Enhancing High Water Content Biomass Gasification with Impregnated Ca in Fuel Drying

Guangwen Xu, Takahiro Murakami, Toshiyuki Suda, Yoshiaki Matsuzawa, and Hidehisa Tani
Research Laboratory, Ishikawajima-Harima Heavy Industries Co., Ltd., Isogo-Ku, Yokohama 235-8501, Japan

Yutaka Mito
Coal and Energy Project Dept., Kobe Steel Co., Ltd., Takasago-Shi, Hyogo 676-8670, Japan

Masami Ashizawa
Central Research Institute of Electric Power Industry, Yokosuka-Shi, Kanagawa 240-0196, Japan

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In view of energy conversion efficiency, the gas production from high water content (>60 wt.%) biomass via gasification is necessarily conducted with fuel drying in advance. In regard to this kind of processes, the present study was devised to impregnate Ca onto fuel during fuel drying and thereby to increase fuel's gasification reactivity to raise the gas production efficiency with minimal additional cost. By employing wet coffee grounds as a model biomass fuel and slurry dewatering in kerosene as the adopted drying technology, the Ca impregnation was implemented through dosing $Ca(OH)_2$ into a fuel-kerosene slurry and in turn treating the slurry in the same way as for the case without Ca addition. The resulting Ca (4.0 wt.% load in CaO base) exhibited high dispersion through the fuel matrix in both SEM-EDX image and XRD spectrum. Gasification of the fuel in a pilot dual fluidized gasification setup further demonstrated that the fuel possessed distinctively high reaction reactivity. This led it to show C and H conversions of 91% and 138%, respectively, at a reaction temperature of about 1083 K, whereas these conversions were only 70% and 92% for the fuel with a similar amount of physically mixed CaO. The catalytic effect of the impregnated Ca manifested also on hydrocarbon reforming and water gas shift, making the resulting product gas evidently rich in H_2 and lean in CO and hydrocarbons. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3555–3561, 2006

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Process Philosophy

It has long been recognized that dispersed calcium on coal greatly catalyzes coal pyrolysis and char gasification reactions.[1-7] The dispersion of Ca onto coal particles can be implemented with either ion exchange[2,3] or impregnation/kneading.[2,4] Only through these technical means can the added Ca be bound to carboxylic sites of fuel molecular matrix to allow its pronounced catalytic effect on fuel gasification.[5,6] Obviously, either of these means implies somehow a complicated pretreatment of the fuel,[7] which surely increases the running cost. Hence, more than 30 years after the quoted catalytic effect was observed, coal catalytic gasification has not yet seen any practical application.

Correspondence concerning this article should be addressed to G. Xu at gwxu@home.ipe.ac.cn.

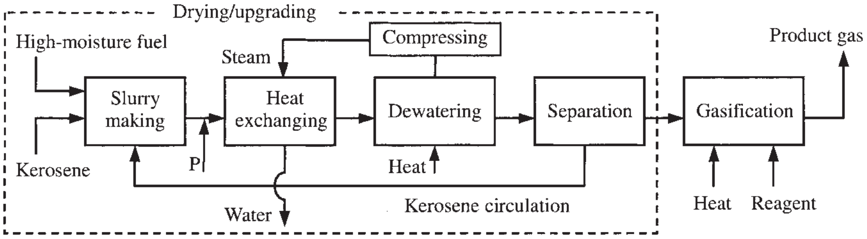


Figure 1. An innovative process for efficient conversion of high water content biomass into product gas.

Nonetheless, we have been looking at a possible exception for high water content fuels. For fuels containing water more than 50 wt.%, it is usually difficult to gasify them directly. If gasifying the fuel directly, the water with the fuel has to be converted into steam inside the gasifier to let it mix with the product gas. Limited by the dew point of tars presenting in the product gas (generally over 373 K), the recoverable energy from the steam is at most part of its explicit heat. The latent heat consumed in vaporizing the water becomes fully wasted in the downstream gas-cleaning scrubbers. There, the scrubbing liquid, which is water usually, absorbs the heat carried with the steam completely. Against this, drying the fuel in advance would allow more energy to be recovered from the vaporized water to lead to higher overall energy efficiency.

