	Methodology
Tier 1~2	$E_i$ : CO <sub>2</sub> emission(tCO <sub>2</sub> ) from lime(i) production $Q_i$ : Lime(i) production(ton) $EF_i$ : CO <sub>2</sub> emission factor(tCO <sub>2</sub> /t-lime(i) production)
Tier 3	$E_i$ : CO <sub>2</sub> emission(tCO <sub>2</sub> ) by carbonate in lime(i) production $Q_i$ : Pure carbonate(i) usage(ton) in burning process $EF_i$ : CO <sub>2</sub> emission factor(tCO <sub>2</sub> /t-Pure carbonate) $Fi$ : Calcine Fraction(%) of carbonate(i) in burning process $Q_{LKD}$ : Washed LKD amount(ton) in lime(i) production $EF_{LKD}$ : CO <sub>2</sub> emission factor on washed LKD in lime(i) production(Default value 0.440 tCO <sub>2</sub> /t-LKD) $F_{LKD}$ : Fraction(%) of Washed LKD

goods as optimizing the production process technique. It will be possible to approach to an optimized kin technique more closely, which can reduce fuel consumption to apply lime stone with a wide range of particle size to the process. In this study, the emission estimation calculation methodology in the slacked lime production unit of the industrial process of IPCC 2006 guideline was quoted in order to evaluate greenhouse gas reduction for the recycling of paper process of oyster shells. The use of slacked lime for soft water is a reaction of CO<sub>2</sub> and lime; thus, it does not generate CO<sub>2</sub> net emission in the air by regenerating calcium carbonate (CaCO<sub>3</sub>). In addition, lime kiln dust (LKD) will be generated during the

lime production period; thus, this should be taken into consideration when estimating emission quantity. The estimation calculation methodology for greenhouse gas emission is classified as Tier 1 to 4 calculation methodologies and each estimation calculation methodology is as Table 1.(NIER, 2007; Lee, 2012)

First, Tier-1 estimates greenhouse gas emission by applying CO<sub>2</sub> emission coefficient (tCO<sub>2</sub>/t-lime production) to the amount of produced lime. In this case, the accuracy of Tier-2 will be enhanced by applying the national emission coefficient that is the unique value at national level as the emission coefficient to be applied. The estimation method is

**Table 2.** The CO<sub>2</sub> emission factor of each Tier

Level	Emission factors (EF <sub>i</sub> )
Tier 1	Using the IPCC default factors (Lime production per CO <sub>2</sub> emissions) - Lime production per CO <sub>2</sub> emissions: 0.750 tCO <sub>2</sub> /t-Quicklime * Source: 2006 IPCC guidelines for national greenhouse gas inventories
Tier 2	Using the country specific emission factors $Fi$ : Fraction purity of limestone (%) $MwCO_2$ : CO <sub>2</sub> molecular weight (=44.01) $MwCaO$ : CaO molecular weight (=56) $MgO$ molecular weight (=40)
Tier 3	Analysis of the material and adjunct material go into lime burning structures and using according to below equation of the inherent emission factors
Tier 4	Using the Continuous Emission Monitoring (CEM)

classified as Tier-1 when applying the emission coefficient to be applied in IPCC. On the other hand, Tier-3 is a method to estimate emission in consideration of the input of fuel (pure carbonate) for lime production based on actual production plants. In this case, it is possible to estimate CO<sub>2</sub> emission that is closer to an actual value through reducing the amount of lime kiln dust to be lost in the production process. Theoretically, it is more accurate than Tier-1 and Tier-2.<sup>[3-6]</sup> (Lee, 2012; Ministry of Environment(ME); Korea Environment Corporation(KECO), 2012)

Tier-3 can be applied when estimating the emission for each workplace. In this case, it will be inevitable to develop a unique emission coefficient (EF<sub>i</sub>) for each workplace through experiment and analysis reflecting the nature of target workplace. In this regard, it will be possible to estimate it through the following equation.(NIER, 2007)

- \* Assumption: Molecular formula of carbonate (i)  
 $= X_Y(CO_3)_Z$   
 EF<sub>i</sub>: CO<sub>2</sub> emission coefficient (tCO<sub>2</sub>/t-carbonate material) of carbonate that is injected as fuel (i)  
 MwCO<sub>2</sub>: Molecular weight of CO<sub>2</sub> (44 g/mol)  
 MwX: Molecular weight of X (alkali metal or alkaline earth metal) (g/mol)  
 MwCO<sub>3-2</sub>: Molecular weight of CO<sub>3-2</sub> (60 g/mol)  
 Y: Stoichiometric coefficients of X (alkaline earth metal "1" and the alkali metals "2")  
 Z: Stoichiometric coefficients of CO<sub>3-2</sub> (1)

