# BIOMASS VOLATILE GASIFICATION USING DOLOMITE AND DOLOMITE-NI/$AL_2O_3$ COMBINATIONS

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## ABSTRACT

Biomass volatile decomposition and gasification were discussed in a fixed reaction system using calcined dolomite and a combination of dolomite and Ni/$Al_2O_3$. Biomass volatiles converted effectively under calcined dolomite at catalytic temperatures between 600-800°C, and $H_2$ was obtained as the dominant product gas. The higher temperature of dolomite resulted in more volatile gasification and less carbon distribution in undecomposed tar and coke deposits. The combined use of dolomite and Ni/$Al_2O_3$ catalyst resulted in efficient tar conversion at relatively low temperatures, e.g., at 650°C, carbon distribution in the undecomposed tar was obtained as low as 0.8%. Furthermore, by placing dolomite upstream of the nickel catalyst, more biomass volatiles were converted into gases, and coke deposition on the catalysts was suppressed notably. Consequently, long-term catalyst stability was achieved with the combined use of these two catalysts.

**Keywords:** *biomass volatile gasification, catalyst stability, coke suppression, dolomite*

## INTRODUCTION

Gasification offers huge potential benefits when it is utilised to process biomass waste, produce sustainable energy, and reduce greenhouse gas or pollutant emissions cost-effectively [1]. Biomass gasification commonly includes a series of thermochemical reactions such as pyrolysis, water-gas shift reaction, char gasification and tar cracking, reforming and gasification to gain synthesis gases (mainly CO and $H_2$). The product gases from gasification progress can be used as fuel for heat and power generation or advanced applications such as the synthesis of chemicals and biofuels [2]. However, tar substances in the gaseous product are undesirable because they are sticky and may clog downstream equipment [3]. Tar substances also account for the energy content of feedstocks [4]. Tar conversion is important for process operation, environmental impact reduction and energy efficiency.

In situ, catalytic tar cracking/gasification is a practical and feasible technology for converting tar into valuable gases, and product gas quality can also be improved by using catalysts [1],[5]. Natural minerals such as olivine, dolomite and limestone have recently been commonly discussed in biomass catalytic gasification because of their low cost and anti-agglomeration abilities [6]-[7]. Among them, dolomite is widely used due to its excellent tar decomposability. Compared with olivine, dolomite exhibits higher catalytic performance for the cracking of heavy hydrocarbons, gaining high yields of total gas and $H_2$ [8]. Simell et al. [9] demonstrated efficient tar conversion using dolomite in a bench-scale pressurised reactor. However, dolomite generally requires an operation temperature above 850°C for efficient tar gasification in the fluidised bed gasification processes, which (the high-temperature operation) is not favourable for improving system thermal efficiency and cold gas efficiency [10]. Besides that, the characteristics of dolomite, such as being brittle and fragile, are another obstacle inhibiting its applications in fluidised beds (FB).

Catalysts based on Group VIII metals, e.g. Fe, Co, and Ni, are effective for tar gasification at lower temperatures. Gusta et al. [11] reported that the reaction temperature can be lowered to 750°C for the tar conversion and water-gas shift reaction using Fe-loaded dolomite (Fe, <0.9 wt.%). Nickel-based catalysts were confirmed effective for tar removal at a mild temperature condition around 600°C [12]-[13]. Due to their high activity, nickel catalysts are widely used in commercial steam reforming processes [14]. Meanwhile, suffering from deactivation due to coke deposition and/or sulfur poisoning narrows their way to commercialisation [15]-[16]. Coke deposition is caused by the subsequent dehydrogenation reaction of hydrocarbons (polycyclic aromatic compounds) adsorbed on the catalyst. That cannot be prevented thermodynamically. Therefore, catalyst design is important in selecting the catalyst that causes less coke precipitation [17].