Illustrated in Figure 1 is a process based on such a concept, whose aim is to efficiently convert high water content fuels into product gas. The fuels considered here are biomass like various residues from beverage, seasoner, and food industries containing water of about 60 wt.%. The conversion process consists of an upstream drying/upgrading pretreatment and a downstream pyrolytic gasification of the resulting dry fuel. The drying/upgrading proceeds with slurry dewatering in kerosene, a technology developed by Kobe Steel Co., Ltd.[8] As indicated in the figure, high water content fuel is first mixed with kerosene to make fuel-oil slurry. Undergoing further the operations of preheating, dewatering, separation (in centrifuge), and deep oil recovery in a steam-tube dryer, in succession, the slurry is finally converted into dry upgraded fuel for gasification, collected kerosene for recirculation, and water for drainage. The residual oil content in the dried fuel is as low as 0.2 wt.% so that more than 99.5% kerosene is in fact circulated. The water with wet fuel is first vaporized in the dewatering unit (under about 423 K and 0.3 Mpa), but the formed steam is in turn compressed and sent to preheat the slurry. This allows the steam to be finally drained as water at tens of Celsius degrees. The water, having CODCr, CODMn, and BOD of about 800, 3500, and 2400 mg/L, respectively, can be mixed into the waste water of the factory generating the wet fuels (residues) for cleanup. Compared to the direct gasification strategy depicted above, the process with drying in advance allows more heat to be recovered and thereby definitely lowers the sacrifice of energy efficiency due to fuel's high water content.

Now that drying fuel in advance is required, the dispersion of Ca or any other catalytic element onto the fuel can be economically performed with fuel drying. Figure 2 outlines the method of Ca impregnation with the fuel drying/upgrading specified in Figure 1. The exemplified fuel was wet coffee grounds containing water of about 65 wt.%, which is representative of various kinds of high water content biomass fuels like tea grounds, soy sauce lees, vinegar lees, bagasse, and so on. In Figure 2, the left inset typifies the drying/upgrading operation without Ca impregnation, which matches to the boxed details in Figure 1 (with broken lines). When impregnation is required (the right inset), CaO or $Ca(OH)_2$ is first dosed into kerosene to form a calcium-oil emulsion. The wet fuel, rude coffee grounds, is then mixed into the emulsion to make the fuel slurry that was forwarded to a drying/upgrading procedure carried on in the same way as for the case without Ca addition. In this means, the impregnation does not incur much additional complexity to lead to extra cost. Its consequence is that the catalytic gasification may circumvent its cost barrier to make it realistic and applicable. Many early studies[1-7] on coal gasification demonstrated that the increased reaction rate through catalytic gasification enables smaller reactor size, lower reaction temperature, less tar generation, and more H_2 production. All of these indicate, in fact, a great viability to increase the energy conversion efficiency and to lower the capital and operational costs involved in fuel gasification.

The present article is devoted to demonstrating, in a pilot gasification plant, whether the calcium impregnated with fuel drying according to the procedure highlighted in Figures 1 and 2 is efficiently catalytic towards fuel gasification. Meanwhile, characterization of the impregnated Ca through XRD, XRF,

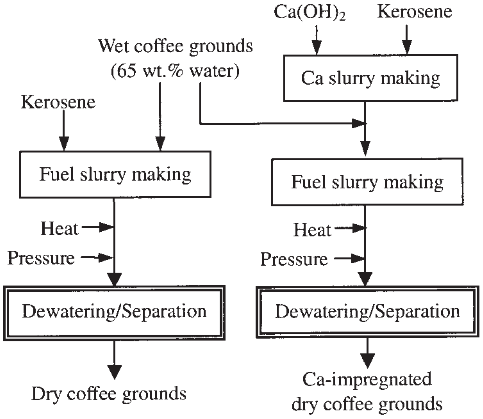


Figure 2. Method to prepare dry coffee grounds with (right side) or without (left side) impregnated Ca.

Table 1. Compositions of Dry Upgraded Coffee Grounds

	No Ca	Impregnated
Proximate [wt.%]		
Moisture	10.5	14.8
VM	71.8	64.9
FC	16.7	15.8
Ash	1.0	4.5
Ultimate [wt.%]		
C	52.97	50.17
H	6.51	6.07
N	2.80	2.78
S	0.05	0.08
O	36.62	35.78
HHV [MJ/kg] (dry)	21980	20457

Fuel sizes were below 1.0 mm for both, and $Ca(OH)_2$ was used in impregnation.

and SEM-EDX is conducted to clarify the effectiveness of the adopted impregnation method. Because the tested fuel is coffee grounds, a kind of biomass, the work hopes also to show the catalytic effects of impregnated Ca on biomass fuel gasification. Although extensive studies were done on Ca-catalyzed coal gasification, very limited efforts were directed to the gasification of Ca-impregnated biomass. In the literature a few relative reports are available.[9,10] What they tackled, however, was mostly about pyrolysis and gasification of ion-exchanged biomass in a micro reactor, such as in TGA. On the other hand, noticeable works have been contributed to tar elimination in biomass gasification using physically mixed ores or calcined ores like limestone, dolomite, and olivine.[11-14] Following the mechanism disclosed for catalytic coal gasification,[5,6] we may anticipate that the physically blended Ca-base additive would hardly speed up the biomass gasification reaction due to its loose contact with fuel particles. To experimentally verify this formulates thus the quaternary point to which the present article likely addresses.