As for the control standard for emission coefficient, workplace measurements are utilized in calcination modulus (F<sub>i</sub>) and calcination modulus of lime kiln dust (F<sub>LKD</sub>) of each carbonate as to Tier 3 calculation methodology. When there is no measurement, 1.0 can be applied. The CO<sub>2</sub> emission coefficient for pure carbonate component presented from IPCC guideline is as follows.(ME and KECO, 2008)

Furthermore, the emission coefficient (EFLKD) of lime kiln dust to be lost when applying Tier-3 can be estimated through the following equation.(NIER, 2007)

- EF<sub>LKD</sub>: Emission coefficient of lime kiln dust (CKD) to be lost during lime production (tCO<sub>2</sub>/t-LKD)  
 LKDCaO: CaO content of LKD that is not recycled in kiln (wt%)  
 LKD<sub>n</sub>CaO: CaO content that is not fired for LKD that is not recycled in kiln (wt%)  
 - CaO that is not fired is a kind of CaO and non-carbonate that is left in LKD in the form of CaO and CaCO<sub>3</sub>. It means CaO in LKD at kiln  
 LKDMgO: MgO content of LKD that is not recycled in kiln (wt%)  
 LKD<sub>n</sub>MgO: MgO content that is not fired for LKD that is not recycled in kiln (wt%)  
 - MgO that is not fired is a kind of MgO and non-carbonate that is left in LKD in the form of MgO and MgCO<sub>3</sub>. It means MgO in LKD at kiln

**Table 3.** The CO<sub>2</sub> emission factor for pure carbonate

Carbonate(i)	Emission factor (tCO <sub>2</sub> /tCarbonate)
CaCO <sub>3</sub>	0.4397 (tCO <sub>2</sub> /tCaCO <sub>3</sub> )
MgCO <sub>3</sub>	0.5220 (tCO <sub>2</sub> /tMgCO <sub>3</sub> )
CaMg • (CO <sub>3</sub> ) <sub>2</sub>	0.4773 (tCO <sub>2</sub> /tCaMg • (CO <sub>3</sub> ) <sub>2</sub> )
C	3.6640 (tCO <sub>2</sub> /tC)

\* Source: 2006 IPCC guidelines for national greenhouse gas inventories

### 3. Results and Discussion

The calculation methodology used for estimating the greenhouse gas emission estimation is as follows. (ME and KECO, 2008; ME, 2012)

First, as for the greenhouse gas emission generated from the lime production, the precipitated calcium carbonate produced by the oyster shell recycling process could replace lime; thus, the reducible quantity of greenhouse gas when using the precipitated calcium carbonate instead of lime in the paper mills was estimated. To this end, 「Tier 2 (CO<sub>2</sub> emission coefficient per lime production: 0.785 tCO<sub>2</sub>/t-quicklime)」 in the emission coefficient control standards was applied. And the greenhouse gas emission generated from the pre-processing for recycling oyster shells was estimated based on the following equation. As for the applied fuel, LNG was reflected in the estimation equation.

$E_{ij}$ : Emission for each greenhouse gas (j) in accordance with fuel (i) combustion (CO<sub>2</sub>-eq ton)

$Q_i$ : Fuel (i) amount (measurements and m<sup>3</sup>-fuel)

$EC_i$ : Calorie coefficient of fuel (i) (fuel net calorific value and MJ / m<sup>3</sup>-fuel)

$EF_{ij}$ : Greenhouse gas(j) emission coefficient for each fuel (i) (kg-GHG / TJ-fuel)

$f_i$ : Oxidation coefficient of fuel (i)

$F_{eqj}$ : CO<sub>2</sub> equivalent coefficient for each greenhouse gas (j) (CO<sub>2</sub>=1, CH<sub>4</sub>= 21, N<sub>2</sub>O = 310)

Each coefficient for the above emission estimation

equation is as shown in the following Table (ME and KECO, 2008; ME, 2012)

The detailed process diagram for installing 100 ton/day sized facilities for recycling oyster shells is as shown in the following Fig. 2.

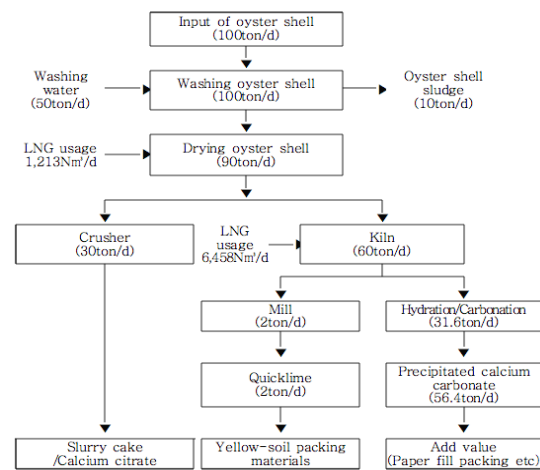


Fig. 2. Oyster Shell Recycling Process.

