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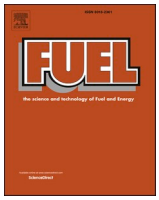
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Full Length Article

Catalysis/sorption enhanced pyrolysis-gasification of biomass for H_2-rich gas production: Effects of various nickel-based catalysts addition and the combination with calcined dolomite

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ABSTRACT

The effects of addition of various Ni-based catalysts and their combination with calcined dolomite on H_2-rich gas production were investigated during catalysis/sorption enhanced pyrolysis-gasification of sawdust. It was found that catalyst support greatly affected the catalytic performance of Ni-based catalysts, the highest H_2 concentration and yield was obtained by NiO/SiO_2, followed by NiO/γ-Al_2O_3 and NiO/ZSM-5. Additional active sites on Ni-based catalyst would be formed by introduction of secondary metals onto NiO/γ-Al_2O_3. Positive synergistic effect between secondary metals and Ni was observed, especially for Mg and Co, resulting in further improved H_2 production. Calcined dolomite was further introduced into the process to enhance H_2 production, simultaneous catalysis and sorption was found to be better for H_2 production than sequential catalysis and sorption. The addition of calcined dolomite could offset the catalytic performance difference for varied Ni-based catalysts due to its catalysis/sorption enhancing effect. Comparatively, bimetallic catalysts were more effective than monometallic catalysts when combined use with calcined dolomite, the H_2 concentration was significantly improved despite of the slight changes in H_2 yield. Ni-Cu/γ-Al_2O_3 and Ni-Zn/γ-Al_2O_3 with good performance on WGS reaction showed better synergistic effect with calcined dolomite, a highest H_2 concentration of 87.06 vol.% was achieved by Ni-Cu/γ-Al_2O_3 catalyst.

1. Introduction

Hydrogen is an ideal clean energy resource as its combustion only generates water [1,2]. It is expected to play a very important role in the future energy consumption system, especially for the global carbon neutrality [3,4]. The sufficient supply/production of green H_2 from clean renewable resources is thus urgently required [5-7]. As an alternative energy resource, biomass has the advantages of abundant resources, accounting for 170 billion metric tons of biomass worldwide per year, zero carbon emissions throughout its whole lifecycle, and being the only carbon renewable in nature, etc. [8-10]. It can be easily used as a cheap carbonaceous feedstock to produce green H_2.

Gasification of biomass has long been used as an effective way for H_2 production [11-13]. The similarity in chemical structure of biomass and coal makes it easy to copy the experiences in coal gasification when developing biomass gasification [10]. However, biomass has its unique characteristics that differs from coal, including its fibrous structure, low volumetric density and high oxygen content [14,15]. The product gas from biomass gasification often suffers from low H_2 content, low carbon conversion rate and high CO_2 and tar content [16-18]. Introduction of catalyst/sorbent into the gasification process, or using catalytic gasification of biomass, has been widely regarded as a promising way to improve the H_2 content in the product gas, increase the gasification reaction rate and product selectivity, and catalytically remove the tar [13,19-21]. Different catalysts have been developed in the gasification process, among them, Ni-based catalysts are highlighted as one of the

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most used catalysts due to their effectiveness in H_2 production and tar removal with an affordable cost [22,23]. Miccio et al. [24] reported that the introduction of Ni/Al_2O_3 catalyst into air-steam gasification of Spruce wood pellets could significantly improve the H_2 content by around 50% with a large reduction in tar yield as well. Chen et al. [25] claimed that Ni/HZSM-5 catalyst could achieve a tar removal efficiency of 91.52% at a very low temperature of 500 ^oC through catalytic cracking.

However, the product gas from catalytic gasification of biomass normally still contains a considerable amount of carbonaceous gases including CO, CO_2 and CH_4, etc. [26], which largely dilute the H_2 in the product gas. A long conversion chain including gasification, tar removal, WGS reaction, CO_2 removal/separation would thus be required for the production of a high-purity H_2, but in the meantime makes the process economically infeasible when using biomass as feedstock. How to integrate the above processes and largely reduce the cost are the main challenging issues needing to be solved currently. Sorption enhanced gasification of biomass is such a process that integrates the gasification, WGS reaction and CO_2 removal into one reactor and produces a high-purity of H_2 by one-step [19,27-29]. CO_2 absorbent such as CaO is introduced into the gasification process, the in situ removal of CO_2 by CaO immediately after its generation during the gasification process would on the one hand shift the equilibrium of WGS reaction as well as the gasification process to produce more H_2, on the other hand concentrate the H_2 in the product gas [30]. Our previous studies have demonstrated that the optimal temperature for sorption enhanced gasification process is around 600-700 ^oC at atmospheric pressure [31]. A high H_2 concentration could be achieved, but the H_2 yield still needs to be improved due to the lower carbon conversion rate at such temperature [32]. Sorption enhanced catalytic gasification of biomass for H_2 production is thus proposed recently, the combined use of catalyst and absorbent is expected to directly obtain a high purity and yield of H_2 from the process [32,33]. Li et al. [34] reported that by use of a bifunctional catalyst of Ni/CaO, a H_2 concentration and yield of 63.7 vol.% and 341.30 mL/g biomass respectively could be produced. The catalytic activity of Ni-based catalysts and the CO_2 removal efficiency of CaO-based absorbent are expected to both affect the H_2 production performance during the process. To the best of our knowledge, there are a lot of studies available where Ni-based catalysts were introduced into the biomass gasification process for H_2-rich gas production with CaO using as an absorbent to reduce the CO_2 in the end product gas. Most of the works focus on the enhanced H_2 production by evaluating the parameters such as temperature, steam to biomass ratio, biomass and absorbent types, Ni loading amount and amount of catalyst addition [35-40]. Unfortunately, very limited studies concentrate on the modification of catalysts during this process, the influence of catalyst supports and the possible interactions between active Ni metal and support as well as the influence of other active metal doping on the catalyst activity are not well understood. In particular, the effects of the combination of mono-/bi-metallic catalysts with calcined dolomite on the sorption-enhanced gasification process for H_2 production are still required to be studied in more details.