Considering the above issues, in this study, we investigated the conversion of biomass volatiles in a fixed-bed reactor, which can easily adjust the gas residence time according to the tar decomposition status and prevent collisions between catalyst particles and surface destruction. In the catalysts combined use cases, dolomite was placed upstream of the Ni catalyst, where heavy hydrocarbons (polycyclic aromatic compounds, glucose, benzene, benzene diol (phenols), etc.) in the biomass volatiles first contact the dolomite and crack/gasify on it, prior to Ni/$Al_2O_3$. It is expected to protect the Ni catalyst from severe coke deposition or

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sulfur poisoning and prolong the catalyst service time. On the other hand, calcinated dolomite has the potential as a cyclically stable $CO_2$ sorbent, which may enhance reactions such as sorbent-enhanced water-gas shift or sorbent-enhanced reforming by lowering the $CO_2$ partial pressure in the reaction system at the temperature below 800°C [18]. Based on the $CO_2$ absorption effect of dolomite and the effective decomposition temperature of tar, the catalyst temperature in this study is varied from 600°C to 800°C [18]. The gas yields, gas compositions and carbon distributions are discussed. Catalyst stability and the protective effect of dolomite on Ni catalyst are also investigated at 650°C with increasing biomass feed.

## EXPERIMENTAL

### Materials

Cypress sawdust, less than 1.4 mm in size, and a waste woody biomass were used as the pyrolysis sample. The proximate and ultimate analyses of cypress sawdust are shown in Table 1. This residue from the wood processing industry offers the typical woody analyses as a high volatile content (70.5%) with lower ash content (1.7%) compared to agriculture waste (rice husk, sugarcane bagasse, and corn cob) [19]. High volatile content is preferred for a high yield of volatile liquid. Low ash content indicates less ash formation and its derivatives during biomass gasification. High carbon, hydrogen and oxygen content with much lower nitrogen and sulphur contents also indicate its suitability for pyrolytic conversion and gas product generation.

**Table 1** Proximate and ultimate analyses of cypress sawdust sample

| Proximate analysis (wt %) | | | | Ultimate analysis (wt %, d.a.f.[a]) | | | | |
|---|---|---|---|---|---|---|---|---|
| Mois. | V.M. | F.C. | Ash | C | H | N | S | O[b] |
| 9.7 | 70.5 | 18.2 | 1.7 | 51.8 | 7.1 | 0.1 | 0.2 | 40.7 |

[a]d.a.f.: dry ash free basis;
[b]: by difference

A natural dolomite ore (provided by Yoshizawa Lime Industry CO., LTD.) was crushed to 1-2 mm and used as a catalyst. Dolomites were analysed using X-ray fluorescence, RIX3000, and Rigaku Corporation. The main components of the dolomite were determined as CaO, MgO and $SiO_2$ (Table 2). The carbonate compositions were obtained from their oxides.). The other components consisted mainly of $CO_2$. As a pre-treatment, the dolomite ore was decarboxylated at 830°C for one hour to obtain magnesium and calcium oxides. Inert gravel (no activity for tar material conversion) as a reference sample, and a commercial Ni/$Al_2O_3$ catalyst (C13-4, Sud-Chemie Catalysts Japan, Inc.; 20±2 wt% nickel) was also used [13]. These two samples were crushed and sieved to 1-2 mm. Porous alumina particles were packed near the reactor outlet to capture the undecomposed tar materials, and the carbon amount in the captured tar was quantified by the combustion method.

**Table 2** Main components (wt %, by XRF) of raw dolomite

| | | | | |
|---|---|---|---|---|
| CaO | 51.73 | → | $CaCO_3$ | 61.58 |
| MgO | 14.02 | → | $MgCO_3$ | 29.44 |
| $SiO_2$ | 4.93 | | | |
| $Al_2O_3$ | 0.21 | | | |
| $Fe_2O_3$ | 0.09 | | | |
| $K_2O$ | - | | | |
| $Na_2O$ | - | | | |
| Others | 29.90 | | | |

### Apparatus and Methods

Experiments were carried out in a two-stage fixed-bed quartz reactor with an inner diameter of 30 mm and a length of 900 mm. A schematic diagram of the two-stage fixed bed is shown in Figure 1. An internal quartz reactor with a porous filter bottom (with a porosity level of less than 5 μm) is set in the upper stage(first stage) for biomass pyrolysis. The lower stage (second stage) with a melted porous filter bottom is for catalytic conversion. The temperature of the two stages is controlled by two electric furnaces, respectively. About 1.0 g of biomass sample was slowly dropped in each run and pyrolysed at 500°C. The released volatiles flowed with fed $N_2$ (140 ml/min, NTP) to the second stage for catalytic cracking and gasification, where the catalyst bed was preheated to 600-800°C. The height of the catalyst bed in the reactor was 3 cm to provide a residence time >1 s for volatiles in the catalyst bed. Steam was generated and flowed directly to the catalyst bed for gasification. Steam concentration in the flowing nitrogen is controlled at 30 vol %. GC/FID and GC/TCD collected and analysed product gases. After each biomass feeding, gas collection continued for an additional 30 minutes. The combustion method evaluated the carbon amounts of coke deposits in the catalyst bed and trapped tar in the outlet alumina adsorbent.

