

The Effect of Na_2CO_3 on the Catalytic Gasification of Rice Straw over Nickel Catalysts Supported on Kieselguhr

Seung Woo Lee, Sang Sung Nam, Seong Bo Kim, Kyu Wan Lee[†] and Cheong Song Choi*

Catalyst Research Division 1, Korea Research Institute of Chemical Technology, P.O. Box 107, Taejeon 305-600, Korea

*Department of Chemical Engineering, Sogang University, Seoul 121-742, Korea

(Received 21 July 1999 • accepted 21 December 1999)

Abstract—Rice straw was catalytically gasified over nickel catalysts supported on kieselguhr. Ni catalyst activated the gasification step from the formed oil. The effect of sodium carbonate on the formation of carbonized solid, oil and gas composition was also investigated. With the addition of sodium carbonate, the gas yield was largely increased and the formation of oil through liquefaction also increased. A reaction pathway on the gasification of rice straw was discussed.

Key words: Biomass, Rice Straw, Pyrolysis, Gasification, Sodium Carbonate, Nickel Catalyst Supported on kieselguhr

INTRODUCTION

Biomass such as wood, grasses, agricultural and food wastes, manure, ocean plants, and garbage has been an important renewable resource as a substitute for fossil fuel. Biomass can be changed into alternative energy by incineration, and thermochemical and biological methods. However, direct incineration creates an environmental pollution problem because of the generation of sulfur and nitrogen compounds. Biological methods, which use microorganisms have a rate problem: The reaction is very slow. Thermochemical conversion of biomass can be divided into carbonization, liquefaction and gasification [Dote, 1997; Elliott, 1994; Garcia, 1998; Ogi, 1985]. Oils and solids obtained through carbonization and liquefaction contain many nitrogen and sulfur compounds which cause environmental problems. Meanwhile, gasification produces a clean synthesis gas which contains a high concentration of hydrogen. Therefore, it may be a better method than liquefaction and carbonization. But gasification requires high-energy consumption. To solve this problem, a number of investigations have been tried. The use of a catalyst in the pyrolysis process could be an interesting approach to increase gas yield. Most metals, their oxides and salts could serve as catalysts. Elliott et al. [1998] reported that nickel catalyst showed an excellent activity on the gasification. Recently, it has been published that the addition of Na_2CO_3 greatly increased the reaction rate. Minowa et al. [1997, 1998] gave a detailed description on the cellulose liquefaction using Na_2CO_3 catalyst in hot compressed water at different temperatures and established a chemical mechanism based on the product distribution. Jean Claude et al. [1998] reported that obtained oil yield was more than 50% by the pyrolysis of bitumen with K_2CO_3 , Li_2CO_3 , Na_2CO_3 at 350-400 °C. Yokoyama et al. [1986] reported about stillage which was treated with Na_2CO_3 under pressure of nitrogen at 300 °C. As a result, the yield of oil was about 52% and the energy recovery of heavy oil ex-

ceeded 75% of the starting material. Catalytic gasification at low temperatures was also studied. Elliott et al. [1993, 1994] reported that the rate of gas production increased greatly with the addition of Na_2CO_3 . In the gasification of bagasse, Lihong [1990] found how to enhance CH_4 yield, and reported that Na_2CO_3 gave a good activity on liquefaction. However, there are not many reports which explain the reason for this result. Therefore, our research has focused on the effect of Na_2CO_3 and the reaction pathway in the gasification of rice straw was studied.

EXPERIMENTAL

1. Experimental Procedures

The gasification of rice straw was conducted in a conventional stainless steel autoclave (2 L) as shown in Fig. 1. The autoclave had a stirrer with a magnetic drive system and a gas reservoir. Nitrogen was used as purge gas and additional nitrogen was added to achieve the initial pressure. Rice straw (50 g), catalyst (5 g) and distilled water (500 ml) were introduced into the autoclave and heated with an electric heater at 300 °C for 30 min. Then, reaction mixtures were intensively extracted with dichloromethane. After this, the mixtures were allowed to stand for several hours and filtered. The cake on the filter glass was dried at 105 °C for 5 hrs. Finally, the solid residue was obtained. The dichloromethane was recovered from the filtrate of extract by using a rotary evaporator (Buche RE 111).