Therefore, in this study, the catalysis/sorption enhanced pyrolysis-gasification of sawdust for H_2-rich gas production was studied in a two-stage fixed-bed reactor. Several Ni-based catalysts with different supports of γ-Al_2O_3, ZSM-5, and SiO_2 were prepared and tested for H_2 production. Furthermore, secondary transition metals of Cu, Mg, Zn, Co, Fe, and Ce were introduced onto NiO/γ-Al_2O_3 catalysts to form bimetallic catalysts, and their effectiveness in H_2 production was also evaluated. Moreover, the combination of Ni-based catalyst and calcined dolomite (as a CO_2 absorbent) was also studied to further reduce the CO_2 concentration in the product gas. Both monometallic and bimetallic catalysts were used during the process to enhance the H_2 production and find out the possible synergistic effect between catalyst and absorbent as well. The results reported in this study are expected to gain more in-depth understanding on the sorption enhanced catalytic gasification process in terms of both catalysis and sorption enhancing effects and their possible synergistic effect. It should be also noted that this study is more used to screen the possible catalysts applied in the catalysis/sorption enhanced gasification process. While the detailed characterizations of the catalysts before and after the process will be investigated in the future.

2. Experimental

2.1. Materials

The biomass feedstock used in the pyrolysis-gasification process was sawdust with a particle size of 90-180 μm. It was dried at 105 ^oC for at least 12 hours before use. The elemental composition of sawdust has been reported in our previous studies, with 49.97 wt.% C, 6.14 wt.% H, 0.07 wt.% N, 0.19 wt.% S, 41.02 wt.% O, and 1.73 wt.% Ash, on a dry basis [41].

Different metal nitrates and catalyst supports were used to prepare the Ni-based catalysts in the study. Analytically pure metal (including Ni, Fe, Cu, Co, Zn, Mg, and Ce) nitrates (hydrates) were purchased from Macklin Co., Ltd. and Sinopharm Chemical Reagent Co., Ltd., respectively. The catalyst supports included γ-Al_2O_3, ZSM-5, and SiO_2, where γ-Al_2O_3 and SiO_2 was bought from Macklin Inc., and ZSM-5 was purchased from Nankai University Catalyst Co. Ltd., the porous structure of the support would provide a better distribution of those metal active components.

The dolomite used in the study was purchased from a local company, it was used to prepare the CO_2 absorbent.

2.2. Preparation of Ni-based catalysts and CO_2 absorbent

Impregnation method was used to prepare the Ni-based catalysts in the study. Two types of supported catalysts were prepared, including single active metal (Ni) catalysts and bimetallic (Ni-Fe, Ni-Co, Ni-Cu, Ni-Zn, Ni-Mg, and Ni-Ce) catalysts. For all the catalysts, the loading amount of Ni on the catalyst support was consistent as 15 wt.% [42]. The detailed procedure for the single active metal (Ni) catalysts preparation could be summarized as follows: controlled amount of analytically pure $Ni(NO_3)_2{\cdot}6H_2O$ was accurately weighed and dissolved in deionized (DI) water to form a Ni nitrate solution. 10 g of various supports (γ-Al_2O_3, ZSM-5 and SiO_2) were weighed and impregnated in the solution. The mixture was stirred and kept for 24 hours for sufficient impregnation. It was then dried overnight at 105 ^oC in an oven. The dried catalyst precursors were subsequently calcined at 650 °C under air atmosphere for 30 minutes with a heating rate of 10 °C/min in a maffle furnace. The 15 wt.% of Ni-based catalysts of NiO/γ-Al_2O_3, NiO/ZSM-5, and NiO/SiO_2 were finally obtained [43]. The bimetallic (Ni-Fe, Ni-Co, Ni-Cu, Ni-Zn, Ni-Mg, and Ni-Ce) catalysts were prepared following the same procedure. The Ni and second metal (Fe, Co, Cu, Zn, Mg and Ce) were co-impregnated during the process. The Ni nitrate and second metal nitrate were simultaneously dissolved in DI water to form a mixed solution. The mass ratio of Ni to second metal ranged from 1:0.25 to 1:1. The catalyst support was chosen as γ-Al_2O_3 according to its better performance during the preliminary experiment results [44]. The remained impregnation, drying and calcination process were kept the same. Six types of bimetallic catalysts of Ni-Fe/γ-Al_2O_3, Ni-Co/γ-Al_2O_3, Ni-Cu/γ-Al_2O_3, Ni-Zn/γ-Al_2O_3, Ni-Mg/γ-Al_2O_3, and Ni-Ce/γ-Al_2O_3 were finally prepared. It should be noted that the catalysts were not reduced into metal element form before use, but directly used in their oxide forms.

The CO_2 absorbent used in the study was calcined dolomite. It was prepared by calcination of 10 g of dolomite at 850 °C for 60 minutes in a horizontal tube furnace under a N_2 flow rate of 500 mL/min.

2.3. Biomass pyrolysis-gasification experiments

The catalysis/sorption enhanced pyrolysis-gasification of biomass

experiments were conducted on a two-stage fixed-bed reaction system, as illustrated in Fig. 1. It was mainly composed of an inert carrier gas N_2 supply system, a steam generator metered by a HPLC pump, a two-stage fixed bed reactor with an electric furnace maintaining the temperature, a tar trapping and condensation system, and a gas bag for product gas collection. During the experiment, biomass was located in the top stage and pyrolyzed to generate volatiles and char, the volatiles were directly carried by N_2 gas and mixed with steam, they would then pass through the catalyst/absorbent bed in the bottom stage and were gasified/reformed to produce H_2-rich product gas. This process is so-called catalysis/sorption enhanced pyrolysis-gasification of biomass for H_2-rich gas production.