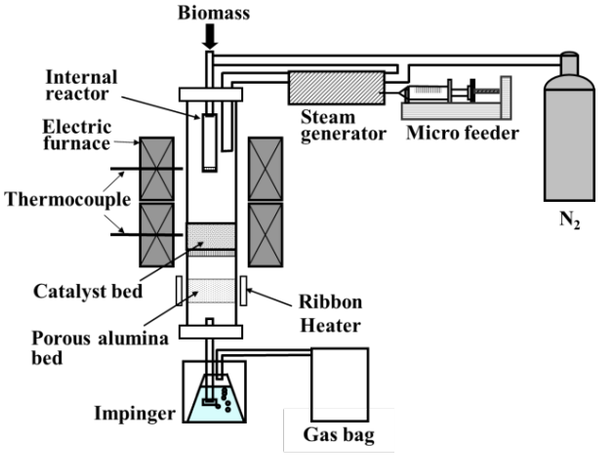



**Figure 1** Schematic diagram of biomass pyrolysis and the volatiles gasification in a fixed-bed reactor

### Material Characterisation

A thermogravimetry analysis apparatus (TGD-9600S, Advance Riko, Inc. Japan) was used. Sample analysis was conducted in flowing nitrogen, and the TGD heating rate was set at 20°C/min. Gas sorptometry was measured using the $N_2$ isotherm adsorption method at -196°C to examine the sample Brunauer-Emmett-Teller (BET) surface area and pore size distribution on a TriStar II 3020 instrument (USA). Before that, degas treatment was carried out in a vacuum at 300°C for one hour.

## RESULTS AND DISCUSSION

### Thermogravimetric Analysis and Changes in Pore Distribution During Dolomite Calcination

Decarbonisation (calcination) treatment for dolomite was carried out before it was used for volatile gasification. According to relevant literature, dolomite calcination analysis was performed from room temperature to 950°C under flowing $N_2$ [18],[20]. Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) curves are shown in Figure 2. Two major weight changes were observed at temperatures around 500°C and around 700-830°C. These were attributed to converting $CaMg(CO_3)_2$ to MgO-$CaCO_3$ and MgO-$CaCO_3$ to MgO-CaO, respectively [21]. TG profile shows that calcination is complete after a 15-minute holding at 830°C, and no weight change is observed in the further temperature steps. Considering that a lower temperature may prevent the sample from overheating, 830°C is deemed sufficient for dolomite calcination in flowing $N_2$ [21]. Consequently, in this work, the dolomite pre-treatment was carried out at 830°C for 30 minutes in flowing $N_2$.

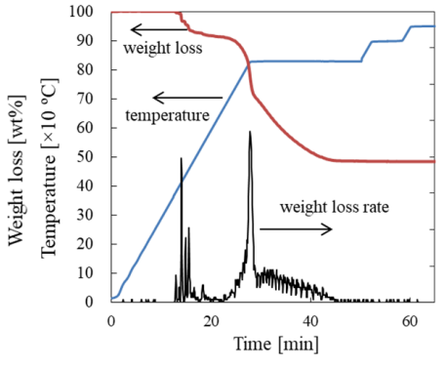
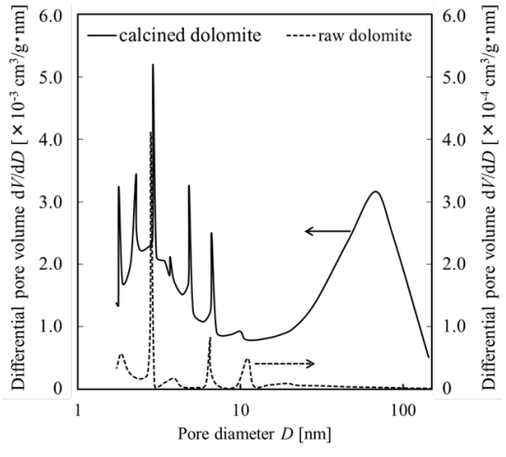



**Figure 2** TGA/DTG curves of dolomite measured in following $N_2$

Figure 3 shows the Barrett-Joyner-Halenda (BJH) pore distributions of raw and calcined dolomite based on adsorption isotherms. This result indicates that the calcination treatment opened more pores in the dolomite over a wide pore size range. The differential pore volume increased significantly in the calcined dolomite for both pores with diameters <10 nm and >20 nm.