Dark brown heavy oil and solvent soluble material were obtained in this manner. The amount of formed gas was measured

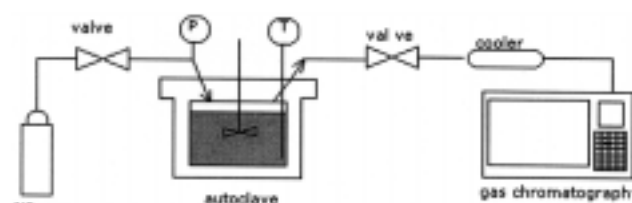


Fig. 1. Experimental scheme for the gasification of rice straw.

[†]To whom correspondence should be addressed.

E-mail: kwlee@pado.kRICT.re.kr

with a gas meter and the composition of evolved gases was determined by gas chromatography with TCD (Donam DS 6000; silica gel column of 60/80 meshes). Conversion to gas, oil and carbonized solid was calculated by the following equation:

$$\text{Conversion (\%)} = \frac{\text{Weight of material obtained from each phase}}{\text{Weight of drying biomass}} \times 100$$

Moisture content of rice straw was measured after drying at 105 °C for 5 hrs and the measured value was 8%. Ash was analyzed after heating at 600 °C for 5 hrs and its value was 3% (ASTM D1102-84).

2. Preparation of Catalysts

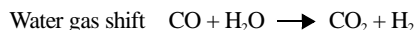
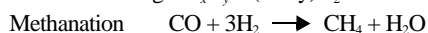
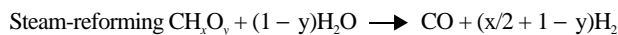
The nickel catalyst (about 50 wt% nickel on kieselguhr) was prepared by an ordinary precipitation method. Sodium carbonate solution was added to a slurry of kieselguhr and nickel nitrate solution at 70 °C and precipitate was obtained. This precipitate was washed with water thoroughly and then was dried at 105 °C for 12 hrs, crushed to 60-150 mesh, calcined at 350 °C for 4 hrs. This catalyst was activated with 100% hydrogen at 200, 300 and 350 °C for 4 hrs. These catalysts were stored in nitrogen atmospheric bottle and desiccator.

3. Characterization of Catalyst: Temperature Programmed Reduction (TPR)

For TPR studies, 50 mg of the calcined catalyst was loaded in a quartz reactor and heated at 673 K for 6 hrs, followed by cooling down to room temperature in argon gas. A high purity pre-mixed gas containing 95% argon and 5% hydrogen was used as a reducing agent. Traces of oxygen and water vapor were removed by passing the gas through an activated molecular sieve trap kept in an ice bath. The catalyst bed was heated linearly at 5 K/min under the feedback control of a temperature programmer. A continuous TPR response profile was obtained when the difference in H₂ concentrations in the gas streams between reference and sample sides of the TCD, resulted from the reduction of metal oxide by H₂.

RESULTS AND DISCUSSION

Gasification of biomass involves pyrolysis, steam reforming, methanation, and a water gas shift reaction.



The composition of gas formed during gasification of biomass was affected by properties of catalysts and reaction conditions. It is known that among various catalysts, nickel has the highest activity in the steam reforming of a wide range of volatile hydrocarbons, methanation of synthesis gas, and hydrogenation of numerous organics. In this study, the effect of sodium carbonate on the catalytic gasification of rice straw over nickel catalysts supported on kieselguhr was examined to increase the gas yield formed from gasification.

1. Influence on Addition of Na₂CO₃

The effect of sodium carbonate on the formation of gas, oil and carbonized solid was examined in the catalytic gasification of rice

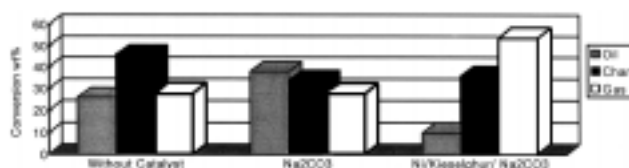


Fig. 2. Effects of Na₂CO₃ on the gasification of rice straw.