For each trial, the temperature of the reactor for both stages (pyrolysis and gasification) was maintained constant at 650 ^{o}C, which is the optimum temperature for H_2 production as illustrated by our previously studies [31]. Three kinds of trails were done in the study: (1) biomass pyrolysis coupled with steam gasification of volatiles, without any catalyst/absorbent addition; (2) biomass pyrolysis coupled with catalytic steam gasification of volatiles, using different Ni-based catalysts; (3) biomass pyrolysis coupled with catalysis/sorption enhanced gasification of volatiles, using both Ni-based catalyst and calcined dolomite. In fact, the reactions in the top stage were all the same as fast pyrolysis of sawdust. While the main difference for them were the reactions taking place in the bottom stage with/without catalyst and/or absorbent. The detailed procedure for each trial could be described as follows:

4 g of Ni-based catalyst or 4g of Ni-based catalyst plus 4 g of calcined dolomite were accurately weighed and loaded into the bottom stage of the reactor in advance. 1 g of dry sawdust was also weighed and put into a stainless-steel basket. It was then hanged on the top of the reactor to avoid overheating before experiment start. The reactor was then heated to the target temperature of 650 ^{o}C with a heating rate of 10 ^{o}C/min under a N_2 flow rate of 50 mL/min and kept isothermal. The HPLC pump was switched on to inject water into the reactor to generate steam once the reactor temperature was stable. The water flow rate of the pump was calibrated in advance and maintained constant at 0.075 mL/min. To ensure the steam was filled in the bottom stage, the trial started after water injection for 10 min. The basket with sawdust inside was promptly put into the middle of the heating zone of top stage. The sawdust was thus fast pyrolyzed to generate volatiles, they were quickly carried by N_2 to the bottom stage and firstly mixed with steam, and then passed through the catalyst/absorbent bed. Catalysis/sorption enhanced steam gasification of biomass volatiles would take place to produce a H_2-rich gas. The resulted gas then went through a solvent (analytical pure acetone) trap with ice-bath condensing to capture the tar. It was finally collected by a gas bag for further analysis. Each trial lasted for 30 min to ensure the completion of pyrolysis-gasification of biomass. After the trial finished, the gas bag was firstly closed and removed from the reaction system, then the HPLC pump was immediately switched off to stop the steam generation, and the furnace was also turned off to naturally cool down the reactor. Once the reactor temperature was less than 50 ^{o}C, the reactor was taken out of the furnace and dismantled to collect the sawdust char and reacted catalyst and absorbent.

The product gas collected in the gas bag was evaluated with a gas chromatography (GC) equipped with a Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID) to get its volumetric composition. The model of the GC was GC-9790II, which was manufactured by Zhejiang Fuli Analytical Instrument Co. Ltd. Before analyzing the product gas, the GC was calibrated with a standard gas via

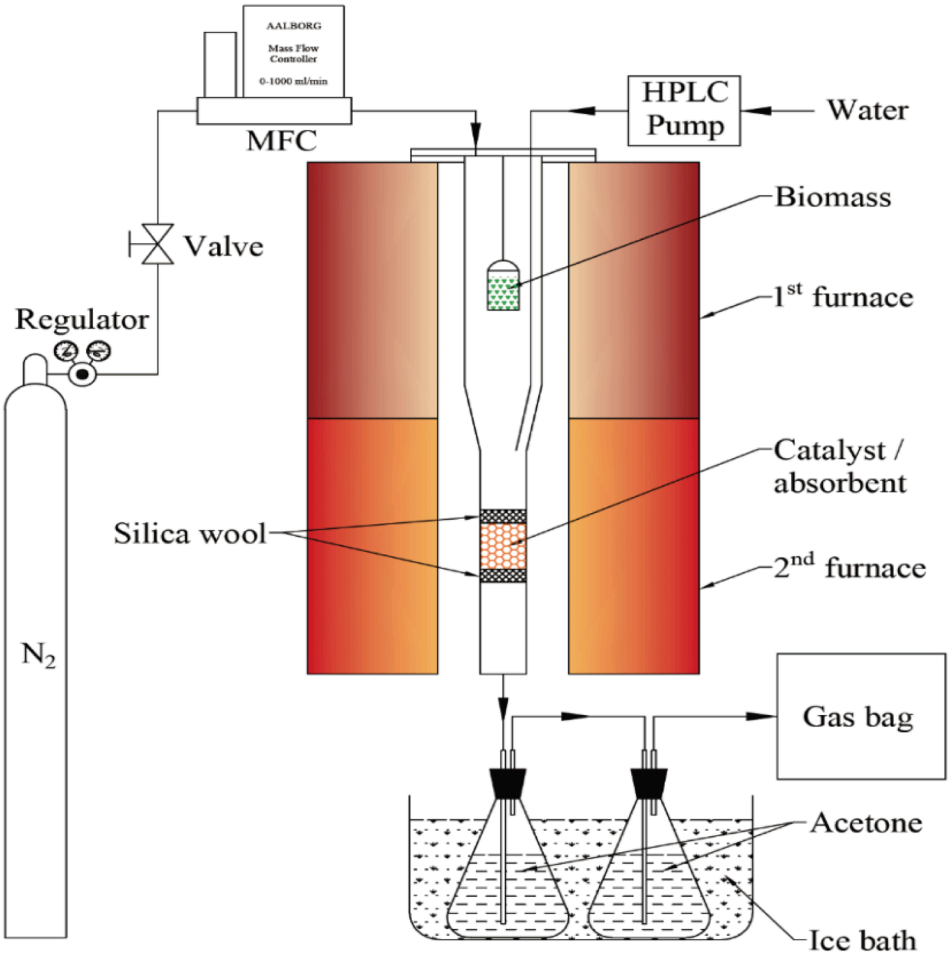


Fig. 1. Schematic diagram of a two-stage fixed-bed pyrolysis-gasification system

the external calibration method. The main gas components detected by the GC included H_2, N_2, CO, CO_2, CH_4, and C_{2+} (C_2H_4, C_2H_6, C_3H_6 and C_3H_8) gases. The yield of the product gas could be directly calculated according to the gas composition through N_2 balance, the detailed procedure could be found elsewhere [19,27,45]. Briefly, the total volume of N_2 in the product gas could be calculated as 50 mL/min × 30 min = 1500 mL. The N_2 concentration in the product gas was known (obtained from GC analysis). The total gas volume excluding N_2 would be thus calculated as the N_2 volume divided by its concentration minus the N_2 volume. It should be noted that the product gas yield was defined as the volume of the gas produced per gram of biomass (mL/g biomass).