*Note*: The left and right axes are on different scales

**Figure 3** Comparison of pore volume distribution between raw dolomite and calcined dolomite by BJH method

**Table 3** Structural comparison of raw dolomite and calcined dolomite

| Sample | BET surface area [$m^2$/g] | Cumulative pore volume [$\times 10^{-3}$ ml/g] | Average pore diameter [nm] |
|---|---|---|---|
| Raw dolomite | 0.25 | 0. 81 | 12.67 |
| Calcined dolomite | 31.32 | 298.06 | 38.06 |

Table 3 shows the calcination enlarged the sample's Brunauer-Emmett-Teller (BET) specific surface area significantly from 0.25 to 31.32 $m^2$/g and cumulative pore volume from 0. 81 to 298.06 [$\times 10^{-3}$ ml/g]. Correspondingly, the average pore diameter of calcined dolomite was calculated as 38.06 nm due to more pore openings.

### Activity of the Calcined Dolomite on Biomass Volatile Conversion

Figure 4 shows the gas yields from biomass and its volatiles, further gasification over inert gravel (Figure 4a) and calcined dolomite (Figure 4b, about 24.5 g dolomite ore was used in one run). The second stage gasification temperature varied from 600 to 800°C. In the gravel cases, gas yields increased gradually as the temperature increased in the second stage, despite the gradual gas increase trend and small change in gas composition. The increase in gas is mainly attributed to the further thermal cracking of volatiles at higher temperatures. The main gas products are $H_2$, $CH_4$, and CO.

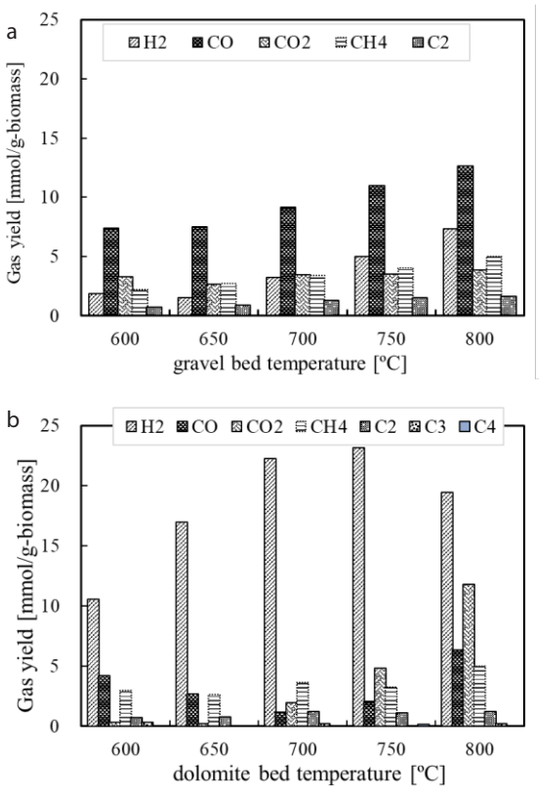



**Figure 4** Comparison of gas yields obtained with inert gravel (a) and calcined dolomite (b) at various temperatures

In contrast, when calcined dolomite was packed in the second stage, hydrogen was produced significantly in the wide temperature range (Figure 4b). Even at a low temperature of 650°C, calcined dolomite improved $H_2$ yield by 11.25 times compared to the gravel, reaching 16.99 mmol/g biomass. This indicates that dolomite converts biomass volatiles at 650°C in the fixed bed. It is significantly lower than the temperatures required in the fluidised bed system with dolomite catalysts, above 850°C for apparent conversion of biomass volatiles [22]. The superficial velocity of flow gas is controlled at about 8.5 mm/s in this fixed bed reaction system, which is much slower than that of a few meters to tens of meters in a fluidised bed system, to provide sufficient contact of biomass volatiles and dolomite, resulting in the effective conversion of biomass volatiles even at lower temperatures. Hydrogen yield continued to increase with dolomite bed temperature, reaching a peak value at 750°C and then decreasing at 800°C. At the same time, more $CO_2$ was detected in the gas products at 800°C. In addition to thermal cracking pyrolysis and gasification advancement at high temperatures, $H_2$ yield generation is also attributed to $CO_2$ absorption by the calcined dolomite. Which improves reactions such as sorbent-enhanced reforming or sorbent-enhanced water-gas shift ($CO + H_2O \leftrightarrow H_2 + CO_2$) by lowering $CO_2$ partial pressure in the reaction system. On the other hand, the higher temperature of 800°C will weaken the $CO_2$ absorption into dolomite and then affect the shift reaction equilibrium, resulting in less hydrogen and more CO [18].