Fuel Characterization

Through the fuel drying/upgrading procedure specified in Figures 1 and 2, wet coffee grounds (65 wt.% water) can be converted into a kind of granular fuel with moisture of about 10 wt.%. This drying/upgrading procedure, according to Mito and coworkers,[8] not only removes water but also lowers the oxygen-to-carbon ratio of the fuel. Consequently, there is also an accompanied increase in fuel heating value. Shown in Table 1 are the results of proximate and ultimate industrial analyses on the acquired fuels without and with Ca impregnation. As it should be, the addition of Ca raised the fuel's ash content. Accordingly, the fuel with impregnated Ca had lower C and H contents and lower HHV. The added Ca was from chemical $Ca(OH)_2$ according to a mass ratio of 0.04 of $Ca(OH)_2$ to dry fuel. Overall, we can see that the coffee grounds fuel is rich in volatile matters (up to 70 wt.%) and oxygen. The latter implicates a potential good Ca dispersion on the fuel because the dispersion is subject to chemical connection of Ca to the fuel's carboxylic sites.[5,6] Besides, the dried/upgraded fuels with and without Ca impregnation both had sizes below 1000 μm and the size distribution was also similar for them.

Against impregnated Ca, physical Ca was made through mixing CaO into the dry upgraded fuel without Ca impregnation. The adopted CaO for this mixing was lightly calcined limestone ore, which had sizes below 1000 μm, specific surface area of 2.0-5.0 m^2/kg, and pore volume of about 0.01 L/kg (see Table 2). The mixing ratio of CaO to fuel was 0.05 kg/kg so as to simulate the Ca load in Ca-impregnated fuel. Table 3 shows the weight percents of oxides of the major elements detected with X-ray fluorescence (XRF) analysis for the fuels with physically mixed and impregnated Ca. Obviously, the data confirmed that both the fuels had very close contents in Ca, and Ca was also dominantly more than the other metals. Thus, for the quoted fuels, calcium must be the catalytic element but its form was different from each other (this will be clarified below). Furthermore, Table 3 shows that the contents of all the other elements were slightly different between the two fuels. This might be due to the fact that different virgin Ca sources were applied to them. That is, while chemical $Ca(OH)_2$ was used for impregnation, a kind of lightly calcined limestone ore, whose properties are shown in Table 2, provided the Ca for physical mixing.

Table 2. Test Conditions and Properties of Sand and CaO

BFB Gasifier	Riser combustor
Temp.: $\sim$1083 K	Temp.: $\sim$1093 K
Steam: 4.0 kg/h	Airflow: 70 nL/min
Fuel: $\sim$4.0 kg/h	(Air ratio to 25 wt.% fuel carbon: $\sim$1.1)
Argon: 10.6 nL/min	

Silica sand	Sauter mean diameter = 187 μm, Bulk density = 1600 kg/m^3, Total load: $\sim$24 kg.
CaO for physical mixing	Lightly calcined $CaCO_3$ ore, Bulk density = 1050 kg/m^3, Sizes $<$ 1.0 mm (Sauter mean: 70 μm), Specific surface area = 2.0–5.0 m^2/kg, Pore volume = 0.01 L/kg.

Figure 3 shows the X-ray diffraction (XRD) patterns of the fuels with physically mixed (diagram a) and impregnated (diagram b) Ca. For the physical situation, not only CaO (○) but also $CaCO_3$ (●) and $Ca(OH)_2$ (■) were detected. The result is reasonable because in the lightly calcined limestone ore there should be residual $CaCO_3$ not decomposed, while a small part of the formed CaO may absorb moisture from air to form $Ca(OH)_2$ during the period preserving the material. In diagram b there is no distinctive peak for any of such calcium chemicals, although the fuel definitely contains Ca at a content similar to that of the CaO-mixed fuel (see Table 3). It is indicative of a high degree of Ca dispersion through the fuel

Table 3. Major Element Composition from XRF for Fuels with Physically Mixed CaO and Impregnated $Ca(OH)_2$

	Physically Mixed CaO	Impregnated $Ca(OH)_2$
CaO	86.3	85.0
K_2O	4.86	7.11
MgO	3.08	2.40
SiO_2	0.32	0.41
Al_2O_3	0.20	0.13
Fe_2O_3	0.52	0.31
MnO	0.20	0.22
P_2O_5	1.75	2.38

All listed values refer to weight percents [wt.%] estimated for oxides of the detected elements.