Table 1. Composition of gas produced on the gasification of rice straw

Catalyst	Composition of gas (mmol)			
	H ₂	CO	CH ₄	CO ₂
Without	35	185	Trace	200
Na ₂ CO ₃	12	305	Trace	115
Ni/kieselguhr	170	52	Trace	300
Ni/kieselguhr/Na ₂ CO ₃	307	500	0.6	278

straw over nickel catalyst. As shown in Fig. 2, without a catalyst, rice straw was converted to oil (26 wt%), carbonized solid (46 wt%), and gas (28 wt%). With Na₂CO₃, oil yield (38 wt%) was increased and carbonized solid (33 wt%) was decreased. The addition of Na₂CO₃ to the nickel catalyst largely enhanced gas yield (53 wt%) and decreased oil yield (10 wt%).

Table 1 also shows that addition of Na₂CO₃ has a great influence on the formation of carbon monoxide and hydrogen, but there are no reports to explain clearly this effect. Thus, our research focused on the reason why Na₂CO₃ increases the gasification activity.

2. The Effect of Amounts of Na₂CO₃

First, the effect of amounts of Na₂CO₃ on this reaction was investigated. Fig. 3 shows that gas yield was gradually increased until weight ratio of Na₂CO₃ per nickel is one and carbonized solid was sharply decreased. Fig. 4 shows the addition of Na₂CO₃ to nickel on kieselguhr largely increased the formation of carbon monoxide.

We also tried to understand the role of nickel. Two catalyst systems, Na₂CO₃ and Ni/kieselguhr + Na₂CO₃, were compared in this gasification. As shown in Fig. 5, Na₂CO₃ increased the formation of oil and the nickel promoted the formation of gas products. This result suggests that Na₂CO₃ promotes the oil formation step and nickel increases the gas formation from oil and char.

3. The Effect of Various Alkali Metal Carbonates

Na₂CO₃ showed an excellent reactivity on the gasification over nickel catalyst. Thus, various alkali metal carbonates were examined to understand the role of Na₂CO₃ on this gasification. The results are presented in Table 2. It is clear from Table 2 that the

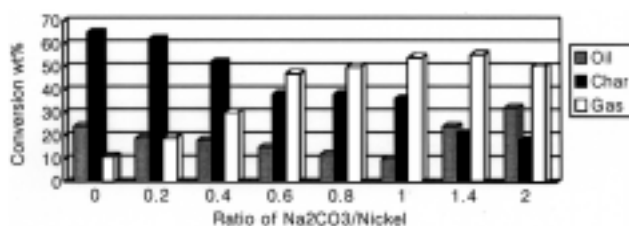


Fig. 3. The effects of amounts of Na₂CO₃ on the gasification of rice straw.

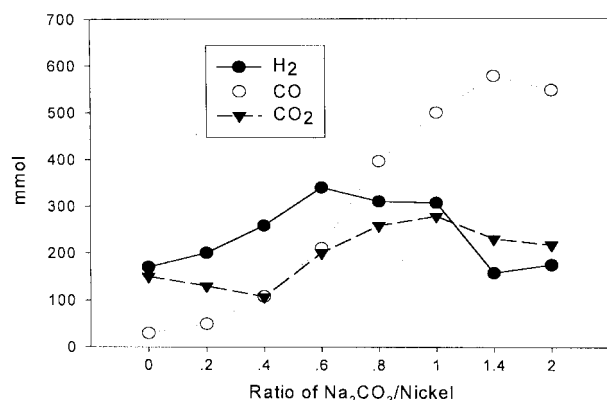


Fig. 4. Composition of formed gases depends on amounts of Na₂CO₃ during catalytic gasification of rice straw.

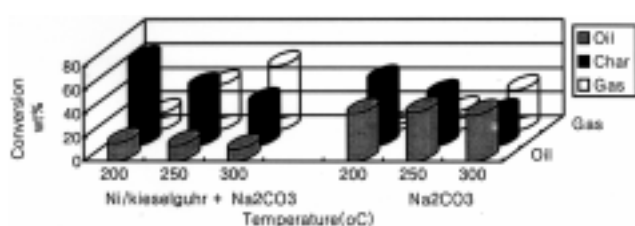


Fig. 5. Effect of reaction temperature and Na₂CO₃ on the gasification of rice straw.