Carbon amounts in the coke deposits on the catalyst and the undecomposed tar trapped near the reactor outlet were quantified by combustion. The results at various temperatures with dolomite are compared in Table 4.

**Table 4** Comparison of carbon distribution in coke deposits on dolomite and undecomposed tar captured on alumina adsorbent at reactor outlet at different catalyst temperatures

| Dolomite bed temperature [°C] | 600 | 650 | 700 | 750 | 800 |
|---|---|---|---|---|---|
| In the coke deposits [%] | 5.92 | 3.15 | 3.57 | 2.78 | 1.03 |
| In the undecomposed tar [%] | 7.09 | 5.64 | 3.97 | 1.60 | 0.87 |

*Note*: Carbon distribution is calculated as the percentage of carbon in each product to carbon in biomass volatiles.

As shown in Table 4, the higher catalytic temperature results in sufficient conversion of biomass volatiles and less tar. E.g., For varying the catalytic temperature from 650 to 800°C, the carbon content in the undecomposed tar decreased by 87.7% to 2.9 mg-carbon/g-biomass (occupying about 0.87% carbon of the total carbon in biomass volatiles). At the same time, coke deposition tended to decline with temperature increase. These results are consistent with the report that dolomite was effective in tar diminution at a suitable temperature [23]. In other words, high temperatures promote tarry matter's decomposition and steam gasification, producing more light gases and less carbon.

On the other hand, undecomposed tar was still detected in dolomite, even at 800°C with dolomite. Therefore, it is thought that there is a limitation to converting biomass volatiles using dolomite only. The addition of nickel catalysts was discussed in the next section, considering the high activity of nickel catalysts in coal volatile conversion [12].

## Combination Use of Dolomite and $Ni/Al_2O_3$ Catalyst

The feasibility of low-temperature conversion of biomass volatiles and improved process thermal efficiency was discussed by combining dolomite and $Ni/Al_2O_3$ catalysts. When using dolomite and nickel catalyst in combination, dolomite was placed upstream of the $Ni/Al_2O_3$ catalyst to avoid rapid deactivation of the nickel catalyst due to coke deposition from the decomposition of heavy hydrocarbons. Also, the Ni catalyst was reported to be highly dependent on the catalyst temperature for tar decomposition. It showed the highest activity at 650°C in converting coal volatile matter. Further, an increase in temperature led to the Ni catalyst's rapid deactivation due to Ni's sintering and carbon deposition on the catalyst. [12],[15]. Based on these, the catalytic temperature was set at 650°C using the combination of dolomite and $Ni/Al_2O_3$ catalyst.

The gas yield is summarised in Figure 5. The X-axis shows the dolomite and nickel catalyst bed information, and the total catalyst bed height was 3 cm. Carbon distributions in the products are shown in Table 5.

The biomass volatiles progressively decomposed and gasified on a $Ni/Al_2O_3$ catalyst. Compared to dolomite alone (case of dolomite-

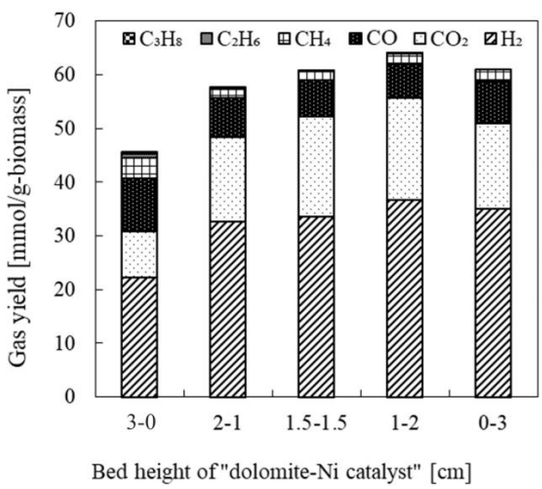



**Figure 5** Comparison of gas yields with different usage ratios of dolomite/nickel catalyst at 650°C

**Table 5** Carbon distributions in product gases, coke deposits on dolomite and undecomposed tar captured on alumina adsorbent at reactor outlet at different catalyst usage ratios at 650°C