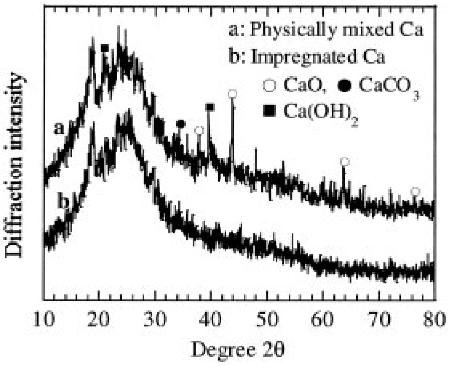
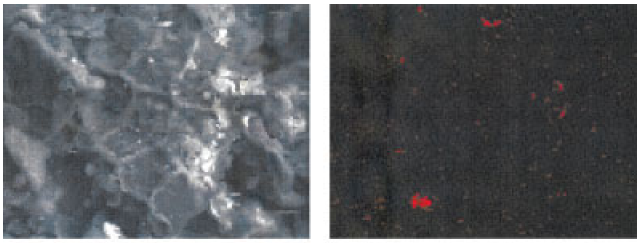


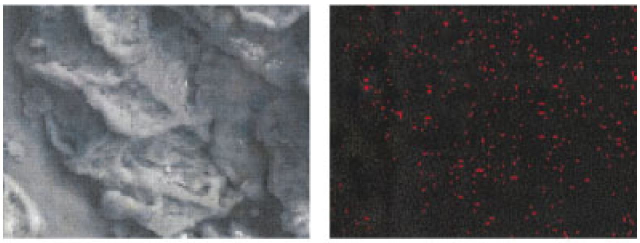
Figure 3. XRD patterns of the fuels with (a) physically mixed CaO and (b) impregnated $Ca(OH)_2$.

matrix. The phenomenon of no X-ray diffraction from loaded Ca was widely identified for Ca-impregnated coal and char,[1-3,15] unless the Ca load was too high ($>$7.0 wt.%)[2] or the loaded Ca was sintered afterwards in heat treatment.[15]

The different dispersion degrees of physically mixed and impregnated Ca are visible also from the SEM-EDX images displayed in Figure 4, where the left and right insets show, respectively, the fuels' SEM photographs and Ca distribution images through the fuel matrix. As for the physically mixed case (4a, upside), some white spots are obviously seeable in the SEM photograph, indicating that the Ca species is present among fuel particles. This was verified by its corresponding Ca distribution image, which reveals that the element, shown as red dots, was not evenly scattering over the scanned section. Corresponding to this, in Figure 4b (downside) no white spot is visible in the SEM photo, but the Ca element (that is, the red dot) was uniformly detected in the entire imaged section. The latter provides firm evidence for the highly dispersed Ca on the Ca-impregnated fuel. According to literature,[1-7] this highly dispersed Ca should catalyze fuel gasification efficiently, as is shown below with gasification of the fuel in a pilot dual fluidized bed gasification (DFBG) facility. The DFBG technology was adopted here because it allows the production of middle-caloric product gas (that is, HHVs $>$ 3000 kcal/m^3_n, m^3_n: normal cubic meter), even if air is used to combust part of the unreacted char to generate the endothermic heat required by gasification reactions.[13,16]

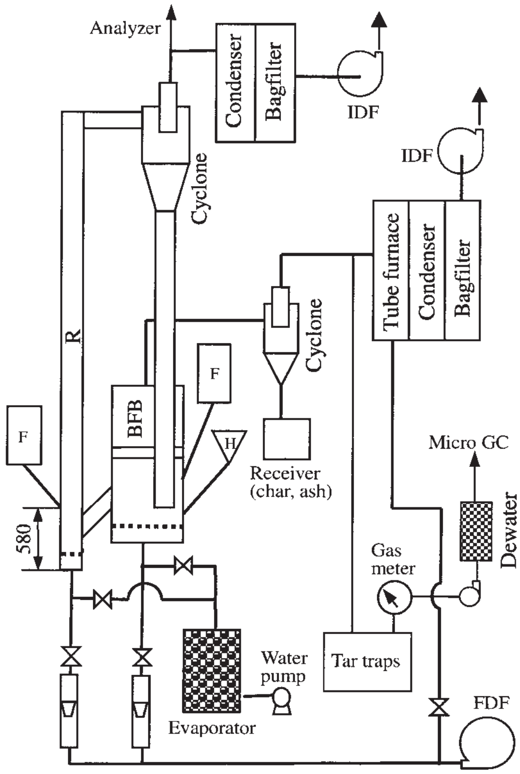


(a) With physically mixed Ca



(b) With impregnated Ca

Figure 4. SEM-EDX photographs (×1000) of the fuels with (a) physically mixed CaO and (b) impregnated $Ca(OH)_2$.



F: Feeder, **H:** Hopper, **BFB:** Bubbling fluidized bed, **R:** Riser

Figure 5. Employed pilot dual fluidized bed gasification setup in gasification tests.