3. Results and discussion

3.1. Effect of catalyst support on the H_2-rich gas production during pyrolysis-gasification of biomass

The ideal catalyst support would largely promote the Ni distribution on its surface, form strong bonds to Ni component, prevent Ni leaching and agglomeration, provide possible acidic and/or basic sites, filling oxygen vacancies, and all in all improve catalytic performance [46]. In this study, three Ni-based catalysts with different supports were tested to figure out the suitable support for Ni-based catalyst using during the gasification process. A blank experiment without any catalyst addition was also done for comparison. The results are shown in Table 1.

From the table, it can be clearly seen that the addition of catalyst significantly affected the composition and yield of the product gas during pyrolysis-gasification of biomass. With no catalyst addition, the sawdust pyrolysis and subsequent volatiles steam gasification only produced a relatively lower H_2 content of 21.93 vol.% with a H_2 yield of 127.32 mL/g biomass in the product gas, the total gas yield was 580.43 mL/g biomass. The lower gasification temperature of 650 °C was the main reason. As demonstrated in our previous studies [31,33], this temperature was more favorable for the sorption enhanced gasification process (in situ CO_2 removal) for the production of H_2-rich syngas. However, a lower carbon conversion rate would be obtained at such temperature as illustrated by the results. The introduction of Ni-based catalysts significantly promoted the volatiles gasification to generate more H_2 with a high total gas yield as expected. The H_2 concentration in the product gas largely increased to 41.95-54.35 vol.%, the concentrations of CO, CH_4 and C_{2+} decreased remarkably, and the CO_2 concentration increased obviously from 12.16 to 24.14 vol.%. It implied that Ni-based catalysts could enhance the steam reforming of CO and light hydrocarbon gases to produce more H_2 and CO_2, the volatiles achieved a more sufficient conversion as well [47]. With Ni-based catalysts addition, the H_2 yields were several times bigger than that without catalyst addition, and the total gas yields were close to or more than doubled.

Comparatively, different catalyst supports surely affected the catalytic performance of Ni-based catalysts during the sawdust pyrolysis-volatiles gasification process. NiO/SiO_2 catalyst generated the highest H_2 concentration and yield of 54.35 vol.% and 693.19 mL/g biomass and the highest total gas yield of 1275.46 mL/g biomass, followed by NiO/γ-Al_2O_3 catalyst with the H_2 concentration and yield of 51.13 vol.% and 598.71 mL/g biomass and a total gas yield of 1170.96 mL/g biomass, NiO/ZSM-5 catalyst showed the lowest catalytic performance with the H_2 concentration and yield of 41.95 vol.% and 428.46 mL/g biomass and a total gas yield of 1021.30 mL/g biomass. As mentioned above, Ni-based catalysts significantly enhanced the volatiles steam gasification to produce more H_2 and product gas, the hydrocarbon gases also notably decreased due to the catalytic effect of the catalysts, especially for NiO/SiO_2 and NiO/γ-Al_2O_3. However, the product gas still contained a large amount of CO and CO_2, which diluted the H_2 in the product gas. Further removal of carbonaceous gases would be required to obtain a high purity H_2 gas.

Table 1
Effects of Ni-based based catalyst addition and catalyst support on the H_2-rich gas production from pyrolysis-gasification of sawdust.

Catalyst	Product gas composition (vol.%)					Gas yield (mL/g biomass)	
	H_2	CO	CO_2	CH_4	C_{2+}	H_2	Total
No catalyst*	21.93	46.11	12.16	13.06	6.75	127.32	580.43
NiO/SiO_2	54.35	23.74	18.27	3.22	0.41	693.19	1275.46
NiO/γ-Al_2O_3	51.13	22.13	21.37	4.99	0.46	598.71	1170.96
NiO/ZSM-5	41.95	25.17	24.14	7.31	1.43	428.46	1021.30

* Only 1 g of sawdust was used in the top stage without catalyst.

3.2. Effect of secondary active metal addition onto Ni-based catalyst on the H_2-rich gas production during pyrolysis-gasification of biomass

Compared to monometallic catalyst, bimetallic catalyst often offers higher catalytic activity, good coking resistance and anti-sintering stability due to new active sites introduction and formation of physical barriers between active components [48,49]. In this study, several transition metals, such as Cu, Mg, Zn, Co, Fe and Ce, were introduced onto NiO/γ-Al_2O_3 catalyst through co-impregnation method, different doping ratios expressed as the mass ratio of Ni to secondary metal (M, g/g) were tested and the results are presented in Fig. 2 and Table 2.

From Fig. 2, it can be observed that the introduction of secondary metal onto NiO/γ-Al_2O_3 catalyst significantly altered the product gas composition. It is clear that the H_2 concentration in the product gas did not always increase but decrease in some cases. For instance, Ni-Cu, Ni-Zn, Ni-Fe and Ni-Ce bimetallic catalysts all obtained a lower H_2 concentration of less than 50 vol.% in the product gas, while only Ni-Mg and Ni-Co bimetallic catalysts got a H_2 concentration higher than that of just NiO/γ-Al_2O_3 catalyst (as presented in Table 1). More importantly, with the addition amount of secondary metal increasing, the H_2 concentrations in the product gas decreased as well for Ni-Cu, Ni-Zn, Ni-Fe and Ni-Ce catalysts, while the H_2 concentration increased slightly for Ni-Mg, and the Ni-Co got a highest H_2 concentration at the mass ratio of Ni/Co of 1:0.5. As the Ni content on the catalyst surface kept constant at 15 wt.%, the additional secondary active metal with the increasing loading amount was expected to gain more new active sites on the catalyst surface, which thus further enhanced the volatiles gasification. But the reality is that the increased amount of Cu, Zn, Fe and Ce active metals did not show further enhancing effect on the steam gasification of volatiles. It might be attributed that part of the Ni active sites were covered by the other metals, a lower amount of secondary metal might exhibit better synergistic effect between Ni and secondary metal during the gasification process [50]. Overall, the introduction of Mg and Co onto the NiO/γ-Al_2O_3 catalyst was proven as a good way to further enhance the volatiles gasification to produce more H_2.