Table 2. Effect of various carbonates on the gasification of rice straw

Alkali metal carbonate	Composition of gas (mmol)				
	Conversion to gas (wt%)	H ₂	CO	CH ₄	CO ₂
Li ₂ CO ₃	32	160	90	3	301
Na ₂ CO ₃	54	307	500	0.6	278
K ₂ CO ₃	53	160	480	0.6	292
CS ₂ CO ₃	39	140	178	0.3	320

gasification conversion depends on the nature of the alkali metal carbonates.

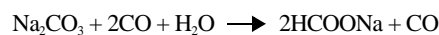
Introduction of alkali metal ions has drastically changed the conversion to gas and the composition of the gas. The formation of gas was dominated and increased in the order: Li<Cs<K<Na. In case of lithium, formation of methane showed the largest value. Various sodium compounds were compared and shown in Table 3. Only Na₂CO₃ showed an excellent conversion. But other com-

Table 3. Effects of various carbonates on the gasification of rice straw

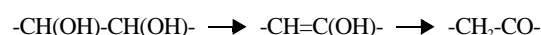
Ni/kieselguhr	Composition of gas (mmol)				
	Conversion to gas (wt%)	H ₂	CO	CH ₄	CO ₂
NaOH	18	79	29	Trace	172
Na ₂ CO ₃	54	307	500	0.6	278
NaHCO ₃	27	117	108	Trace	237
Na ₂ SO ₄	25	100	11	Trace	273

pounds including the strong alkali compound represented a lower value. This result suggests that strong basicity of the catalyst is not required in gasification of rice straw. This can also be explained from the mechanism which Appell and coworkers [1971] proposed for sodium carbonate-catalyzed conversion of carbohydrate to heavy oil in the presence of ambient CO:

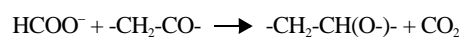
i) Reaction of sodium carbonate and water with carbon monoxide to yield sodium formate:



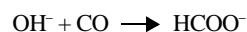
ii) Dehydration of vicinal hydroxyl groups in a carbohydrate to an enol, followed by isomerization to ketone:



iii) Reduction of newly formed carbonyl group to the corresponding alcohol with formate ion and water:



iv) The hydroxyl ion reacts with additional carbon monoxide to regenerate the formate ion:



3. Comparison of Various Reducing Temperatures of Nickel

Since biomass contains higher contents of oxygen than petroleum and coal, in our previous work some oxygen was produced during gasification. It was expected that nickel catalyst was deactivated by oxygen during gasification. Thus, nitrogen was used to prevent the deactivation of nickel catalysts by oxygen. The effect of initial pressure of nitrogen for conversion and composition of gas formed was examined at 300 °C and at a reaction time of 30 min. Cellulose instead of rice straw was charged as feedstock. The results are summarized in Table 4.

The formation of hydrogen and methane was sharply increased and carbon monoxide was decreased with the addition of nitrogen. This result means that the oxidation state of nickel catalyst influences the formation of gas. Thus, the effect of reducing temperature on nickel catalyst was investigated. Fig. 6 shows that gas

Table 4. Effect of nitrogen on gasification of rice straw

Purge condition	Composition of gas (mmol)			
	H ₂	CO	CH ₄	CO ₂
Without purge	37	155	6	360
Purge using N ₂	72	62	12	366
Add 200 psi N ₂	98	37	12	354

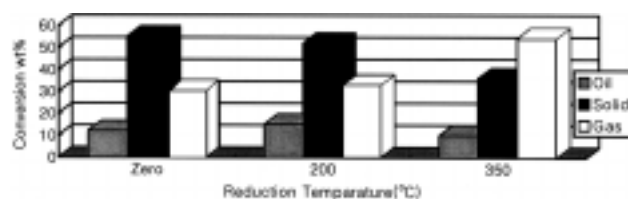


Fig. 6. Effect of reduction temperature of nickel catalyst on the gasification.