Pilot Gasification Test

Apparatus and methodology

Figure 5 shows a schematic diagram of the employed 5.0 kg/h pilot gasification plant, whose details are available in Xu and coworkers.[16] It was a dual fluidized bed system consisting of a pneumatic riser (R) and a bubbling fluidized bed (BFB) that had as well the function of a siphon (thus called a reactor siphon[17]). Both the riser and BFB had cape-type gas distributors. A distinctive feature of the plant was that it was able to arrange either the riser or the BFB as the fuel gasifier.[16] Nonetheless, the deployment of fuel gasification into the BFB and its accompanying char combustion into the pneumatic riser was shown to be the superior technical choice for DFBG in terms of promoting gasification and suppressing tar generation.[16] Herein, the gasification tests follow thus this superior technical deployment to take the BFB as the fuel gasifier and the riser as the char combustor. Between these two reactors, silica sand (see properties in Table 2) was circulated as heat carrier particles. In principle the tested gasification plant is

Table 4. Typical Molar Composition and Its Corresponding HHV of Rude Product Gas from the Gasifier

Ca Form*	Temp. [K]	Fuel [kg/h]	Molar Concentration [vol.%]										HHV [kcal/m^3_n]
			H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	O_2	N_2	Ar	
W	1083	3.80	18.6	29.3	10.5	13.2	4.79	2.47	0.03	0.34	1.74	18.7	3850
Ph	1083	4.05	21.7	26.3	11.6	13.2	4.90	2.50	0.03	0.29	1.75	17.8	3909
Im	1080	4.05	31.9	24.0	14.5	10.1	3.50	1.84	0.02	0.37	1.32	12.6	3540

*The symbols "W", "Ph", and "Im" represent "without Ca", "physically mixed Ca", and "impregnated Ca", respectively. For the cases of "Ph" and "Im", their time-series compositions are available in Figure 6.

consequently similar to the FICFB gasifier developed in Vienna University of Technology.[13]

The riser was 52.7 mm in i.d. and 6400 mm high, and the BFB had a rectangular cross section of 80 × 370 mm^2 and a height of 1800 mm, of which the top 700-mm-long section of 180 × 370 mm^2 was a freeboard. All ducts connecting the riser and BFB had the same i.d. of 52.7 mm. The riser and BFB had their independent cyclones, heat exchangers, bagfilters, and induction fans. Hence, independent adjustment of pressures in both such reactor vessels was possible. The reactors were both electrically heated, and bed temperatures of up to 1173 K were allowed. The product gas from the gasifier was first burned off in a tube furnace and in turn sent to a downstream condenser. This would reduce the CO emission with final venting.

A table feeder was used to feed the fuel quantitatively and continuously, and the fed fuel was carried into the freeboard of the BFB via an argon stream monitored in a mass flow meter controller. The argon stream was also a gas tracer for determining the volume (that is, moles) of produced gas. Steam at about 673 K was the gasification reagent adopted, while air was applied to the char combustor as the oxidant. Nonetheless, in heating (before steam feed) and cooling (after test) the facility, both the riser and BFB were fluidized with air. The airflows to both the beds were controlled with their respective rotameters. Steam was generated in a water evaporator heated with a SiC heater, and its rate was controlled by measuring the water feed rate in a metering pump. The steam feeding line was warmed to 523 K to avoid condensation.

Sampling the product gas was through a suction pump connected to the gas exit of the gasifier's cyclone. The sampled gas entered a tar trap system (detailed in the next paragraph) to have its tar-intake dropped. Until tar traps external heating via tape heaters was applied to the involved gas line to keep the sample gas temperature above 523 K. The tar-stripped gas was finally led to a micro gas chromatography (micro GC) for measuring its molar composition after it was detected for volumetric flow rate (1-2 normal-liter/min) in a wet gas volumeter and dewatered in a $CaCl_2$ column.

The adopted tar trap system was made of, in succession, a condenser and three water bubblers immersed in an ice-water bath. The condenser worked at temperatures below 278 K so that nearly all steam and most tars carried with the sample gas could be dropped in this step. With controlled gas flow rate, it was guaranteed that the sampled gas could reside in the tar trap system for at least 2 min. Hence, we believed that the tar trapping from the sample gas was efficient, although not thoroughly completed.

The trapped tars were extracted by following a procedure of collecting the tarry water, washing the condenser, water bubblers, and silicon rubber tubes for connection using acetone, filtration of water/acetone liquid, vacuum evaporation of water and acetone at temperatures below 333 K, and drying the tars (the residual of evaporation) in an airflow of 323 K. The tar content of the product gas (tracer free) reported herein refers to the ratio of the extracted dry tar weight over the sample gas volume free of argon tracer determined from the volume and molar composition of the sampled gas. That is,

$$\text{Tar content} = \frac{\text{dry tar weight}}{(\text{gas volume}) * (1 - \text{Ar fraction})}.$$