In Table 2, the product gas yield from pyrolysis-gasification of sawdust with the addition of the above bimetallic catalysts is presented. It should be noted that only the results for the mass ratio of Ni to secondary metal of 1:0.25 were shown here as a representative. From Table 2, it can be found that all the H_2 yields were improved with bimetallic catalysts compared to that with just NiO/γ-Al_2O_3 catalyst (Table 1), although the H_2 concentration in the product gas decreased with some of the bimetallic catalysts (Fig. 2). The introduction of secondary active metals onto NiO/γ-Al_2O_3 catalyst indeed enhanced the volatiles gasification, as more H_2 and carbonaceous gases were produced with a higher total gas yield obtained. The yields of CO and CO_2 increased greatly as well. However, the product gas still had a considerable amount of hydrocarbon gases such as CH_4, which did not actually decrease but increase mostly. It would infer that the volatiles/tar would be more sufficiently gasified/converted to form the small molecular permanent gases due to the additional metal active sites and/or the synergistic effect of the two kinds of metal active sites, while the steam reforming of hydrocarbon gases was not significantly enhanced as expected, properly because of more hydrocarbon gases forming from the tar cracking. Overall, from the perspective of H_2 production, the

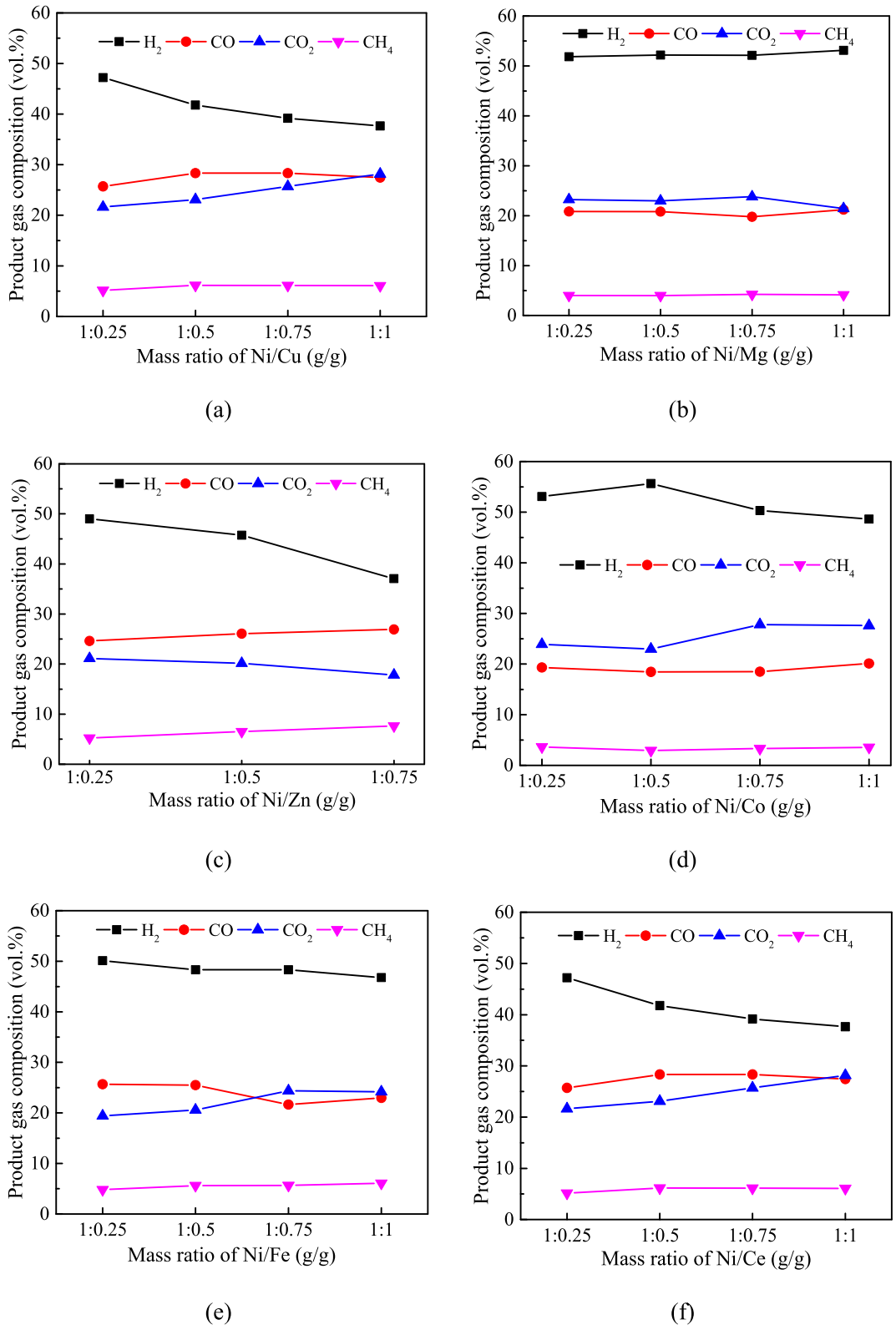


Fig. 2. Effect of mass ratio of Ni to secondary active metal (Cu, Mg, Zn, Co, Ce, and Fe) for Ni-M/γ-Al_2O_3 catalysts on the H_2-rich gas production from pyrolysis-gasification of sawdust: (a) Ni-Cu, (b) Ni-Mg, (c) Ni-Zn, (d) Ni-Co, (e) Ni-Fe, and (f) Ni-Ce.

catalytic performance of different bimetallic catalysts showed a following sequence: Ni-Co/γ-Al_2O_3 > Ni-Mg/γ-Al_2O_3 > Ni-Fe/γ-Al_2O_3 > Ni-Ce/γ-Al_2O_3 > Ni-Zn/γ-Al_2O_3 > Ni-Cu/γ-Al_2O_3. The addition of Zn and Cu onto Ni/γ-Al_2O_3 catalyst did not show comparable enhancing effect on H_2 production compared with other active metals during volatiles gasification.