| Catalyst bed height of dolomite-$Ni/Al_2O_3$ [cm-cm] | Carbon distribution in products [%, based on carbon content in the biomass volatiles] | | | |
|---|---|---|---|---|
| | gas | coke | tar | total |
| 3-0 | 89.3 | 3.2 | 5.6 | 98.2 |
| 2-1 | 90.1 | 1.8 | 2.4 | 94.3 |
| 1.5-1.5 | 96.0 | 1.9 | 1.0 | 99.0 |
| 1-2 | 96.8 | 2.1 | 0.8 | 99.7 |
| 0-3 | 92.5 | 6.2 | 0.7 | 99.4 |

Ni catalyst of 3-0 cm-cm), gas yields show an apparent increase in all cases with a nickel catalyst. $H_2$ and $CO_2$ increased, particularly with methane hydrocarbons, and $C_2$ and $C_3$ gases decreased. The combined use of 1 cm height dolomite on a 2 cm Ni catalyst gave a higher gas yield than that of the Ni catalyst alone. This means the volatiles decompose sequentially on the dolomite and nickel catalyst layers, producing more gases and reducing carbon deposition (coke).

Along with the efficient conversion of volatiles, carbon distribution changes also occurred in the tar and coke products. For 1cm height dolomite on 2 cm height Ni catalyst, up to 96.8% of carbon in biomass volatiles is converted to gas products. The total carbon balance in the product gas, coke deposits, and captured undecomposed tar reached as high as 99.7%. The carbon amount in the undecomposed tar gradually decreases as the proportion of Ni catalyst usage increases. On the other hand, in the absence of dolomite, high coke content was demonstrated in the nickel sample after the reaction. Some literature suggested that the reactor for tar removal should be heated at temperatures above 800°C to reduce coke formation, avoiding premature catalyst deactivation, or a guard bed should be useful [24]. High temperatures are not suitable for nickel catalysts due to thermal agglomeration. Other studies on dolomite have shown that under appropriate steam/carbon (S/C) molar ratios, it is possible to reduce the thermodynamic propensity for coking to a reasonably low level, even at temperatures as low as 600-650°C [25]. In addition, reactive oxygen species have been generated at high-temperature conditions [26]. These reactive oxygen species, including superoxide $O_2^-$, singlet oxygen, etc., act as oxidants and suppress coke formation.

### Effect of Catalyst Position in Combination Use of Catalysts

For further confirmation, we compared the upstream and downstream dolomite placements with the same catalyst ratio of dolomite and Ni catalyst at 650°C. The bed heights of dolomite (1 cm) and nickel catalyst bed (2 cm) were fixed in both cases. Gas yields and carbon amounts deposited in the catalyst bed and outlet alumina absorbent are compared in Figure 6 and Table 6. Compared to the upstream installation, placing dolomite downstream of the nickel catalyst bed resulted in less hydrogen and $CO_2$ production and a noticeable decrease in total gas yield. The carbon amount changed slightly in the undecomposed tar but changed clearly in the coke deposits. More coke deposits were formed when the biomass volatiles directly passed through the Ni catalyst bed.

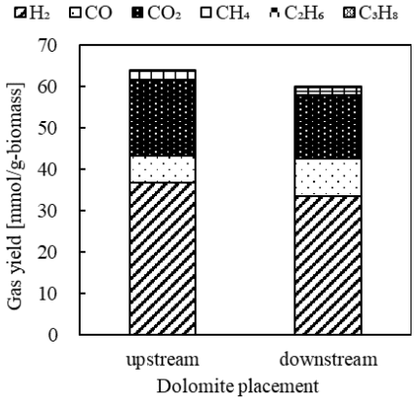



**Figure 6** Comparison of gas yields with dolomite placed upstream and downstream of nickel catalyst at 650°C (1 cm dolomite and 2 cm Ni catalyst bed height were set in the reactor)

**Table 6** Effect of dolomite placement on carbon distribution in the product gas, coke and tar in the combination of 1cm height dolomite and 2 cm height $Ni/Al_2O_3$ at 650°C

| Dolomite placement | Carbon distribution in products [%, based on carbon content in the biomass volatiles] | | | |
|---|---|---|---|---|
| | gas | coke | tar | total |
| upstream | 96.8 | 2.1 | 0.8 | 99.7 |
| downstream | 94.5 | 3.7 | 0.9 | 99.1 |

Therefore, the dolomite placed upstream of the nickel catalyst bed partially decomposes/gasifies some heavy hydrocarbons prior to $Ni/Al_2O_3$ and guards the nickel catalyst against rapid deactivation due to coke deposition.