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Results and discussion

In order to demonstrate the reactivity of different fuels, the gasification tests for all fuels were conducted under similar conditions. Table 2 summarizes the major operating parameters, indicating a gasification temperature of about 1083 K and a fuel feed rate around 4.0 kg/h. The steam rate was 3.4 kg/h, implying a steam-to-carbon molar ratio of about 1.5. The riser combustor was controlled at a temperature of about 1093 K. The temperature profiles along the bed elevation in both the BFB gasifier and riser combustor are similar to those reported in Ref. [16]. At the mentioned bed temperatures, the superficial gas velocities in the gasifier and combustor were 0.17 and 2.8 m/s, respectively. Through measuring the particle circulation rate at the operating temperature,[18] the explicit fuel particle residence time in the fluidized particles of BFB, which is

$$\frac{\text{Particle amount in gasifier}}{\text{Circulated particles in 1.0 s}},$$

was estimated to be about 1000 s under the employed particle load of 24.0 kg in the facility.

The tested fuels were those characterized in Table 1 and Figures 3 and 4, including upgraded dry coffee grounds without Ca, with physically mixed Ca, and with impregnated Ca. Table 4 and Figures 6 and 7 report the acquired results. Figure 6 exemplifies the time-series molar composition of produced gas (tracer free) by taking the two fuels with Ca as examples. Table 4 and Figure 7 compare further the composition of rude product gas from the gasifier, and its corresponding fuel conversion (without tars included) and tar content in the gas for all the examined fuels. The C and H conversions plotted in Figure 7 were estimated according to

$$\frac{\text{Moles of C (H) in product gas}}{\text{Moles of C (H) in treated fuel}} \times 100\%.$$

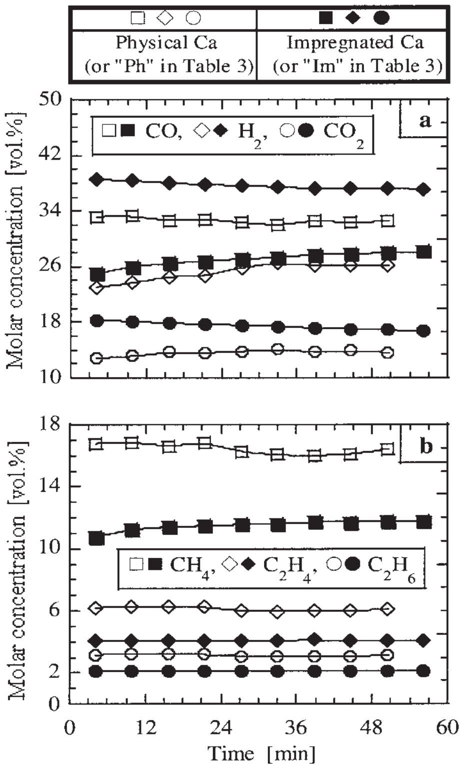

Figure 6. **Time-series compositions of product gases free of Ar tracer for the fuels with physically mixed CaO (open marks) and impregnated $Ca(OH)_2$ (solid marks).**

The H conversion refers to an explicit value because part of fuel H has to become H_2O in pyrolysis and some H in the product gas would also come from steam through the reactions of reforming, char gasification, and water gas shift. Figure 6 shows that the operation for each fuel tended to reach its quasi-steady state in 1 h, revealing that the one-hour test would be enough to assure the steady-state result. Table 4 mentions the actual reaction temperature and fuel feed rate for each specified test, confirming further that the experimental conditions were similar for all the quoted cases.

The produced gases, even with Ar tracer, had HHVs above 3500 kcal/m^3_n in Table 4. Furthermore, the composition matrix in the table reveals that the gases contained trace amounts of O_2 and N_2. Both of these demonstrate just the advantages of the examined dual fluidized bed gasification (DFBG) technology. That is, even if air is employed to combust part of the fuel char from the BFB gasifier in the riser combustor to generate endothermic heat, the technology still enables the production of high caloric product gas without serious N_2 dilution. Table 4 clarifies also that the HHV was slightly lower for the fuel with impregnated Ca ("Im" Ca). Corresponding to this is the product gas containing distinctively more H_2 and CO_2 and evidently less CO and hydrocarbons (CH_4 to C_3H_6). The results, as will be analyzed hereafter, reflect rightly the excellent catalytic effects of the impregnated Ca.

Figure 6 delivers a clearer comparison for the molar compositions of the product gases from the fuels with physical ("Ph", open marks) and impregnated ("Im", solid marks) calcium. Here, the displayed composition refers to the case free of Ar tracer so that the concentrations of H_2, CO, CO_2, and hydrocarbons (CH_4 to C_3H_8) can be normalized to 100% to typify the possible gas composition in a commercial plant whereto no tracer gas should be applied. The figure shows obviously that the gas produced from the fuel with physical Ca was featured with higher CO (6a) and hydrocarbon (6b) intakes but lower H_2 (6a) content in the entire period of the test. It is particularly noticeable that for "Im", its H_2 concentration approached 40 vol.% and CH_4 intake was only 11 vol.% compared to an H_2 content of 25 vol.% and a CH_4 content of 17 vol.% for "Ph". Although no concentration value was shown here for C_3H_6 (<1.0 vol.%), it was confirmed that the "Im" case had constantly less C_3H_6, as one may see from Table 4 (no C_3H_8 being detected).