Table 2
Product gas yield (mL/g biomass) from pyrolysis-gasification of sawdust with addition of bimetallic catalysts under a mass ratio of Ni to secondary metal of 1:0.25.

Bimetallic Catalysts	Ni-Fe/γ-Al_2O_3	Ni-Cu/γ-Al_2O_3	Ni-Ce/γ-Al_2O_3	Ni-Mg/γ-Al_2O_3	Ni-Zn/γ-Al_2O_3	Ni-Co/γ-Al_2O_3
H_2	720.00	600.13	713.67	765.25	660.52	783.97
CO	369.02	326.74	304.32	307.67	331.56	285.24
CO_2	278.00	274.93	328.65	342.76	284.63	352.79
CH_4	68.95	65.63	71.27	59.18	70.33	53.69
C_{2+}	0.04	3.78	0.16	0.93	0.30	0.95
Total gas yield	1437.01	1271.19	1418.08	1475.79	1347.35	1476.64

3.3. Determination of the sequence of catalysis and sorption during sorption enhanced catalytic gasification process

Besides catalyst addition, calcined dolomite, as a CO_2 absorbent, was also introduced into the process to produce a higher purity of H_2 [16,36]. The position of catalyst and absorbent placing inside the reactor was tested to determine the appropriate sequence of catalysis and sorption during the process to achieve better H_2 production performance, the typical results are shown in Fig. 3.

Three kinds of catalyst and absorbent positions of (1) with catalyst on top of absorbent, (2) with catalyst at bottom of absorbent, and (3) with unique mixture of catalyst and absorbent were set during the experiment, corresponding to three reaction modes of (1) catalysis followed with sorption, (2) sorption followed with catalysis, and (3) simultaneous catalysis and sorption. From Fig. 3, it can be observed that the position

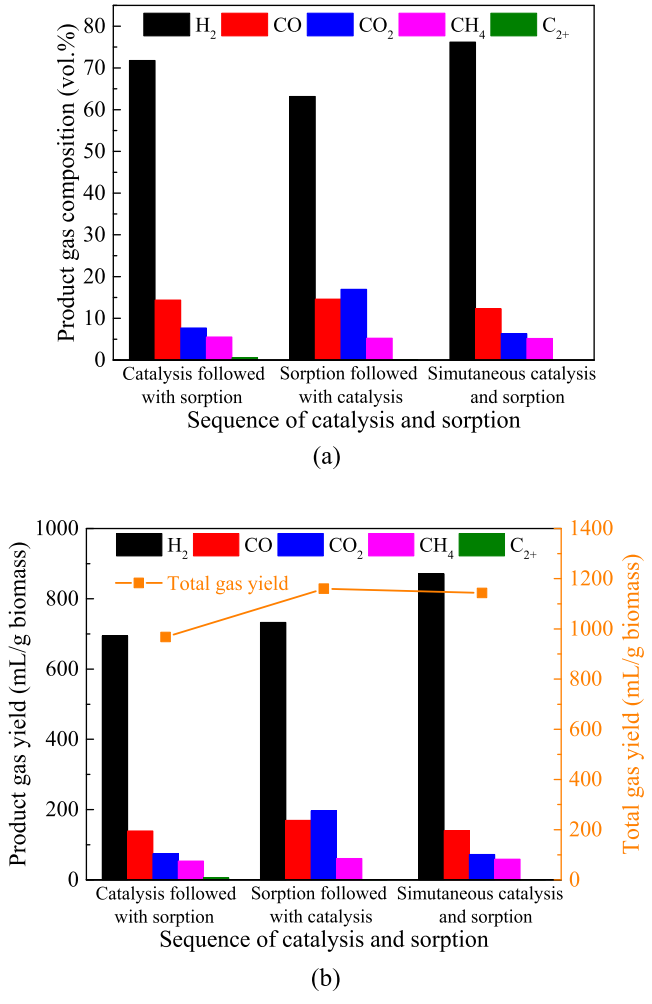


Fig. 3. Effect of the position of catalyst (NiO/γ-Al_2O_3) and absorbent (calcined dolomite) on the H_2-rich gas production from pyrolysis-gasification of sawdust: (a) product gas composition, and (b) product gas yield.

of NiO/γ-Al_2O_3 catalyst and calcined dolomite significantly affected the formation of H_2-rich gas production, resulting in very different product gas composition and yield. For instance, in the case of catalysis followed with sorption, the concentration and yield of H_2 in the product gas were 71.81 vol.% and 694.70 mL/g biomass, with lower contents of CO and CO_2 of 14.38 and 7.67 vol.%, respectively. While in the case of sorption followed with catalysis, the H_2 content decreased to 63.16 vol.%, with a slightly higher H_2 yield of 732.59 mL/g biomass, the CO_2 content in the product gas increased greatly to 16.95 vol.%. Comparatively, in the case of simultaneous catalysis and sorption, the H_2 concentration and yield obtained their maximum values of 76.20 vol.% and 871.27 mL/g biomass with the lowest contents of carbonaceous gases. NiO/γ-Al_2O_3 catalyst mainly catalyzed the volatiles gasification to produce more small molecule permanent gases, while the calcined dolomite would concentrate the product gas by in situ absorbing the CO_2 from the product gas and promote the water-gas shift (WGS) reaction to produce more H_2 [32,34]. First catalysis to achieve a high carbon conversion rate and subsequent sorption to further enhance its H_2 production were proven to be an effective way to produce a H_2-rich gas as illustrated from the results presented in Fig. 3. While oppositely, namely first sorption followed with catalysis, although the calcined dolomite showed certain catalytic effect during gasification process, part of unreacted volatiles was subsequently catalyzed to produce more CO_2 which would again dilute the H_2 in the product gas. By contrast, simultaneous catalysis and sorption with better matching achieved the best H_2 production performance. Also, the addition of calcined dolomite indeed significantly enhanced the production of H_2 in terms of both concentration and yield. Thus, physical mixing of catalyst and calcined dolomite would be conducted for all the rest experiments for combining catalysis and sorption during the process.