Table 5. Composition of gas obtained at different reduction temperatures of Ni-catalyst

Reducing temperature (°C)	Composition of gas (mmol)			
	H ₂	CO	CH ₄	CO ₂
350	307	500	0.6	278
300	187	210	Trace	323
250	190	58	Trace	302
200	45	19	Trace	360
No reduction	40	48	Trace	260

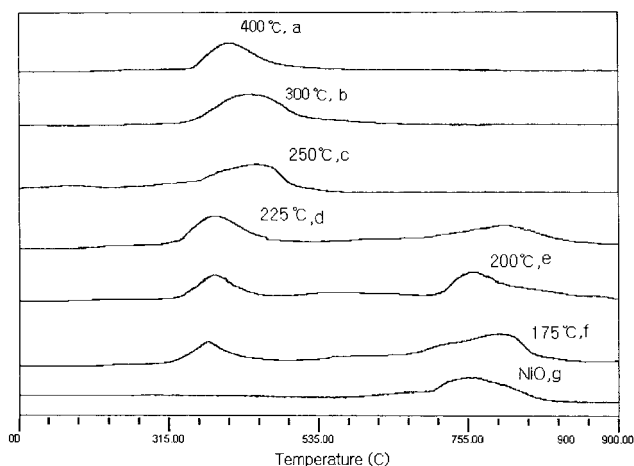
yield was increased with higher reduction temperatures of nickel catalyst.

In Table 5, compositions of gas obtained at different reduction temperatures of nickel catalyst are also summarized. The amounts of hydrogen and carbon monoxide had larger values in higher reducing temperatures. This indicates that the oxidation state of the nickel catalyst is a major factor in the gasification of biomass.

Temperature programmed reduction (TPR) experiments of prepared Ni catalysts supported on kieselguhr were performed to understand the reduction degree and the strength of metal support interaction. There is general agreement [Jenwei Chen, 1988] that the reduction of bulk phase NiO proceeds in the following steps.



In this catalyst, pure NiO supported on kieselguhr (Fig. 7g) catalyst shows one peak at 800 °C indicating the presence of strong metal support interaction. This main peak is found to shift gradually to lower temperature with reduction temperature above 175 °C, which indicates that metal support interaction becomes weaker after reduction. In particular, reduction of Ni supported on kieselguhr below 250 °C shows two peaks that indicate weak and strong metal support interaction are coexisting. Chang-Wei Hu et al. [1997] reported that this weak peak at 400 °C is a crystalline Ni₂O₃. Hence, the reducing condition greatly influences the catalyst activity. The reduction peak in the profiles around 400 °C appears to be very important in generating active nickel species

**Fig. 7. TPR profiles of Ni supported on kieselguhr catalyst with various reducing temperatures.****Table 6. Gasification of char and oil formed from the pyrolysis of rice straw**

Feedstock	Composition of gas (mmol)				
	Conversion to gas (wt%)	H ₂	CO	CH ₄	CO ₂
Char	0.0001	20	Trace	0	Trace
Oil	10.7	25	114	0	Trace

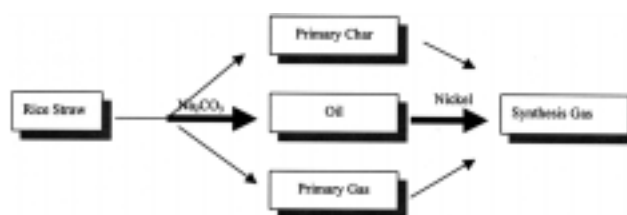
by reduction of NiO which are responsible for producing hydrogen and carbon monoxide from gasification of rice straw. Larger quantity of weak metal support interaction may be responsible for increased catalytic activity. The pure Ni supported on kieselguhr phase is not favorable, whereas reduced Ni supported on kieselguhr phase is more active for this reaction. From these results, a close correlation seems to exist between the reduction characteristics and the activity of the catalyst. The NiO supported on kieselguhr phase is not favorable, whereas reduced Ni supported on kieselguhr phase is more favorable for this reaction.

4. Reaction Pathway of Gasification

Reaction pathway of gasification was examined to understand the role of catalyst. Oil and char obtained from pyrolysis at low temperatures were used as feedstocks. Addition of Na₂CO₃ increased gas yields. As shown in Table 6, in case of char as feedstock, conversion to gases was very low. However, oil as feedstock showed a high gas conversion of 10.7%. These results suggest that Na₂CO₃ activates the liquefaction step to produce oil and nickel catalyst increased the gasification. Therefore, oil formation must be an important factor for enhancing the reactivity in the gasification of biomass. Therefore, formation of gas through oil from rice straw (→) is the main reaction to produce gas as shown in Fig. 8.