Figure 7 clarifies that the fuel's C and H had much higher conversions (left Y) in the Ca impregnated case (solid bar). Its C conversion was as high as 91%, while H conversion reached 138%. The H conversion over 100% indicates that the H converted into gas included a considerable proportion from H_2O (steam), implying that inside the gasifier steam gasification, reforming and water gas shift reactions occurred to a great degree. In the other two cases, the C and H conversions were about 70% and 90%, respectively. Compared to Ca-free fuel (open bar), the physically mixed CaO (shaded bar) according to a mass ratio of CaO:Fuel = 1:20 tended to increase the fuel conversion, but the effect was truly slight. The resulting increment was, in fact, only 1% or so for C conversion and not beyond 7% for H conversion.

The tar content in the product gas (right Y, Figure 7) was lowest for the Ca-impregnated fuel and highest for the Ca-free fuel. While the impregnated Ca led to a tar content of 11 g/m^3_n (Ar tracer free base), the other two cases stopped at tar contents of about 40 g/m^3_n. Physically mixed Ca only lowered the gas's tar content from 42 g/m^3_n (for Ca-free fuel) to 37 g/m^3_n. Compared to literature reports,[1-14] this is a very weak effect of physical-form Ca additive, and it is probably due to the employed lower Ca amount (<5.0 wt.% of fuel) than literature's (about 30 wt.% of bed material). As a consequence, we can see that in Table 4 the "Ph" Ca only slightly increased the H_2 and CO_2 concentrations and weakly decreased CO content of the product gas. However, hydrocarbon contents remained nearly the same for both the physical-Ca and Ca-free fuels.

What the preceding results demonstrate is that the fuel with

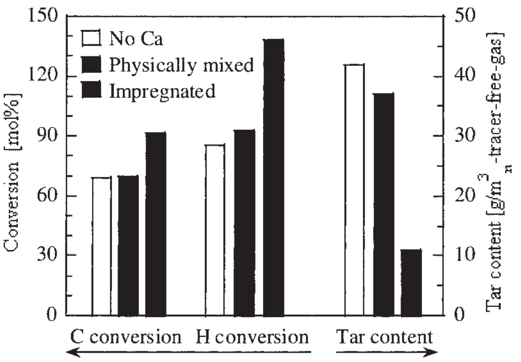

Figure 7. **Fuel C and H conversions (left two insets) and tar contents in product gases free of Ar (the right inset) corresponding to the molar compositions of Table 4.**

impregnated Ca exhibited very high gasification reactivity, low tar production, and greatly raised H_2 yield. All of these resulted surely from the comprehensive catalytic effects of the impregnated Ca on the reactions of fuel pyrolysis, char gasification, tar destruction/reforming, and CO water gas shift, as early similarly identified for coal.[1-7] Against this, the physically mixed Ca at the similar amount (about 4.0 wt.%) displayed much lower activity in catalyzing such reactions. Consequently, the highly dispersed catalytic metal, here Ca, over the fuel's matrix is a necessary precondition for catalytic gasification of biomass. The impregnated Ca in our case catered well to this precondition, as is shown in Figure 4b through Ca dispersion profiles. Thus, it not only assured the above-identified distinctively good catalysis effects but confirmed also that the impregnation with drying of high water content fuel is sufficiently viable to disperse the catalytic element onto the fuel matrix.

Based on all of the preceding facts, we believe then that the Ca impregnation with fuel drying would provide an economic and technical feasible way to gasify various high water content fuels efficiently. It makes not only the catalyst impregnation be free of large extra cost but reduces also the gasifier size by taking advantage of the resulting fuel's high gasification reactivity. On the other hand, CaO or $Ca(OH)_2$ is cheap and at the Ca addition ratios below 5.0 wt.% the impregnation itself does not incur much additional cost. Hence, with the reported technology we may see some realistic prospects for catalytic biomass gasification.

Conclusions

A NEDO-financed technical program is underway to develop an advanced upgrading and pyrolytic gasification system to convert high water content biomass into middle-caloric product gas. The overall system consists of an upstream fuel drying/upgrading processor based on slurry dewatering in kerosene and a downstream dual fluidized bed gasification (DFBG) plant that coupled a bubbling fluidized bed fuel gasifier and a pneumatic riser char combustor. In regard to this process, the present study devised to impregnate Ca onto fuel with fuel drying and thereby to improve fuel's reactivity without bearing much additional cost. The Ca impregnation was implemented by blending $Ca(OH)_2$ or CaO into a fuel-kerosene slurry and subsequently treating the slurry in the same procedure as applied to the case without Ca addition.