3.4. Effect of catalyst support on the H_2-rich gas production during sorption enhanced catalytic gasification process

As stated previously, the catalyst support greatly affected the catalytic performance of the Ni-based catalysts during volatiles gasification, it is expected that it would exhibit different H_2 production characteristics when combined use with calcined dolomite during sorption enhanced catalytic gasification process. Three above-mentioned Ni-based supported catalysts were thus firstly tested here to find out the possible effect of catalyst support on the H_2-rich gas production during sorption enhanced catalytic gasification process, the results are shown in Fig. 4.

From Fig. 4, it can be found that the H_2 concentrations and yields were significantly higher with the combination of Ni-based catalyst and calcined dolomite compared with those with only Ni-based catalysts (Table 1). The values were all over 75 vol.% and 845 mL/g biomass, respectively. The addition of calcined dolomite along with Ni-based catalyst further greatly enhanced the H_2 production, while the concentrations and yields of CO and CO_2 for all cases decreased significantly, which are very similar with the results shown in Fig. 3. It might be because of the in-situ removal of CO_2 from product gas and simultaneously shifting the reaction equilibrium of WGS reaction to produce more H_2 through the addition of calcined dolomite. However, other than with only Ni-based catalysts, the product gas composition and yields

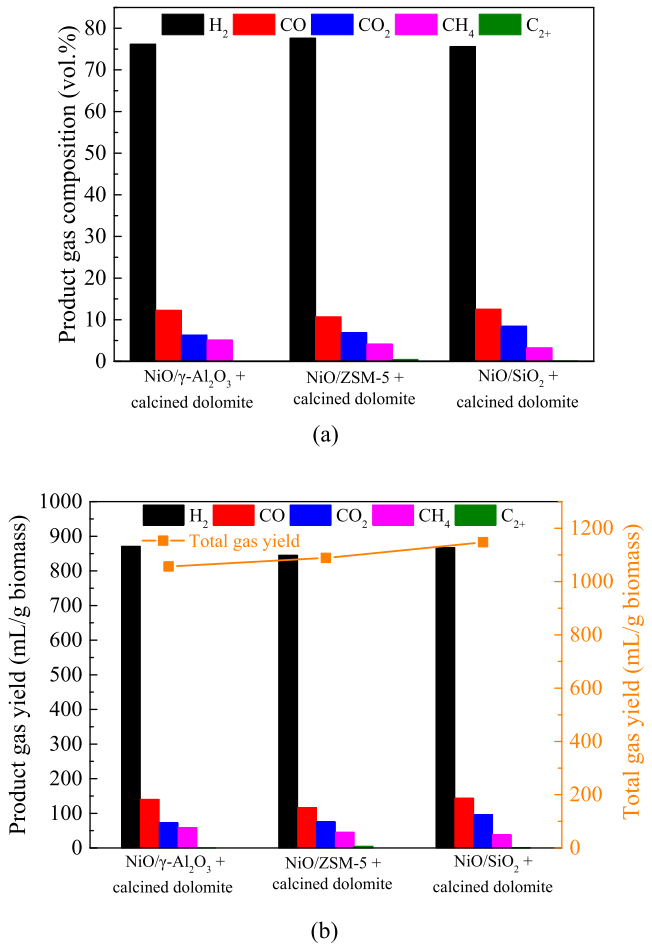


Fig. 4. Effect of catalyst support on the H_2-rich gas production from pyrolysis-sorption enhanced catalytic gasification of sawdust: (a) product gas composition, and (b) product gas yield.

with different catalysts and calcined dolomite showed relatively less variations, the addition of calcined dolomite reduced the catalytic performance difference for different supported catalysts as presented in Table 1. The sorption enhancing effect of calcined dolomite during the gasification process as well as its catalytic effect on the H_2-rich gas production might be the main reason. Similar H_2 content and yield were obtained for the catalysts with different supports together with calcined dolomite, despite of other carbonaceous gases varied somehow. The combination of catalysis and sorption indeed significantly improved the H_2 production from biomass gasification with a H_2 content and yield of around 77 vol.% and 870 mL/g biomass.

3.5. Addition of bimetallic catalyst with calcined dolomite during sorption enhanced catalytic gasification process

To further enhance the H_2 production, bimetallic catalysts were also introduced into the sorption enhanced catalytic gasification process together with calcined dolomite. The above 6 bimetallic catalysts were evenly mixed with calcined dolomite in advance and tested for H_2 production, the results are presented in Table 3.

From Table 3, it can be observed that the addition of bimetallic catalyst and calcined dolomite obtained significantly higher H_2 concentrations and lower concentrations of CO and CO_2 in the product gas compared with the cases with only bimetallic catalysts addition (Fig. 2 and Table 2). A highest H_2 concentration of 87.06 vol.% was achieved by Ni-Cu/γ-Al_2O_3 catalyst and calcined dolomite, followed by Ni-Zn/γ-Al_2O_3 catalyst and calcined dolomite (81.80 vol.%). While the catalytic effect of Ni-Cu/γ-Al_2O_3 and Ni-Zn/γ-Al_2O_3 for the volatiles gasification was found to be relatively lower than the other bimetallic catalysts (Fig. 2 and Table 2). The sequence for the H_2 production performance with the bimetallic catalysts and calcined dolomite was very different with only bimetallic catalyst. Again, the catalysis and absorption of calcined dolomite could enhance the volatiles/tar reforming, CO_2 absorption and WGS reaction to generate more H_2 and concentrate the H_2 in the product gas, a high H_2 concentration was thus obtained [32]. In addition, the catalytic effect of calcined dolomite as well as its sorption enhancing effect could supplement the difference in catalytic effect of various bimetallic catalysts [51], resulted in a high H_2 content for a lower activity catalyst, such as Ni-Cu/γ-Al_2O_3. It also indicated that better synergistic effect existed between calcined dolomite and Ni-Cu/γ-Al_2O_3 and Ni-Zn/γ-Al_2O_3 catalysts. At the reaction temperature of 650 °C, despite of the catalytic effect of calcined dolomite, the sorption enhancing effect of calcined dolomite was dominated during the gasification, which could in situ absorb the CO_2 generated during the process and shifted the WGS reaction to produce more H_2 [52]. While ZnO and CuO are regarded as effective catalysts for WGS reaction by forming surface -OH to promote the WGS reaction [53]. Although the catalytic effect of Ni-Cu/γ-Al_2O_3 and Ni-Zn/γ-Al_2O_3 on the volatiles/tar reforming somehow was sacrificed compared with other bimetallic catalysts, their enhancing effect on WGS reaction might be the main reason for the better synergistic effect with calcined dolomite. A very low concentrations of CO and CO_2 of 3.36 vol.% and 1.05 vol.% were achieved with Ni-Cu/γ-Al_2O_3 and calcined dolomite. The total gas yield for the combination of bimetallic catalyst and calcined dolomite was significantly lower as well due to the enhanced WGS reaction (consuming CO) and in situ CO_2 removal (CO_2 fixation into solid phase).