### Catalyst Stability Evaluation

The stability of the catalysts was also investigated at the catalytic temperature of 650°C, in which 1 cm height dolomite (4.6 g) was placed upstream of 2 cm height $Ni/Al_2O_3$ catalyst (10.7 g). The catalysts were repeatedly used for catalytic conversion of biomass volatiles, and 1 g of dry biomass sample was fed in each cycle. The gas yields for 24 cycles are presented in Figure 7.

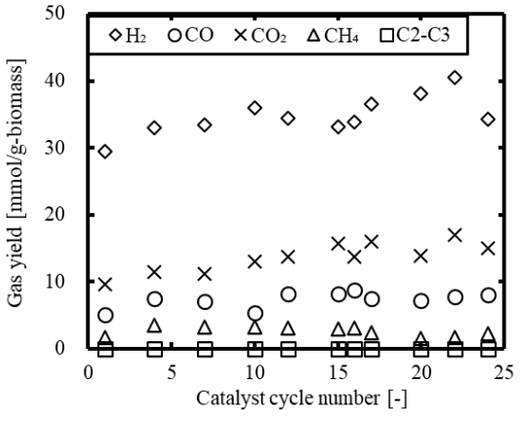



**Figure 7** Change of gas yields during repeated use of the combined dolomite-Ni catalyst at 650°C (1 cm height dolomite upstream of the 2 cm height $Ni/Al_2O_3$ catalyst)

The catalysts show significant stability for volatile catalytic decomposing. There is no noticeable decrease in gas yield, and $H_2$ and $CO_2$ gases slightly increase with small fluctuations in later cycles. The fluctuation in gas yield is thought to be due to the gasification reaction (Equation 1) of the biomass char and the steam released from the newly supplied biomass pyrolysis in the first-stage internal reactor and water gas shift reaction (Equation 2).

$$C + H_2O \rightarrow H_2 + CO \quad (1)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (2)$$

The carbon amount of coke deposits on the catalyst after 24 cycles was determined to be 9.15 mg carbon per gram catalyst. It is less than 1/6 of the carbon in the spent $Ni/Al_2O_3$ catalyst that was deactivated due to severe coke deposition after several cycles of coal volatile decomposition [12]. The combined use of dolomite and $Ni/Al_2O_3$ protected them from severe pore channel coverage or blockage by coke, and the catalysts maintained the developed pore structure ($S_{BET,\ Ni/Al_2O_3} = 69.9\ m^2/g$, $S_{BET,\ dolomite} = 9.1\ m^2/g$) after 24 cycles use, which contributed to their improved stability.

## CONCLUSIONS

Calcination enlarged the texture structure of dolomite ore, and the calcined dolomite showed obvious performance for biomass volatiles cracking/gasification in a fixed bed reaction system. Hydrogen, as the main gas, increased its yield with increasing dolomite temperature, reaching a peak at 750°C. At 800°C, the $H_2$ yield decreased due to changes in the $CO_2$ partial pressure in the reaction system, and undecomposed tar was still detected with dolomite only.

The combined use of dolomite and $Ni/Al_2O_3$ catalyst converted the biomass volatiles progressively at a lower temperature of 650°C, a preferred temperature to protect the Ni catalyst from high-temperature sintering. Less than 1.0% carbon of the volatiles was detected in the undecomposed tar, and 96.8% of the carbon was converted into gas products. Dolomite placed upstream of the Ni catalyst layer acted as a guard bed to suppress coke deposition on the catalysts, contributing to long-term stability. Consequently, placing a dolomite layer upstream of the nickel catalyst efficiently converted biomass volatiles to gases at a relatively low reaction temperature, extending the catalyst's lifetime.

## ACKNOWLEDGEMENT

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