Using wet coffee grounds containing 65 wt.% water as a model fuel, the impregnated Ca at a CaO load of about 4.0 wt.% exhibited distinctively high dispersion on the upgraded dry coffee grounds both in SEM-EDX image and in XRD spectrum. Pilot gasification tests in a 5.0 kg/h DFBG setup then demonstrated that the impregnated Ca dramatically increased the fuel's gasification reactivity. Compared to the fuel blended physically with a similar amount of CaO, the C and H conversions for the Ca-impregnated fuel increased by 20% (valued to 91%) and 45% (reached 138%), respectively, at the tested reaction temperature of about 1083 K. The tar content in the product gas was conversely one fourth (about 11 $g/m^3{}_n$) of that from the fuel with physically mixed CaO. The distinctive catalytic effects of the impregnated Ca manifested also on reactions of hydrocarbon reforming and water gas shift so that the resulting product gas contained obviously more H_2 but less CO and hydrocarbons. Against these, only slight improvement on fuel conversion and tar elimination was identified for the physically mixed CaO at the similar amount (about 4.0%) in comparison with the case without using any type of Ca. As a consequence, the Ca impregnation with fuel drying was supposed to be an efficient, economic, and technical prospective way to upgrade the conversion efficiency of high water content biomass fuels into product gas.

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Literature Cited

1. Ohtsuka Y, Asami K. Highly active catalysts from inexpensive raw materials for coal gasification. *Catal Today.* 1997;39:111-125.
2. Salinas-Martínez de Lecea C, Almela-Alarcónh M, Linares-Solano A. Calcium-catalysed carbon gasification in CO2 and steam. *Fuel.* 1990; 69:21-21.
3. Ohtsuka Y, Tomita A. Calcium catalysed steam gasification of Yallourn brown coal. *Fuel.* 1986;65:1653-1657.
4. Shibaoka M, Ohtsuka Y, Wornat MJ, Thomas CG, Bennett AJR. Application of microscopy to the investigation of brown coal pyrolysis. *Fuel.* 1995;74:1648-1653.
5. Clemens AH, Damiano LF, Matheson TW. The effect of calcium on the rate and products of steam gasification of char from low rank coal. *Fuel.* 1998;77:1017-1020.
6. Lang RJ, Neavel RC. Behavior of calcium as a steam gasification catalyst. *Fuel.* 1982;61:620-626.
7. Hengel TD, Walker Jr. PL. Catalysis of lignite char gasification by exchangeable calcium and magnesium. *Fuel.* 1984;63:1214-1220.
8. Mito Y, Komatsu N, Hasegawa I, Mae K. Slurry dewatering process for biomass. 2005 Int. Conference on Coal Science and Technology (ICCS&T), London: IEA-Clean Coal Center, 2005: Paper 2E01.
9. Richards GN, Zheng G. Influence of metal ions and of salts on products from pyrolysis of wood: applications to thermochemical processing of newsprint and biomass. *J Anal Appl Pyrol.* 1991;21:133-146.
10. Risnes H, Fjellerup J, Henriksen U, Moilanen A, Norby P, Papadakis K, Posselt D, Sørensen LH. Calcium addition in straw gasification. *Fuel.* 2003;82:641-651.
11. Devi L, Ptasinski KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy.* 2003;24:125-140.
12. Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. *Fuel Process Technol.* 2001;73:155-173.
13. Pfeifer C, Pourmodjib M, Rauch R, Hofbauer H. Bed material and additive variations for a dual fluidized bed steam gasification in laboratory, pilot and demonstration scale. In: Cen K. *Circulating Fluidized Bed Technology VIII.* Beijing: Beijing World Publishing Co.; 2005:482-489.
14. Corella J, Aznar MP, Gil J, Caballero MA. Biomass gasification in fluidized bed: where to locate the dolomite to improve gasification. *Energy Fuels.* 1999;13:1122-1127.
15. Devi TG, Kannan MP. Calcium catalysis in air gasification of cellulosic chars. *Fuel.* 1998;77:1825-1830.
16. Xu G, Murakami T, Suda T, Matsuzawa Y, Tani H. The superior technical choice for dual fluidized bed gasification. *Ind Eng Chem Res.* 2006;45:2281-2286.
17. Xu G, Murakami T, Suda T, Matsuzawa Y. Reactor siphon and its control of particle flow rate when integrated into a circulating fluidized bed. *Ind Eng Chem Res.* 2005;44:9347-9354.
18. Xu G, Murakami T, Suda T, Matsuzawa Y. Particle circulation rate in high-temperature CFB: measurement and temperature influence. *AIChE J.* 2006;52: in press.

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