From the perspective of product gas yield, different bimetallic catalysts with calcined dolomite did not show very remarkable differences in the H_2 yield, as stated previously, the addition of calcined dolomite did offset the catalytic performance difference for different catalysts during volatiles gasification. Compared with NiO/γ-Al_2O_3 and calcined dolomite (Fig. 3 or Fig. 4), bimetallic catalysts did not show unique

Table 3
Product gas composition and yield from sorption enhanced catalytic gasification of sawdust with addition of calcined dolomite and bimetallic catalysts under a mass ratio of Ni to secondary metal of 1:0.25.

Catalyst and absorbent used	Ni-Cu/γ-Al_2O_3+ calcined dolomite	Ni-Mg/γ-Al_2O_3+ calcined dolomite	Ni-Zn/γ-Al_2O_3+ calcined dolomite	Ni-Co/γ-Al_2O_3+ calcined dolomite	Ni-Fe/γ-Al_2O_3+ calcined dolomite	Ni-Ce/γ-Al_2O_3+ calcined dolomite
Product gas composition (vol. %)						
H_2	87.06	78.55	81.80	75.81	80.81	76.69
CO	3.36	8.81	6.84	11.69	8.78	9.61
CO_2	1.05	6.13	5.83	4.66	6.36	6.64
CH_4	8.09	6.51	5.52	7.84	4.04	7.06
Product gas yield (mL/g biomass)						
H_2	861.44	880.80	907.19	803.09	878.71	866.66
CO	33.27	98.74	75.88	123.79	95.49	108.62
CO_2	14.71	68.79	64.64	49.37	69.21	74.99
CH_4	80.04	73.00	61.20	83.04	43.94	79.77
Total gas yield	989.52	1121.35	1109.05	1059.31	1087.35	1130.05

advantage in term of H_2 yield, while the concentrations of CO and CO_2 decreased with bimetallic catalysts, especially for Ni-Cu/γ-Al_2O_3 and Ni-Zn/γ-Al_2O_3, as well as Ni-Fe/γ-Al_2O_3, resulting in a higher H_2 concentration in the product gas. It indicated that the synergistic effects of two metal actives and metal actives with calcined dolomite would more affect the WGS reaction to produce H_2 at the expense of consuming of CO and CO_2. Overall, bimetallic catalysts showed better performance for generating high purity and yield of H_2 when used with calcined dolomite during the sorption enhanced catalytic gasification process [52].

4. Conclusions

Catalysis/sorption enhanced pyrolysis-gasification of sawdust for H_2-rich gas production was conducted in a two-stage fixed-bed reactor, the effects of addition of various Ni-based catalysts including monometallic and bimetallic catalysts and their combination with calcined dolomite were tested in this study. The results showed that catalyst support surely affected the catalytic performance of Ni-based catalysts during the sawdust pyrolysis-volatiles gasification process, NiO/SiO_2 obtained the highest H_2 concentration and yield, followed by NiO/γ-Al_2O_3 and NiO/ZSM-5. The addition of secondary active metals (Cu, Mg, Zn, Co, Fe and Ce) onto NiO/γ-Al_2O_3 introduced additional active sites on the catalyst surface and exhibited synergistic effect with Ni sites, which further improved the H_2 production. The introduction of Mg and Co was demonstrated to be better than other metals, while the addition of Zn and Cu did not show comparable enhancing effect on H_2 production compared with other active metals. Calcined dolomite was also introduced into the process to further enhance the H_2 production, it was proven that simultaneous catalysis and sorption was better for H_2 production than both catalysis followed by sorption and sorption followed by catalysis. The self-catalytic performance and sorption enhancing effect of calcined dolomite on volatiles gasification were found to be able to offset the catalytic performance difference for different Ni-based catalysts, the H_2 concentrations and yields with different catalysts and calcined dolomite showed relatively less variations of around 77 vol.% and 870 mL/g biomass. Compared to monometallic catalysts with calcined dolomite, the bimetallic catalysts together with calcined dolomite did not significantly improve the H_2 yield, but further increased the H_2 concentration in the product gas. The Ni-Cu/γ-Al_2O_3 and Ni-Zn/γ-Al_2O_3 catalysts with good performance on WGS reaction showed better synergistic effect with calcined dolomite, a highest H_2 concentration of 87.06 vol. % was achieved by Ni-Cu/γ-Al_2O_3 catalyst. The absorption capacity of calcined dolomite was further demonstrated by the results obtained with the Ni-Cu/γ-Al_2O_3 catalyst with and without calcined dolomite. A sharp drop in CO_2 yield was observed from 274.93 mL/g (Ni-Cu/γ-Al_2O_3) to 14.71 mL/g (Ni-Cu/γ-Al_2O_3 + calcined dolomite).

CRediT authorship contribution statement

Christian Fabrice Magoua Mbeugang: Writing – original draft, Investigation, Formal analysis, Data curation. **Bin Li:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Funding acquisition, Formal analysis, Conceptualization. **Xing Xie:** Writing – review & editing. **Juntao Wei:** Writing – review & editing, Supervision, Methodology. **Yusuf Makarfi Isa:** Writing – review & editing. **Alexander Kozlov:** Writing – review & editing. **Maxim Penzik:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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