CONCLUSIONS

1. Addition of Na₂CO₃ enhanced activity for catalytic gasification of rice straw over nickel catalyst and largely increased the formation of gas.
2. Na₂CO₃ activates the oil formation step and nickel catalyst increases the gas formation from oil and char.
3. The formation of gas depends on the nature of alkali metal carbonates and is increased in the order of Li < Cs < K < Na.
4. Main reaction course to produce gas from rice straw is the formation of gas from the oil step.
5. Reducing condition of the catalyst gives influences the oxidation state of the catalyst, and the oxidation state of the nickel

**Fig. 8. Reaction pathway on gasification of rice straw over Na₂CO₃ + Ni/kieselguhr.**

catalyst is a major factor in the gasification of biomass. These results are further supported by our observations in gasification of rice straw. The pure NiO supported on kieselguhr phase is not favorable, whereas reduced Ni supported on kieselguhr phase is more favorable for this reaction.

REFERENCES

- Appel, H. R., Fu, Y. C., Friedman, S., Yuvorsky, P. M. and Wender, I., "Report of Investigation 7560," U.S. Bureau of mines, Pittsburgh (1971).
- Chang-We Hu, Yao, J., Yang, H. Q., Chen, Y. and Tian, A. M., "On the Inhomogeneity of Low Nickel Loading Methanation Catalyst," *J. of Catalysis*, **166**, 1 (1997).
- Chen, I. and Shiue, D. R., "Reduction of Nickel-Alumina Catalyst," *Ind. Eng. Chem. Res.*, **27**, 429 (1988).
- Dote, Y., Inoue, S., Ogi, T. and Yokoyama, S., "Distribution of Nitrogen in the Liquefaction of Albumin," *Dev. Thermochem. Biomass Convers.*, **1**, 320 (1997).
- Elliott, D. C., Butner, R. S. and Sealock, L. J., Jr., "Low Temperature Gasification of High Moisture Biomass," *Res. Thermochem. Biomass Convers.*, 696 (1988).
- Elliott, D. C., Sealock, L. J., Jr. and Eddie, G. B., "Chemical Processing in High Pressure Aqueous Environmental 2," *Ind. Eng. Chem. Res.*, **32**, 1542 (1993).
- Elliott, D. C., Phelps, L. J., Sealock, L. J., Jr. and Eddie, G. B., "Chemical Processing in High-Pressure Aqueous Environmental 4," *Ind. Eng. Chem. Res.*, **33**, 566 (1994).
- Garcia, L., Salvador, M. L., Bilbao, R. and Arauzo, J., "Influence of Calcination and Reduction Condition on the Catalyst Performance in the Pyrolysis Process of Biomass," *Energy & Fuels*, **12**, 139 (1998).
- Jean-Claude, C. and Esteban, C., "Fraction of Peat-derived Bitumen into Oil and Asphaltenes," *Fuel*, **57**, 304 (1978).
- Lee, S. W., Kim, S. B., Lee, K. W. and Choi, C. S., "Catalytic Gasification of Rice Straw at Low Temperature," *Environ. Eng. Res.*, **4**(4), 293 (1999).
- Lihong, X., Yongjie, Y., Lei, Z. and Piya, C., "Development of Energy from Biomass. III. Catalytic Pyrolysis of Bagasse in Aqueous Solution," *Huadong Huagong Xueyuan Xuebao*, **16**, 528 (1990).
- Minowa, T., Fang, Z., Ogi, T. and varhegyi, G., "Liquefaction of Cellulose in Hot Compressed Water Using Sodium Carbonate," *J. Chem. Eng. Japan*, **30**, 186 (1997).
- Minowa, T., Fang, Z. and Ogi, T., "Hydrogen Production from Wet Cellulose by Low Temperature Gasification Using a Reduced Nickel Catalyst," *J. of Chem. Eng. Japan*, **31**, 131 (1998).
- Ogi, T., Yokoyama, S. and Koguchi, K., "Direct Liquefaction of Wood by Alkali and Alkaline Earth Salt in an Aqueous Phase," *Chem. Lett.*, 1199 (1985).
- Yokoyama, S. Y., Suzuki, A. and Murakami, M., "Liquid Fuel Production from Ethanol Fermentation Stillage," *Chemistry Letters*, 646 (1986).