Those oyster shells, which are supplied to the oyster shell recycling facility, will be decomposed into salts and organic matters through the crushing and cleaning process. Then, water will be removed through the drying process. Some of them will be ground to produce cement raw material or calcium citrate. Some of them will be used to produce slacked lime through the firing process at a high temperature of at least 850 °C. Slacked lime produced through the firing process will be used to produce high value

Table 4. The emission factor for greenhouse gas calculation

Greenhouse gas	$Q_i$ (m <sup>3</sup> -fuel)	$EC_i$ (MJ/m <sup>3</sup> )	$EF_{ij}$ (kg/TJ)	$f_i$	$F_{eqj}$
CO <sub>2</sub>			56,100		1
CH <sub>4</sub>	7,671	39.4	1	0.98	21
N <sub>2</sub> O			0.1		310

\* Source: The guidelines for managing the target management system in Korea

**Table 5.** The emission factor for greenhouse gas calculation

Greenhouse gas	$Q_i$ (m <sup>3</sup> -fuel)	$EC_i$ (MJ/m <sup>3</sup> )	$EF_{ij}$ (kg/TJ)	$f_i$	$F_{eq,j}$
CO <sub>2</sub>			56,100		1
CH <sub>4</sub>	7,671	39.4	1	0.98	21
N <sub>2</sub> O			0.1		310

\* Source: The guidelines for managing the target management system in Korea

-added precipitated calcium carbonate(56.4 ton/day) through the slacked lime reaction and carbonation reaction. Those produced precipitated calcium carbonates can be utilized as a paper filler instead of lime. To estimate the reducible greenhouse gas amount, 「Tier-2 (CO<sub>2</sub> emission coefficient per lime production: 0.785 tCO<sub>2</sub>/t-quicklime)」 described in "the greenhouse gas reduction estimation calculation methodology" was applied. The equation thereof is as follows.

As shown in the Fig. 2. it is possible to produce precipitated calcium carbonate of 56.4 tons when recycling 100 tons of oyster shells. It was found that it would be possible to reduce greenhouse gas of 44.27 tCO<sub>2</sub> when taking into consideration the greenhouse gas emission generated from lime production.

Reduction = 0.785 tCO<sub>2</sub>/t x 56.4 ton when recycling 100 tons of oyster shells in the paper mills On the other hand, they become 1,213 Nm<sup>3</sup>/day and 6,458 Nm<sup>3</sup>/day respectively when drying 100 tons of oyster shells and operating kiln; thus, it was found that a total of 7,671 Nm<sup>3</sup>/day of LNG fuel was utilized. The following equation was applied to calculate the greenhouse gas emission generated herein.(NIER, 2007)

$E_{ij}$ : Emission for each greenhouse gas (j) in accordance with fuel (i) combustion (CO<sub>2</sub>-eq ton)

$Q_i$ : Fuel (i) amount (measurements and m<sup>3</sup>-fuel)

$EC_i$ : Calorie coefficient of fuel (i) (fuel net

calorific value and MJ / m<sup>3</sup>-fuel)

$EF_{ij}$ : Greenhouse gas(j) emission coefficient for each fuel (i) (kg-GHG / TJ-fuel)

$f_i$ : Oxidation coefficient of fuel (i)

$F_{eq,j}$ : CO<sub>2</sub> equivalent coefficient for each greenhouse gas (j) (CO<sub>2</sub> = 1, CH<sub>4</sub> = 21, N<sub>2</sub>O = 310)

Based on the above equation, it was found that approximately 16.3 tCO<sub>2</sub>-eq tons of greenhouse gas were generated by the use of LNG fuel when drying 100 tons of oyster shells and operating kiln. The detailed calculation process is as follows.

In conclusion, it was found that it would be possible to reduce greenhouse gas by approximately 27.97 tCO<sub>2</sub>[=44.27 tCO<sub>2</sub> (greenhouse gas reduction by production of precipitated calcium carbonate) - 16.3 tCO<sub>2</sub> (greenhouse gas emission by the use of LNG in the oyster shell recycling process)] through operating 100 ton sized oyster shell recycling facility.

#### 4. Conclusions

This study found that there would be a reduction of greenhouse gas by 27.97 tCO<sub>2</sub> by collecting all of oyster shells generated in Korea and recycling them as converting them into alternative resource for lime stone in those 100 t sized paper factories. The amount of oyster shells generated in Korea was estimated to be about 308,277 tons annually as of 2011. Based on the aforementioned result finding, we assumed that all the oyster shells would be converted into resource as paper filler. Under this assumption, we confirmed

that it would be possible to reduce greenhouse gas by about 86,225 tCO<sub>2</sub> annually.

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